A small-angle scattering analysis of the influence of manufacture and thermal induced morphological changes on the thermal conductivity of EB-PVD PYSZ Thermal Barrier Coatings

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A small-angle scattering analysis of the influence of manufacture and thermal induced morphological changes on the thermal conductivity of EB-PVD PYSZ Thermal Barrier Coatings

by Arturo Flores Renteria

Abstract

The deposition of Electron Beam – Physical Vapor Deposition Thermal Barrier Coatings (EB-PVD TBCs) on metallic turbine blades of aero engines is a viable additional method to improve the internal cooling effect on these components. Thus, an increase of the efficiency of aero engines can be achieved by rising the inlet temperature in the turbine.

This work exhibits the influence of process parameters of the EB-PVD process, i.e. rotation speed and temperature of the substrate, on the columnar microstructure, and the geometry and distribution of the porosity in the deposited coatings. These process parameters influence the kinetic of the condensation process during the vapor deposition. The produced morphological changes consequently induce alterations in the thermal conductivity values of the manufactured coatings.

A detailed quantitative analysis of the anisotropic configuration of the porosity contained in these coatings was achieved by the combination of sophisticated measuring techniques such as Ultrasmall-angle x-ray scattering (USAXS) and small-angle neutron scattering (SANS), and SEM micrographs analysis. The results indicate that the pores exhibit a strong anisotropic configuration at the cross-sections oriented in the directions perpendicular and parallel to the axis of substrate rotation.

A theoretical approximation based on Maxwell’s theory was used to determine the thermal conductivity of the analyzed EB-PVD coatings based on the obtained USAXS data. This approximation allows the analysis of the influence of geometrical and spatial characteristics of the pores on the thermal conductivity. The calculated values correspond well with the experimental values. This approximation indicates that the intra-columnar pores and the deepest section of the voids between feather-arms are the principal contributors to the thermal isolating capability of the EB-PVD TBCs. Inter-columnar gaps influence only slightly the thermal conductivity.

Furthermore, it was demonstrated that the activation of thermal induced processes during ageing, like sintering, induces additional morphological and thermal conductivity changes to the manufactured EB-PVD coatings. The reduction of the surface area of the pores produced by the changes in the geometry during ageing was analyzed via SANS method. The results indicate that the thermal activated mass diffusion mechanism responsible for such changes is surface diffusion, which is activated at temperatures \( \geq 900^\circ\text{C} \). The achieved low aspect ratio geometry of the intra-columnar pores and voids between feather-arms after ageing exhibit a noticeably lower effect on the reduction of the thermal conductivity of the EB-PVD coatings.
Kleinwinkelstreuungsanalyse des Einflusses der herstellungs- und wärmebehandlungsinduzierten Änderungen der Morphologie auf die Wärmeleitfähigkeit von EB-PVD-PYSZ-Wärmedämmsschichten

von Arturo Flores Renteria

Zusammenfassung
Die Abscheidung von elektronenstrahlaufgedampften Wärmedämmsschichten (EB-PVD WDS) auf metallischen Turbinenschaufeln von Triebwerken führt zu einer Verbesserung der Schaufelinnenkühlung, d.h. die Eintrittstemperatur der Gase in der Turbine kann erhöht werden und somit die Effizienz des Triebwerks gesteigert werden.


Eine detaillierte quantitative Analyse der Porositätsverteilung in der WDS wurde mittels moderner Messmethoden wie Ultrakleinwinkelröntgenstreuung (USAXS), Kleinwinkel-neutronenstreuung (SANS), und Rasterelektronenmikroskopie (SEM) durchgeführt. Die Ergebnisse zeigten eine stark ausgeprägte anisotrope Konfiguration der Poren im Querschliff parallel und senkrecht zur Rotationsachse des Substraträgers.


1 Introduction

According to the technical report written by Penner et al. [1] as requested by the International Civil Aviation Organization (ICAO), the global passenger air travel is projected to grow about 5% per year between 1990 and 2015, whereas the total aviation fuel use (passenger, freight, and military) is projected to increase by 3% per year over the same period. The difference between these two percentage data is largely influenced by improvements in the aircraft efficiency. Projected scenarios indicate that technological improvements leading to reduced emissions per revenue passenger-km will continue in the future and that optimal use of airspace availability (i.e. ideal air traffic management) can be achieved by 2050. Moreover, studies of the possible impact of aviation on the atmosphere indicate the needs to optimize the consumption of the fuel energy for the aircraft transportation. There have also been several recent assessments of the impacts of aviation in Europe, Asia, and America (Brasseur et al. [2]; Schumann et al. [3]; Sorokin et al. [4] Carslaw et al. [5]; Itano et al. [6]; and Yu et al. [7]). Furthermore, air transportation plays an essential role in the economic activities of the society. In 1994, more than 1.25 billion passengers used the world's airlines for business and vacation travel, and well in excess of a third of the value of the world's manufactured exports were transported by air. The aviation industry accounted for 24 million jobs for the world's workforce and provided US$1,140 billion in annual gross output. By the year 2010, aviation's global impact could exceed US$1,800 billion and more than 33 million jobs (The International Air Transport Organization, IATA, 1994, 1996) [1].

Aircrafts are a major investment with a useful economic life of 25 years or more. Optimal operation of an aircraft includes an adequate airframe and efficient engine performance. The capacity of an aircraft must address the principal issue of safety, as well as engine efficiencies, economics, and environmental objectives. Modern aircraft engines represent some of the most demanding and sophisticated applications for structural materials applied in any engineering system manufactured nowadays. The optimization of such engines exhibit a continuous demand of an increasing in-service temperature and the usage of lightweight materials while upholding a specific product reliability [8]. The efficiency of these aero engines is directly related to the thrust-to-weight ratio and the effectiveness (reduction) in the combustion of the fuel (see Fig. 1.1).

Higher inlet temperatures induce an increase in the kinetic energy of the combustion gases, and consequently increase the thrust-to-weight ratio. The principal obstacles in using higher turbine entry temperatures is the thermal activated phenomena induced in the nozzle and principally in the turbine blades, e.g. fatigue and creep failure, oxidation, and hot gas corrosion. Even tough the used Ni-basis single-crystals superalloy used to manufacture the turbine blades exhibit excellent high temperature creep resistance, since these components work in-service conditions near to the melting temperature 0,9Tm (Tm = melting temperature) [9, 10], an additional temperature increment causes a significant reduction in the creep resistance. The high speed rotation during in-service conditions imparts tensile stresses (centrifugal force) to these features which is also an important limiting factor of the in-service conditions.
Figure 1.1: Trends in aircraft engine efficiency (after Pratt & Whitney). SFC = specific fuel consumption (mass flow rate fuel / thrust), Thermal efficiency (rate of production of kinetic energy / fuel power), Propulsive efficiency (propulsive power / rate of production of propulsive kinetic energy), Overall efficiency (thermal efficiency × propulsive efficiency).

One of the techniques utilized for the reduction of the temperature at these turbine blades is the integration of an air in- and film-cooling method, which induces lost in the efficiency of the engine since it uses pressurized air from the compressor. An alternative technique is the use of ceramic based thermal barrier coatings (TBCs) deposited on the surface of the metallic blades. These coatings induce a temperature reduction at the surface of the metallic blades due to their intrinsic low thermal conductivity by intermediately interacting with the hot combustion gases (see Fig. 1.2). The use of TBCs on turbine blades facilitates the optimization of the efficiency of aircraft engines by opening the interaction field between the air cooling volume, the gas temperature, and metallic blade temperature [9, 11-13].

Figure 1.2: Trend of the inlet temperatures according to the employed alloys and the benefit of the usage of TBCs [14].

Thermal barrier coatings are comprised by several components interacting with their particular thermo-mechanical properties. These components are: bond coat, deposited on the
surface of the metallic turbine blades; thermally grown oxide, which forms on the surface of the bond coat by the diffusion/oxidation of aluminum ions contained in the bond coat; and ceramic top coat, deposited on the formed TGO. The nowadays used standard metallic alloys for the manufacture of the bond coat are: MCrAlY and (Ni,Pt)Al. Both alloys exhibit a capability to create a TGO at the surface, while maintaining appropriated tensile resistance to accommodate the induced tensions by the differences in the thermal expansion coefficient between the TGO and the metallic blades. The TGO is principally comprised of Alumina with small insertions of ZrO2 and Y2O3. Moreover, the top coat is manufactured with a standard 3-4 mol% Y2O3 - ZrO2 ceramic material exhibiting a meta-stabilized tetragonal phase (t’). This crystalline solid solution displays high thermal expansion coefficient and low intrinsic thermal conductivity. The ceramic top coat can be deposited by using two alternative methods: Electron-Beam Physical Vapor Deposition (EB-PVD) and Air Plasma Spray method (APS). Ceramic deposited by EB-PVD exhibit a cyclic thermal spallation lifetime 8-15 factor higher than APS coatings, whereas the thermal conductivity is around factor approx. 2 higher for coatings in as-coated conditions and approx. 1.3 after thermal stabilization of the porosity during ageing, respectively. It has been shown that elements composing TBCs exhibit degradation of their mechanical and thermal properties at high temperature conditions. Then, an optimization of the materials and manufacture conditions must be done to assure the safety and capacity reliabilities of these coatings during in-service conditions.

In this work, the EB-PVD process was utilized for the manufacture of the TBCs. This method utilizes a concentrated high energy electron beam to fuse the surface of a ceramic ingot containing the same chemical composition as the deposited material. The created vapor particles condensate in the substrates positioned above the vapor cloud. The condensation process is accomplished by the reduction of the kinetic energy of the particles until they find a low energy crystallographic position within the structure of the growing crystals. The substrate holder was positioned above the vapor cloud aligned to the ingot axis in a conventional constant rotating mode during the deposition of the coatings. Individual crystals in form of columns grow in a preferred crystallographic direction. The shapes of the columns tips are determined by the geometrical configuration that guarantees that constant amounts of vapor flux impinge the constituent facets and ridges. In the case of conventional rotated substrates, it has been demonstrated that the preferred crystallographic direction is the <100> at deposition temperatures from 900°C to 1100°C [15].

The aim of this work is intended to the engineering of the manufacturing process and the thermal properties of EB-PVD PYSZ TBCs. The accomplishment of this objective can be only assured by gaining basic knowledge of the creation of the porosity and the effect of ageing in the microstructure of these coatings. Then, an analysis of the influence of process parameters and ageing on the microstructure and thermal properties of such coatings has been done. Additionally, the application of a thermal conductivity approximation exhibited the effect of the spatial and geometrical characteristics of the porosity on the thermal conductivity of these coatings in as-coated conditions and after ageing. Congruently, the state-of-the-art of EB-PVD TBCs top coats has been mainly developed in the reduction of the thermal conductivity in the last years. The use of alternative ceramic materials that improve the thermo-mechanical properties of the top coats has been investigated. Variations of the vapor transportation-condensation process (e.g. zig-zag structures) have been investigated with the aim to reduce the thermal conductivity of EB-PVD PYSZ coatings. Also, investigations of alteration of the substrate temperature and rotation speed have demonstrated the influence of this process parameter on the thermal conductivity of these columnar structured coatings.

The information presented in this work is largely oriented to the generation of basic knowledge on the nucleation and growth processes principally of nano-sized pores created within the primary columns of the EB-PVD coatings. Also, the anisotropic character of the
primary columns and all pores with the coatings is exposed via the usage of a micrographic-quantitative analysis.

Furthermore, an analysis of the effect of irreversible thermal processes such as sintering on the microstructure and thermal properties of the EB-PVD TBCs is applied. A study of the influence of temperature and time on changes in the surface area of the pores allows identifying the governing mass diffusion mechanism during sintering. This aim is achieved by applying basic principles originated to describe the sintering phenomenon of powder particles within compacts.
2 Background and literature survey

2.1 Use of TBCs on aircraft gas turbine engines

The aircraft gas turbine is basically a heat engine that utilizes air as the working fluid to overcome the aircraft drag. This condition is achieved by increasing the kinetic energy (velocity) of the air passing through the engine via four systems working together: (1) compressor, (2) combustion chamber, (3) turbine, and (4) exhaust nozzle. The compressor increases the pressure and heat energy (200°C to > 660°C) of the inlet air in direction to the combustion chamber. This process takes place in several stages by increasing air velocity until the diffuser inlet is reached at the end of the compressor. Here the velocity of the air is reduced as the pressure increases toward the diffuser outlet. Pressured primary air mixes with the fuel introduced in a highly atomized spray form in the combustion chamber. The resulting combustion high-speed hot gases subsequently delivered into the turbine should not exceed the allowable limit inlet-temperature (850°C to 1700°C). This is regulated by the addition of an extra amount of secondary air into the combustion chamber which is not used for the combustion process, but for controlling the temperature operating range within the combustion chamber (i.e. cooling) (1800°C to 2000°C [16-18]). The heat energy added to the air volume by the combustion process induces an expansion of the formed gases which transforms in kinetic energy. A great portion of this energy is extracted by the turbine blades and converted to shaft power to drive the compressor and inlet fan. This configuration exposes all these components to extreme thermo-mechanical loads during in-service conditions, especially the blades situated directly after the combustion chamber (high-pressure sector) [18]. In modern civil aircraft turbofans, the main trust is obtained by the fan-bypass arrangement. Nevertheless, the configuration of the exhaust nozzle increases the velocity the combustion gases producing additional propulsion power (see Fig. 2.1).

![Figure 2.1: Modern Pratt & Whitney PW4084 turbofan jet engine used to power Boeing 777 aircrafts](http://www.allstar.fiu.edu, NASA/LTP).

The claim of highly-efficient gas aero-engines requiring higher inlet temperatures demands the turbine blades to be working at extreme thermal conditions during long periods of in-service lifetime [19]. One of the methods employed to reduce the temperature in the turbine blades is via an interior and surface cooling system. High-pressure cool air is extracted from the compressor and fractioned in two cooling systems. Specific volume fraction is forced through several serpentine passages inside the blades extracting the heat. The rest is blown...
out to the exterior surface through small holes, forming a cooling film at the surface of the blades \((T^\circ = 1100-1200\,^\circ C)\) that is in thermal equilibrium with the hot combustion gases at \(~1500\,^\circ C\). However, the extraction of air from the compressor represents a great penalty in the efficiency of the turbine. The use of thermal barrier coatings (TBCs) is suggested as an alternative method to achieve an additional reduction in the temperature of the metallic substrate and mitigate the effect of hot spots [20]. This improvement enhances the durability of the protected metallic blades since its lifetime in creep conditions is halved for every 10-15°C increase in temperature [21]. The concept of TBCs first appeared in the 1960’s. These have been used since then in the turbines to reduce metal temperatures, extending the in-service life of the protected stationary components (combustion chamber walls and burner cans). Moreover, increase use of the TBCs has occurred since the 1980’s as protecting medium first in stationary and later in mobile highly loaded components within gas turbines (turbine nozzles and blades) [22, 23]. Two manufacturing methods emerged as the principal processes capable to create stable protecting coatings: Electron-Beam Physical Vapor Deposition (EB-PVD) and Air Plasma Spray (APS). For components exposed at extreme thermo-mechanical conditions, e.g. high-pressure sector turbine blades, EB-PVD coatings are considered to be the best suitable protecting medium due to their better thermo-cyclic capacities (Fig. 2.2) [23-25]. EB-PVD TBCs are widely used to optimize the aircraft engine technology as part of advanced designs, like in Pratt & Whitney 4000-series engines, General Electric/SNECMA’s CMF56-7 [26]. These coatings are also being successfully used in industrial gas turbines for power generation in the Westinghouse and Siemens designs [27].

![Diagram of Thermal Barrier Coating System](image)

**Figure 2.2:** Application of EB-PVD thermal barrier coatings in gas turbine engines [28].

### 2.2 Description of the TBC system

Especially during starting and maneuvering, the turbine inlet-temperature of the gases in military and commercial aircraft turbines reaches approx. 1600°C and 1500°C, respectively. Future developments regarding gas turbines requires the increase of inlet-temperatures well beyond 1600°C [25]. The maximum operational temperature level for refractory single-crystal Ni-base superalloys used for blade manufacture is 1100°C \((T_m \sim 1300\,^\circ C)\), setting the upper limits of their practical use [26]. Although the Ni-based metallic blades are high-temperature creep resistant [29, 30] and microstructural stable at temperatures up to 1100°C, they need to be protected by thermal barrier coatings (TBCs) to keep these temperature conditions within
Thus, the low thermal conductivity of TBCs is the principal property influencing the in-service reliability of turbine blades. Due to their low thermal conductivity, 250-300 μm thickness TBCs ceramic top coats can yield a temperature decrease of 100-200°C at the protected metallic surface during their superficial interaction with the hot combusted gases [9, 11, 12, 31-34]. Thermal barrier coatings (TBCs) are functional systems composed by several interacting components that jointly contribute to the coatings reliability. These materials achieve their final physical properties by taking advantage of the constituent elements (metallic and ceramic materials). An improvement in the capabilities of the coatings represents a real challenge due to the strong interrelation between these component features (see Fig. 2.3). The ceramic top coats (TC) are made with a standard oxygen-transparent [35-38] 7-8 wt% Y2O3- ZrO2 ceramic, which possesses a meta-stable tetragonal (t') crystalline structure, high thermal expansion coefficient (10,7x10^-6 /K, at 1000°C [39]) and low thermal conductivity (2 W/(mK) [40, 41]). Compatibility between these two metallic and ceramic features is achieved by using a metallic bond coat (BC) in between. Currently, there are two bond coats used as standard materials: MCrAlY and (Ni,Pt)Al alloys [42-45]. In the case of MCrAlY alloys, the microstructure of such bond coats is composed of distributed finely β-NiAl particles within a γ-Ni (Co, Cr, Al) or γ'-Ni3Al solid solution. The presence of γ-phase improves the thermal fatigue resistance by increasing the ductility of the coating. The β-phase acts as Al-reservoir for the formation of the thermal grown oxide (Al2O3-TGO) at the surface of the bond coat [46-48]. Furthermore, in the case of (Ni,Pt)Al alloys, β-(Ni, Pt)Al and γ-Ni phases are formed within the coating, and PtAl2 near the surface which is considered in this case to act as Al- reservoir for the formation of the Al2O3-TGO at the interface BC and TC (surface of BC). Moreover, this bond coat component adheres to the substrate by forming an inter-diffusion zone (IDZ) composed of solid solution phases through the diffusion of Al and alloying elements. The exposure of the substrates at elevated temperatures during the preparation process for the ceramic top coat deposition produces the formation of the Al2O3-TGO film (max. 1 μm) at the surface of the bond coats. This component is considered as the principal factor influencing the durability of the TBC system [49-52]. It develops large residual compressions (3-6 GPa) because of the thermal expansion misfit with the metallic substrate [53-57]. Finally, the PYSZ top coat is deposited on the prior formed Al2O3-TGO forming a fine-grain Al2O3-ZrO2 “mixed zone” [45, 58].

Figure 2.3: Schematic representation of the TBC system showing the interfaces between the components (inter-diffusion zone, IDZ; interface bond coat (BC)/TGO; and interface TGO/top coat (TC)), and the required individual characteristics for a functional protecting system [24].
There are characteristic limitations/capabilities of both competing manufacturing processes, i.e. EB-PVD and APS, making them economically and physically suitable for specific in-service conditions. APS coatings possess lower thermal conductivity due to the normal orientation of their interfacial porosity to the heat flow (inter-splat porosity). However, intra-columnar gaps oriented parallel to the heat flux gives EB-PVD coatings a higher strain tolerance (lower in-plane elasticity modulus [49, 59-61]), which is required for the accommodation of the strains produced by the thermal expansion mismatch with the underlying stressed TGO film [49, 62-64]. EB-PVD outperform APS coatings in cyclic thermal spallation lifetime tests by a factor of 8-15 [65, 66] within lower uncertainties [67]. Nevertheless, for EB-PVD TBCs, inter-columnar gaps formed through the complete coating thickness allow corrosive foreign materials to enter within the columns up to the deepest bottom zone of the coating, attacking the coated metallic material [30].

2.3 EB-PVD process

The EB-PVD process belongs to the manufacturing process group that employs the deposition of material from a gas phase (PVD) [68]. The use of the EB-PVD process was first developed for the deposition of MCrAlY coatings in the USA in the 1960’s. Subsequently, Airco Temescal and Pratt & Whitney implemented the use of this process for the deposition of thermal barrier coatings during the end of the 1970’s and beginning of the 1980’s [69]. This method concentrates a programmed high energy electron-beam following a scanning pattern upon the surface of a cylindrical ingot located within a water-cooled crucible. An homogeneous vapor-cloud phase is developed by using an adequate beam power/scanning pattern relation together with a controlled and continuous feeding-in movement of the ingot within the coating chamber. The vaporized particles condense on the surface of previously pre-heated substrates fixed to a holder positioned above the vapor cloud (see Fig. 2.4).

Figure 2.4: Schematic representation of the principal components in an EB-PVD process.

The parameters defining the interrelation between the substrates and the vapor flux during the coating deposition can be arranged differently (i.e. pattern of vapor incidence). These parameters can be established to obtain a conventional rotating mode, perpendicular and oblique stationary mode, and oblique rotating mode (see Fig. 2.5). Investigations revealed that the relative position of the substrates to the vaporizing source influences the growth process of the columnar structure [15, 70, 71]. During the coating deposition, addition of condensed
atoms in the growing crystal structure (lattice) occurs due to the temperature gradient between the vapor cloud and the substrate. The kinetics of this process is determined by the interrelation between thermodynamic lower energy conditions of the growing surface and by the preferable crystal growth directions. Furthermore, adjusted oxygen flow into the coating chamber is required to uphold the stoichiometry of the manufactured coatings while obtaining the desired vacuum level.

**Figure 2.5:** Schematic representation of different substrates/vapour cloud arrangements and the respective incident vapour flux pattern: (a) conventional rotating mode, (b) oblique rotating mode [71], and (c) stationary mode.

### 2.3.1 Fundamentals

EB-PVD technology utilizes the interaction of high-energy electrons to fuse the surface of an evaporation source, which is generally a cylindrical shaped ingot. This energy interaction produces a vaporized phase which is thereafter deposited on a substrate localized above the vapor cloud. High energy electron-beam is produced by thermo-ionic emission at the filament of the high-voltage electron gun. Electrons are subsequently accelerated and concentrated via electromagnetic fields, and finally directed to the surface of a vaporizing ingot. A fraction of the kinetic energy \( E = eU_B \) of the electrons incoming at the ingot’s surface transforms into heat energy. This conversion effect melts and evaporates the solid material at the surface of an induced small interaction volume (see **Fig. 2.6**). Hence, a scanning movement pattern of the electron beam on the surface of the vaporizing target is required for a homogeneous melting/vaporization process. A constant vaporization rate is achieved by equilibrating this process and a controlled feed-in movement of the ingot in the water-cooled crucible. For ZrO₂ ceramic targets, 5-25 μm/min ingot feed-in rates are considered technically adequate [69]. Higher rates at high electron gun power produce dents on the melted surface of the vaporizing ingot, which intermittently explode generating spatters on the surface of the substrates.

The mean free path length of the vaporized particles, which is inversely proportional to the chamber pressure, should be larger than the distance between the substrate and the ingot surface to achieve efficient vapor transporting conditions. The influence of energy interchanges between vapor particle-vapor particle, and electrons-vapor particles are mainly avoided by conserving this space relationship. Moreover, at oxygen partial pressure lower than 1x10⁻⁷ bar, the effect of energy lost from interactions between the generated electron-
beam with oxygen molecules can be neglected [45]. Nevertheless, a certain amount of oxygen is required for the reactive vaporization/deposition of stoichiometric ceramic oxides. In the case of ZrO₂, an oxygen partial pressure of min. 2x10⁻⁵ bar is needed [72]. Finally, vapor particles condensate at the substrate’s surface by giving a part of their kinetic energy and transforming into adatoms. These adatoms exchange their remaining energy with the atoms at the surface of the substrate. By this energy exchange, the adatoms can loose energy (exchange) and diffuse until they occupy low energy positions within the growing crystal lattice, or gain energy (rejection) and re-evaporate into the vapor phase and become particles.

**Figure 2.6:** Schematic representation of the interaction between the electron beam and the vaporizing solid material target.

### 2.3.2 Growth of PYSZ columnar crystals in EB-PVD coatings

EB-PVD PYSZ coatings enclose a microstructure composed of single crystal individual columns [70, 73, 74] growing in a preferred crystallographic direction. The configuration of the surfaces and ridges at the tip of the individual columns guarantees that equal amounts of vapor flux impinge all the constituent facets during the growing process ensuring the persistency of the growth direction <hkl> (see Fig. 2.7) [15]. According to the periodic bond-chain analysis (PBC) developed by Hartman and Perdok [75], the fluorite crystal structure contains PBCs lying in the <110> directions. These connect the anion tetrahedral arrangements, and coordinate the cations within the unit cell [76]. Thus, it is expected that the preferred growing facets are {111} since these planes contain multiple interacting PBCs. It can be assumed that these conditions are also valid for the meta-stable tetragonal crystalline structure of EB-PVD PYSZ coatings since its deviation from the fluorite structure is sufficiently small [15]. The final morphology and orientation of the columns depends primarily on the relative position of the substrates to the vaporizing source, i. e. vapor incidence angle (VIA), which is the angle between the substrate normal and the average direction of vapor incidence [71]. The data in Table 2.1 demonstrate a clear relationship between the orientation of the columnar growth texture with the VIA and substrate temperature in the case of stationary mode. In this case, a fibrous column texture with mainly <111> and <110> preferred growth directions were achieved for coatings deposited via stationary perpendicular and oblique modes. Moreover, coatings deposited at different
substrate temperatures and rotation speeds in a conventional rotating mode exhibit a $<100>$ preferred column growth direction. Under these coating conditions, the $<100>$ orientation of the columns is parallel to the averaged vapor flux, i.e. normal to the substrates surface, and the ridges of the columns are oriented perpendicular and parallel to the axis of substrate rotation [77]. The resulting pyramidal morphology assures that all {111} facets capture equal amounts of integrated vapor flux and the appearance of an in-plane orientation [77-81]. Additionally, the alignment of the c-axis of the meta-stable tetragonal crystalline structure changes from the in-plane to the out-of-plane by depositing at $1100^\circ$C [15].

![Figure 2.7: Schematic representation of the persistence of $<100>$ truncated octahedral tips under conventional rotated mode. “Sunrise” and “sunset” patterns acting together create opposing pairs of $<110>$ rooftops arrangements of {111} facets [15]. The lines in the rotation pattern figure (right) represent the column ridges and the surfaces in between are the growing facets.](image)

### Table 2.1: Trends of the preferred growth direction under stationary and rotating conditions from various investigations on EB-PVD PYSZ TBCs.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Substrate Temperature, °C</th>
<th>VIA$^a$</th>
<th>Texture$^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCrAl-alloy</td>
<td>900</td>
<td>0°, 45°</td>
<td>$&lt;111&gt;, &lt;111&gt; + &lt;110&gt;$</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0°, 45°</td>
<td>$&lt;111&gt; + &lt;110&gt;, &lt;110&gt;$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>0°, 45°</td>
<td>$&lt;110&gt;, &lt;110&gt;$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900-1100</td>
<td>8 rpm (0°)</td>
<td>$&lt;100&gt;$</td>
<td></td>
</tr>
<tr>
<td>Ni-basis + NiCoCrAlY</td>
<td>~ 1000</td>
<td>0°, 31°, 12 rpm (27°)</td>
<td>$&lt;113&gt; + &lt;111&gt; + &lt;100&gt;$</td>
<td>[70]</td>
</tr>
<tr>
<td>Ni-basis</td>
<td>~ 938</td>
<td>0° - 30°, 40 - 80°</td>
<td>$&lt;110&gt; + &lt;111&gt;$</td>
<td>[82]</td>
</tr>
<tr>
<td>Ni-basis + NiCoCrAlY</td>
<td>995</td>
<td>12rpm (0°)</td>
<td>$&lt;100&gt;$</td>
<td>[71]</td>
</tr>
<tr>
<td>Ni-basis</td>
<td>935</td>
<td>12rpm (57-64°)</td>
<td>$&lt;100&gt;$</td>
<td>[83]</td>
</tr>
<tr>
<td>Ni-basis</td>
<td>~ 993</td>
<td>0°</td>
<td>$&lt;111&gt;$</td>
<td>[84]</td>
</tr>
<tr>
<td>Ni-basis</td>
<td>~ 993</td>
<td>0 - 10 rpm (0°)</td>
<td>$&lt;100&gt;$</td>
<td>[85]</td>
</tr>
<tr>
<td>PYSZ</td>
<td>950</td>
<td>0, 1, 5, 10 rpm (0°)</td>
<td>$&lt;100&gt;$</td>
<td></td>
</tr>
<tr>
<td>Fused quartz</td>
<td>700, 950</td>
<td>0°</td>
<td>$&lt;111&gt;, &lt;111&gt;$</td>
<td>[86]</td>
</tr>
<tr>
<td>Plcrts. Alumina</td>
<td>700, 950, 1050, 1150</td>
<td></td>
<td>$&lt;111&gt;, &lt;111&gt;, &lt;100&gt;, &lt;100&gt;$</td>
<td></td>
</tr>
<tr>
<td>(0001) Saphire</td>
<td>700, 950, 1050, 1150</td>
<td></td>
<td>$&lt;111&gt;, &lt;100&gt;, &lt;100&gt;$</td>
<td></td>
</tr>
<tr>
<td>(111) Zirconia</td>
<td>700, 950, 1150</td>
<td></td>
<td>$&lt;111&gt;, &lt;100&gt;, &lt;100&gt;$</td>
<td></td>
</tr>
<tr>
<td>(100) Zirconia</td>
<td>700, 950, 1050, 1150</td>
<td></td>
<td>$&lt;111&gt;, &lt;111&gt;, &lt;111&gt;$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ vapor incidence angle  
$^b$ preferred crystallographic growth direction
2.3.3 Microstructure of the EB-PVD coatings

During the EB-PVD coating process, primary columns start to grow on the substrate surface following a nucleation stage. An equiaxed-zone of grains with no preferred crystal orientation forms initially at the bottom of the deposited coating of specimens produced under both, conventional rotating mode [70, 73, 86] and stationary mode [15]. The appearance of this zone is assumed to be influenced by the low temperature of the substrate at the beginning of the EB-PVD deposition process, thermal stresses produces at this zone, and interactions of diffusion elements between the TGO and the initially deposited top coat [87].

For perpendicular stationary mode, the morphology of the coatings is sensitive to the substrate material and the preparation of the surface to be coated [70]. Since the substrate is continuously exposed to the vapor flux, shadowed regions are only created at line-of-sight configurations behind grain tips extended slightly from the main column bodies, producing a competitive growth process between columns. This effect governs the appearance of porosity within the deposited coating, i.e. inter-columnar gaps, voids between feather-arms and intra-columnar pores.

In the case of conventionally rotated samples, the rotating movement strictly controls the crystallographic texture and morphology of the columns [70]. The previously formed TGO creates a “roof” topography which interacts with the vapor cloud during the rotating movement. This interrelation enhances the nucleation and growth of a structure formed by individual columns due to the occurrence of a shadowing effect at the developed localized roughness [88]. The growth process of individual columns occurs in a preferred direction governed by the developed rooftop configuration of the tips (see Fig. 2.7). An enlargement of the columns diameter and elimination of non-favorable oriented columns occur due to a selective process influenced by the “sunrise-sunset” line of sight shadowing effect of the neighboring columns during the rotation movement. Whereas this effect enhances the creation of the same pore types as in the stationary perpendicular mode, there arise significant differences in the geometrical and spatial characteristics of the created pores [15]. The principal difference between these two deposition modes occurs in the intra-columnar pores.

Rotation of the specimens creates periodic overlapped arrays of enlarged intra-columnar pores along the columns length, whereas in stationary mode these pores are randomly created under unstable micro-shadowing conditions. Furthermore, the dimensions of inter-columnar gaps and voids between feather-arms are affected by the deposition mode since these features are principally originated due to a shadowing effect between primary columns. The pattern of such shadowing phenomenon is clearly different at the mentioned deposition methods.

The physical model based on microstructural features by Movchan and Demchisin [89] exhibits the effect of the substrate temperature in the microstructure of EB-PVD coatings deposited in stationary mode (see Fig. 2.8). This approximation considers that the substrate temperature is directly related to the melting temperature of the deposited material (T_m). This model includes three microstructural zones emerging by the increase in the substrate temperature during the EB-PVD process (Zone 1, Zone 2, and Zone 3). Such formed zones are separated by two transition temperatures (T_1 and T_2). These transition temperatures were experimentally determined to be T_1 \sim 0.3 T_m and T_2 \sim 0.5 T_m for metals and T_1 \sim 0.26 T_m and T_2 \sim 0.45 T_m for oxides [15]. Zone 1 films are characterized by low surface diffusivity of the deposited adatoms on the growing surface. The resulting grains are cone-shaped with rounded tips, enclosing a highly porous (fibrous) cross section. In the Zone 2, the activation of surface diffusion defines the appearance of parallel columnar grains with faceted tips, containing lower porosity volumes. The thicknesses of these columnar grains enlarge by increasing the temperature. Zone 3 is characterized by the additional activation of volume diffusion. The resulting microstructure is composed by re-crystallized equiaxed grains with a flat top surface.
Background and literature survey

Figure 2.8: Movchan structural zone model describing the influence of the substrate temperature on the morphology of the deposited EB-PVD films [89].

Furthermore, the deterministic model for polycrystalline growth developed by Van der Drift [90] has been considered for the detailed analysis of the Zone 2 described in the Movchan and Demchisin’s model [69]. This considers that the growth of the EB-PVD coatings under stationary conditions is controlled by surface diffusion influencing the nucleation and growth of columnar crystals. Such conditions are controlled by the combined effect of vapor deposition direction, surface diffusion, conditions for columnar structure formation and crystallographic condensation coefficients. **Fig. 2.9a** shows the parallel columnar structure with rounded tips resulting from a combination of the absence of surface diffusion, a diffuse vapor deposition direction and isotropic condensation coefficients. The structure displayed in **Fig. 2.9b** corresponds to the vapor deposition under the presence of anisotropic crystallographic condensation coefficients. The resulting sharp faceted surfaces at the edges of the individual columns correspond to crystallographic planes with the slowest shift velocity. Furthermore, the activation of surface diffusion enhances the filling up of the inter-columnar spacing deposition creating a dense columnar structure (see **Fig. 2.9c**). The re-nucleation process of additional columns along the coating thickness during the deposition process creates a structure like the one displayed at the **Fig. 2.9d**.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYSZ</td>
<td>&lt; 773 K</td>
<td>773 – 1340 K</td>
<td>&gt; 1340 K</td>
</tr>
<tr>
<td>NiCoCrAlY</td>
<td>&lt; 472 K</td>
<td>472 – 708 K</td>
<td>&gt; 708 K</td>
</tr>
</tbody>
</table>

**Figure 2.9:** 2D growth of EB-PVD coatings under conditions corresponding to Zone 2 in Movchan’s diagram [90].
2.3.4 Distribution of porosity in EB-PVD coatings

Generally, the shadowing effect and the activation of surface diffusion are considered to be the controlling factors in the emergence of pores within EB-PVD coatings [91, 92]. Features like column tips affect the line-of-sight nature deposition of vapor particles in the EB-PVD process by interacting with the vapor flux. This effect is enhanced when the vapor incidence angle is non-zero, generating pores at the deposited material due to local variations in the vapor flux. Moreover, the activation of surface diffusion determines the final geometry and size of the created pores. This effect controls the capacity of the deposited atoms to migrate to crystal structure sites giving a lower surface energy of the pores (e.g. low aspect ratio).

Figure 2.10: SEM-micrographs showing the columnar microstructure of EB-PVD coatings. The geometrical and spatial characteristics of the pores is perceptible in a fractured cross-section of the complete coating thickness (a), polished cross-section close to the bottom (b), and top (c) zones.

EB-PVD coatings deposited under conventional rotating mode consist of numerous single crystalline columns of very fine diameter that start growing on the previously formed TGO film on the metallic substrate surface (see Fig. 2.10). These created columns grow continuously in a preferred growth direction enlarging their diameter and consequently, reducing the number of columns due to a competitive growing process. Columns with unfavorable orientation are screened out, allowing the gradual broadening of favorably oriented ones. These primary columns are only weakly interconnected to each other, displaying inter-columnar gaps produced by the enhancement of the shadowing effect due to the produced “sunrise-sunset” pattern of the vapor flux during each rotation movement. The distribution of the inter-columnar gaps follows the same sequence as the primary columns. These are numerous and narrow at the substrate side. Their width increases and their amount reduce approaching to the tip of the coating. Additionally, the shadowing effect of the neighboring column tips impedes the vapor flux to reach the bottom of the valleys between the column tips. This effect enhances the creation of nano-sized secondary columns and voids.
in-between (so-called feather-arms) along the complete columns periphery [15]. Voids between feather-arms could be designated as opened intra-columnar pores created at the columns periphery due to lower vapor flux available for the complete solid material deposition. At this edge region, the effect of the column-tip shadowing dominates the surface diffusion process on these features and controls the value of the deposition rate over a differential area as function of time during each rotation movement. Therefore, this phenomenon becomes more significant at the limit edge of the columns yielding their conical cross section. In addition, high aspect ratio intra-columnar pores are created inside the columns. These emerge at regions where the vapor with the highest incidence angle (VIA), corresponding to each rotation movement, interacts with the valleys between the edges of the “banana” shaped elements localized at the edge of the previously deposited material. These pores grow parallel to the feather-arms through the deposited material in an elongated curved shape by following the changing direction of the vapor incidence angle (VIA) in a “sunset” pattern.

Furthermore, pore distribution and column size in the coatings manufactured under conventional rotational mode differ in the cross-section perpendicular to the direction of axis of substrate rotation compared to the parallel one (see Fig. 2.11). Inter-columnar gaps of all manufactured morphologies are slightly broader, and contain evidently higher volume fractions perpendicular to axis of substrate rotation compared with the parallel direction [15, 93]. This effect results from the fact that oblique vapor incidence occurs primarily at the direction perpendicular to axis of substrate rotation. The pattern of vapor incidence is the primary factor controlling the anisotropy of the column shape on conventionally rotated substrates (see Fig. 2.12). The material layers deposited after each rotation movement grow uniformly in the direction perpendicular to the axis of substrate rotation, whereas in the parallel direction these exhibit a discontinuous configuration. The arrays of growing surface edges in the direction perpendicular to axis of substrate rotation grow uniformly along the column tip during rotation due to their polar configuration related to the rotation axis. The growing surface edges oriented parallel to the axis of substrate rotation grow independently to each other due to their linear configuration related to the rotation axis (see Fig. 2.11). Thus, this effect creates an elongation of the column profile in this parallel direction. The resulting anisotropy of the in-plane compliance enhances the anisotropy in the strain tolerance of the TBC system due to the differences in the number and configuration of the corresponding inter-columnar pores [94].

Figure 2.11: SEM-micrographs showing the fractured cross-section of the top zone (a) and view from the top (b) of EB-PVD coatings. This last micrograph shows the evident anisotropic distribution of the column tips and the inter-columnar gaps in correlation with the axis of substrate rotation.
2.3.5 Influence of process parameters on the microstructure of EB-PVD coatings

During the EB-PVD process, the physical deposition of atoms onto a substrate surface from a vaporized phase includes vaporization, transport, and condensation processes. The vapor cloud created during the vaporization process must enclose a homogeneous distribution of the elements corresponding to the vaporized phases. Thus, it is indispensable that the intrinsic vaporization pressure of the elements forming the ingot material is approximately the same. Moreover, a saturation vapor pressure forms at the surface of the ingot and is controlled by the vaporized material in equilibrium with the vaporizing and condensation rates. This saturation pressure determines the mean free path length of the vaporized particles, and consequently, the vapor transport to the substrate surface [95]. Furthermore, the condensation process of vaporized particles on a substrate is mainly influenced by the interrelation between the shadowing effect and surface diffusion [96]. Moreover, the competitive growth at the initial stage of the columns creation is reported to be controlled by the surface roughness of the substrate. So that higher substrate surface roughness promotes the formation of a coarse and open structure [97].

EB-PVD TBCs are normally deposited at temperatures (~0.4T_M) near the T_2 transition temperature in the Movchan and Demchisin diagram. This implies that the film produced at stationary conditions should be dense due to the activation of surface diffusion overcoming the effect of the atomistic-scale shadowing. However, additional factors appear when the films are deposited under rotational conditions. The rotation of the substrates produces a “sunrise-sunset” vapor incidence pattern that determines the deposition rate over a differential area as a function of time. Thus, the interplay between neighboring column tips and the vapor incidence angle of the incoming particles enhances the dominance of the shadowing effect over the surface diffusion. This shadowing phenomenon enhances the formation of inter-columnar porosity at thermal conditions that normally yield dense films (T ≥ T_2). Therefore, it is considered that the rotation of the substrates during the EB-PVD process shifts the zones of the Movchan and Demchisin diagram to higher temperatures [88]. Jan et al. found an
enhancement of the cone shape in relation with the rotation speed by constant temperature, although, the size of the columns at the bottom region remains constant [84]. Thus, while the temperature controls principally the amount of porosity, the rotation speed determines the morphology of the porosity. An increase in substrate temperature activates the surface diffusion process. At elevated temperatures this process dominates the shadowing effect, producing denser microstructures in coatings deposited at constant rotation speed and deposition rate [88, 95]. Also, the temperature increase of the substrate reduces the density of created nuclei by reducing the driving force for the nucleation of columns on the TGO. The consecutive competitive growth enhances the formation of columns containing a larger average grain diameter, and consecutively broader inter-columnar pores. Moreover, higher substrate temperatures also reduces the aspect ratio of voids between feather-arms and the spheroidization of intra-columnar pores [15]. The interrelation of “low temperature/low rotation speed” generates irregular, light conical-shaped columns. Increasing both parameters improves the regularity and parallelism of columns, and enlarges their diameter [96].

Moreover, the volume and shape of voids between feather-arms and intra-columnar pores is expected to be determined by the rotation speed, substrate temperature and the angle between the substrate and the vapor during evaporation [15, 88, 98]. Apart from the control of the physical factors, some investigations have dealt with modifications of the morphology by altering the vapor deposition pattern via the shift movement of the substrate during the coating process. Multilayered microstructure was manufactured by means of an “in and out” or “shuttering” method [99]. The interruption of the deposition process creates arrays of nucleated primary columns and, consecutive arrays of pores laying perpendicular to the primary columns axes. Another method used is the creation of a microstructure with a zig-zag inter-columnar porosity by an oscillatory [100-102] or pivoting method [103]. This configuration of the inter-columnar pores alters the heat flux through the coating thickness. Alternatively, the use of additives in the vapor phase to influence the condensation process has been investigated [104]. Here, coatings with extremely high pore volume fraction are created. However, these works remain out of the scope of this study.

2.4 Thermal conductivity

2.4.1 Fundamentals

Heat conduction in crystalline solids via a temperature gradient is carried out by the flux of (a) electrons, (b) phonons, and (c) photons [105, 106]. In the case of ceramic materials, thermal conductivity is mainly governed by phonon conductivity with an additional photon conductivity fraction at high temperatures. In the case of materials with anisotropic microstructure along their thickness, the thermal conductivity measured by standard techniques (e.g., laser flash method) represents the averaged value, which is influenced by the statistical value of the heat flux density. This physical property corresponds to the group of those physical properties where a density flux is defined by a scalar field and a proportional factor like electric conductivity, dielectric constant and magnetic permittivity. Since the density flux represents a local statistical representative value, it is obvious to assume that such properties will not generally obey the rule of mixtures.

Thermal conductivity is a microstructural rather than an intrinsic physical property of a material that quantitatively describes its capacity to transfer the heat energy (dW). This physical property is material and temperature dependent. The heat energy defines a heat flux (\(q\)) by passing through a cross-section area (\(dA\)) within a certain time (\(dt\)). Since the heat flux is not constant across a solid material, a statistical representative value is instead considered: heat flux density (\(j\)) [107]. One-dimensional (z) transport of heat energy in opaque materials is described by Fourier's equation:
The conduction of heat caused by vibration energy in dielectric solids is considered as the propagation of anharmonic elastic waves through a continuum or the interaction between thermal energy quanta-phonons. In the case of thermal isolating ceramic systems, porosity is an important component influencing their physical properties. At temperatures where heat conduction by radiation is neglected, porosity has a lower thermal conductivity than any solid phase comprising a material. Dispersed pores within a solid system create a nearly linear decrease in conductivity by increasing their volume fraction. Nevertheless, flat pores in the form of microcracks oriented perpendicular to the heat flux path have a strong influence on the conductivity despite their small volume fraction. The diffusion of heat energy through the solid material volume must overcome a resistance effect caused principally by phonon-phonon Umklapp processes (collisions between phonons), the scattering of phonons due to anharmonicities caused by lattice imperfections and the dimensions of the solid material [108, 109]. Without these trends, the heat energy (phonons) would be transmitted through a solid material with ultrasonic velocity without the creation of a temperature gradient. Every phonon delivers a certain quantity of energy to the averaged thermal flux density along the transmission direction (z) according to the magnitude of the z-component of its velocity and the location of its last collision. Debye described the phonon conductivity in dielectric materials employing the Drude kinetic theory of gases:

$$\lambda = \frac{1}{3} C v l = \frac{1}{3} C v^2 \tau$$  \hspace{1cm} (Eq. 2.2)

where $C$ is the heat capacity per unit volume of the phonons, which is one of the factors that determines the temperature dependence of $\lambda$; $v$ the phonon velocity, and $l$ the mean free path length, which is directly related to the collision rate $\tau^{-1}$ of the phonons [110].

There is a dependence between the thermal conductivity and the temperature ($T$) described by the Debye’s theory. At low temperatures, the phonons diffusion is affected only by anharmonicities produced by geometric and impurities related factors. Under these conditions, the mean free path length is primarily affected by the edges of the solid material. An increment in the temperature increases the kinetic energy ($v$) of the phonons, and consequently increases the thermal conductivity by increasing the heat capacity proportionally to $T^{-3}$. This relation is valid until the temperature reaches a value (Debye temperature, $T_D$) that activates phonon-phonon Umklapp processes, reducing the phonons mean free path length. The thermal conductivity reaches a maximum value under these conditions. Higher temperatures cause the increment of phonons participating in Umklapp processes according to $e^{T_D/T}$. These phenomena occur until the mean free path length reaches to values near the lattice spacing. Under these conditions, the conductivity is expected to be independent of temperature. Furthermore, differences in atomic weight/ionic radius of the elements comprising a solid material induce anharmonicities in the photon diffusion [111]. In the same way, impurities and vacancies cause phonon scattering due to the differences in mass and the creation of a local elastic strain field around the substituted atom due to differences in size and binding forces.

At high temperatures, a fraction of the overall heat conductance occurs through electromagnetic radiation energy (photons) additionally to the phonon diffusion in solid materials. This phenomenon becomes important at high temperatures ($T$), because of its $T^{-4}$ proportionality with the heat flux density ($j$). Heat energy is emitted in all directions by a unit of volume of material with refractive index $n$. 

$$j = \frac{q}{A} = \frac{\partial^2 W}{\partial t \cdot \partial A} = -\lambda \frac{\partial T}{\partial z}$$  \hspace{1cm} (Eq. 2.1)
\[ j = \frac{q}{A} = 4a\sigma n^2 T^4 \quad (\text{Eq. 2.3}) \]

where \( A \) is the cross-section of the emitted heat flux \( q \), \( a \) is the absorption coefficient and \( \sigma \) the Stephan-Boltzmann constant (1,37x10^{-12} \text{cal/cm}^2\text{-sec-K}^4). By substituting the radiation heat capacity of the material and \( v = c/n \) (\( c \) is the velocity of light) in Eq. 2.2, the radiant energy conductivity with a \( l_r \) mean free path length is given by

\[ \lambda_r = \frac{16}{3} \sigma n^2 T^3 l_r \quad (\text{Eq. 2.4}) \]

The main scattering process occurs at the interface pores-solid material by interrupting the photon diffusion due to the large differences in index of refraction (\( n \)) between these means. Considering the heat transfer across a flat cavity inside of an opaque material with parallel sides and thickness \( dp \), the effective conductivity by radiation is defined by

\[ q = 4n\sigma e_{\text{eff}} A T_m^3 \Delta T = -k_{\text{eff}} \cdot A \frac{\Delta T}{d_p} \quad (\text{Eq. 2.5}) \]

thus,

\[ \lambda_{\text{eff}} = 4d_p n^2 \sigma e_{\text{eff}} T_m^3 \quad (\text{Eq. 2.6}) \]

According to the proportionality between the radiation conductivity and the pore size at Eq. 2.5, smaller size pores act as efficient thermal barriers. Nevertheless, these considerations are valid for opaque materials. Generally the ceramic materials are partially translucent to radiation, transmitting a considerable fraction of the incident energy. Thus, the effect of translucency dominates the isolation efficiency of the pores in diminishing the heat conduction by photons.

### 2.4.2 Thermal conductivity of EB-PVD TBCs

Until now, the standard ceramic material utilized for the manufacture of EB-PVD TBCs is meta-stable tetragonal 3-4 mol\% \( \text{Y}_2\text{O}_3 \) stabilized \( \text{ZrO}_2 \) (PYSZ). The meta-stable equilibrium within the crystal structure of this solid solution occurs from the substitution of two \( \text{Zr}^{4+} \) ions with two \( \text{Y}^{3+} \) ions, creating the incorporation of one oxygen vacancy to keep the electroneutrality:

\[ \text{Y}_2\text{O}_3 \rightarrow 2\text{Y}^{3+}_\text{Zr} + \text{V}^{\bullet\bullet} + 3\text{O}^{\bullet\bullet} \]

This configuration produces the scattering of phonons by the introduction of ions with different atomic masses and vacancies (defects) into the crystal lattice. However, due to the small differences in atomic masses and sizes between yttrium and zirconium this effect is generally neglected. Thus, the insensitivity of the thermal conductivity of PSYZ ceramics to temperature variations is mainly attributed to the presence of \( \text{O}^{\bullet\bullet} \) vacancies in the crystal lattice. Increasing yttrium content (fully stabilized zirconia) reduces the thermal conductivity by creating additional amounts of these crystalline defects [112-115]. Additional to these lattice and crystal-structure-related defects and irregularities, the typical voids and pores created in EB-PVD produced PYSZ coatings defines and alters their overall thermal conductivity. The spatial and geometrical characteristics of porosity is assumed to be responsible for the additional reduction in the thermal conductivity of these coatings compared with the bulk, sintered, and APS deposited materials [116, 117].
Discrepancies between the experimental results obtained for materials possessing similar chemical compositions are therefore related to porosity. EB-PBV TBCs are composed by a parallel arrangement of primary columns and lower volume fraction of inter-columnar gaps. In this configuration, most of the heat flows through the coating thickness via the better conductor (i.e. columns) with the same in-plane thermal gradient between the phases. Thus, as a general practice, the inter-columnar pores orientated parallel to the heat flux are considered to induce only a slight effect on the thermal conductivity [100, 102]. However, recent studies have been controversial regarding this consideration. For instance, significant reduction in the thermal conductivity of EB-PVD PYSZ TBCs was identified by decreasing the coating thickness. It is assumed that this effect emerges because of the fraction increase of inter-columnar pores at the bottom zone of EB-PVD coatings and their deviation of the direction perpendicular to the substrate’s plane [118-120]. Nicholls et al. [119] assumed that an additional factor could be the presence of an un-textured crystal structure within the bottom region of the columns. Nevertheless, micron-scale spatial resolved thermal conductivity measurements via laser time-domain thermoreflectance (TDTR) showed that approx. 95% of the total reduction of the thermal conductivity compared with the bulk value was influenced by the presence of pores within the columns [121].

Moreover, the nano-sized pores within the primary columns interrupt the heat flux because of the inefficient conduction and radiation heat flux through the void due to their size even when these are gas filled [122-124]. The effectiveness of the porosity to interrupt of heat flux depends upon the reduction of the cross sectional area through which the heat flows; thus, altering the local statistical representative heat flux density [85, 100, 101]. This effect is directly related to the volume fraction, and geometrical and spatial characteristics of these pores [15, 122, 125]. Since the atoms at the pore surface contain a different energy due to their atomic coordination conditions, it is also expected that this effect influences the diffusion of phonons around these discontinuities [126]. As a result, control of the pore volume fraction, spatial distribution, orientation and morphology provides an approach to minimize the thermal conductivity of these thermal barrier coatings, and optimize the thermo-mechanical properties of EB-PVD TBCs.

2.4.3 Non-interacting approximation modeling of the thermal conductivity of EB-PVD TBCs

The semi-empirical approximation of Lu [122] based on Maxwell’s non-interaction scheme [127] represents a suitable, simple and reasonably accurate approximation to achieve quantitative assessments on the thermal conductivity of EB-PVD TBCs. This semi-empirical approximation is theoretically presented as an accurate analysis method that describes the thermal conductivity of EB-PVD TBCs. In the current work, experimental and calculated values of the thermal conductivity values are correlated via the use of the obtained USAXS data of the porosity in the theoretical approximation. Such approximation analyses the influence of the volume fraction and stereometric (geometric and spatial) characteristics of thermal insulating pores on the thermal conductivity of these ceramic coatings. It is based on the non-interacting analysis of the influence of randomly distributed spheroids and oriented cylinders by Bakker et al. [123], and the volume fraction mixtures of non-randomly oriented pore shapes by Shafiro et al. [128] on the overall thermal conductivity of solid materials. In this non-interacting approximation, each inclusion is subjected to the same field temperature gradient, unperturbed by the presence of other inclusions. These pore characteristics are tangled together in a non-linear fashion and they must be considered simultaneously.

The overall thermal conductivity tensor $k$ of a material containing pores of given shape and volume fraction, $\Phi$, is given by
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\[
\frac{k}{k_s} = 1 - \sum_i H_i \left( k_p / k_s, \Phi, \text{pore morphology} \right) \tag{Eq. 2.7}
\]

where the summation of all pores within the coating is influenced by the tensor \(H_i\) of the \(i\)th pore group, the effective pore conductivity \(k_p\), which is considered as negligible for nanosized pores in EB-PVD TBCs (see Appendix A1), and the bulk material conductivity \(k_s\). It is important to notice that the prior used term to define the thermal conductivity, \(\lambda\), is changed into \(k\) in the thermal conductivity approximation. Shape and size of pores within real materials (EB-PVD TBCs) are generally distributed within certain values. Then, the “pore morphology” is replaced by probabilities densities (Appendix A2). Thus, the tensor \(H_i\) for a spheroidal isolating pore embedded in an infinite matrix with conductivity \(k_s\) (Appendix A3) is derived as

\[
H_i = \frac{V^{\ast(i)}}{V} \left( 1 - \frac{k_p}{k_s} \right) \left[ 1 + \left( \frac{k_p}{k_s} - 1 \right) F(\gamma^{(i)}) \right]^{-1} \left( 1 - n^{(i)} n^{(i)} \right) + \left[ 1 + \left( \frac{k_p}{k_s} - 1 \right) \left( 1 - 2 F(\gamma^{(i)}) \right) \right]^{-1} n^{(i)} n^{(i)} \right) \right]
\tag{Eq. 2.8}

where \(I\) is the unit tensor, \(n^{(i)}\) is the unit vector along the axis of symmetry for the \(i\)th spheroid, \(n^{(i)} n^{(i)}\) is the dyadic product of \(n^{(i)}\), \(V\) is the reference volume of the porous medium, and \(V^{\ast(i)}\) and \(\gamma^{(i)}\) are the volume and the aspect ratio of the \(i\)th spheroid. The function \(F[\gamma]\) is a shape parameter (Appendix A3). For spherical pores \(F[\gamma] = 1/3\); in the limit \(\gamma \to 0\) (penny-shaped voids), \(F[\gamma] \to 1/2\); and for \(\gamma \to \infty\) (cylinders), \(F[\gamma] \to \pi/4\). Finally, the combination of Eq. 2.7 and Eq. 2.8 can be used to calculate the overall thermal conductivity of a solid matrix containing non-interacting spheroidal pores of arbitrary aspect ratio, orientation and distribution in EB-PVD TBCs.

Primarily, the overall thermal conductivity of the coating \((k_{coat})\) is related to that of the inter-columnar gaps and the individual columns \((k_{col})\) laying in a parallel arrangement with the thermal flux

\[
\frac{k_{coat}}{k_{col}} = (1 - \Phi_{ie}) \sin^2 \omega \tag{Eq. 2.9}
\]

where \(\Phi_{ie}\) is the volume fraction of the inter-columnar gaps, and \(\omega\) is the angle formed by the gaps axis and the substrate’s plane. Moreover, the voids between feather-arms and intra-columnar pores are considered as aligned spatial and size distributed voids (Appendix A4). In this case this approximation considers three morphologies to characterize these features: oblate, prolate and spheres. For the confined thermal conductivity at the domain where the voids between feather arms \((k_{fa})\) interact with the PYSZ bulk solid material \(k_s\), it is considered to be embedded within a domain containing intra-columnar pores having an overall thermal conductivity, \(k_{ia}\).

For oblate shapes:

\[
\frac{k_{fa}}{k_{ia}} = (1 - \Phi_{fa}) \sin^2 \omega + \left[ 1 - \frac{8}{3} \left( \frac{d}{d_w} \right) \Phi_{fa} \right] \cos^2 \omega \tag{Eq. 2.10}
\]

For prolate shapes:

\[
\frac{k_{fa}}{k_{ia}} = (1 - \Phi_{fa}) \sin^2 \omega + (1 - 2 \Phi_{fa}) \cos^2 \omega \tag{Eq. 2.11}
\]
Additionally, for the case of spherical pores

\[
\frac{k_{fa}}{k_{ia}} = 1 - \frac{3\Phi_{ia}}{2}
\]

(Eq. 2.12)

where \(d\) and \(d_w\) are the diameter and thickness of the ellipsoidal pores, respectively; and \(\Phi\) is the angle between the axial dimension of the pores and the substrate’s plane. The conductivity of the domain containing only intra-columnar pores interacting with the PYSZ bulk material is calculated by the same equations (Eq. 2.10), (Eq. 2.11) and (Eq. 2.12) by changing the denominator \(k_{ia}\) to \(k_s\), which is the thermal conductivity of the bulk material, respectively.

Finally, the value of the thermal conductivity of the columns is related to the gaps between feather arms domain \((k_{fa})\) and intra-columnar pores domain \((k_{ia})\) by their corresponding cross-section area fraction perpendicular to the heat flux in each column \((S_{fa}\) and \(S_{ia}\), respectively)

\[
k_{col} = (k_{fa} \cdot S_{fa}) + (k_{ia} \cdot S_{ia})
\]

(Eq. 2.13)

The cross section area fractions can be calculated by determining the horizontal component of the orthogonal feather-arms length.

### 2.5 Review of the effect of heat treatments on the morphology and thermal conductivity of EB-PVD PYSZ TBCs

Ageing of EB-PVD PYSZ TBCs activates different thermal processes in all their components. The ageing effects enhance the creation of numerous degradation modes such as cracking, erosion, thermo-mechanical fatigue, thermo-chemical reactions, etc., which finally lead to failure (spalling) of the TBC system [129]. Both isothermal and cyclic ageing of these coatings activate diffusion related phenomena, which create thermo-mechanical conditions that induce the failure of the system. Such failure conditions are created principally due the 3D-growth of the TGO during ageing and the thermal expansion coefficient mismatch between the bond coat and the TGO. These thermo-mechanical conditions originate cracks in the BC/TGO interface, which propagate through the TGO within the ceramic top coat producing the delaminations of the coating [50, 130-132]. Zhao et al. demonstrate that delaminations at the TGO/BC interface is enhanced by the strain energy density created in the TGO and TC and controlled by the interfacial fracture toughness of TGO/BC [133]. Moreover, phase destabilization of the PYSZ top coat (TC) is another ageing effect which affects the reliability of these coatings. The meta-stable tetragonal (t’) crystalline phase remains unalterable up to 1200°C [134-136]. Higher temperature ageing induces the decomposition of the t’ phase into a mixture of cubic + tetragonal + monoclinic. The diffusion of Yttrium from the crystal sites of the t’ structure into a rich Yttrium cubic phase destabilizes the remaining unit cells, which transform into monoclinic phase during cooling [96, 129]. The transformation to monoclinic is responsible for the formation of cracks due to the change in volume (3-5%) by the alteration of the lattice parameters [137].

Moreover, significant increase of the erosion rate of EB-PVD PYSZ TBCs after ageing of the coatings was reported by Wellman et al. [138]. Such changes in the erosion rate are created by the binding process between primary columns that enables the cracks, nucleated at the feather arms edges, to propagate into neighboring columns. Such failure processes affecting the reliability of EB-PVD TBCs are beyond the scope of this work.

Furthermore, exposure of EB-PVD PYSZ TBCs to temperatures above 900°C activate the sintering process, leading to morphological changes in all pore types within the ceramic top coat [139]. Since the sintering phenomenon is a thermal activated kinetic process, changes in the microstructure of EB-PVD coatings are directly related to the temperature and time of
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ageing. Fritscher et al. [140] analyzed the sintering behavior of standard EB-PVD PYSZ TBCs by ageing samples at different temperatures and times. BET surface area measurements suggested that the surface area recession during the ageing of EB-PVD TBCs is dominated by the voids between feather-arms. Coatings aged 1 h show that the surface area recession is activated at temperatures \( \geq 900^\circ C \). Additionally, Fritscher et al. [94] suggested that surface diffusion is the dominant diffusion mechanism during annealing of EB-PVD PYSZ TBCs at temperatures 700-1100°C for 100 h.

Mass transfer in inter-columnar pores occurs through bonding between primary columns along their length at prior formed contact points. This effect alters the initial distribution of their extreme enlarged shape and averaged volume fraction. Sintering of these features is enhanced mainly at the bottom (foot) zone of the coating because of the higher concentration of finer columns contacting to each other. The aspect ratio of these large shaped gaps decreases via mass transfer supported by the concave curvatures at the gap edge. Fritscher et al. [141] and Schulz et al. [129] described the increment of stiffness (Young’s modulus) of PYSZ top coats after ageing due to sintering-bonding between inter-columnar gaps [94]. Additionally, inter-columnar sintering creates internal stresses within the TC, which seem to trigger the formation of mud-cracking.

At the same time, significant changes occur at intra-columnar pores and voids between the feather-arms during ageing. Finer dimensioned groups of voids between the feather-arms localized deep into the core of the primary columns disappear completely, breaking up into linear arrays of globular pores. Additionally, coarse sections of these voids localized at the edge of the columns evolve into isolated coarse openings with lower aspect ratio. Moreover, cylindrical high aspect-ratio intra-columnar pores (fine “banana” shaped pores) break-up into polydispersed globular pores (detailed description in Chapter 6). The resulting quasi-equilibrium shape with low aspect ratio of these pores corresponds to the most inefficient pore shape acting as thermal barriers together with cylinders oriented parallel to the heat flux [122, 142]. Thermal conductivity of the coatings increases as a consequence of the thermal induced morphological changes of the porosity, reaching a maximum value after an 1100°C/100h heat treatment [143, 144]. Further ageing at higher temperatures or longer time induce light thermal conductivity changes that are within the uncertainties of the measuring method.

In the case of thermal barrier coatings manufactured by air plasma spray method there is an increment of approx. 50% of the as-sprayed thermal conductivity (~0.8-1.0 W/(mK)) after ageing at 1300°C [145, 146]. Moreover, Ahmaniemi et al. [146] reported that in as-coated conditions segmentation cracks created by laser-glazed in APS TBCs influences the thermal conductivity values depending on the orientation of the created cracks in relation to the heat flux direction. Cracks oriented parallel to the heat flux influence only slightly the thermal conductivity, whereas those crack oriented obliquely display a better efficiency to reduce the thermal conductivity of these coatings.

2.6 Sintering phenomena of EB-PVD PYSZ TBCs

According to the sintering theory of Kingery for solid-state sintering [111], if there are several possible parallel reaction paths likely to occur during a thermal activated process, this will be dominated by the one with the lowest energy barrier being the most rapid and the principal contributor. For the case of materials composed of powders, the sintering diffusion mechanisms governing the thermal activated morphological changes of the pores can be determined via the analysis of the surface area reduction and volume’s shrinkage. Investigations carried out on solid state sintering of 3 mol% \( Y_2O_3-ZrO_2 \) powders in air revealed that three different atomic diffusion mechanisms are in operation. These are referred to as surface, lattice and grain-boundary diffusion [147-149]. The influence of these
mechanisms in the overall sintering process is grouped in three stages. The first stage encompasses predominantly surface diffusion between contacting particles forming a compact. This effect causes the formation of necks between particles, which enhance the atomic diffusion along their length. The second sintering stage comprises the diffusion of vacancies through grain boundaries between attained pores. The tendency of these to disappear or grow depends on the dihedral angle formed between the surrounding grains. Finally, a separation of the pores from the grain boundaries normally occurs due to the differences in diffusivity between these features during the grain growth process. At this third sintering stage, the vacancies move between pores and grain boundaries by lattice diffusion.

Moreover, it can be assumed that the changes in the morphology of the inter-columnar gaps and voids between feather-arms caused by ageing are comparable to the first stage sintering of compacts enclosing particles with analogous morphologies. The magnitude of the sintering force (Laplace stresses) depends on the number of necks along the length of each sintering body as well as on the interface PYSZ-pore surface tension, $\gamma_{sv}$, and the ratios of the necks, $r$. For intra-columnar pores, such changes could be similar to particles or pores within solid bulk materials with non-equilibrium morphologies. Following these assumptions, if there is one single diffusion mechanism governing the surface area changes of the porosity present at the EB-PVD top coats, it may be possible to determine it by measuring the surface area reduction after ageing. The reduction in the surface energy is the driving force for sintering and induces changes in the surface area of pores. This energy modifies the morphology of pores until the lowest surface area is obtained for a corresponding volume resulting in an equilibrium shape [150, 151]. For the as coated EB-PVD top coat, it is evident that the shape of the pores is far from the equilibrium as is shown by the micrographs in Fig. 2.10.

Analysis of the diffusion mechanism governing the shape changes of the porosity could be done by utilizing German’s kinetic equation derived from the Kuczynski’s format which is time-dependant for surface area reduction. This sintering model assumes that powder particles are monodispersed spheres and the limit of applicability is up to $\Delta S/S_0 \approx 50 \%$ [152]. Alternatively, changes in activation energy also deliver information about the occurrence of different sintering mechanisms and can be determined by isothermal ageing of coatings at different temperatures for a constant exposure time and by heating at a constant rate [153, 154]. This analysis was made using a constant heating-rate for the heat treatments in order to minimize experimental problems with shifting in atomic transport mechanisms [153]. Also this model is only valid for the first 50 % of area loss and assumes that a single diffusion mechanism is operative during sintering. In this model based on Arrhenius analysis, the slope of the plot represents the values of $Q/\gamma$, where $\gamma$ is the coefficient corresponding to the relevant sintering mechanism produced by the atomic diffusion and Q is the related activation energy.
3 Resume of the different themes and motivation of the investigation

The general purpose of this work is to gain basic knowledge required for the optimization of the thermal properties of standard PYSZ ceramic top coats of EB-PVD TBCs. The implemented investigation approach contemplates the manufacturing conditions, the characterization of the microstructure and the anisotropic character of the produced coatings, the changes induced by sintering, and the resulting effects on the thermal conductivity. The principal aims of this work are the fundamental understanding of the creation of the porosity principally with the primary columns, the changes induced by sintering on these features, and their effect on the thermal conductivity of EB-PVD coatings. The general purpose of these aims is contemplated in the following partial objectives:

- The characterization of the effect of substrate temperature and rotation speed on the microstructure and thermal conductivity of five manufactured EB-PVD PYSZ TBCs.
- The quantitative geometrical and spatial characterization of the anisotropic porosity created within the manufactured EB-PVD coatings in as-coated conditions, and achieved after ageing.
- The quantitative analysis of the effect of the geometrical and spatial characteristics of the porosity on the thermal conductivity of the EB-PVD coatings in as-coated conditions and after ageing.
- The analysis of the effect of sintering in the porosity of the EB-PVD coatings, and the determination of the governing mass diffusion mechanism responsible for the surface and shape changes of the pores.

The experimental description in Section 4 shows the materials, methods, and conditions employed to manufacture the EB-PVD coatings. This section also contains an exhaustive description of the utilized characterization methods and their measuring principles.

The results in Section 5 display the influence of the process parameters and ageing conditions on the microstructure and the thermal conductivity of the manufactured EB-PVD coatings. SEM micrographs exhibit the interrelation between the process parameters and the resulting microstructure by the manufacture of five different EB-PVD coatings. These were created under different conditions by varying the substrate temperature and rotation speed. USAXS, BET, and SANS measurements confirm the differences between the manufactured coatings. Additionally, USAXS modeling displays the anisotropic characteristics of the pores in three analyzed EB-PVD coatings.

These EB-PVD coatings exhibit a manifest anisotropic character that is created by the rotation movement during the deposition process. This anisotropic effect influences the specific spatial and geometrical characteristics of all pores created in the coatings: inter-columnar gaps, voids between feather-arms, and intra-columnar pores. Additionally, the substrate temperature induces the activation of surface mass diffusion, altering principally the geometry and volume fraction of the porosity. USAXS modeling exhibits the anisotropic nature of the porosity in three analyzed coatings.

Moreover, thermal activated phenomena are of great importance in the reliability of TBCs since these are exposed to high temperatures during the in-service lifetime conditions. Investigations of the effect of the thermal activated sintering phenomenon on the microstructure and surface area of the open (inter-columnar gaps and voids between feather-arms) and closed pores (intra-columnar pores) of EB-PVD coatings were carried out.

Thermal conductivity measurements of coatings in as-coated conditions and after ageing demonstrate the influence of the process parameters and the sintering phenomenon in the
value of this physical property of the five manufactured EB-PVD coatings. A non-interacting approximation is applied to analyze the influence of the spatial and geometrical characteristics of the pores obtained by USAXS modeling in three EB-PVD coatings.

Discussion in Section 6 presents an amplification of the Movchan’s diagram for the microstructures of EB-PVD coatings created at different substrate temperatures and rotation speeds.

The anisotropic character of the different pores in three EB-PVD coatings and their nucleation and growth conditions are discussed in accordance to the obtained USAXS modeling results and SEM micrographs.

Analysis of the sintering phenomenon indicates that surface diffusion is the mass diffusion mechanism governing the surface changes of the pores of EB-PVD coatings. This thermal activated phenomenon modifies the surface of the porosity at low temperature as 900°C. USAXS results and STEM/SEM microstructures indicate the non-spherical shape of the nano-sized intra-columnar pores achieved after ageing at 1100°C/100h.

Results of the non-interacting approximation, thermal conductivity measurements and SEM micrographs exhibit the principal geometrical and spatial characteristics of the porosity governing the thermal conductivity of the analyzed EB-PVD coatings.
4 Experimental description

4.1 Manufacture of the coatings

Thermal barrier coatings manufactured by Electron-Beam Physical Vapor Deposition achieve their characteristic reliability by combining a mixture of specific physical properties from their constitutive features. The materials selection and manufacturing criteria utilized in this work is in accordance with standardized configurations employed in real conditions. There is a patented general procedure for the coating of turbine blades with EB-PVD TBCs composed of metallic bond coat and ceramic top coat [62, 155]:

- Substrate cleaning for removal of oxides, grease, and dirt.
- Bond coat deposition at substrate temperature of 871-982°C.
- Air-blasting of the coated surface for compaction of the bond coat columnar structure.
- Heat treatment at 1080°C for 4h in H₂ atmosphere for re-crystallization and relaxation of the microstructure, and formation of a thin dense α-Al₂O₃ film (TGO) at the surface.
- Deposition of the ceramic top coat.

4.1.1 Materials and physical characteristics of the substrates

Two metallic alloys were employed as substrates for the deposition of the EB-PVD coatings: (1) Inconel IN 718, which is a common Ni-base superalloy, and (2) FeCrAl-alloy that develops a dense TGO film after ageing, and displays an efficient capability to be easily chemical etched when free-standing coatings are required. The chemical composition of these alloys is shown in Table 4.1.

Table 4.1: Chemical composition of the metallic substrates utilized for the manufacture of the coatings (data given by the supplier). Values are given in wt%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Cb</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>Ni</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN 718</td>
<td>0.04</td>
<td>0.20</td>
<td>0.30</td>
<td>18.60</td>
<td>3.10</td>
<td>5.00</td>
<td>18.50</td>
<td>0.90</td>
<td>0.40</td>
<td>BAL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeCrAlloy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.00</td>
<td>-</td>
<td>-</td>
<td>72.80</td>
<td>-</td>
<td>5.00</td>
<td>0.10</td>
<td>0.10</td>
<td>-</td>
</tr>
</tbody>
</table>

Moreover, since the employed analysis methods require specimens in specific geometries, the dimensions of the metallic substrates for the manufacture of the coatings were selected according to this restriction as shown in Table 4.2.

Table 4.2: Geometry of the metallic substrates utilized for the manufacture of the coatings selected in accordance to the used analysis methods.

<table>
<thead>
<tr>
<th>Measuring method</th>
<th>Substrate</th>
<th>Bond Coat</th>
<th>Top Coat</th>
<th>Dimensions (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANS¹</td>
<td>IN 718</td>
<td>NiCoCrAlY</td>
<td>7-8wt% PYSZ</td>
<td>7.0 x 45.0 x 2.5</td>
</tr>
<tr>
<td>BET²</td>
<td>IN 718</td>
<td>NiCoCrAlY</td>
<td>7-8wt% PYSZ</td>
<td>7.0 x 45.0 x 2.5</td>
</tr>
<tr>
<td>USAXS³</td>
<td>IN 718</td>
<td>NiCoCrAlY</td>
<td>7-8wt% PYSZ</td>
<td>7.0 x 45.0 x 2.5</td>
</tr>
<tr>
<td>LFA⁴</td>
<td>FeCrAlloy</td>
<td>-</td>
<td>7-8wt% PYSZ</td>
<td>Ø 12.7 x 0.5</td>
</tr>
</tbody>
</table>

4.1.2 Deposition of the bond coats via EB-PVD process

NiCoCrAlY bond coats were manufactured via EB-PVD process by modified LEYBOLD ESC equipment having 60 kW maximum EB-power (see Fig. 4.1) (detailed description in [69]). This equipment is composed of a three chamber system to load, pre-heat, and coat the substrates. The chambers are separated by load locks and evacuated by diffusion- and turbo-molecular pumps. The IN 718 metallic substrates were polished and subsequently cleaned in an ultrasonic bath of alcohol in order to achieve a clean, impurity-free surface to be coated. After the ultrasonic bath cleaning of the substrates, the substrates were fixed in a four flat-edges rotating holder within the loading-chamber. Sequentially, the pre-heating of the substrates takes place at 950°C in vacuum conditions (10^{-4} \text{ mbar}). These conditions induce cleaning and thermal activation of the surface, improving the adhesion of the bond coat. Afterwards, the deposition process was accomplished at 950°C substrate temperature, and 12 rpm rotation speed of the substrate holder in 10^{-5} \text{ mbar} vacuum conditions. Under these conditions, metallic bond coats with 116 \mu m averaged thickness were deposited under an approx. 8\mu m/min deposition rate. The evaporation source was a $\Theta = 50$ mm ingot with 46Ni-22Co-20Cr-12Al-0.1...0.15Y (values in wt%) chemical composition. Moreover, the deposited microstructure of the bond coats display a open columnar structure containing deep irregularities (inter-columnar gaps), which need to be closed in order to achieve a compact surface required for the homogenous deposition of the ceramic top coatings. Thus, the coated surface of the substrates was smoothed by using 2.5 bar - air blasted Zirshot 210 (210-300 \mu m averaged particle size with: 68wt\% ZrO_2 and 32wt\% glassy phase (SiO_2 + \alpha-Al_2O_3). The compacting process induces deformation of the microstructure developing internal stresses within the crystal lattice. Subsequent annealing process of the substrates at 1080°C/4h in 10^{-5} vacuum conditions relaxes and re-crystallizes the microstructure, whereas a thin thermal grown oxide ($\text{Al}_2\text{O}_3$-TGO) is formed on the surface of the bond coat [156, 157]. The deposition of the ceramic top coat occurs on this formed oxide instead on the substrate, improving the thermo-cycling resistance of the TBC system [45].

![Figure 4.1: EB-PVD 60 kV modified LEYBOLD ESC coater.](image)

4.1.3 Deposition of the top coats using different parameters conditions via EB-PVD process (characteristics and equipment)

Partially Yttria Stabilized Zirconia (PYSZ) top coats were deposited on the previously bond coated metallic substrates via EB-PVD process using a “von Ardenne Anlagentechnik GmbH” 150 kW pilot plant (for more information see [158, 159]) (see Fig. 4.2). This equipment possesses a three-chamber system for an adequate processing of the substrates to be coated similarly to the equipment used for the deposition of the bond coats. The
temperature within the coating-chamber is regulated by the radiation heat from the melted volume at the surface of the ceramic ingot, the chamber walls and the substrate, the reflected high-energy electrons, and the solidification heat of the deposited atoms. Thus, the substrate temperature is only indirectly settable, since it is strongly influenced by these factors that are controlled by the power of the applied electron beam and other process parameters (i.e. thermal isolation of the chamber, etc). The vaporization process at the ingot surface is regulated by the physical properties of the vaporizing source and different process parameters such as electron-beam scanning pattern, focus, electron gun power, etc. Therefore, a refined know-how is required for the stabilization of the established coating conditions during the EB-PVD process.

Figure 4.2: EB-PVD 150 kV von Ardenne Anlagentechnik GmbH pilot plant.

Ni-base substrates previously coated with a NiCoCrAlY bond coat, and disc-shaped FeCrAl-alloys substrates (without bond coat) previously roughened via 2.5 bar - sand blasting were cleaned in an ultrasonic bath. Subsequently, the cleaned substrates were fixed on a six flat-edge rotating horizontal holder aligned perpendicular to the ingot axis. These were homogenously pre-heated to 920-1000°C according to the desired final substrate temperature for approx. 10min. in 1x10⁻⁴ mbar in order to clean and activate the surface to be coated. Subsequently, the substrates were coated under conventional rotating mode [71] at different substrate temperatures and rotation speeds, achieving the coating thickness and deposition rate shown in Table 4.3. The oxygen flow entering into the coating chamber was adjusted to obtain the desired vacuum, and also contain the desired stoichiometry in the coating. Deposition of the PYSZ top coatings was carried out by single source evaporation. The evaporating source material was a 7wt.%Y₂O₃-ZrO₂ ingot (Ø = 63.5mm) provided by Phoenix Transtec (TT, USA).

Table 4.3: EB-PVD process conditions and designation of the manufactured coatings.

<table>
<thead>
<tr>
<th>Coating Microstructures</th>
<th>Chamber Pressure (mbar)</th>
<th>Substrate Temperature (°C)</th>
<th>Rotation Speed (rpm)</th>
<th>Deposition rate (μm/min)</th>
<th>Coating Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Feathery”</td>
<td>8x10⁻³</td>
<td>867 ± 21</td>
<td>30</td>
<td>6.6 ± 0.2</td>
<td>447 ± 13</td>
</tr>
<tr>
<td>“Intermediate”</td>
<td>8x10⁻³</td>
<td>942 ± 23</td>
<td>12</td>
<td>5.6 ± 0.11</td>
<td>374 ± 7</td>
</tr>
<tr>
<td>“Coarse”</td>
<td>8x10⁻³</td>
<td>1003 ± 5</td>
<td>3</td>
<td>6.7 ± 0.2</td>
<td>432 ± 13</td>
</tr>
<tr>
<td>“Fine”</td>
<td>4x10⁻³</td>
<td>850 ± 20</td>
<td>3</td>
<td>5.4 ± 0.16</td>
<td>360 ± 11</td>
</tr>
<tr>
<td>“Parallel”</td>
<td>8x10⁻³</td>
<td>992 ± 4</td>
<td>30</td>
<td>7.4 ± 0.37</td>
<td>371 ± 18</td>
</tr>
</tbody>
</table>
Standard deviations in the coating thickness exhibited in Table 4.3 represent the variations of the coating deposited in all metallic substrates (see Table 4.2) corresponding to each of the five manufactured coating microstructures. Correspondingly, since the coating time is the same for each of the manufactured coatings, deviations in the deposition rate values are directly related to the variations in the measured coating thickness.

The names of the five EB-PVD coatings given in Table 4.3 are related to the resulting columnar structure by applying the annotated process parameters during the coating process. SEM micrographs in Fig. 5.1 show these columnar structures in the cross-section oriented perpendicular to the axis of substrate rotation.

### 4.2 Manufacture of the specimens

Specimens were manufactured according to the configurations and requirements of the employed analysis methods. Thick EB-PVD ceramic top coats are required for the USAXS analysis due to the measurement of the specimens by the x-ray beam interacting with the coatings in the in-plane directions perpendicular and parallel to the axis of substrate rotation (details given in Section 4.3.1.2). This method utilizes a micrometer size x-ray beam, which must interact only with the ceramic top coat. The thickness of the specimens utilized for the characterization of the coatings with all used methods was adapted to this requirement.

Moreover, during the EB-PVD process using single source evaporation, a slight gradient in the vapor cloud density along the substrate holder is created. Therefore, in order to reduce the uncertainties between the manufactured coatings due to this effect, substrates located in similar holder position during the coating process were selected for the preparation of the specimens to compare the values of the measured physical properties.

#### 4.2.1 Specimens for thermal conductivity measurements

The thermal conductivity of the coatings was indirectly determined based on their thermal diffusivity ($\alpha$) measured by LFA-method according to Eq. 4.11. A free-standing condition is the best accurate specimen configuration that minimizes the uncertainties for thermal diffusivity measurements of EB-PVD coatings. Thermal diffusivity measurements of coatings attached to the metallic bond coat/substrate delivers significant errors on the obtained values that can be originated by micro-delaminations of the top coat after heat treatments [160], and by thin top coat/thick substrate configurations [161, 162]. In this case, free-standing specimens were obtained by etching out the disc shaped FeCrAl-alloys substrates via immersion in acid solution. For each of the five manufactured coating microstructures, the free-standing specimens were isothermally heat treated at 1100°C for 1h and 100h, respectively. The “free” conditions of these coatings eliminate the thermal stresses at the bottom of the ceramic top coat caused predominantly by the mismatch in coefficients of thermal expansion between the metallic substrate and the formed TGO; however, those between the ceramic top coat and the TGO still remain present [15]. This stress release affects mainly the sintering behavior of the inter-columnar gaps at the bottom of the coatings by controlling the spacing (contact points) between primary columns. Nonetheless, these gaps are considered to influence only slightly the overall thermal conductivity of the coatings.

Finally, the free-standing coatings were additionally coated on both sides with a thin Pt film to avoid penetration of the laser beam during the LFA measurements. These films were deposited using a “von Ardenne Anlagentechnik GmbH” LA 250S Magnetron-sputter instrument (detailed description is given in [163]). The working voltage is optionally obtained via 600W-AC high-frequency generator or 1500W-DC generator. The substrate holder is
fixed in the middle of the coating-chamber. This can be angular positioned along their rotation axis or constantly rotated. The substrates can be additionally cleaned within the isolated coating-chamber by high-frequency sputter-etching. In this work, the free-standing top coats, previously cleaned in an ultrasonic-bath in alcohol, were fixed on a rectangular flat holder and sputter-etched in order to activate the surfaces to be coated. The coating process took place in stationary conditions at 6.7x10^{-3} mbar partial pressure using 270W-DC generator power achieving a 4-5 μm thickness film.

4.2.2 Specimens for SANS-BET measurements

In this case, free-standing top coats were obtained by etching out the NiCoCrAlY bond coats of rectangular shaped Ni-base substrates via immersion in acid solution. The corresponding BET and SANS specimens were also heat treated in a free-standing condition, which encloses the issues discussed at Section 4.2.1. The information obtained by employing these methods corresponds mainly to the voids between feather arms and intra-columnar pores for BET and SANS, respectively. Therefore, since the “free” condition of the coatings affects mainly the sintering of the intra-columnar pores, it is expected that such a configuration affects the results obtained only slightly. The BET method requires this free-standing configuration of the specimens to be analyzed since it takes in account the volume of the complete material to determine its surface area. Moreover, the SANS measurements were carried out using the neutron beam aligned perpendicular to the substrate’s plane (parallel to the columns axis). Thus, specimens in free-standing conditions are required due to the interaction of the radiation with the coatings in a transmission configuration. Also in this case, the free-standing coatings contain a thin TGO film at the bottom zone which is considered to have no influence on the measured values according to its volume fraction compared with the top coat, and the similar scattering length density in the case of SANS.

4.2.3 Specimens for USAXS measurements

USAXS specimens were obtained from coatings deposited on rectangular shaped Ni-base substrates. In this case, the x-ray beam interacts with the specimens in the cross section parallel to the substrate’s plane in a transmission configuration. Since the distribution of the porosity is anisotropic in this in-plane coordinate-system, two specimens oriented perpendicular and parallel to the axis of substrate rotation were cut from the coated substrates. USAXS specimens were cut and polished up to 200 μm thickness from coatings in as-coated conditions and after isothermal ageing at 1100°C/100h (see Fig. 4.3); the dimensioning of the specimens is in accordance to the utilized beam energy (16.9 keV) to obtain a representative transmitted x-ray flux within reasonable measuring times.

![Figure 4.3: Preparation and dimensioning of the USAXS specimens.](image-url)
4.3 Methods of characterization

Measurements of the thermal conductivity of coatings in as-coated and aged conditions were done by the laser flash method (LFA). This technique provides clear reproducibility and accuracy advantages compared with the direct thermal conductivity measuring methods. Accordingly, the characterization of the pores within the corresponding coatings in as-coated and aged conditions was done by small-angle neutron scattering (SANS) - Brunauer-Emmett-Teller (BET), and ultrasmall-angle x-ray scattering (USAXS). The pores surface area subtended to the plane perpendicular to the heat flux was calculated via SANS - BET methods and the stereometric characteristics of three selected coatings were determined via USAXS.

4.3.1 Characterization of the porosity

Due to limits in accessibility to the open and closed pores, differences in size, high aspect ratio shape and anisotropic distribution of the different pores in EB-PVD TBCs, it is necessary to employ adequate techniques which are suitable to quantitatively determine the spatial and geometrical characteristics of these pores. Use of innovative radiation techniques has been reported for the statistically quantification of representative features comprising the microstructures of heterogeneous materials [164-169]. These methods are based on the transmission/scattering of x-rays or neutrons through the coatings. SANS and SAXS techniques represent an alternative to the gas adsorption methods, with some advantages like sensitivity to both closed and open porosity, and in many cases offer a more complete analysis of the measured porosity [170]. SANS has been applied to study the processing-microstructure relations and sintering on plasma sprayed coatings (APS) [171-176]. Particularly, the studies focused on the characterization of voids in a porous material derived from the terminal slope of a Porod scattering SANS spectra [177] yields quantitative information on the corresponding interfacial surface area of pores. In this technique, the fine features in the microstructures are the major contributors to the deduced surface area [174]. Therefore, it is important to establish the minimum size of the scatterers present in the sample in order to ascertain the origin of the scattered apparent Porod surface which dominates the measured intensities. Porod scattering technique does not require a void shape model, which makes this technique especially useful for studies of void systems with complex shapes [171]. Since the obtained information from this technique corresponds mainly to closed intra-columnar pores, additional measurements of the open porosity, i.e. primarily gaps between feather arms, were applied via BET measurements [140]. The combination of these analysis techniques yields quantitative data which can be used to analyze differences between coatings manufactured under varied conditions and the induced changes after an ageing process. Furthermore, the complete analysis of the volume fraction and stereometric (geometrical and spatial) characteristics in a feature scale range from a few nanometers up to more than a micrometer can be characterized and quantified via USAXS. Analysis of the stereometric information for each pore population that comprises the anisotropic porosity within EB-PVD TBCs has been successfully determined by USAXS [178]. Thus, the influence of the surface area and the stereometric characteristics of the pores on the thermal conductivity of EB-PVD TBCs can be studied.

In this case, the ability of the methods that determine only the surface area of the measured specimens is not restricted by the pore size range. These are only restricted by the size of the analysing media. Then, BET method is restricted to the size of the utilized N₂ molecules, whereas SANS method is “restricted” by the angstrom-sized wavelength of the neutrons (see Table 4.4).
Table 4.4: Requirements and capabilities of the used analysis methods.

<table>
<thead>
<tr>
<th>Measuring method</th>
<th>Pore-size range</th>
<th>Pore configuration</th>
<th>Pore orientation</th>
<th>Specimen requirement</th>
<th>Pore characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>USAXS-APS (^a)</td>
<td>6 - 5200 nm</td>
<td>Open + closed</td>
<td>3D</td>
<td>Thick on substrate</td>
<td>Spatial and geometrical</td>
</tr>
<tr>
<td>BET</td>
<td>&gt; 0.45 nm</td>
<td>Open</td>
<td>-</td>
<td>Free-standing</td>
<td>Surface area</td>
</tr>
<tr>
<td>SANS-IPNS (^b) (Porod)</td>
<td>&gt; 0.10 nm</td>
<td>Open + closed</td>
<td>2D</td>
<td>Free-standing</td>
<td>Surface area</td>
</tr>
<tr>
<td>SANS-HMI (^c) (Porod)</td>
<td>&gt; 0.61 nm</td>
<td>Open + closed</td>
<td>2D</td>
<td>Free-standing</td>
<td>Surface area + distribution</td>
</tr>
</tbody>
</table>

\(^a\) APS: Advanced photon source facilities in Argonne National Lab., Illinois, USA.

\(^b\) IPNS: Intense pulsed neutron source facilities in Argonne National Lab., Illinois, USA.

\(^c\) HMI: Hahn-Meitner Institute in Berlin Neutron Scattering Center, Germany.

4.3.1.1 Microscopy

The microstructures were visually characterized by using a Field-Emission Scanning Electron Microscope (FE-SEM, LEITZ LEO 982) and Transmission Electron Microscope (Philips EM 430). Since the columnar structure of the EB-PVD coatings enclose an anisotropic distribution of their porosity, special attention must be taken by preparing the corresponding cross-sections. The anisotropy of the pores (inter-columnar gaps and voids between feather arms, and intra-columnar pores, respectively) is principally related to the directions parallel or perpendicular to the axis of substrate rotation (see Fig. 2.12). Therefore, cross-sections aligned to these two orientations were prepared for all studied microstructures.

4.3.1.2 Ultrasmall-Angle X-rays Scattering

Atomic-scale information obtained from crystalline materials through diffraction techniques is based on the Brag law, \( d = \frac{\lambda}{2 \cdot \sin \theta} \) (\( \lambda \) is the x-rays’ wavelength). In a diffraction experiment, it supports a minimum measured size of \( \frac{\lambda}{2} \), and predicts that information from nano to colloidal-size structures can be seen at \( 2\theta \leq 6^\circ \) in the diffractometer trace. The characteristics of the features within materials at these larger-sized scales are basically different from those at atomic scales. The spatial and geometrical characteristics of the features at atomic scale are characterized by high degrees of order (crystals), formed by simple-shaped atoms. However, complex shapes and distributions are typical on the nano-scale structures. Thus, the resulting features are sharp diffraction peaks in the x-ray diffraction range (XRD) and comparatively diffuse patterns in the small-angle scattering (SAS) range. In the 1930’s Guinier [179] realized that important structural information in form of diffuse scattering was carried in the neighboring zones of a diffracted x-ray primary beam. Later on in the 1950’s, Gunier and Fournet [180] discovered that the detected diffuse patterns not only contain information on the size and shape of the scattering features, but also on the structure of ordered and partially ordered systems. In addition, Porod [181, 182] found that the surface area from sharp interfaces between two phases enclosing different scattering length densities (e.g. pores in solid materials) could be determined.
EB-PVD TBC specimens in as-coated and aged conditions attached to the substrate (1100°C/100h) were measured at 16.9 keV in the 1D USAXS-instrument at the UNICAT sector 33 of the Advanced Photon Source in Argonne National Laboratory, Illinois (USA) (detailed information in [183]). This instrument utilizes the advantages of Bonse-Hart double-crystal diffraction optics [184] to extend the range of the scattering vector $Q$ ($Q = (4\pi/\lambda)(\sin \theta)$), where $\lambda$ is the wavelength of the incident x-ray and 2$\theta$ is the scattering angle) to noticeably lower values ($1.2 \times 10^{-4} \text{Å}^{-1} < |Q| < 0.1 \text{Å}^{-1}$). This configuration decouples the resolution of the instrument from the primary beam size. This enables the analysis of scattering elements at significantly larger scales according to the relation $D = (2\pi/Q)$, where $D$ is the mean open dimension of the scatterers.

After the monochromator (photon energy selection) and the mirrors (harmonic energy selection), the pair Si (111)-crystals at the collimator and analyzer are channel-cut allowing the selection of two, four, six or eight reflections each by placing the x-ray beam in the appropriate horizontal position of the collimator or by adjusting the gap between the crystals of the analyzer, respectively. The number of reflections in the collimator and the analyzer can be selected for high flux (two or four reflections) or high resolution and sensitivity (six or eight reflections) (see Fig. 4.4).

Figure 4.4: Bonse-Hart geometry for USANS and USAXS measurements.

Moreover, to obtain the required low values of the scattering angle, an extremely well-collimated x-ray beam is needed. This is achieved by the use of extremely-small pinhole diameters for the collimation process, which also causes an important reduction of the primary beam intensity (flux). Thus, only a small fraction of the radiation emitted by the source is capable to interact with the samples and generate a scattered beam flux. Hence, the measuring process would require long time to achieve an acceptable level of the detected signal. To overcome this difficulty, the use of a collimating slit system is used. The Bonse-Hart configuration uses a horizontal slit collimating system which can be thought as an array of singular pinholes tightly spaced along a straight line. As a result, the primary beam flux passing through the sample is clearly many times the flux from a single pinhole. The smearing of the scattered beam in the vertical direction can be overcome by moving the detector in the vertical direction. However, spread of the beam in the horizontal direction occurs due to the orientation of the collimating slit (slit-smearing) (see Fig. 4.6a). For isotropic microstructures, the required de-smearing of the USAXS raw data is numerically attainable by well established methods [185].

In contrast, the utilized USAXS-instrument in this work overcomes this slit-smearing effect by adding two horizontally diffracting crystals, which collimate the primary and scattered beam also in the horizontal direction providing an effective pinhole-collimated USAXS-beam (see Fig. 4.6b). Thus, measurements of anisotropic microstructures such as EB-PVD TBCs...
can be achieved. This effective-pinhole configuration allows the measurement of the scattering vector \( Q \) in one direction (1D) within the plane of the coating. Therefore, to determine the 2D distribution of the scattering intensities, rotation of the specimens in small increments around the beam axis in an azimuthal angle \( \alpha \) is required. To obtain the complete characterization of spatial and geometrical anisotropic microstructures such as EB-PVD TBCs, two measuring methods are usually employed: (1) the scattering intensity, \( I(Q) \), is measured as function of the azimuthal angle \( \alpha \) for a constant \( Q \) value (aniso-scans) (see Fig. 4.5); hence, the principal scattering intensities (max. and min.) and their respective \( \alpha \) values are determined, (2) the scattering intensity \( (I(Q)) \) is measured as function of \( Q \) at the principal \( \alpha \) values. By combining the results of these methods, a quantitative mapping of the microstructural anisotropy as function of the pores size can be done [183]. Since the analyzed coatings enclose anisotropic stereometric characteristics at the azimuthal and polar spatial domains, each specimen was measured at two orthogonal directions perpendicular and parallel to the axis of substrate rotation, respectively. Five aniso-scans at different fixed \( Q \)-values were done, which allowed the characterization of the complete size range of the pores within the coatings. Additionally, the scattering intensity at important anisotropic azimuthal orientations was measured.

**Figure 4.5**: Schematic of the rotation of the EB-PVD PYSZ TBCs during the USAXS measurements to obtain the aniso-scans at different scattering vector values, e.g. \( Q = 0.00150 \text{ nm}^{-1} \) (scattering intensity vs. azimuthal angle).

The arrangement of pores in EB-PVD TBCs can be assumed as an ideal two-phase configuration in a dilute particulate system. These materials contain only two phases with constant scattering length density each. The interface between these two regions is sharp with no measurable thickness, and the concentration of the pores is assumed to be sufficient dilute with no long-range correlation between them. Thus, under these conditions the x-rays
scattered from different pores are incoherent among them, and the obtained scattering intensities represent the sum of the individual scattering. By assuming or independently calculating the shape of the scattering pores ($F(Q)$), the scattering intensity from individual pores can be calculated and compared with the measurements through a computer-based model. Moreover, if the shape of the pores is unknown or with irregular shape, measured scattering intensities may be analyzed according to the Guinier law [180] to determine the radius of gyration, characterizing the shape of the pores.

Figure 4.6: Schematics of a Bonse-Hart USAXS-instrument: (a) side view of a slit-smeared primary beam collimation. For the incident beam, the crystal monolith at the analyzer can be rotated by a scattering angle ($\phi_s$) out of the Bragg condition to record the measuring data at the photodiode as function of $Q$ (downwards and approximately in the sample plane). The imaging camera is used to accurately place the sample in the centre of the rotating axis. (b) side and top view of an effective pinhole primary beam collimation using side reflecting crystals to remove the slit-smearing effect perpendicular to the $Q$ scanning direction [186]. APS: Advanced photon source facilities.

Statistically representative and quantitative characterization of the spatial and geometrical values of every pore population within EB-PVD TBCs was determined by employing an Igor Pro computer-based modelling-fitting of the obtained USAXS-raw data. The magnitude of the scattered intensity $I(Q)$ is expressed as the differential SAS (small-angle scattering) cross-section per unit sample volume ($d\Sigma/d\Omega$). This relation is defined by the probability per x-ray flux and sample volume to scatter into a unit solid angle $d\Omega = (dx \times dy / L_d^2)$ perceived at a detector element of dimensions $dx \times dy$ positioned at a distance $L_d$. The objective in a SAS experiment is to determine the differential cross-section $d\Sigma/d\Omega$, since it contains the
information on the size, shape and interactions between the scattering elements in the sample. It is represented by the sum of the scattered intensities from each pore population by [178]

$$I(Q) = \frac{d\Sigma}{d\Omega} = \sum_{p} \left[ N_p \frac{d\sigma}{d\Omega} \right]_p$$  \hspace{1cm} (Eq. 4.1)

where $N_p$ is the number density of scattering elements corresponding to a scattering pores population, $p$. The general form of the differential scattering cross-section for a single pore population is given by

$$\frac{d\sigma}{d\Omega} = V_p^2 \left( \Delta \rho \right)^2 F^2(Q) S(Q) + B_{\text{incoherent}}$$  \hspace{1cm} (Eq. 4.2)

where $V_p$ is the volume fraction of a single pore population, $|\Delta \rho|^2$ is the square of the x-ray scattering length densities difference between pores (air) and the PYSZ bulk phase (scattering contrast) $(4.35718 \times 10^{11} \text{ m}^{-2})$, and $B_{\text{incoherent}}$ is the incoherent scattering background. $F^2(Q)$ and $P(Q)$ are the form factor and structure factors, respectively. These factors are functions that describe how $d\sigma/d\Omega$ is modulated by interference effects between radiation scattered by different parts of the same body and by the arrangement between different scattering bodies, respectively. Scattering form factor functions have been already derived for different shapes of scattering elements such as spheroids, rods, discs, networks, etc [187-190]. Moreover, the scattering structure factor function is dependent on the local order, describing spatial correlations that may exist between scattering elements, e.g. monodispersed population of spherically shaped scatterers [191], arrays of parallel cylindrical shaped scatterers [192], or a fractal system [193]. When a population of uniform scattering elements is evenly distributed at high volume concentration (>10%), $P(Q)$ modulates the overall $d\sigma/d\Omega (Q)$ variation, creating a small-angle diffraction interference peak with a maximum at $2\pi/d$, ($d$ is the mean separation distance between neighboring scattering elements in the direction of $Q$) [186].

Since real spatial and geometrical characteristics of every pore population enclose a certain standard deviation, this computer-based model considers Gaussian distributions for the calculations of the orientation and size values. It uses idealized particle shapes for which small-angle scattering can be reasonably well calculated (ellipsoidal oblate and prolate, and spheres), and allows the optimization of the parameters by a least square fitting [194]. The model allows the use of five independent pore populations composed of individual spheroidal shapes with $R_0$, $R_0$ and $\beta R_0$ axes. In the employed coordinate system the x axis, and y and z axes lay perpendicular (parallel to the columns axis) and parallel to the substrate’s plane, respectively (see Fig. 4.7). Furthermore, the orientation of the pores in the space is described by its $\beta R_0$ axis with respect to the coordinate system by two independent angles $\alpha$ (azimuthal angle) and $\omega$ (polar angle). An anisotropic orientation model is assumed to the solution of the differential scattering cross-section as function of the orientation for each scattering pore population by [178]

$$\frac{d\sigma}{d\Omega} = \int_0^{2\pi} d\alpha \int_0^{\pi/2} d\omega \left( P(\alpha, \omega) \frac{d\sigma(Q, \alpha, \omega)}{d\Omega} \sin \alpha \right)$$  \hspace{1cm} (Eq. 4.3)
This equation relates the orientation probability of the differential scattering cross-section to that of randomly oriented spheroids. As an approximation, it is assumed that \( \alpha \) and \( \omega \) are independent and the probability of finding a pore oriented in any particular direction can be described satisfactorily by multiplying their probabilities \( P(\alpha, \omega) = P(\alpha) \cdot P(\omega) \). Two arbitrary formulae provide a suitably way to optimize \( P(\alpha) \) and \( P(\omega) \) (Eq. 4.4 and Eq. 4.5). These are capable to have a component peaked in any particular orientation with the option to change the width of the peak.

\[
P(\alpha) = C_1 (A_1 \cos(\alpha - A_2) + A_3)
\]

(Eq. 4.4)

\[
P(\omega) = C_2 \left( B_1 \cos\left(\frac{\omega - B_2}{2}\right) + B_3\right)
\]

(Eq. 4.5)

where \( A_2 \) and \( B_2 \) are the values of the azimuthal (\( \alpha \)) and polar (\( \omega \)) angles corresponding to the spatial orientation of the \( \beta R_0 \) pores axis. \( A_1 \) and \( B_1 \) are related to the distribution of the \( \alpha \) and \( \omega \) functions, respectively. \( A_3 \) and \( B_3 \) are the backgrounds of the \( \alpha \) and \( \omega \) probability orientation functions \( P(\alpha) \) and \( P(\omega) \). For a given \( A_1 \), \( A_2 \) and \( B_1 \), \( B_2 \) the functions \( P(\alpha) \) and \( P(\omega) \) are normalized using \( C_1 \) and \( C_2 \). Note that both functions \( P(\alpha) \) and \( P(\omega) \) have to normalize to 1 when they are integrated over \( \alpha \) at 0-180° and \( \omega \) at 0-360°, respectively.

Figure 4.7: Definition of the coordinate system used for the spatial orientation of the pores within the EB-PVD coatings.

4.3.1.3 Small-Angle Neutron Scattering

Neutrons can be obtained from a nuclear reactor and in synchrotron radiation facilities (spallation neutron source). For the production of neutrons in a synchrotron facility, high-energy protons are directed and crashed against a target (e.g. tantalum base). The incident protons blast the target nuclei apart releasing a certain amount of neutrons per incident proton. Nuclear reactors produce neutr ons through the fission of uranium-235. Since this reaction releases neutrons in sufficient quantities required for worthwhile experiments, this characteristic makes this technique the most usable method for neutron production. Neutrons are basically used to study the physics of components of matter and their fundamental interactions. In the case of SANS, this technique utilizes the interaction of neutrons with heterogeneities in matter. An incident neutron beam is scattered at the interfaces between
Experimental description

these heterogeneities and the matrix within the analyzed body. The scattered radiation is collected in a detector for its subsequent analysis. SANS instruments can be configured to measure the scattering intensities at different scattering vector values \( I(Q) \) by using mono- or polychromatic neutron wavelengths: steady-state or pulsed source (time-of-flight), respectively. A steady-state source is usually employed to obtain the \( I(Q) \) curves by scanning the scattering angle using a pre-selected constant wavelength. This is achieved via positioning the detector at different sample-to-detector distances. Moreover, pulsed sources use a fixed geometric configuration (constant sample-to-detector distance; thus constant \( \theta \)), measuring at time-sorting different wavelength values from a polychromatic incident beam. Steady-state source instruments are normally used when the \( Q \)-range (size range of the scattering elements) is known, allowing the optimization of the count rate by utilizing a wavelength close to the peak of the flux distribution. Moreover, pulsed source instruments are ideal for analyzing microstructures where a range of length scales are involved, or even when they are uncertain. These instruments have a greater dynamic \( Q \)-range than the steady-state sources. In SANS measurements, the size of the primary incident beam is regulated by pinhole collimation, which is directly proportional to the neutron flux. For this reason it is important to set up an adequate last collimation of the beam (size), in order that SANS-measurements can be completed within reasonable measuring times. This is important for materials with small dimensions and anisotropic microstructures, which must be analyzed at their three orthogonal directions (3D) to be completely characterized (e.g. EB-PVD coatings). In this case, the specimens were placed in a sample holder by using an intermediate Cadmium Mask with a circular slit during the measurements. Through this configuration, the slit size directly determines the size of the neutron beam interacting with the specimens. The primary neutron beam is targeted perpendicular to the substrate’s plane (parallel to the column axes) in transmission geometry (see Fig. 4.8).

\[
I(Q)_{Q \to a} = \frac{dS}{dQ_{Q \to a}} = \frac{2\pi|\Delta \rho|^2 S_v}{Q^4} + BGD
\]  
(Eq. 4.6)

**Figure 4.8:** Schematic of instrument-specimen transmission geometry configurations for SANS and SAXS measurements with a 2D detector.

At high values of the scattering vector \( Q \), the terminal slope of the \( I(Q) \) graphic becomes proportional to the interfacial surface area \( (S_v) \) between the scattering elements and the matrix per unit of measured volume, regardless of the scattering elements morphologies. This relation is represented by the Porod scattering law [181, 188]:

![Diagram of instrument-specimen transmission geometry configurations for SANS and SAXS measurements with a 2D detector.](image-url)
where $BGD$ is the background parasitic scattering. The scattering intensity, $I(Q)$, is a function of the magnitude and direction of the scattering vector $Q$. Therefore, for anisotropic microstructures it is necessary to carry out an orientational averaged analysis over all solid angles (3D) in order to calculate the overall value of the interfacial surface area. The values of $S_v$ and $BGD$ can be obtained by determining the intercept and slope of a $I(Q)\cdot Q^4$ vs. $Q^4$ graphic [173]. The intercept of this graphic represents the value of the Porod Constant ($P_c$) which is related to the surface area ($S_v$) by [195, 196]

$$S_v = \frac{P_c}{2\pi|\Delta \rho|^2} \quad \text{(Eq. 4.7)}$$

where $\Delta \rho$ is the difference in scattering length densities between the pores and the PYSZ bulk material. In this method, the measured Porod scattering intensity $I(Q)$ is linearly proportional to the interfacial surface area projection in a plane perpendicular to the scattering vector $Q$, corresponding to dimensions measured parallel to it [177, 197]. In view of the fact that the Porod scattering measured in one direction does not reflect the total surface area of the scatters but yields a projection in the plane perpendicular to the scattering vector $Q$, it is often called Apparent Porod Surface Area (APSA), which can be calculated from its corresponding Porod constant by Eq. 4.7. The total specific area of the scatterers within the sample can be obtained from the apparent Porod constant by averaging over all 3D-directions in the material [198]. However, this apparent surface area is useful to analyze microstructural changes between samples by measuring them under the same conditions. The Fig. 4.9 shows the types of information to obtain at different zones in a $I(Q)$ vs. $Q$ graphic.

![Figure 4.9](image-url)

**Figure 4.9:** Typical absolute-calibrated $I(Q)$ vs. $Q$ graphic showing the generic information obtainable through the application of respective models.

EB-PVD TBC free-standing specimens in as-coated and aged conditions (900°C-1400°C/1hr and 1100°C/20min, 1h, 3h, 10h, 100h) were measured at the time-of-flight (pulsed) Small-Angle Neutron Diffractometer (SAND) of the Intense Pulsed Neutron Source in Argonne National Laboratory, Illinois (USA) (detailed description in [199]). Since the primary neutron beam was targeted perpendicular to the substrate’s plane (parallel to the columns axes) in transmission geometry (see Fig. 4.8), it was required to have the specimens in free-standing conditions to avoid measurement of entities different from the EB-PVD TBC top coat. In this case, the two-dimensionally distributed APSA-values in the plane perpendicular to the substrate plane were averaged over the analyzed azimuthal angle ($\alpha$). The information
obtained from these SANS-measurements was used to characterize the atomic diffusion mechanism governing the sintering process of pores in EB-PVD TBCs at high temperatures. The reduction of the surface area of pores within solid materials aged at high temperature conditions is recognized as the driving force for sintering [111]. Small-angle neutron scattering has been employed to study the sintering of ceramics [187, 191, 193, 200-203]. Particularly, studies focused on measurements of Porod scattering, which are derived from the terminal slope in SANS spectra, yields quantitative information of the interfacial surface area. This technique does not require a void shape model, which makes it appropriated for the study of systems with complex-shape voids. Although this method is sensitive to open and closed pores, the obtained surface area values are primarily sensitive to the smallest pores within the analyzed materials (larger surface-to-volume ratios). In our case it reflects principally the surface area of the nanometer-sized intra-columnar pores (closed porosity).

Furthermore, additional EB-PVD specimens in as-coated and aged conditions (1100°C/1h and 100h) conditions were characterized by this technique at the SANS instrument V4 of the Berlin Neutron Scattering Center (BENSC) in the Hahn-Meitner Institute (for detailed information see [204]) to determine the value and the anisotropic distribution of the apparent Porod surface area. The corresponding specimens were also measured in free-standing conditions by targeting the primary neutron beam perpendicular to the substrate’s plane (parallel to the column axis) in transmission geometry (see Fig. 4.8) over two-sample detector distances: 1m and 4m, employing a $\lambda = 0.605$ nm neutron wavelength. During the measurements, the specimens were placed on the sample holder by means of a Cadmium mask with a circular slit of 6 mm diameter. The obtained results were corrected due to uncertainties from background scattering, transmission and detector efficiency; and normalized to absolute units by using water as calibration standard procedure. Quantitative information of the surface area corresponding to the intra-columnar pores was achieved in the form of the corresponding Porod Constant ($P_c$) as a function of the azimuthal angle by converting the 2D data to 1D scattering profiles averaged over $5^\circ$.

### 4.3.1.4 Brunauer-Emmett-Teller Method

This method employs the physical adsorption of gas (e.g. N$_2$) at the surface of a porous material to measure its surface area / mass relation (m$^2$/g) (see Fig. 4.10). The adsorption process does not have activation’s barrier, it is a reversible process activated through Van der Waal attraction forces and its potential energy ($E_p$) depends only on the distance between the gas molecules and the analyzed surface. For its practical application the following assumptions are taken into account:

- Adsorption takes place on the surface lattice and molecules remain fixed at their first occupied position.
- The first monolayer is adsorbed onto the solid surface and each layer can start forming before another is finished.
- Except for the first layer, a molecule can be adsorbed on a given site in a layer ($n$) if the same site also exist in the ($n-1$) layer, at saturation pressure ($P_0$), the number of adsorbed layers is infinite (i.e. condensation).
- Except for the first layer, the adsorption enthalpy ($H_L$) is identical for each layer.

During the measurements, the specimens are isothermally heated and several ($P/P_0$) vs. ($P/n(P_0-P)$) points are measured. The next equation is used to evaluate the BET-isotherm:
\[ \frac{P}{n(P_0 - P)} = \frac{1}{n_m \cdot C} + \frac{(C - 1) P}{n_m \cdot C P_0} \]  

(Eq. 4.8)

where \( n \) is the amount of gas adsorbed at the pressure \( P \), \( n_m \) is the amount of gas in a monolayer, \( P_0 \) is the saturation’s pressure, and \( C = \exp \left( -(H_1-H_L)/(RT) \right) \), where \( H_1 \) and \( H_L \) are the adsorption enthalpy of the first and subsequent layers. The values of \( C \) and \( n_m \) are evaluated from the slope \((c-1/n_mC)\) and the intercept \( (1/n_mC)\) of the isotherm plot usually obtained for \( P/P_0 < 0.2 \) (linearity range), respectively. Thus, the BET-surface area \( (S_{BET}) \) is given by [205]

\[ S_{BET} = \frac{n_m \cdot \sigma \cdot N_L}{n_o \cdot m} \]  

(Eq. 4.9)

where \( \sigma \) is the molecular cross-section (for \( N_2, \sigma = 0.162 \) \( \text{nm}^2/\text{mol} \)), \( N_L \) is the Avogadro’s number, \( n_o \) is the ideal gases volume \( (n_o = 22.41 \text{ l}) \), and \( m \) is the sample mass.

Isothermal heated (300°C) EB-PVD specimens in as-coated and aged conditions were measured in an Accelerated Surface Area Porosimeter System instrument (ASAP 2010) by using \( N_2 \) as analysis gas. The isothermal heating of the specimens eliminates the humidity attached to the surface area of the specimens. In the case of EB-PVD coatings, this technique mainly describes the characteristics of the voids between feather arms due to their evidently higher surface area fraction [140].

Figure 4.10: Schematic of the BET-measurement principles. (a) Section of an enlarged solid, (b) adsorbed \( N_2 \) molecules forming a monolayer (approx. 30% saturation), and (c) total pore volume filling (approx. 100% saturation).

4.3.1.5 Archimedes Method

The hydrostatic weighing technique based on the Archimedes principle was used for the calculations of the bulk density. This method requires that the specimens are measured in different conditions: dried, soaked, and suspended in water. Theoretically, the specimens should be boiled for two hours to replace the air into the open pores by water. However, since the free-standing EB-PVD coatings are extremely fragile, these were immersed in de-ionized water for 72 hours with slight periodic agitation allowing a better penetration of the water into the open porosity of the specimens. Specimens were weighed in suspended conditions in de-ionized water \( (W_{wi}) \). Additionally, the specimens were weighed in soaked conditions \( (W_s) \) by
taking the samples out of the water and removing the excess of water at the surface by using the edge of a filter paper. Finally, the specimens were dried in an air oven at 120°C and weighed in dried conditions \( (W_d) \). The measurements of the different specimen conditions enclose an standard deviation of ± 0.35% based on the average of ten repetitions. The bulk volume is the combined volume of solid material and closed and open porosity [206]:

\[
\text{Bulk Volume} = \left( \frac{W_d - W_{iw}}{\rho} + \frac{W_s - W_d}{\rho} \right) = \frac{W_s - W_{iw}}{\rho} \quad \text{(Eq. 4.10)}
\]

where \( \rho \) is the density of the immersion liquid that in this case is de-ionized water, 1 g/cm³. Then, the corresponding bulk density is given by:

\[
\text{Bulk Density} = \frac{W_d \cdot \rho}{W_s - W_{iw}} \quad \text{(Eq. 4.11)}
\]

Errors can be induced by the temperature dependence of the immersion liquid density, variations in the deep level during the in-water weighing, and air bubbles in the specimen.

### 4.3.2 Measurements of the thermal conductivity

There are direct and indirect methods to measure the thermal conductivity of solid materials. Laser Flash Analysis method is an indirect ASTM standard method (E1461) that provides some important advantages compared with the direct measurement of the thermal conductivity. It requires easier specimen forms and shorter measuring times; it has good reproducibility and accuracy; and it is usable over an extremely large range of diffusivity values and measurement temperatures compared with the direct thermal conductivity measuring methods (e.g. 3-omega and photo-acoustic techniques). Over one-half of the conductivities measured in the world since 1980 have been obtained by this technique [162].

#### 4.3.2.1 Laser Flash Analysis Method (LFA)

The thermal conductivity (\( \lambda \)) of the coatings was calculated indirectly by measuring the thermal diffusivity (\( \alpha \)) via Laser Flash Analysis Method (LFA) employing a Netzsch - LFA 427 equipment and using the relation

\[
\lambda = \alpha \cdot \rho \cdot C_p \quad \text{(Eq. 4.12)}
\]

where in this case, \( \rho \) represents the bulk density of the free-standing coating measured by the Archimedes Method, and \( C_p \) is the specific heat measured by Differential Scanning Calorimeter (DSC). The values of the \( C_p \) vs. \( T \) curve were taken from Krell [207]. These were obtained from DSC measurements of heat-treated 7-8 wt% PYSZ pellets (free of internal stresses) by using a Netzsch-DSC 404 apparatus. The standard deviation in this method varies between 3-5% according to the manufacturer. The acquired data are in good agreement with those corresponding to a material of the same chemical composition proposed by Touloukian [208] and Raghavan et al. [112] (see Fig. 4.11). Furthermore, the Archimedes Method was used for the calculations of the bulk density.
Figure 4.11: Specific heat of a 8 wt% mass Y2O3 stabilized ZrO2 material according to the measurements of Krell (measured via a Netzsch-DSC 404 apparatus) and the literature by Touloukian.

During the LFA-measurements, the front side of a disc-shaped specimen, positioned in a furnace and heated to a desired temperature, is additionally heated homogeneously through the adsorption of radiation energy from a short and high-energized laser impulse (irradiation times are typically less than 1 ms). The heat generated at the front surface fluxes through the material thickness, principally in form of phonons, to the rear side of the specimen producing a maximum temperature change ($\Delta T$) (typically about 1°C) measured by an IR-detector within a certain time ($t$) (see Fig. 4.12).

The heat balance equation for transient conditions of a solid material without internal heat sources and sinks may be written as [161]

$$\nabla \lambda \cdot \nabla T = C_p \rho \frac{dT}{dt} \quad \text{(Eq. 4.13)}$$

For homogeneous materials of which the thermal conductivity is nearly independent of temperature for small temperature increments, $\lambda$ may be treated as constant. Then

$$\lambda \nabla^2 T = C_p \rho \frac{dT}{dt} \quad \text{(Eq. 4.14)}$$

where $\alpha = \lambda/C_p \rho$ is the thermal diffusivity. For one-dimensional heat flow

$$\alpha \frac{d^2 T}{dx^2} = \frac{dT}{dt} \quad \text{(Eq. 4.15)}$$
Figure 4.12: Scheme of the thermal diffusivity measurements configuration via laser impulse method by using a Netzsch - LFA 427 Instrument.

During the measurements, the relation ($\Delta T$) vs. ($t$) (see Fig. 4.13a) is influenced by the thermal diffusivity of the specimen, the duration of the laser impulse, and the loss of heat to the periphery by radiation. The mathematical analysis of the temperature gradient ($\Delta T$) evolution vs. the time required to reach its maximum value ($t$) allows the determination of the thermal diffusivity of the specimen. The approximation developed by Parker et al. [209] is used for this analysis by considering the following assumptions:

- Measurements of a homogeneous material exposed to one-dimensional thermal conduction.
- Non-loss of heat by radiation.
- The laser energy is homogeneously adsorbed and distributed at the exposed surface of the specimen.
- The laser impulse duration is shorter compared to the time required for the heat-transport process.

Thus, under adiabatic conditions the following relation is valid

$$\alpha = 0.1388 \frac{l^2}{t_{0.5}} \quad (\text{Eq. 4.16})$$

where $\alpha$ is the thermal diffusivity (cm$^2$/s), $l$ is the specimen’s thickness in (cm), and $t_{0.5}$ is the required time to reach the 50% of the maximum temperature increment at the rear surface.

However, uncertainties in the thermal diffusivity from deviations of the ideal conditions can not be corrected by this relation. Such deviations are:

- **Finite pulse-time effect.** The laser impulse has a determined finite impulse-width. The distribution of its intensity vs. time, normally enclosing a maximum value, influences the distribution of the temperature within the analyzed specimen. Thus, if the laser...
impulse duration is longer compared to the time required to increase the 50% of temperature at the emitting surface, this effect must be corrected.

- **Heat loss by radiation and convention.** A fraction of the energy generated by the laser impulse is emitted to the surroundings through the overall surface of the specimen via radiation and convection, i.e., cooling process. In this case, the heat loss occurs only by radiations since the specimens were measured in vacuum (approx. $5 \times 10^{-4}$ mbar). Under these conditions the temperature at the emitting rear surface will decrease after the maximum temperature state. Then, the one-dimensional thermal conduction is no longer valid and corrections must be applied.

- **Non-uniform heating.** The non-uniform heating of the specimen’s adsorbing surface also produces a non-definable a three-dimensional heat conduction process. This effect results from the wrong setting of the laser, and a non-homogenous and reflecting surface.

- **Radiation transparency.** As PYSZ is a translucent material, visible light is not absorbed within the first atomic layers whereas it is scattered and transmitted to depths of several hundreds of micrometers [117]. Conventional LFA data modeling assumes light to be converted into heat just on the surface of the specimen. Thus, a low emission (opaque) thin Pt layer (4-5 μm) was sputtered on the front and rear surfaces of the specimens prior performing the thermal diffusivity measurements. This avoids the laser beam penetration at the front surface, and prevents the infrared detector from viewing into the sample thickness at the rear surface. Another radiation transparency effect during the LFA measurements at temperatures above approx. 500-600°C is the radiation heat transport additional to conduction, especially in translucent and semi-translucent materials, i.e., PYSZ (see Fig. 4.14). In this case, a direct radiation-interchange between the front and rear surfaces occurs. This effect is visible by an abrupt increase at the beginning of the $\Delta T$ vs. $t$ curve (see Fig. 4.13b). Then, additional factors which take into account this effect should be considered in the data modeling.

![Figure 4.13](image_url)

**Figure 4.13:** Relation ($\Delta T$) vs. ($t$) during the LFA measurements in normal heat conduction conditions (a), and influenced by additional radiation transparency effect (b).

Measurements of free-standing specimens in as-coated conditions and aged at 1100°C for 1h and 100h were carried out. Due to the extreme fragility of the specimens in free-standing conditions, only one specimen per condition was measured. The combined iteration approximation developed by Dusza [210] was used to the fitting of the obtained $\Delta T$ vs. $t$ curves (see Fig. 4.13). This model takes into account the finite pulse-time effect and radiation heat loss to determine the thermal diffusivity. The effect of radiation transparency was not corrected due to the incapability of the used LFA instrument to accomplish this operation. The
analyzed temperature range was 20-1000°C for specimens in as-coated conditions and 20-1200°C for aged specimens. Measurements were applied under vacuum conditions at $5 \times 10^{-4}$ mbar. This configuration eliminates the possibility of heat transfer by convection during the measurements.

Figure 4.14: Effect of the radiation on the thermal conductivity of EB-PVD PYSZ TBCs measured at different temperatures.
5 Results

5.1 Morphology of the five manufactured EB-PVD PYSZ TBCs

Fig. 5.1 shows SEM micrographs of the manufactured EB-PVD PYSZ coatings having morphological differences in their column diameter size and shape. These were produced by altering the process parameters during the EB-PVD coating process according to the data specified in Table 4.3. Variations in the substrate’s temperature and rotation speed influence principally the condensation process of vaporized particles in the growing surfaces of the columns. Specifically, the number of nucleated columns on the previously formed TGO, and the interrelation between the shadowing effect of the columns tips and the diffusion process in the growing surfaces are altered by such modifications.

Figure 5.1: SEM micrographs of the analysed PYSZ EB-PVD-coatings in as-coated conditions displaying cross sections of the top zone (left), and bottom zone (middle) perpendicular to the axis of substrate rotation; and top view (right): “intermediate” (A), “fine” (B), “coarse” (C), “feathery” (D), and “parallel” (E). Axis of substrate rotation is oriented vertically to the top view micrographs (right).
The “intermediate” coatings exhibit a morphology comprised by symmetrically distributed primary columns of about 10 µm diameter at the top region. Feather-arms surrounding the columns core display an elongated shape embedded from the columns edge toward the columns core occupying approx. 1/4 of the columns cross-section (see Fig. 5.1A). The coatings produced by employing lower substrate temperature and rotation speed designated as “fine” exhibit non-symmetrical distribution of the columns with column diameters of approx. 5 µm, as well as very short feather-arms (see Fig. 5.1B). The coatings designated as “coarse”, which was produced by employing higher substrate temperatures combined with slower rotation speed, display a symmetrical arrangement of larger column diameter of around 22 µm and broader inter-columnar gaps. The feather-arms of this morphology show are embedded toward the core of the primary columns occupying approx. 1/7 of their cross-section (see Fig. 5.1C). Moreover, primary columns in “feathery” coatings exhibit approx. 15 µm diameter at the top region. Especially in these coatings, the feather arms features occupy almost 1/2 of the primary columns cross-section (see Fig. 5.1D). Finally, “parallel” coatings exhibit symmetrically distributed primary columns of approx. 9 µm at the top region. The principal characteristics of the manufactured coatings are listed in the Table 5.1.

**Table 5.1:** Principal microstructural characteristics of the manufactured EB-PVD coatings.

<table>
<thead>
<tr>
<th>Coating Microstructures</th>
<th>Bulk Density a (g/cm³)</th>
<th>Total Porosity (%)</th>
<th>Columns Diameter b Top/Bottom c (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Intermediate”</td>
<td>4.37 ± 0.13</td>
<td>27.2</td>
<td>~10 / 2</td>
</tr>
<tr>
<td>“Coarse”</td>
<td>4.65 ± 0.23</td>
<td>22.5</td>
<td>~ 22 / 2.5</td>
</tr>
<tr>
<td>“Fine”</td>
<td>4.50 ± 0.13</td>
<td>25.0</td>
<td>~ 5 / 1.5</td>
</tr>
<tr>
<td>“Feathery”</td>
<td>4.35 ± 0.10</td>
<td>27.5</td>
<td>~ 15 / 1.5</td>
</tr>
<tr>
<td>“Parallel”</td>
<td>4.60 ± 0.004</td>
<td>23.3</td>
<td>~ 9 / 2</td>
</tr>
</tbody>
</table>

a Measured by Archimedes Method.
b Diameter of the columns in the direction perpendicular to axis of substrate rotation.
c Dimensions at 40 µm of coating thickness (total thickness = 400 µm).

**5.2 Effect of the sintering phenomena on the morphology of “intermediate” EB-PVD PYSZ TBCs**

In order to define the governing diffusion mechanism, changes in the surface area (ΔS/S₀) of the different porosity types after isothermal ageing at 1100°C for various holding times (see Fig. 5.2), as well as at different temperatures varying from 900°C to 1400°C for a constant holding time, were measured (see Fig. 5.4). The specimens were analyzed in free-standing condition to avoid measurements of entities different from the TBC top coat. The surface area changes after isothermal ageing were determined via Small-Angle Neutron Scattering method (SANS) mainly for the closed intra-columnar pores, and Brunauer-Emmett-Teller method (BET) principally for the open voids between feather arms.

**Fig. 5.2** shows the surface area recession of intra-columnar pores and voids between feather arms measured by SANS (Porod method) and BET, respectively. According to the surface area fraction remaining in the EB-PVD coatings after different ageing times, it is observed that significant surface area reduction takes place at 1100°C within extremely short periods of
time, i.e. 20 min. Subsequent isothermal ageing induces only slight surface area reduction. Therefore, slight differences in the slope of the graphs corresponding to both measuring methods are perceptible at ageing times exceeding 1h. SEM micrographs in Fig. 5.3 display the cross-section of the coatings in as-coated conditions and after ageing at 1100°C for 1h and 100h.

![Figure 5.2](image_url)

**Figure 5.2**: Surface area reduction of open (measured by BET) and closed pores (calculated by SANS-Porod) during ageing of EB-PVD top coats at 1100°C for various times. Deviations from the calculated values of the surface area using the data fitting process are represented by the vertical bars.

![Figure 5.3](image_url)

**Figure 5.3**: Scanning electron micrographs of the cross sections of the EB-PVD standard top coat displaying the morphological changes in the columnar microstructure in (a) as-coated state and (b) after ageing at 1100°C for 1h and (c) for 100h.
Fig. 5.4 shows the changes in surface area reduction (ΔS/So) as a function of temperature under constant heating rate conditions (5°C/min). The trend of the surface area reduction at the measured temperatures displays an abrupt change at 1100°C/1h. The slope of the data at the right hand section indicates that the surface area changes of the measured pore groups occur rapidly in the temperature range of 900-1100°C. Above 1100°C, the rate of surface area reduction diminishes drastically indicating a change in the driving force and/or the diffusion mechanism for the sintering process. Scanning electron microscopy investigations of the coatings aged at 1100°C for 1h showed that voids between feather-arms and intra-columnar closed pores became coarser in comparison with those in the as-coated state (Fig. 5.3a and 5.3b). In contrast, no considerable porosity changes were observed in the coatings on further ageing at 1100°C for 100h (Fig. 5.3c).

Fig. 5.4 shows an Arrhenius plot of the surface area reduction of intra-columnar pores (SANS-Porod) and voids between feather arms (BET) corresponding to 900-1400 °C ageing temperatures during 1h. Using the Arrhenius equation suggested by German [153], the ratios between the activation energy and the mechanism constant (Q/γ) for the two different slopes of the curve were calculated. Based on morphology models [211, 212], the surface area reduction as a function of a diffusion mechanism can be expressed as

\[
\frac{\Delta S}{S_0} = \frac{g\Omega D_0 \exp(-Q/RT)}{kT} \left(\frac{\delta}{a}\right)^m
\]

(Eq. 5.1)

where ΔS/So is the surface area loss divided by the initial as-coated surface area value, γ is a diffusion mechanism-dependent exponent, g is a constant dependent on mass transport mechanism and powder packing coordination, Q is the surface energy, t is the time, D0 is the diffusion pre-exponential frequency factor, Q is the activation energy, R is the gas constant, K is Boltzmann’s constant, δ is the atomic diameter, a is the particle size, and m is the Herring scaling law exponent. Moreover, for an isochronal case, Eq. 5.1 can be simplified as:

\[
\frac{\Delta S}{S_0} \approx C \exp(-Q/RT)
\]

(Eq. 5.2)

where C incorporates a 1/T dependence to the Eq. 5.2, which can be ignored since the Arrhenius temperature dependence is dominant. Thus, taking logarithms and rearranging terms the relation (Q/γ) can be calculated from the slope of the ln(ΔS/So) vs. (1/T) plot:

\[
\ln(\Delta S / S_0) \approx C' - \frac{Q}{(γR)\ln(1/T)}
\]

(Eq. 5.3)

The application of the Eq. 5.3 to the temperature range of 900-1100°C yield average calculated (Q/γ)-ratios of 114 kJ/mol and 120 kJ/mol for the BET and SANS data, respectively. At the temperature range of 1100-1400°C, the calculated (Q/γ)-ratio values for BET and SANS was approx. the same ~ 9 kJ/mol. Microstructural observation of the coatings aged at different temperatures for one hour shows that substantial changes in the morphology and distribution of the porosity occur at temperatures between 900°C to 1100°C (see Fig. 5.5a and Fig. 5.5b). Considering the slope change in Fig. 5.4 and micrographs in Fig. 5.5c and Fig. 5.5d, it can be assumed that the morphological alteration becomes rather insignificant in the temperature range between 1100°C and 1400°C.
Figure 5.4: Surface area reduction data plotted against temperature is used as a basis to calculate the apparent activation energy for surface area loss with a heating rate of 5°K/min. Deviations from the calculated values of the surface area using the data fitting process are represented by the vertical bars.

Figure 5.5: Scanning electron micrographs of the cross sections of the EB-PVD standard top coats showing the changes in columnar after annealing for one hour at (a) 900°C, (b) 1100°C, (c) 1200°C and (d) 1400°C.
5.3 Manufacture and thermally induced morphological changes

5.3.1 Results of the microstructural analysis via SANS-BET on five morphologies

Characterization of all pores within EB-PVD ceramic coatings requires the employment of adequate techniques due to the anisotropy, accessibility (open and closed pores) and size differences between the pore groups. In this work, small-angle neutron scattering (SANS) and BET methods were applied to measure principally the surface area of closed (intra-columnar pores) and open (inter-columnar gaps and voids between feather arms) porosity in EB-PVD coatings, respectively. SANS is an alternative analyzing method that is sensitive to both open and closed surfaces, and is able to describe the configuration of nano-size features three dimensionally within solid materials. Additionally, the SANS method analyses the orientation dependence of the pore surface area. This information is of great importance to determine specifically the origin of the measured surface area values in the case of materials containing anisotropic distributed pores. This technique is capable to analyze nanometer-sized features due to the small neutron wavelengths (\(\lambda\)) normally utilized (e.g. in this case \(\lambda = 0.605\) nm). Intra-columnar pores in EB-PVD coatings are considered as the main contributors to the obtained information due to their higher surface area/volume ratio.

During the SANS measurements, the so-called Porod surface area emerges from the interfaces between individual pores and solid bulk material. Intensities of the Porod constant displayed at different angle values in polar figures represent the orientation of the corresponding pores region containing a determined related surface fraction. Porod constant intensities are perpendicular to the surface area region of the corresponding scattering pores. Higher intensities correspond to higher surface area fractions, and vice versa. Moreover, distribution of the pores orientation influences the sharpness of the resulting intensity peaks.

![Figure 5.6: Porod Constant values as a function of the azimuthal angle built at the plane parallel to the columns axis (perpendicular to substrate’s plane) of EB-PVD coatings measured in as-coated conditions. Orientation 0-180° corresponds to the direction perpendicular to axis of substrate rotation. The polar figures shown in the Fig. 5.6 exhibit the distribution of the surface area corresponding mainly to the closed intra-columnar pores measured in the direction parallel to the column axis for the analyzed coatings in as coated conditions. The surface area of the “fine” and “feathery” coatings possesses the highest value and the “coarse” the lowest. “Intermediate“ and “parallel” coatings contain a slightly higher surface area than the “coarse”. Differences between the maximum surface area values (horizontal axis 0-180°) between “fine” and “coarse“ microstructures lie by 75%. It is evident that in the as-coated conditions, the distribution of the surface area for the five analyzed microstructures is anisotropic with its highest value in the direction parallel to axis of substrate rotation. The aspect ratio and shape of the curves indicate the presence of a preferential orientation of non-spherical intra-](image-url)
columnar porosity. The anisotropic distribution of the Porod scattering depends on the shape/orientation of the individual pores and its polydispersity.

Ageing of the coatings at 1100°C for 1h produces an abrupt decrease of the surface area and a narrower distribution of the preferential orientation of the scattering features (narrow intensity peaks). The effect of such phenomena exhibits clear differences between the analyzed EB-PVD coatings as shown in the distribution of the Porod constant in **Fig. 5.7a**. Intra-columnar pores in “feathery”, “parallel” and “coarse” coatings display a clear preferentially oriented surface area at the directions perpendicular and parallel to the axis of substrate rotation. Nevertheless, the surface area distribution (shape of the peaks) of intra-columnar pores in “parallel” and “coarse” coatings is narrower than those in “feathery”. “Fine” coatings additionally display an intermediate preferential orientation between the directions perpendicular and parallel to axis of substrate rotation. Conversely, surface area distribution of “intermediate” coatings displays a slight enlarged distribution oriented perpendicular to the axis of substrate rotation. Furthermore, prolonged ageing (i.e. 100 hours) of the EB-PVD coatings diminishes and alters the interrelation between the surface area of the measured pores observed after 1100°C/1h ageing (see **Fig. 5.7b**). However, the orientation of the maximum intensity peaks remains unchanged. This effect indicates the stability of the achieved shape and orientation of the scattering pore-arrays. The surface area of the intra-columnar pores in all EB-PVD coatings still display a preferential orientation in the directions perpendicular and parallel to axis of substrate rotation (90-270° and 0-180° directions, respectively). An additional intensity peak is clearly perceptible at oblique orientations in all coatings. Nevertheless, differences in the distribution of the surface area between the coatings are still observed. “Parallel” coatings display a fine defined distribution, whereas “intermediate” coatings exhibit a quasi isotropic distribution.

**Figure 5.7:** Porod Constant values as a function of the azimuthal angle built at the plane parallel to the columns axis (perpendicular to substrate’s plane) of EB-PVD coatings measured after ageing at 1100°C for 1 hour (a) and 100 hours (b). Orientation 0-180° corresponds to the direction perpendicular to axis of substrate rotation.

Furthermore, EB-PVD coatings contain an important fraction of their overall porosity as open cavities that can be measured by BET method. This open porosity is formed by inter-columnar gaps and voids between feather arms. The last features are conceived as the main contributors to the surface area of the open porosity due to their size, aspect ratio, and distributions along the periphery of the columns surface. BET surface area of the coatings exhibit an abrupt decrease after 1h ageing at 1100°C. BET measurements exhibit considerable differences between the open surface areas of the EB-PVD coatings (see **Fig. 5.8**). In as-
coated conditions, “fine” and “feathery” coatings display the highest surface area. “Coarse” and “parallel” coatings exhibit the lowest values, whereas “intermediate” display an in-between value. Again the surface area values seem to be correlated with the substrate temperature during the EB-PVD coatings process. Low-temperature coatings show the highest values, whereas high temperature coatings the lowest values.

**Figure 5.8**: Values of the BET-Surface Area of the five analysed EB-PVD TBC coatings measured in as-coated conditions, and after ageing at 1100 °C for 1 hour and 100 hours.

### 5.3.2 Results of the microstructural analysis via USAXS measurements on three morphologies

USAXS analysis enables the possibility to determine the anisotropic stereometric characteristics of all pores within EB-PVD coatings. The complete mapping of these features was achieved by measuring two orthogonal directions per specimen (i.e. parallel and perpendicular to the axis of substrate rotation), and employing two complementary analysis methods for each direction: (1) Five aniso-scans were obtained at different scattering vector values \( Q \) to collect information of the anisotropy dominated by the corresponding pore size \( Q = \frac{2\pi}{D} \), where \( D \) is the mean pore dimension. (2) Scattering intensity was measured as function of the scattering vector, \( Q \), at specific azimuthal angles selected from the aniso-scans.

#### 5.3.2.1 USAXS measurements on coatings in as-coated conditions

USAXS aniso-scans graphs in Fig. 5.9 display the polar distribution of the scattering intensity vs. azimuthal angle. Polar graphics clearly exhibit the differences between the anisotropic intensity and distribution of the scattered radiation in the two measured orthogonal directions, i.e. perpendicular and parallel to the axis of substrate rotation. This complex anisotropic configuration shows the variability of the microstructure and the complexity of the quantitative analysis of these materials. In the case of SANS, the information obtained is dominated by the smallest features due to the utilized instrument configuration with only high \( Q \) values (smallest pores). The description of the anisotropic nature of these materials by USAXS method agrees with the results obtained by SANS measurements. Though, USAXS method analyses specifically the different pore groups by measuring at different scattering vector values.
Figure 5.9: USAXS aniso-scans measured at different scattering vector (Q) values in specimens in as-coated conditions. These display the anisotropic distribution of the scattering intensities in the direction perpendicular (blue) and parallel (red) to axis of substrate rotation for the (a) “intermediate”, (b) “coarse” and (c) “feathery” coatings. Axis 0-180° is oriented parallel to the substrate plane, whereas the axis 90-270° is oriented parallel to the column axis.

The characteristics of the scattering intensity graphs displayed in the USAXS aniso-scans enclose valuable qualitative information of the anisotropic character of the pores. In this case, the intensity is directly proportional to the volume and size distribution of the corresponding scattering pores. The angular distribution is related to the orientation of the measured features based on the orientation of the substrate’s plane lying in the 0-180° axis. Thus, scattering intensity peaks oriented in the vertical direction (~ 90°-270°) correspond to inter-columnar pores. The prevalence of this peak at higher Q values indicates that these features enclose a wide conical size distribution (broad/narrow cross section at the top/bottom of the coating). Clear differences in the scattering intensity of this features between the two analyzed orthogonal directions is perceptible in all microstructures. Moreover, maximum peaks obliquely oriented (42-60°) correspond to scattered radiation from the gaps between feather arms. By inter-columnar pores it is likely that their sizes also enclose a wide conical size distribution. These features display a broad/narrow cross section at their outside/inside edges. However, since these features have the same orientation as the intra-columnar pores, it is not possible to dissociate the mixture effect between them by solely analysing the aniso-scans.
The orientation of the peaks corresponding to these features displays a divergence between the direction perpendicular and parallel to axis of substrate rotation. Those at the perpendicular direction display lower azimuthal angles ($\alpha$). Moreover, the width of the peaks is directly related to the distribution of the scatterer (pores) orientation. Narrow peaks correspond to small distribution of the pore orientation and vice versa. According to the shape of the scattering intensity peaks, all pores included in the “feathery” coatings show a broader orientation distribution compared with the “intermediate” and “coarse” coatings.

Figs. 5.10 to 5.12 show microstructures of cross sections obtained in the direction perpendicular and parallel to the axis of substrate rotation of the analysed coatings. These also clearly demonstrate the anisotropic character of the coatings microstructure. Differences in the size distribution of the pores between the two analyzed directions are clearly observable. The cross section parallel to the axis of substrate rotation display narrower dimensions at the inter-columnar gaps in all coatings. Especially in the case of the “feathery” coatings, these gaps display an irregular shape. This configuration is perceptible by the absence of intensity peak oriented parallel to the vertical axis in the corresponding aniso-scans at high $Q$ values (see Fig. 5.9c). In the case of the “coarse” microstructure, the scattering intensity peak corresponding to fine-size inter-columnar pores is larger in the direction parallel to axis of substrate rotation. This configuration is contrary to the tendency observed at the other two microstructures (see Fig. 5.9b). In the direction perpendicular to the axis of substrate rotation, inter-columnar pores in the bottom zone of the coatings are noticeably broader than those in the parallel one (see Fig. 5.11). Thus, the absence of scattering intensity peak in the perpendicular direction corresponding to narrower sizes (higher $Q$ values) indicates the narrower size distribution of such features at this microstructure.

**Figure 5.10:** SEM-micrographs showing the tip (up) and bottom (down) regions of the “intermediate” coatings at the directions perpendicular (left) and parallel (right) to the axis of substrate rotation in as-coated conditions.
5.3.2.2 USAXS measurements on coatings after ageing conditions

Furthermore, USAXS measurements of the specimens after ageing at 1100°C/100h display the scattering intensity distributions as shown in the aniso-scans in Fig. 5.13. The observed changes in intensity compared to specimens in as-coated conditions are attributed to variations in volume fraction and size distribution of the pores. The remaining elongated shaped peaks parallel to the vertical axes indicate the shape-stability of the elongated inter-columnar pores during the ageing process. However, in the case of gaps between feather arms and intra-columnar pores, the elongated shape of the scattering intensity peak at the oblique directions drastically changes into lower aspect ratios (42-60°). Differences in the scattering...
intensities between the directions parallel and perpendicular to axis of substrate rotation are still noticeable in all coatings. The anisotropic characters of the coatingspersevere after the applied heat treatment. Contrary to the as-coated conditions, scattering intensity peaks corresponding to the cross section perpendicular (blue) to the axis of substrate rotation in “coarse” coatings exhibit evidently higher values than those in the parallel (red) direction after ageing (see Fig. 5.13b). An abrupt reduction of the scattering intensity is evident in the aniso-scans corresponding to the direction parallel (red) to the axis of substrate rotation. For “intermediate” and “feathery” coatings, the original configuration created in as-coated conditions persists after ageing. Although, after the applied ageing process, the intensity of the scattering peaks and their interrelation at the parallel and perpendicular cross sections exhibit an obvious alteration in all analyzed coatings (see Fig. 5.9 and Fig. 5.13).

**Figure 5.13**: USAXS aniso-scans measured at different scattering vector (Q) values in specimens after ageing at 1100°C for 100h. These display the anisotropic distribution of the scattering intensities in the direction perpendicular (blue) and parallel (red) to the axis of substrate rotation for the “intermediate” (a), “coarse” (b) and “feathery” (c) “coatings”. Axis 0-180° is oriented parallel to the substrate plane, whereas the axis 90-270° is oriented parallel to the column axis.

Micrographs corresponding to the USAXS measured coatings after ageing conditions at 1100°C/100h are shown in Fig. 5.14 to 5.16. Apparent modifications in the microstructure are observable in all EB-PVD coatings after ageing. The high temperature ageing activates thermal-induced microstructural changes such as sintering. Detailed description of the effect of such phenomenon on the morphology of EB-PVD coatings is given in Section 5.2.
of inter-columnar gaps due to sintering seems to be particularly enhanced at the cross section parallel to the axis of substrate rotation by the prior formed multiple contact points and narrower spacing between primary columns in this section of the coatings. Nevertheless, occasionally occurring sinter bridges are also observable in the cross section perpendicular to axis of substrate rotation. Moreover, deepest section of voids between feather arms break into low aspect ratio pores, whereas the external section changes into lower aspect ratio enlarged pores.

Figure 5.14: SEM-micrographs showing the tip (up) and bottom (down) regions of the directions perpendicular (left) and parallel (right) to the axis of substrate rotation of the “intermediate” coatings after ageing at 1100°C/100h.

Figure 5.15: SEM-micrographs showing the tip (up) and bottom (down) regions of the directions perpendicular (left) and parallel (right) to the axis of substrate rotation of the “coarse” coatings after ageing at 1100°C/100h.
5.3.3 Modeling of the USAXS data on three morphologies

Statistical representative stereometric characteristics of the pores within EB-PVD coatings were determined by a computer based modeling through parallel fitting process of the obtained aniso-scans, and $I = f(Q)$ curves. This model utilizes three spheroid-shapes: oblate, prolate or sphere; and five pore populations: $P1$ … $P5$, for the fitting process to determine the dimensions and volume fraction of pores in EB-PVD TBCs. Additional to the accuracy of the pore shape observed at the micrographs, the selected shapes contain a characteristic slope of the $I(Q)$ curves, which is conditioned for the appropriated selection of the pore shapes. The equations describing the form factor, $F(Q)$, of these features are already known, and the structure factor $S(Q)$ was taken as one (non-interaction between the pores). Thus, the fitting of the scattering intensity vs. scattering vector data, $I(Q)$, is achieved by substituting the accurate geometrical values in $F(Q)$, and the accurate value of the volume fraction of each pore population in Eq. 4.2. At the same time, the orientation of the pores should fulfill the Eq. 4.3, and the aniso-scan curves must also be fitted by the stereometric characteristics of the selected pore shape. The fitted $I(Q)$ graphs and aniso-scan figures for as-coated conditions and after ageing conditions at 1100°C/100h are shown in Appendix B1 and Appendix B2, respectively. There were only three pore groups identified in the EB-PVD coatings: inter-columnar gaps, voids between feather arms and intra-columnar pores. Therefore, the results obtained by measuring the two orthogonal directions correspond to the same pore kinds. Moreover, one pore kind is frequently represented by two USAXS populations measured in one direction due principally to its wide size distribution containing a fine and a coarse section (see Fig. 5.17). Furthermore, the resulting volume fractions of each pore population in both orthogonal analyzed cross-sections calculated with the USAXS model were scaled for the two analyzed orthogonal directions to the corresponding total porosity volume measured using the Archimedes Method for all coatings, (27.46% for “feathery”, 27.15% for “intermediate”, and 22.55% for “coarse”) in the as-coated and aged conditions.
Figure 5.17: Scheme of the USAXS populations representing the wide distribution of inter-columnar gaps and voids between feather arms in EB-PVD coatings.

5.3.3.1 Modeling of the USAXS data for coatings in as-coated conditions

In as-coated conditions, inter-columnar gaps formed at the flat surfaces between columns can be represented as oblate shaped cavities (see Fig. 5.18a). The best accurate shape to represent the voids between feather arms was also an oblate geometry (see Fig. 5.18b). Intra-columnar pores exhibit two preferred orientations in the cross-section perpendicular and parallel to the axis of substrate rotation. In the case of the perpendicular direction, intra-columnar pores are oriented parallel to the voids between feather arms across the complete cross-section (see Fig. 5.18c). In the parallel direction, features created in the middle volume of the primary columns oriented parallel to the inter-columnar gaps are observed. These features exhibit an oblate shape oriented in the vertical directions parallel to the inter-columnar gaps. Such pores are specifically observed at the cross-section oriented in the direction parallel to axis of substrate rotation (see Fig. 5.18d). Additional intra-columnar pores near the origin of voids between feather-arms are oriented parallel to these open voids.

Figure 5.18: SEM-Micrographs showing the best accurate approximation of the pores shape for the USAXS modeling. Fractured cross-sections: (a) inter-columnar gaps (oblate) and (b) voids between feather arms (oblate), and polished cross-sections: inter-columnar pores in the cross sections (c) perpendicular to the axis of substrate rotation (prolate), (d) parallel to the axis of substrate rotation (oblate).
USAXS modeled data shown in Table 5.2 demonstrate that “intermediate” coatings contain coarse inter-columnar gaps with similar width in both orthogonal analyzed directions. Cross-sections perpendicular to the axis of substrate rotation contain higher volume fraction of these features. However, intra-columnar pores display a broader size distribution in the parallel cross-section represented by a second thin section.

Voids between feather arms are composed of two populations in the two cross-sections, but these are much deeper and with a higher volume fraction in the perpendicular cross-section. These features display an orientation of 42° in the perpendicular and 56° in the parallel cross-sections, respectively. Moreover, both directions contain intra-columnar pores oriented parallel to voids between feather arms with similar volume fractions in both directions (11.5% and 14%), but larger aspect ratios (20 and 8.8) and dimensions in the perpendicular cross-section (260 nm and 156 nm). These features exhibit a prolate shape in both directions. Furthermore, an additional group of intra-columnar pores created in the middle volume of the primary columns exhibit an oblate shape oriented in the vertical directions parallel to the inter-columnar gaps. Circles in SEM-micrographs of these coatings show the corresponding USAXS populations in both analyzed directions (see Fig. 5.19a and Fig. 5.19b).

Table 5.2: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to the axis of substrate rotation of the “intermediate” EB-PVD coatings in as-coated conditions. P1-P5 are the scattering-pore populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

Table 5.2a – Cross section parallel to the axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>86</td>
<td>8957</td>
<td>671</td>
<td>0.075</td>
<td>2.3</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>86</td>
<td>974</td>
<td>117</td>
<td>0.12</td>
<td>2.8</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>56</td>
<td>613</td>
<td>86</td>
<td>0.14</td>
<td>4.8</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>86</td>
<td>342</td>
<td>41</td>
<td>0.12</td>
<td>3.2</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Prolate</td>
<td>56</td>
<td>18</td>
<td>156</td>
<td>8.8</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Figure 5.19a: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “intermediate” EB-PVD coatings in as-coated conditions.
Table 5.2b – Cross section perpendicular to the axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>82</td>
<td>13460</td>
<td>673</td>
<td>0.05</td>
<td>8.5</td>
</tr>
<tr>
<td>P2: Voids between feather arms-1</td>
<td>Oblate</td>
<td>42</td>
<td>1300</td>
<td>118</td>
<td>0.91</td>
<td>1.2</td>
</tr>
<tr>
<td>P3: Voids between feather arms-2</td>
<td>Oblate</td>
<td>42</td>
<td>705</td>
<td>46</td>
<td>0.065</td>
<td>4.2</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Prolate</td>
<td>42</td>
<td>13</td>
<td>260</td>
<td>20.00</td>
<td>11.5</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>42</td>
<td>34</td>
<td>15</td>
<td>0.45</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 5.19b: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction perpendicular to the axis of substrate rotation of the “intermediate” EB-PVD coatings in as-coated conditions.

In the case of “coarse” coatings, the modeled USAXS data representing the characteristics of the porosity exhibit a sectioning of the different features in both analyzed directions (see Table 5.3). The thickness of inter-columnar gaps is broader (602/154 nm and 436/80 nm) and contains a slightly higher volume fraction (5.9/2.7% and 0.2/7.6%) in the cross-section perpendicular to the axis of substrate rotation. Voids between feather arms display deeper sections (1600 nm and 719 nm) in the perpendicular section with equal volume fractions in both directions (6.8 both). Intra-columnar pores oriented parallel to voids between feather arms display higher volume fractions (5.8% and 4.4%) and larger dimensions in the perpendicular cross-section. These features display a similar orientation being 50° in the perpendicular and 52° in the parallel cross-sections, respectively. In this case, all measured intra-columnar pores can be fitted as oblate shapes, except those joining the pores arrays formed after each rotation movement at the perpendicular direction, which are prolate shaped. Circles in SEM-micrographs of these coatings show the corresponding USAXS populations in both analyzed directions (see Fig. 5.20a and Fig. 5.20b).
Table 5.3: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to the axis of substrate rotation of the “coarse” EB-PVD coatings in as-coated conditions P1-P5 are the scattering-pore populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

Table 5.3a – Cross section parallel to axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>84</td>
<td>8714</td>
<td>436</td>
<td>0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>84</td>
<td>1600</td>
<td>80</td>
<td>0.05</td>
<td>7.6</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>52</td>
<td>576</td>
<td>58</td>
<td>0.10</td>
<td>6.8</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>84</td>
<td>381</td>
<td>25</td>
<td>0.065</td>
<td>3.5</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>52</td>
<td>199</td>
<td>30</td>
<td>0.15</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 5.20a: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “coarse” EB-PVD coatings in as-coated conditions.

Table 5.3b – Cross section perpendicular to axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>86</td>
<td>12044</td>
<td>602</td>
<td>0.05</td>
<td>5.9</td>
</tr>
<tr>
<td>P2: Voids between feather arms-1</td>
<td>Oblate</td>
<td>50</td>
<td>1622</td>
<td>154</td>
<td>0.095</td>
<td>2.7</td>
</tr>
<tr>
<td>P3: Voids between feather arms-2</td>
<td>Oblate</td>
<td>50</td>
<td>719</td>
<td>54</td>
<td>0.075</td>
<td>6.8</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Prolate</td>
<td>50</td>
<td>22</td>
<td>446</td>
<td>20.00</td>
<td>5.8</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>50</td>
<td>210</td>
<td>63</td>
<td>0.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Figure 5.20b: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction perpendicular to the axis of substrate rotation of the “coarse” EB-PVD coatings in as-coated conditions.

USAXS modeled data of “feathery” coatings is shown in Table 5.4. In this case, the thickness inter-columnar gaps are much broader in the cross-section parallel to the axis of substrate rotation (638 nm and 1636 nm). Inter-columnar gaps comprise a broader size distribution (two USAXS populations) and higher volume fraction (2.7% and 5.4/3.2%) in the cross-section oriented in the direction perpendicular to the axis of substrate rotation. Voids between feather arms display similar lengths (oblate diameters) in both directions (1859/226 nm and 1149/1082 nm), but higher volume fraction in the parallel direction (0.9/1.3% and 4.8 and 2.7%). Intra-columnar pores oriented parallel to voids between feather arms display similar volume fractions and larger dimensions in the parallel direction. These features display an orientation of 42° in the perpendicular and 60° in the parallel cross sections, respectively. Also in these coatings, all intra-columnar pores exhibit an oblate shape, except those at the perpendicular direction, which join the pores array formed after every rotation movement. Circles in SEM-micrographs of these coatings show the corresponding USAXS populations in both analyzed directions (see Fig. 5.21a and Fig. 5.21b).

Table 5.4: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to axis the of substrate rotation of the “feathery” EB-PVD coatings in as-coated conditions via USAXS. P1-P5 are the scattering-pore populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

Table 5.4a – Cross section parallel to axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps</td>
<td>Oblate</td>
<td>90</td>
<td>10910</td>
<td>1636</td>
<td>0.15</td>
<td>2.7</td>
</tr>
<tr>
<td>P2: Voids between feather arms-1</td>
<td>Oblate</td>
<td>60</td>
<td>1149</td>
<td>195</td>
<td>0.17</td>
<td>4.8</td>
</tr>
<tr>
<td>P3: Voids between feather arms-2</td>
<td>Oblate</td>
<td>60</td>
<td>1082</td>
<td>54</td>
<td>0.05</td>
<td>2.7</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>60</td>
<td>358</td>
<td>18</td>
<td>0.05</td>
<td>13.9</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>90</td>
<td>160</td>
<td>8</td>
<td>0.05</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Results

Figure 5.21a: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “feathery” EB-PVD coatings in as-coated conditions.

Table 5.4b – Cross section perpendicular to axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>84</td>
<td>6378</td>
<td>638</td>
<td>0.10</td>
<td>5.4</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>84</td>
<td>422</td>
<td>59</td>
<td>0.14</td>
<td>3.2</td>
</tr>
<tr>
<td>P3: Voids between feather arms-1</td>
<td>Oblate</td>
<td>42</td>
<td>1859</td>
<td>93</td>
<td>0.05</td>
<td>0.9</td>
</tr>
<tr>
<td>P4: Voids between feather arms-2</td>
<td>Oblate</td>
<td>42</td>
<td>226</td>
<td>32</td>
<td>0.14</td>
<td>1.3</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Prolate</td>
<td>42</td>
<td>6</td>
<td>126</td>
<td>20.00</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Figure 5.21b: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction perpendicular to the axis of substrate rotation of the “feathery” EB-PVD coatings in as-coated conditions.

5.3.3.2 Modeling of the USAXS data for aged coatings

Modeling of the USAXS data obtained from the measurements of EB-PVD coatings after ageing was applied similarly to the as-coated conditions (see Appendix B2). It was observed that the inter-columnar gaps remain open after the ageing process (see Fig. 5.22a). Nevertheless, according to the USAXS results, these features exhibit a broader size distribution in both analyzed directions after ageing. Finer dimension group of voids between feather-arms observed in the as-coated state disappears completely. This section breaks into arrays of quasi-spherical intra-columnar pores at their inner pyramidal ends, leaving isolated openings with lower aspect ratio at the edge of the feather-arms (see Fig. 5.22b). Finally, high aspect ratio cylindrical intra-columnar pores (fine “banana”-shaped pores in Fig. 5.18c)
connecting the two rows of pores created by each rotation phase break into two groups of quasi-spherical pores (see Figs. 5.22c). SEM-micrographs in Fig. 5.22c and 5.22d show that low aspect ratio inter-columnar pores enclose both, rounded and right-angled edges. Therefore, the USAXS fitting process of these features is normally approached by the use of low aspect ratio spheroids.

Figure 5.22: SEM-Micrographs showing the best accurate pores shape for the USAXS modeling. Fractured cross-sections: (a) inter-columnar gaps (oblate) and (b) voids between feather arms (oblate), and polished cross-sections: inter-columnar pores in cross sections (c) perpendicular to axis of substrate rotation (prolate), and (d) parallel to the axis of substrate rotation (oblate).

According to the USAXS modeled data of the “intermediate” coatings (see Table 5.5), inter-columnar pores exhibit similar thickness and volume fraction in the directions perpendicular and parallel to the axis of substrate rotation (8.7/5.4 % and 5.9/8.3%). Narrow pores contain the biggest volume fraction in the parallel direction; and a contrary distribution tendency is observable in the perpendicular direction. Voids between feather arms are deeper in the perpendicular direction (580 nm and 352 nm), but they contain higher volume fraction in the parallel direction (3.1% and 5.3%). These features display an orientation of 45° in the perpendicular and 61° in the parallel cross-section, respectively. Intra-columnar pores are represented by two sized groups in the two analyzed directions (see Fig. 5.23a and Fig. 5.23b), which contain higher volume fraction in the perpendicular direction (4.7/5.3% and 1.8/5.9%).
Table 5.5: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to the axis of substrate rotation of the “intermediate” EB-PVD coatings after ageing at 1100°C/100h. P1-P5 are the scattering-pore populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

**Table 5.5a – Cross section parallel to the axis of substrate rotation**

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>87</td>
<td>6000</td>
<td>450</td>
<td>0.075</td>
<td>5.9</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>87</td>
<td>480</td>
<td>101</td>
<td>0.21</td>
<td>8.3</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>61</td>
<td>352</td>
<td>88</td>
<td>0.25</td>
<td>5.3</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Sphere</td>
<td>-</td>
<td>90</td>
<td>-</td>
<td>1.00</td>
<td>1.8</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Sphere</td>
<td>-</td>
<td>48</td>
<td>-</td>
<td>1.00</td>
<td>5.9</td>
</tr>
</tbody>
</table>

**Figure 5.23a**: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “intermediate” EB-PVD coatings after ageing at 1100°C/100h.

**Table 5.5b – Cross section perpendicular to the axis of substrate rotation**

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>84</td>
<td>9384</td>
<td>470</td>
<td>0.05</td>
<td>8.7</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>84</td>
<td>480</td>
<td>125</td>
<td>0.26</td>
<td>5.4</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>45</td>
<td>580</td>
<td>174</td>
<td>0.30</td>
<td>3.1</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>45</td>
<td>121</td>
<td>96</td>
<td>0.80</td>
<td>4.7</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Sphere</td>
<td>-</td>
<td>42</td>
<td>-</td>
<td>1.00</td>
<td>5.3</td>
</tr>
</tbody>
</table>
USAXS data for the “coarse” coatings are shown in Table 5.6. According to the resulting values, inter-columnar gaps display similar thickness in the cross-sections oriented in the direction perpendicular and parallel to the axis of substrate rotation (563/156 nm and 553/97 nm). Inter-columnar pores in the perpendicular cross-section contain noticeably higher volume fraction (7.0/1.5% and 1.2/3.6%). Voids between feather arms are deeper in the perpendicular direction (993 nm and 400 nm), but with lower volume fraction (4.9% and 8.3%). These features display an orientation of 53° in the perpendicular and 54° in the parallel direction, respectively. Intra-columnar pores exhibit a slightly higher volume fraction in the parallel direction (5.3/3.8% and 4.7/4.7%). Nevertheless, bigger sizes were calculated for the coarse group in the perpendicular direction (see Fig. 5.24a and Fig. 5.24b).

Table 5.6: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to the axis of substrate rotation of the “coarse” EB-PVD coatings after ageing at 1100°C/100h. P1-P5 are the scatter populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

Table 5.6a – Cross section parallel to the axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>98</td>
<td>11060</td>
<td>553</td>
<td>0.05</td>
<td>1.2</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>98</td>
<td>880</td>
<td>97</td>
<td>0.11</td>
<td>3.6</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>54</td>
<td>400</td>
<td>200</td>
<td>0.50</td>
<td>8.3</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>54</td>
<td>160</td>
<td>128</td>
<td>0.80</td>
<td>4.7</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Sphere</td>
<td>-</td>
<td>48</td>
<td>-</td>
<td>1.00</td>
<td>4.7</td>
</tr>
</tbody>
</table>
**Results**

**Figure 5.24a:** SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “coarse” EB-PVD coatings after ageing at 1100°C/100h.

**Table 5.6b – Cross section perpendicular to the axis of substrate rotation**

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>92</td>
<td>11261</td>
<td>563</td>
<td>0.05</td>
<td>7.0</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>92</td>
<td>600</td>
<td>156</td>
<td>0.26</td>
<td>1.5</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>53</td>
<td>993</td>
<td>130</td>
<td>0.13</td>
<td>4.9</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>53</td>
<td>261</td>
<td>209</td>
<td>0.80</td>
<td>5.3</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>53</td>
<td>51</td>
<td>46</td>
<td>0.90</td>
<td>3.8</td>
</tr>
</tbody>
</table>

**Figure 5.24b:** SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction perpendicular to the axis of substrate rotation of the “coarse” EB-PVD coatings after ageing at 1100°C/100h.

Modeled USAXS data for the “feathery” coatings (see Table 5.7) exhibit that inter-columnar pores in the perpendicular direction display a broader size distribution (591/85 nm and 220 nm) and volume fraction (4.5/11.1% and 2.8%) compared to the parallel one. Contrarily, voids between feather arms display higher volume fraction (1.1% and 3.3/8.7%) and broader size distribution (161 nm and 157/149 nm) in the parallel direction. These features display an orientation of 52° in the perpendicular and 60° in the parallel directions, respectively (see Fig. 5.25a and Fig. 5.25b). Intra-columnar pores exhibit a higher volume fraction (5.3/5.4% and 4.6/8.1%) in the direction parallel to the axis of substrate rotation.
Table 5.7: Calculated stereometric characteristics from USAXS modeling of the porosity at the cross-sections parallel (a) and perpendicular (b) to the axis of substrate rotation of the “feathery” EB-PVD coatings after ageing at 1100°C/100h. P1-P5 are the scatter populations utilized for the USAXS modeling. 1 = coarse and 2 = fine.

Table 5.7a – Cross section parallel to the axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>90</td>
<td>4400</td>
<td>220</td>
<td>0.05</td>
<td>2.8</td>
</tr>
<tr>
<td>P2: Voids between feather arms-1</td>
<td>Oblate</td>
<td>60</td>
<td>1120</td>
<td>157</td>
<td>0.14</td>
<td>3.3</td>
</tr>
<tr>
<td>P3: Voids between feather arms-2</td>
<td>Oblate</td>
<td>60</td>
<td>373</td>
<td>149</td>
<td>0.40</td>
<td>8.7</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>60</td>
<td>80</td>
<td>72</td>
<td>0.9</td>
<td>4.6</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Sphere</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>1.00</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Figure 5.25a: SEM-micrographs of the cross-section at the middle region of the EB-PVD coating thickness corresponding to the direction parallel to the axis of substrate rotation of the “feathery” EB-PVD coatings after ageing at 1100°C/100h.

Table 5.7b – Cross section perpendicular to the axis of substrate rotation

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Shape</th>
<th>Azimuthal Angle</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect Ratio</th>
<th>Vol. Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1: Inter-columnar gaps-1</td>
<td>Oblate</td>
<td>88</td>
<td>11827</td>
<td>591</td>
<td>0.05</td>
<td>4.5</td>
</tr>
<tr>
<td>P2: Inter-columnar gaps-2</td>
<td>Oblate</td>
<td>88</td>
<td>386</td>
<td>85</td>
<td>0.22</td>
<td>11.1</td>
</tr>
<tr>
<td>P3: Voids between feather arms</td>
<td>Oblate</td>
<td>52</td>
<td>1467</td>
<td>161</td>
<td>0.11</td>
<td>1.1</td>
</tr>
<tr>
<td>P4: Intra-columnar pores-1</td>
<td>Oblate</td>
<td>52</td>
<td>123</td>
<td>99</td>
<td>0.80</td>
<td>5.3</td>
</tr>
<tr>
<td>P5: Intra-columnar pores-2</td>
<td>Oblate</td>
<td>52</td>
<td>37</td>
<td>30</td>
<td>0.80</td>
<td>5.4</td>
</tr>
</tbody>
</table>
5.4 Thermal conductivity of EB-PVD PYSZ TBCs

Alterations in the process parameters vary the resulting thermal conductivity of EB-PVD coatings. Considerable microstructural differences can be achieved by depositing the same ceramic material by altering the deposition process. Additionally, ageing of such morphologically different coatings induces distinctive changes in their thermal conductivity.

5.4.1 Results of the measured thermal conductivity

Thermal conductivities of the five analyzed EB-PVD coatings measured at different temperatures in as-coated conditions are shown in Figure 5.26. According to the displayed graphs, it is evident that “feathery” coatings exhibit the lowest thermal conductivity values, whereas “coarse” coatings the highest. Considering the values measured at 200°C, a difference of 32% between the thermal conductivity of these two coatings has been determined. Moreover, “parallel” coatings display a slight higher thermal conductivity values than “intermediate” and “fine”, which are very near to each other at the measured temperature range. Thermal conductivity values of all coatings, except “coarse”, remain almost constant even at the low temperature range. This configuration indicates that the thermal conductivity of these EB-PVD coatings is independent of temperature at the measured as-coated microstructural conditions. Furthermore, a slight increase in the thermal conductivity at temperatures above 800°C is perceptible in all analyzed coatings.
During the thermal conductivity measurements of the as-coated specimens it was detected that the curves corresponding to heating and cooling periods do not overlap (see Fig. 5.27). Thermal conductivity values corresponding to the cooling period display higher values, which markedly increase toward lower temperatures.

**Figure 5.27**: Thermal conductivity vs. temperature graphs of the heating and cooling periods of an “intermediate” EB-PVD coating in as-coated conditions.

Ageing at 1100°C for 100h induces an increase in the thermal conductivity in all analyzed EB-PVD coatings (see Fig. 5.28). Thermal conductivity increase at temperatures above 800°C is no more perceptible in the graphs corresponding to aged conditions. Moreover, the slope of the graphs at low temperatures changes into higher inclination arrangements. “Coarse” EB-PVD coatings still exhibit the highest thermal conductivity values as well as “parallel” coatings. Thermal conductivity of “fine” and “feathery” coatings fall close to each other, whereas “intermediate” display slightly higher values. Taking into account the process parameters used for the manufacture of these EB-PVD coatings, the dependence of thethermal conductivity of these materials on ageing seems to be grouped according to the substrate temperature during the EB-PVD process. The coatings deposited at higher temperatures (“parallel” and “coarse”) exhibit higher thermal conductivity values.

**Figure 5.28**: Thermal conductivities of the analyzed EB-PVD coatings at different measuring temperatures after ageing conditions at 1100°C for 100h.
Additional thermal conductivity measurements at intermediate ageing conditions (1100°C/1h) were applied. Such measurements exhibit the effect of shorter ageing time in the thermal conductivity increase in the different EB-PVD coatings (see Fig. 5.29). The increase in the thermal conductivity differences toward lower temperatures between as-coated conditions, and after ageing at 1100°C for 1h and 100h is observed in all analyzed coatings, except in “coarse” coatings.

Figure 5.29: Thermal conductivities at different measuring temperatures of the analyzed EB-PVD coatings in as-coated conditions and after ageing at 1100°C for 1h and 100h: (a) “intermediate”, (b) “coarse”, (c) “fine”, (d) “feathery”, and (e) “parallel”.

“Feathery” and “coarse” EB-PVD coatings display the extreme configurations according to the graphs in Fig. 5.29. While “coarse” coatings exhibit no perceptible changes in thermal
conductivity changes after ageing at 1100°C/1h, “feathery” coatings seem to reach a stable configuration of the pores after this ageing process. This configuration remains even after further ageing at 1100°C for 100h. “Intermediate”, “fine” and “parallel” coatings show an intermediate increase in thermal conductivity after ageing at 1100°C/1h. Furthermore, it is evident that the slope of the thermal conductivity values at low measuring temperatures of all coatings after such intermediate ageing conditions (1100°C/1h) exhibit similar decay to the thermal conductivity graphics corresponding to 1100°C/100h.

5.4.2 Modeling of the thermal conductivity
Ceramic top coats of thermal barrier coatings deposited by EB-PVD process are composed principally of three groups of discontinuities (porosity): inter-columnar gaps, voids between feather arms, and intra-columnar pores. The quantitative data obtained from the USAXS analysis was utilized to model the thermal conductivity of such coatings. In this case, two orthogonal directions: parallel and perpendicular to the axis of substrate rotation were analyzed in order to accurately characterize the anisotropic geometrical and spatial characteristics of the pores within EB-PVD coatings. Then, the data corresponding to a single EB-PVD coating is comprised by the characteristics of the three pores groups corresponding to each of the two analyzed orthogonal cross-sections in as-coated conditions (see Table 5.2 to Table 5.4) and after ageing (see Table 5.5 to Table 5.7). Accordingly, the equations of the thermal conductivity modeling listed in Section 2.4.3 indicate that all pores analyzed in the two orthogonal directions can be grouped in the three mentioned groups: inter-columnar gaps, voids between feather arms, and intra-columnar pores. Nevertheless, the total sum of the volume fractions of all pores within a single EB-PVD coating evidently exceed the total volume fraction determined by the Archimedes method. Then, the thermal conductivity factor of each population was calculated by the corresponding equations listed in Section 2.4.3. Afterward, the rule of mixtures was applied to obtain the representative thermal conductivity value of one pore group ($k_r$) by substituting the calculated thermal conductivity factor ($k_i$) and volume fraction ($V_i$) of each single USAXS-population forming a group in the following equation:

$$k_r = \sum_{i=1}^{n} k_i \left( \frac{V_i}{\sum_{i=1}^{n} V_i} \right)$$

(Eq. 5.1)

The data shown in Table 5.8a exhibit the influence of each USAXS-population in the thermal conductivity factors corresponding to each pore group of the analyzed EB-PVD coatings in as-coated conditions. The factor influenced by the inter-columnar pores ($k_{coil}$/kcoil) is partially maintained despite the differences in the microstructure of the coatings. The factor corresponding to the voids between feather arms ($k_{fa}$/kfa) is mainly governed by the deepest region of these features located in the cross-section perpendicular to the axis of substrate rotation in the “intermediate” and “coarse” coatings. Additionally, thermal conductivity factor of the intra-columnar pores ($k_{ia}$/kia) is principally affected by the prolate shaped features measured at the cross-section perpendicular to the axis of substrate rotation.
**Table 5.8a:** Modeling factors of the non-interacting approximation corresponding to the different USAXS pore populations in each pore group used to calculate the thermal conductivity of the EB-PVD coatings in as-coated conditions.

<table>
<thead>
<tr>
<th>USAXS Populations</th>
<th>Inter-columnar gaps, ( \frac{k_{\text{coat}}}{k_{\text{col}}} )</th>
<th>Voids between feather arms, ( \frac{k_{\text{fa}}}{k_{\text{ia}}} )</th>
<th>Intra-columnar pores, ( \frac{k_{\text{ia}}}{k_{s}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“Intermediate”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.89728 (IEC-PE)</td>
<td>0.94826 (FA-PE1)</td>
<td>0.82149 (IAC-PE1)</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.97225 (IEC-PA1)</td>
<td>0.75042 (FA-PE2)</td>
<td>0.97788 (IAC-PE2)</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.96727 (IEC-PA2)</td>
<td>0.89876 (FA-PA1)</td>
<td>0.96763 (IAC-PA1)</td>
</tr>
<tr>
<td>Population 4</td>
<td>-</td>
<td>-</td>
<td>0.81622 (IAC-PA2)</td>
</tr>
<tr>
<td>( k_r )</td>
<td>0.92437</td>
<td>0.84498</td>
<td>0.84360</td>
</tr>
<tr>
<td><strong>“Coarse”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.93642 (IEC-PE)</td>
<td>0.91982 (FA-PE1)</td>
<td>0.92196 (IAC-PE1)</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.98710 (IEC-PA1)</td>
<td>0.75608 (FA-PE2)</td>
<td>0.98196 (IAC-PE2)</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.91390 (IEC-PA2)</td>
<td>0.79369 (FA-PA1)</td>
<td>0.96514 (IAC-PA1)</td>
</tr>
<tr>
<td>Population 4</td>
<td>-</td>
<td>-</td>
<td>0.96206 (IAC-PA2)</td>
</tr>
<tr>
<td>( k_r )</td>
<td>0.92467</td>
<td>0.79889</td>
<td>0.94900</td>
</tr>
<tr>
<td><strong>“Feathery”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.93566 (IEC-PE)</td>
<td>0.93269 (FA-PE1)</td>
<td>0.74077 (IAC-PE1)</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.95742 (IEC-PA1)</td>
<td>0.96153 (FA-PE2)</td>
<td>0.45330 (IAC-PA1)</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.97300 (IEC-PA2)</td>
<td>0.91906 (FA-PA1)</td>
<td>0.96600 (IAC-PA2)</td>
</tr>
<tr>
<td>Population 4</td>
<td>-</td>
<td>0.89381 (FA-PA2)</td>
<td>-</td>
</tr>
<tr>
<td>( k_r )</td>
<td>0.95075</td>
<td>0.91899</td>
<td>0.64577</td>
</tr>
</tbody>
</table>

IEC: Inter-columnar gaps   FA: Voids between feather arms   IAC: Intra-columnar pores
PE, PA: Perpendicular and parallel to the axis of substrate rotation
1: Coarse   2: Fine

**Table 5.8b** displays the influence of each pore population in the different factors utilized for the thermal conductivity modeling of the EB-PVD coatings after ageing at 1100°C for 100h. The ageing process of the coatings induces the dissolution of the insulating effect created by the voids between feather arms and prolate shaped intra-columnar pores observed in the coatings in as-coated conditions. Differences in the values of the thermal conductivity factors in all coatings after ageing are now influenced solely by the volume fraction and spatial distribution of the low aspect ratio pores. The previous influence of the shape and orientation of these features in as-coated conditions vanishes.
Table 5.8b: Modeling factors of the non-interacting approximation corresponding to the different USAXS pore populations in each pore groups used to calculate the thermal conductivity of the EB-PVD coatings after ageing at 1100°C/100h.

<table>
<thead>
<tr>
<th>USAXS Populations</th>
<th>Inter-columnar gaps, $k_{coat}/k_{col}$</th>
<th>Voids between feather arms, $k_{fa}/k_{ia}$</th>
<th>Intra-columnar pores, $k_{ia}/k_{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“Intermediate”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.90302 {IEC-PE1}</td>
<td>0.95161 {FA-PE}</td>
<td>0.95780 {IAC-PE1}</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.93566 {IEC-PE2}</td>
<td>0.92774 {FA-PA}</td>
<td>0.92050 {IAC-PA2}</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.93842 {IEC-PA1}</td>
<td>-</td>
<td>0.97300 {IAC-PA1}</td>
</tr>
<tr>
<td>Population 4</td>
<td>0.91449 {IEC-PA2}</td>
<td>-</td>
<td>0.91150 {IAC-PA2}</td>
</tr>
<tr>
<td>$k_r$</td>
<td>0.91999</td>
<td>0.93655</td>
<td>0.93274</td>
</tr>
<tr>
<td><strong>“Coarse”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.92887 {IEC-PE1}</td>
<td>0.88503 {FA-PE}</td>
<td>0.95074 {IAC-PE1}</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.98380 {IEC-PE2}</td>
<td>0.91382 {FA-PA}</td>
<td>0.96584 {IAC-PE2}</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.96886 {IEC-PA1}</td>
<td>-</td>
<td>0.95435 {IAC-PA1}</td>
</tr>
<tr>
<td>Population 4</td>
<td>0.94533 {IEC-PA2}</td>
<td>-</td>
<td>0.92950 {IAC-PA2}</td>
</tr>
<tr>
<td>$k_r$</td>
<td>0.94313</td>
<td>0.90313</td>
<td>0.94936</td>
</tr>
<tr>
<td><strong>“Feathery”</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Population 1</td>
<td>0.95384 {IEC-PE1}</td>
<td>0.96904 {FA-PE}</td>
<td>0.95110 {IAC-PE1}</td>
</tr>
<tr>
<td>Population 2</td>
<td>0.87929 {IEC-PE2}</td>
<td>0.93773 {FA-PA1}</td>
<td>0.95018 {IAC-PA1}</td>
</tr>
<tr>
<td>Population 3</td>
<td>0.97200 {IEC-PA}</td>
<td>0.90013 {FA-PA2}</td>
<td>0.95737 {IAC-PA1}</td>
</tr>
<tr>
<td>Population 4</td>
<td>-</td>
<td>-</td>
<td>0.87850 {IAC-PA2}</td>
</tr>
<tr>
<td>$k_r$</td>
<td>0.91163</td>
<td>0.91539</td>
<td>0.92699</td>
</tr>
</tbody>
</table>


The overall thermal conductivities of the analyzed coatings were calculated by using 2 W/(mK) as the value of bulk PYSZ materials ($k_s$), and the cross-section area fractions occupied by the voids between feather arms ($S_{fa}$) and intra-columnar pores ($S_{ia}$) listed in the Table 5.9. Such surface area distribution was calculated by considering the average of the projection of the voids between feather arms length in the horizontal cross-section of the primary columns in each of the two analyzed orthogonal directions. This consideration was applied for each coating in as-coated conditions and after ageing. Thus, according to the schema displayed in Fig. 5.30, the 2D cross-area sections $S_{fa}=2l_{fa}$ and $S_{ia}=(1-S_{fa})$. In the case of voids between feather arms comprised by two USAXS populations, the value of $S_{fa}$ is the sum of the two fitted oblate shaped features. Then, the average value of both cross-sections oriented perpendicular and parallel to the axis of substrate rotation is considered as the final value of each cross section.
Figure 5.30: Schematic representation of the projection of the voids between feather arms length ($d_{fa}$) on the horizontal cross-section of the primary columns ($l_{fa}$).

Furthermore, observing the micrographs of the cross sections parallel and perpendicular to the axis of substrate rotation in as coated and after ageing it is obvious that the intra-columnar pores occupy the majority of the primary column volume (see Figs. in Section 5.2). Thus, it is obvious that the value of the factor corresponding to the thermal conductivity of the primary columns ($k_{col}$) is mainly affected by the intra-columnar pores by applying the Eq. 2.13 (see Table 5.9).

Table 5.9: Values of the thermal conductivity factors of the primary columns ($k_{col}$) calculated from the factors and the cross-section area fractions corresponding to the voids between feather arms and intra-columnar pores of the EB-PVD coatings in as-coated conditions and after ageing at 1100°C/100h.

<table>
<thead>
<tr>
<th>EB-PVD Coatings</th>
<th>Condition</th>
<th>$k_{fa}$</th>
<th>$S_{fa}$</th>
<th>$k_{ia}$</th>
<th>$S_{ia}$</th>
<th>$k_{col}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Intermediate”</td>
<td>As coated</td>
<td>1.425</td>
<td>0.172</td>
<td>1.697</td>
<td>0.828</td>
<td>1.597</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.747</td>
<td>0.050</td>
<td>1.865</td>
<td>0.950</td>
<td>1.853</td>
</tr>
<tr>
<td>“Coarse”</td>
<td>As coated</td>
<td>1.516</td>
<td>0.110</td>
<td>1.898</td>
<td>0.890</td>
<td>1.816</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.714</td>
<td>0.890</td>
<td>1.899</td>
<td>0.910</td>
<td>1.882</td>
</tr>
<tr>
<td>“Feathery”</td>
<td>As coated</td>
<td>1.187</td>
<td>0.410</td>
<td>1.291</td>
<td>0.590</td>
<td>1.254</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.697</td>
<td>0.270</td>
<td>1.854</td>
<td>0.730</td>
<td>1.819</td>
</tr>
</tbody>
</table>

Finally, the modeled overall thermal conductivity value ($k_{coat}$) are determined by the interrelation between the thermal conductivity factor of the primary columns ($k_{col}$), and the factor of the inter-columnar pores ($k_{coat}/k_{col}$). Modeled thermal conductivity values of the coatings in as-coated and aged conditions accurately agree with the corresponding measured values as shown in Table 5.10.
Table 5.10: Modeled and measured thermal conductivities of the EB-PVD coatings in as-coated conditions, and after ageing at 1100°C/100h.

<table>
<thead>
<tr>
<th>EB-PVD Coatings</th>
<th>Condition</th>
<th>Measured at 200°C ( \lambda ), W/(mK)</th>
<th>Modeling ( \lambda ), W/(mK)</th>
<th>( \frac{k_{coat}}{k_{col}} )</th>
<th>( k_{col} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Intermediate”</td>
<td>As coated</td>
<td>1.23 ± 0.08</td>
<td>1.47</td>
<td>0.924</td>
<td>1.597</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.56 ± 0.10</td>
<td>1.70</td>
<td>0.919</td>
<td>1.853</td>
</tr>
<tr>
<td>“Coarse”</td>
<td>As coated</td>
<td>1.64 ± 0.09</td>
<td>1.67</td>
<td>0.924</td>
<td>1.816</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.76 ± 0.11</td>
<td>1.77</td>
<td>0.943</td>
<td>1.882</td>
</tr>
<tr>
<td>“Feathery”</td>
<td>As coated</td>
<td>1.11 ± 0.05</td>
<td>1.19</td>
<td>0.950</td>
<td>1.254</td>
</tr>
<tr>
<td></td>
<td>1100°C/100h</td>
<td>1.46 ± 0.07</td>
<td>1.65</td>
<td>0.911</td>
<td>1.819</td>
</tr>
</tbody>
</table>
6 Discussion

6.1 Influence of the process parameters on the columnar microstructure of EB-PVD PYSZ TBCs

Differences in the manufactured coatings presented in Fig. 5.1 and the corresponding data in Table 5.1 were achieved by varying the process parameters, principally the substrate temperature and rotation speed during the EB-PVD process. The process parameters of the EB-PVD process are the factors controlling the spatial and geometrical characteristics of the created porosity. Rotation speed influences mainly the shadowing effect between neighboring columns, which is accountable for the number, size and shape of the created intra-columnar pores, and voids between feather-arms, and consequently the inter-columnar gaps composing the EB-PVD TBCs. Furthermore, substrate temperature influences the number of nucleated primary columns, and the activation of surface mass diffusion that influences the persistency of the nucleated intra-columnar pores and voids between feather-arms. Mass diffusion phenomenon binds the created “banana” shaped elements, closing the corresponding coupled pores in form of intra-columnar pores and voids between feather arms. Then, the distribution of the pores within the primary columns is mainly affected by the period of time that each section of the growing surface is exposed to the vapor phase, and the diffusion of the attached atoms to reduce the created surface area. Investigations of the EB-PVD PYSZ TBCs processing by Schulz et al. [213] reported the creation of microstructures analogous to “fine”, “intermediate” and “parallel” obtained by the use of similar process parameters. Schematic representation of the influence of the substrate temperature and rotation speed on the columnar microstructure of EB-PVD coatings observed in this work is shown in Fig. 6.1. This information complements the tendency reported by Schulz et al. [96] at intermediate rotation speed and substrate temperatures. In this work, different microstructural tendencies are observed principally at high rotation speed along the investigated substrate temperature range. An enhanced conical shape of the primary columns in “feathery” coatings was observed, which is different from the microstructure obtained at intermediate substrate temperatures-rotation speed (950°C/12rpm). Moreover, higher substrate temperature promotes the formation of finer primary columns grown in a parallel arrangement.

Figure 6.1: Schematic representation of the influence of the rotation (rpm) speed and substrate temperature (K) in the microstructure of EB-PVD PYSZ TBCs.
Rotation of the substrates during the coating process alters the interrelation between the different zones of the Movchan’s diagram (see Fig. 2.8). At low rotation speed, the microstructure changes from Zone 1 to the corresponding high temperature limit of Zone 2. Alternatively, the microstructure seems to remain unchanged among the limits of Zone 1 and the neighboring low temperature region of the Zone 2 at high rotation speed. Monte Carlo simulation of the effect of the process parameters in the microstructure of EB-PVD coatings by Cho [88] also demonstrates the tendency of the rotation to move the zones of the Movchan’s diagram toward lower temperatures.

Furthermore, Fig. 6.2 exhibits that there is a clear interrelation between the process parameters: rotation speed and substrate temperature, and the bulk density of the manufactured EB-PVD coatings. Similar substrate temperature-bulk density tendency is also reported by Schulz et al. [214] by EB-PVD coatings deposited on flat substrates at the same chamber pressure (8x10^-4 mbar). Additionally, results reported by Jang et al. [215] also indicate the linear dependence of the bulk density on the rotation speed utilized during the deposition of EB-PVD coatings at 950°C. Moreover, the low and high bulk density values of the coatings manufactured under boundary manufacture conditions: “feathery” and “coarse” respectively, indicate a strong interrelation between the rotation speed and substrate temperature as previously indicated in this section.

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**6.2 Analysis of the effect of sintering phenomena on the morphology of “intermediate” EB-PVD PYSZ TBCs**

The microstructure of “intermediate” EB-PVD TBCs is formed by a 7-8 wt.% Y_2O_3 partially stabilized ZrO_2 ceramic material grown from the vapor phase in form of single crystal columns. This ceramic consist mainly of a single meta-stable tetragonal phase stabilized by the partial substitution of two Y^{3+} ions in two Zr^{4+} sites, creating one O^{2-} vacancy to keep electroneutrality within the unit cells. Exposure to in-service high temperature conditions of this meta-stabilized crystalline material enclosing equilibrated lattice defects will cause the reduction of the overall surface area. The first sintering stage under ageing occurs primarily through the consolidation of bonding necks between individual primary columns at the bottom region of the coating (see Fig. 6.3b), as well as at previously formed contact points along the voids between feather-arms (secondary columns) at dense regions formed by the material deposited after each rotation movement (see Fig. 6.3c). As in the case of solid-state sintering of powder compacts, the effect of the surface tension along the periphery of the formed necks provides a driving force that acts to attach sections together. Moreover, fine
intra-columnar pores break up into arrays of low aspect ratio voids due to the increase in amplitude of developed periodical perturbations produced by Rayleigh instabilities (see Fig. 6.3d).

Figure 6.3: SEM micrographs displaying cross-sections of different zones in EB-PVD PYSZ top coats in as-coated conditions: top region (a), bottom region of the coating (b), feather-arms (c), and intra-columnar pores (d). Arrows indicate the formed contact points during the coating deposition.

Thermal induced stabilization of the inter-columnar spacing occurs mainly at the bottom region by the created necks at the prior formed contact points. Rayleigh instabilities are unable to join the columns due to the large dimensions of the inter-columnar gaps (see Fig. 6.4b). The configuration of these grain boundaries encloses broad enlarged gaps along their length. Thus, it is rather unlikely that considerable mass diffusion occurs through grain boundaries between the columns. Moreover, grain-boundary diffusion can be directly ruled out for the analysis of the voids between feather-arms and intra-columnar pores within the single crystal columns since these features do not interact with grain boundaries. Furthermore, open exterior sections of voids between feather-arms tend to smooth due to Laplace stresses created by the presence of concave-convex curvatures. This effect is enhanced by the remaining high aspect ratio of these features (see Fig. 6.4c). The only diffusion mechanism capable to activate and enhance these changes is surface diffusion. In turn, intra-columnar pores distributed within the cross-section of the primary columns can be eliminated only by lattice diffusion due to their closed isolated nature (see Fig. 6.4d).
Figure 6.4: Scanning electron micrographs of EB-PVD PYSZ top-coat cross-sections displaying the evolution of the pores during ageing conditions at 1100°C for 1h: at the top region (a), at the bottom region of the coating where the bonding between primary columns at the previously formed contact points principally occurs (b), and at the region between feather-arms (c). Isolated intra-columnar pores exhibit a low aspect ratio shape (d). Arrows indicate the formed sintering bridges in (b), and the remaining voids between feather-arms in (c).

Considering the abrupt decrease of the surface area during isothermal ageing at 1100°C shown in Figure 5.2, it appears that mass diffusion has already started during the heating period before the selected exposure temperature was reached. It is evident that the low surface area configuration of the open and closed pores after ageing for 1h at the given temperature reaches a partial equilibrium (i.e. smoothness) state. Regarding to the surface area changes occurring during the investigated ageing time, such partial equilibrium is more pronounced in open pores (measured by BET) than in closed ones (determined by SANS) (see Fig. 5.2). Thermal stabilization of the surface area of open pores (BET) is achieved in shorter ageing times (1 h).

This partial equilibrium state indicates that the specific surface energy corresponding to the achieved curvature of the pore surfaces is not high enough to drive atomic diffusion within a reasonable time at the applied ageing temperature. Analogous results were found by Akash et al. [147], who demonstrated that an equilibrium shape (smoothing) of the pores of tetragonal structured 3mol% YSZ powder compacts was reached after different but defined periods of time at various ageing temperatures. This effect was assumed to occur if sintering is governed solely by surface diffusion. Moreover, Gregory et al. [216] stated that in the case of pores with a non-equilibrium morphology, transfer of atoms must occur from rough to smooth surfaces. For the occurrence of material transfer between different surface morphologies, a
nucleation energy barrier must be overcome. If this barrier is not overcome, the morphology change of the pores will be achieved only at a fraction of the final equilibrium shape.

Furthermore, measurements of the surface area reductions after ageing of the EB-PVD coating at different temperatures during a constant time provides information of the activation temperature and energy of the mass diffusion processes. Microstructural observation of the coatings aged at different temperatures for one hour shows that substantial changes in the morphology and distribution of the porosity occur at temperatures between 900°C to 1100°C (see Fig. 5.5a and Fig. 5.5b). Moreover, the change in the slope in Fig. 5.4 and micrographs in Fig. 5.5c and Fig. 5.5d indicate that the morphological alteration becomes rather slight in the temperature range between 1100°C and 1400°C. The \( \langle \Delta S/S_0 \rangle \) values in Fig. 5.4 indicate that the sintering process of the analyzed EB-PVD coatings begins at 900°C. Similar results were reported by Fritscher et al. [94, 140] and Schulz et al. [217]. Using the model suggested by German [153], the ratios between the activation energy and the mechanism constant \((Q/\gamma)\) for the two different slopes of the curve were calculated. At the temperature range of 900-1100°C, the yield average calculated \((Q/\gamma)\)-ratios are 114 kJ/mol and 120 kJ/mol for the BET and SANS data, respectively. Comparing the calculated \((Q/\gamma)\)-ratios with those of the literature data [153] \((Q_{SD} \approx 430 \text{ kJ/mol})\) and the coefficients suggested by Hillman and Herman (3.6 for surface diffusion) [153, 154], one can postulate that surface diffusion (120 kJ/mol) is the most suitable diffusion mechanism to occur during ageing of PYSZ EB-PVD coatings at the temperature range of 900°C and 1100°C. Similar conclusions were previously reported by Lughi et al. [218]. At the temperature range of 1100-1400°C, the surface area reduction exceeds the limit of applicability of the model used. Nevertheless, the resulting extreme low \(Q/\gamma\) value (~ 9 kJ/mol) does not fit with any of the different mass diffusion mechanism transport typical for these types of ceramic materials. Moreover, even this low \(Q/\gamma\) value still indicates that a certain mass transport still occurs. STEM micrographs in Fig. 6.6 show that some intra-columnar pores interconnect to each other during their shape evolution to lower aspect ratio geometry. The new concave-convex configuration created within these colloidal features enhances the additional surface area changes detected at these high temperature ageing conditions. It is likely that at this range, mass transport in the low aspect ratio pores is rate-limited due to the lower aspect ratio geometry achieved by all pores within the coatings. Morphology of isolated pores seems to reach a partial equilibrium shape after 1h ageing at 1100°C. Pores with anisotropic surface energy containing flat surfaces or those with isotropic energy with curved surfaces may become meta-stable after ageing at determined conditions.

The presence of complex pore morphologies in EB-PVD PYSZ top coats should be regarded for interpretation of the influence of surface diffusion on pore morphology changes and consequently on sintering. It is likely that in different pore groups different morphological changes occur although the driving force for their initiation might be the same, namely the reduction of the surface area. The transition state of the mass transport between the facets of isolated pores is governed by diffusion-limited shape changes and attachment-detachment limited shape changes. Dramatic differences in the evolution of complex shapes take place with ageing time when surface diffusion is rate-limiting or attachment-detachment of atoms from a facet source to a sink facet is rate limiting. Bullard and Searcy [219] state that whenever both convex and concave facets are present on a crystalline surface, the created edges (terraces) provide favorable sites for the formation of monolayer ledges at which detachment and attachment of molecules (or atoms) can occur during diffusion process. This configuration is similar to the terrace-ledge-kink model proposed by German et al. [153] (see Fig. 6.5). Therefore, by the sintering of enlarged pores within a solid material, mass transport between faceted surfaces is unlikely to be rate limited by the nucleation of ledges. This configuration provides the driving force for surface diffusion due to the significant differences
in curvature. Thus, it is reasonable to assume that the coarsening process of voids between feather-arms is a result of surface diffusion driven matter transport leading to detachment/attachment process from convex to concave facets. This process takes place until one of the mass transport rate-limiting effects occur.

**Figure 6.5**: Schematic of the configuration created at a free surface composed by ledges and kinks between flat terraces, and vacancies and adatoms at the intermediate flat surfaces. This arrangement provides active sites for atomic detachment and reattachment during surface diffusion [153].

Furthermore, it is important to establish if the intra-columnar pores close up by lattice diffusion during the ageing conditions. STEM micrographs show that during the shape evolution activated by the sintering process several pores get connected to each other creating bigger cavities after ageing at 1100°C for 1h (see **Fig. 6.6a**). These newly created features require additional energy to reach the equilibrium Wulff shape [220] due to their larger curvatures. Pores attain this equilibrium Wulff condition by achieving a shape which ensures that the specific surface energy of the involved facets divided by the distance to the center of the pore remains constant. In the case of isotropic specific surface energy, an enlarged particle or void shape will change to spheres by constant volume. However, pores with anisotropic surface energies will often persist in meta-stable shapes [221]. The shape of isolated, nano-size intra-columnar pores reaches the equilibrium state during ageing at 1100°C/100h. Pores with approx. 5 nm size remain present within the cross-section of the primary columns (see **Fig. 6.6b**). The attained geometry of these features displays the typical configuration of a Wulff shape enclosing anisotropic surface energies (non-spherical shapes). This effect results in a meta-stable shape configuration because different crystallographic faces have different surfaces energies. Planes of densest atomic packing are also planes of lowest surface energy, and consequently are usually the most stable.

**Figure 6.6**: Transmission electron micrographs of EB-PVD PYSZ top coats cross-sections displaying the size, shape and distribution of intra-columnar pores after ageing at (a)1100°C/1h, and (b)1100°C/100h. Arrows indicate the pores that are approx. 5 nm sizes.
6.3 USAXS analysis of the anisotropic nature of the porosity in three EB-PVD PYSZ TBCs

USAXS analysis and SEM micrographs in Section 5.1 indicate that basically all three investigated coatings show variation in the spatial and geometrical characteristics of the pores and column density in the in-plane directions perpendicular and parallel to the axis of substrate rotation. USAXS analysis method collect information from the EB-PVD coatings through the x-rays scattered at the pores/solid material interface. The scattering intensity collected at the aniso-scans and \( I(Q) \) curves enclose the information from the in-plane section of openings oriented parallel to the x-ray beam. In the as-coated state, the inter-columnar gaps are slightly broader, and evidently contain higher volumes at the cross-sections of the direction perpendicular to the axis of substrate rotation compared with the parallel direction at the three analyzed coatings. Similarly, the qualitative results reported by Terry [15] also indicate the anisotropic distribution of the porosity in EB-PVD PYSZ TBCs, relying solely on microstructural investigations. Furthermore, it was observed that the USAXS modeling calculates a higher overall volume fraction than the value obtained by the Archimedes method in the orientation perpendicular to the axis of substrate rotation, whereas the overall volume fraction calculated for the parallel direction is lower than the Archimedes method value. This interrelation between the perpendicular and parallel analyzed directions corresponds to the anisotropic nature of the porosity distribution in these coatings. The anisotropic configuration of the columns and porosity in EB-PVD TBCs results mainly because of the rotation movement [15]. This movement creates a varying oblique vapor pattern interacting along each column ridge and shadowed by the neighboring column tip. This effect is supported by the relative position between the tips of the primary columns oriented parallel and perpendicular to the axis of substrate rotation, and the incidence of the vapor cloud into a specific zone of the growing surfaces during a certain period of time.

The enlarged column tip profile oriented parallel to the axis of substrate rotation exhibits a smoother decay of its height compared with the tip oriented perpendicular to the axis of substrate rotation. The scheme presented in Fig. 6.7 exhibits this spatial configuration between the tips of neighbouring primary columns manufactured in rotated conditions. The ridges and the surfaces attached in the perpendicular direction are mainly time dependent (ridge CF), whereas those at the parallel direction are principally influenced by the shadowing effect of the neighboring column tip (ridges AC and CE). The BC and CD zones of the ridges oriented parallel to the axis of substrate rotation get simultaneously in contact with the vapor phase, whereas the infinitesimal regions comprising the AB and DE zones and the CF zone in the perpendicular direction are time dependent. Thus, contact of the vapor cloud with the infinitesimal zones composing the complete length of the ridges oriented in the direction perpendicular to the axis of substrate rotation occurs within shorter periods of time than those at the parallel direction. Consequently, the columns cross-section is elongated in a direction parallel to the axis of substrate rotation (see Fig. 6.7). This configuration corresponds to an anisotropic distribution of the porosity. Enlarged inter-columnar gaps oriented parallel to the axis of substrate rotation are created together with a higher density of corresponding voids between feather-arms at their periphery, and intra-columnar pores within the enlarged columns. In accordance, Terry [15] described the enlargement of the profiles of the columns in the directions parallel and perpendicular to the axis of substrate rotation by the differences in the decrease of the incident vapor flux angle. Moving away form the center of the column tip (point C) in the direction perpendicular to the profile changes results in a steady decrease of the incident vapor flux angle, whereas moving in the parallel direction does not immediately results in a decrease of incident vapor flux angle.
Figure 6.7: Schematic distribution of the tips of the EB-PVD TBCs primary columns in top view (top) and in the direction perpendicular to the axis of substrate rotation (bottom). Letters indicate the different interacting zones of the columns ridges produced by the rotation movement during the deposition process.

SEM micrographs in Fig. 5.10 to Fig. 5.12 show the cross-sections oriented in the directions parallel and perpendicular to the axis of substrate rotation of the analyzed EB-PVD coatings in as-coated conditions. Inter-columnar gaps are more clearly defined and wider in the direction perpendicular than in the direction parallel to the axis of substrate rotation. This specific configuration is mainly influenced, likely by the columns tips, by the shadowing effect and the orientation of the ridges comprising the primary columns tips during the rotation of the substrates. The vapor deposition process at the periphery of the columns is particularly rate- and geometrically limited by the unfavorable contact of these regions with the vapor phase. Differences in both analyzed directions are created by divergences in the profile (slope and length) of the columns tips oriented perpendicular and parallel to the axis of substrate rotation. Taking into account that the height of each primary column tip is the same in both directions, especially Fig. 5.10 and Fig. 5.11 clearly show that the meeting point between the parallel edges of neighboring columns is shifted upwards in the parallel direction due to the larger and flatter profile of the columns edges in this direction. The scheme presented in Fig. 6.8 displays the arrangement between columns tips both orthogonal directions. This configuration allows the vapor phase to be in contact with the peripheral edges of the columns during larger periods of time. Thus, a fill-up effect of the gaps in-between the primary columns occurs in this meeting point between the ridges oriented parallel to the axis of substrate rotation. This hypothesis agrees well with the information published by Terry [15] who reported that the shadowing effect the dimensions of the inter-columnar gaps is the profile of the columnar grain tips, which makes it more difficult or easy for the vapor flux to reach the bottom of the valleys in between.

Figure 6.8: Schematic configuration of the EB-PVD TBCs primary columns tips in the direction perpendicular and parallel to the axis of substrate rotation showing the differences in the height of the meeting point between column ridges and the incident vapor flux angle (γ) at these points.
The characterization of the porosity solely by observation of micrographs would contain significant uncertainties due to the presence of macro-defects (see Fig. 6.9), micro-variations along the columns length (see Fig. 5.10 to Fig. 5.12 top and bottom), and at the complete periphery of the primary columns (see Fig. 5.10 to Fig. 5.12 left and right). Normally, features comprising real materials enclose anisotropic spatial and geometrical characteristics. In this case, USAXS analysis determines the statistical representative values of the geometrical and spatial characteristics of the porosity in EB-PVD coatings. Therefore, this analysis method is better suitable for the characterization of anisotropic systems like the porosity within EB-PVD TBCs. In the case of inter-columnar pores and voids between-feather arms, the cross-section changes from thin dimensions toward broader sizes at their edge zone. Then, since this configuration encloses in some cases a broad size distribution, the corresponding configuration is accomplished by the USAXS analysis through the use of two populations. However, this case also implies that there is a high concentration of fine and coarse sections, which can not be grouped in a single population for their analysis. This fact is accounted by fitting process since it considers the statistically representative values representing the dimensions accounted for all measured features.

![Figure 6.9](image)

**Figure 6.9**: SEM micrograph top view of a “parallel” EB-PVD PYSZ coating showing the enlarged tips of the primary columns and their inter-columnar gaps. Arrows show macro-defects between primary columns.

The geometrical characteristics obtained by the fitting of the USAXS data corresponds to the dominating dimensioning of the scattering pores, which are normally not the extreme values observed in the top or the bottom region of the EB-PVD TBCs. Since the primary columns and their corresponding inter-columnar gaps are enlarged in the direction perpendicular to the axis of substrate rotation (see Fig. 6.7), and the profile (slope and length) of the columns tips, such calculated diameters and volume fraction are normally larger in this direction in all analyzed coatings.

### 6.3.1 Inter-columnar gaps

USAXS analysis shows that there is a common distribution of the inter-columnar gaps in the three analyzed EB-PVD coatings: “intermediate”, “coarse” and “feathery”. This indicates that fine width features dominate the direction parallel to the axis of substrate rotation, whereas broad features dominate the perpendicular direction. This tendency is in agreement with the microstructural observations in SEM micrographs (see Fig. 5.10 to Fig. 5.12) and the shadowing effect exposed in Fig. 6.7. In the case of “intermediate” and “coarse” coatings, inter-columnar gaps are represented by two USAXS populations: fine and coarse. However, the absence of such coarse sections of inter-columnar gaps in the corresponding micrographs in Figs. 5.10 to Fig. 5.11, and Fig. 5.19 to Fig. 5.20, and the low volume fractions of these coarse populations indicate that the obtained dimensions in the USAXS modeling do not
correspond to representative inter-columnar gaps, but to inter-columnar macro-defects. Large widths of the resulting inter-columnar gaps in the parallel direction in “feathery” coatings confirm that these are accounted for macro-defects. The absence of fine USAXS population in these “feathery” coatings is originated by the extreme irregularities in the enlarged shape of the inter-columnar gaps (see Figs. 5.12 and 5.21). This irregular configuration does not accomplish the shape homogeneity required for the detection of representative features by USAXS. The low substrate temperature utilized for the vapor deposition enhances the attachment of particles at the peripheral edges of the columns oriented parallel to the axis of substrate rotation without the required energy to migrate to places that satisfy lower surface energy configurations. This configuration creates the resulting differences in the size distribution and volume in each of the analyzed orthogonal directions by USAXS. Moreover, two populations (fine and coarse) represent the distribution of the inter-columnar gaps oriented in the direction perpendicular to the axis of substrate rotation of these “feathery” coatings. This specific characteristic indicates the enhanced competitive growth process between the nucleated primary columns during the coating deposition. This tendency is also exhibited by the largest conical relation between the dimension of the primary columns at the bottom and top regions of these coatings (see Table 5.1). Similar values showing the enhancement of the conical section of the primary columns by increasing the substrate rotation were reported by Jang et al. [222].

According to the aniso-scans shown in Fig. 5.9, the orientation of the inter-columnar pores in all analyzed coatings tends toward azimuthal angles perpendicular to the substrate plane, which is in good agreement with the observed angles in the corresponding SEM micrographs. Correspondingly, higher volume fractions of the USAXS populations representing the inter-columnar gaps in the direction perpendicular to the rotation axis confirms the anisotropic configuration of such features in the EB-PVD TBCs. Volume fractions of the inter-columnar gaps in the “intermediate” and “feathery” coatings exhibit an evident dominance of the features oriented in the perpendicular direction by considering only the representative fine USAXS populations in the parallel direction. This configuration is created by the finer dimensions and lower density of inter-columnar gaps determined in the cross-section oriented in the direction parallel to the axis of substrate rotation.

In the case of “coarse” coatings, the volume fraction of the fine USAXS population in the parallel direction is slightly higher than the volume fraction of the inter-columnar gaps in the parallel direction. Aniso-scans in Fig. 5.9b demonstrate that in the cross-section oriented perpendicular to the axis of substrate rotation the inter-columnar gaps exhibit an extremely narrow size distribution. It seems that toward the top region of the coatings, the broad section of the inter-columnar gaps is particularly large and contains a significant volume fraction of the inter-columnar gaps. The calculated volume fraction of gaps corresponding to this perpendicular cross-section is restricted by the low nucleation and enhanced width of the gaps by the growth of fewer primary columns under these specific manufacturing conditions (e.g. high temperature/low substrate rotation). Thus, the modeling of this coarse section is not possible by the USAXS method since it is restricted by the size, shape, and volume fraction of the modeled gaps. Such a configuration is produced by the nucleation and growth of fewer primary columns under the fixed manufacturing conditions, which enhances the extreme enlargement of the created inter-columnar gaps toward the top of the coating.

6.3.2 Voids between feather-arms

Voids between feather-arms are created at the periphery of the primary column edges (see Fig. 5.18). Spatial and geometrical characteristics of these voids are directly related to the anisotropy of the primary columns, and consequently, also to the intra-columnar gaps.
USAXS analysis exhibits clear differences in the orientation and length of these voids by measuring the cross-sections oriented in the in-plane directions perpendicular and parallel to the axis of substrate rotation. Normally, voids in the parallel direction display higher azimuthal angles and shorter lengths compared to the voids in the perpendicular direction. This configuration exhibits an alteration in the interaction of the different zones of the column peripheral edges with the vapor phase caused by the rotation movement during the EB-PVD process. Differences in the shape and height of the primary column ridges modifies the duration of vapor deposition at the peripheral edges of the primary columns, and the angular range of vapor incidence during the rotation movements (see Fig. 6.8). Similar deduction is exposed by Schulz et al. [223] about the direct influence of the vapor incidence angle (VIA) on the geometrical characteristics of the feather-arms.

Voids between feather-arms observed in the direction perpendicular to the axis of substrate rotation are nucleated at the created intra-columnar pores in the growing front of the column tips (e.g. for “intermediate” coatings see Fig. 5.19b). The persistence of such features is assured by the short exposition period of the incident vapor in this direction. Thus, the length of voids between feather-arms in the perpendicular direction is larger because these start growing from intra-columnar pores deep in the columns core. Moreover, voids between feather-arms in the parallel direction also start growing at intra-columnar pores located near the edge of the primary columns in the zone D toward the zone E of the Fig. 6.7. In this direction, it is observed that the middle region of the columns core is occupied by intra-columnar pores oriented parallel to the column axis located in the zones BCD of the Fig. 6.7 (e.g. for “intermediate” coatings see Fig. 5.19a). Thus, the created voids between feather-arms exhibit shorter lengths than those in the perpendicular direction. Hence, the orientation of the voids between feather-arms is governed by the orientation of the intra-columnar pores. Furthermore, voids between feather-arms in the parallel direction are nucleated by intra-columnar pores slightly oriented toward oblique angles from the direction parallel to column axis. Then, these features exhibit orientations at higher azimuthal angles in the parallel direction. In the perpendicular direction, the orientation of the voids between feather-arms is determined by the number of arrays created after each rotation movement comprising the length of the feather-arms. In the case of “intermediate” and “feathery” coatings, the total length of the feather-arms contains several of these arrays (see Figure 5.19b and Fig. 5.21b). However, in the case of “coarse” coatings, most of the voids between feather-arms comprise the void section formed within a single rotation movement due to the employed slow rotation speed. Thus, the resulting feather-arms display only a section of the large curved “banana” shaped geometry that corresponds to higher azimuthal angles (see Fig. 5.20b). The assumed interrelation between intra-columnar pores and voids between feather-arms as nucleus for the formation of these open voids contradicts the conception considered by Terry [15]. Terry’s work describes the nucleation of feather-like pores between terraces created by previously formed multilayered steps on the four surfaces comprising the column tip.

In the three analyzed EB-PVD coatings, the voids between feather arms created at the direction perpendicular to the axis of substrate rotation are represented by the USAXS analysis as composed by two populations: fine and coarse. This configuration exhibits the triangular cross-section of such features, especially in the perpendicular direction. In the case of “intermediate” and “feathery” coatings, these two sections comprise the total length of the measured voids (see Fig. 5.19b and 5.21b). The two determined populations in “coarse” coatings correspond to a mixture of individual features instead of sections of single voids (see Fig. 5.20b). The enhanced depth of these features into the column core occurs due the low values of the angle of vapor incidence and the corresponding period of time for the vapor deposition in this perpendicular direction to the axis of substrate rotation. This configuration avoids the close-up of the created intra-columnar pores during their growing process toward
the periphery of the columns. Moreover, in the direction parallel to the axis of substrate rotation, the voids between feather arms are represented by one single USAXS population in the “intermediate” and “coarse” coatings. The short length of these features in this direction is a consequence of the longer exposure time to the vapor phase of the region where these voids nucleate and grow. Then, the nucleation and growth conditions occur near the periphery of the columns where the incidence of the vapor phase is insufficient to close-up the created intra-columnar pores. However, in “feathery” coatings, these features are comprised by a fine and coarse section likely in the perpendicular direction. In this case, the enlargement of these voids is a consequence of an irregular deposition of the vapor phase due to the used process parameters (e.g. low substrate temperature/high rotation speed). The voids nucleated deep into the primary columns core are able to propagate until they reach the edge of the columns due to the absence of surface diffusion at the corresponding low substrate temperature.

Volume fraction of the voids between feather-arms in the perpendicular direction exhibit higher values than in those in the parallel direction of the “intermediate” and “coarse” coatings. This effect is in agreement with the two fine and coarse USAXS populations representing the large voids in the perpendicular direction, whereas a single population is accounted for the short voids in the parallel direction. In “feathery” coatings, the volume fraction of voids accounted in the perpendicular direction is slightly lower than in the parallel direction. This configuration is mainly acquired by the external coarse section of the voids in the parallel direction. The deposition of the vapor phase in these “feathery” coatings is particularly irregular in this region, which enhances the creation of high number of these coarse features. Generally, higher volume fractions were calculated for the fine section (fine USAXS population) of voids between feather-arms in the perpendicular direction. This effect indicates the regularity of the nucleation process of these voids deep in the core of the columns, and their continuous growth capability toward the edges of the columns.

6.3.3 Intra-columnar pores

Intra-columnar pores are created in the core of the primary columns. The formation of these features is directly influenced by the anisotropic contact of the growing tips of the columns with the vapor phase due to the rotation movement. Analyzed EB-PVD coatings exhibit the anisotropic character of such features in the 3D space, and the presence of two groups composing these pores type:

(a) “Cut-shaped” intra-columnar gaps oriented in the direction parallel to the primary column axis (yellow A figures in Fig. 6.11). These can be most easily observed in the cross-sections oriented in the direction parallel to the axis of substrate rotation of the middle region of the primary columns core (see Fig. 5.18d). These gaps exhibit two sections: (1) broad nucleation and (2) fine growth section composing the total length (see Fig. 6.11). Therefore, only the coarse section was characterized by the USAXS analysis due to the restricted number of void populations utilized for the modeling. The geometry of such features was represented by an oblate shape.

(b) Enlarged intra-columnar pores oriented oblique to the substrate plane (orange B1 and B2 figures in Fig. 6.10). These pores are observable at both cross-sections oriented in the directions perpendicular and parallel to the axis of substrate rotation (see Fig. 5.18c). Nevertheless, these features occupy the complete core of the primary columns in the perpendicular direction, whereas they are created near the peripheral edge of the primary columns in the parallel direction. These intra-columnar pores nucleate between the tips of the “banana” shaped elements of the last deposited material and grow in between the next formed “banana” shaped features created during each rotation movement. The achieved
The geometry is similar to a curved “sperm-cell” 3D shape composed of a nucleation oblate section followed by a growing enlarged prolate section (see Fig. 6.10). The Fig. 6.10 displays the USAXS-SEM determined shapes and sections of the intra-columnar pores. The formation and growth of such intra-columnar pores is directly related to the deposited material in form of individual “banana” shaped elements after each rotation movement (see Fig. 6.12). This individual curved structure represents the primary elements shaping the overall growth process of EB-PVD coatings during the vapor deposition. The existence of these features was also reported by Terry [15] as nano-sized “fingers” created at the periphery of the primary columns on stationary conditions at VIA = 45°. The tips of individual nano-sized bananas are the first and the last regions getting exposed to the vapor phase during the “sunrise-sunset” period along the growing surface. In this way, such elements assure their continuous growth from the column core until they reach the periphery of the primary columns in form of feather-arms. A nano-shadowing effect takes place between tips of the “banana” shaped features similar to the shadowing between the pits of individual columns. Analogous deductions are reported by Schulz et al. [223] about the similitude in the shadowing mechanism during the growth of the primary columns and the feather-arms.

![Image](image1.png)

**Figure 6.10**: SEM micrograph of the cross-section oriented in the direction perpendicular (left) and parallel (right) to the axis of substrate rotation of the “coarse” EB-PVD coatings showing the determined intra-columnar pores sections and shapes. Figure B1 and B2 comprise the single “sperm-cell” shaped pores, and A represents the “cut-shaped” intra-columnar pores.

![Image](image2.png)

**Figure 6.11**: SEM micrographs showing the nucleation and growth section of enlarged shaped intra-columnar pores created during the vapor condensation in “coarse” coatings: sperm-cell intra-columnar pores in the cross-sections oriented in the direction perpendicular (a) and “cut-shaped” intra-columnar pores localized in the cross-section oriented in the direction parallel to the axis of substrate rotation.

Intra-columnar pores in the cross-section oriented parallel to the axis of substrate rotation in the three analyzed coatings are represented by two USAXS populations. Particularly in this
parallel direction, these pores are created at different regions within the core of the primary columns. One “cut-shaped” group is located in the middle region of the columns core in-between the “banana” shaped elements arrays. The shape of these pores can be approximated by a thin oblate spheroids oriented parallel to the axis of the primary columns. In the case of “coarse” coatings, the created intra-columnar pores in the middle of the columns core are shaped by the activated surface diffusion mechanism due to the attained high substrate temperature during the EB-PVD process. These pores display a low size in relation to the length of the attached “banana” shaped elements, due to the mass transference between these elements (see Fig. 5.20a right). The length of the “cut-shaped” intra-columnar pores in “intermediate” and “feathery” coatings exhibit similar dimensions to the “banana” shaped elements. The second group is located at the external region of the primary columns located in-between individual “banana” shaped elements oriented oblique to the substrate plane behind the voids between feather-arms. The geometry of these pores can be approximated by oblate or prolate shapes. In the case of “intermediate” coatings, this second group of intra-columnar pores is represented by a prolate shape. This configuration indicates that there is a misalignment of the created pores in-between the “banana” shaped elements in the direction perpendicular toward their growing axis. Intra-columnar pores composing this second oblique group are represented by oblate spheroids in “coarse” and “feathery” coatings. In these cases, the pores between individual “banana” shaped elements bind to each other, producing an array configuration that originates the oblate shape.

**Figure 6.12**: SEM micrographs showing the enlarged individual “banana” shaped elements created during the vapor condensation in “intermediate” coatings. These features are visible at the feather-arms (a) and at the cross-section of the column core in the direction perpendicular to the axis of substrate rotation (b).

In the cross-section oriented perpendicular to the axis of substrate rotation, enlarged “sperm-cell” shaped intra-columnar pores occupy the complete core of the primary columns. These features are comprised by two sections: oblate shaped nucleation section and prolate shaped growing section, represented by two USAXS populations in the “intermediate” and “coarse” coatings (see Fig. 5.19b right, and Fig. 5.20b right). In these coatings, the detected nucleation section displays noticeably-small length and aspect ratio oblate shapes, whereas the growing section exhibits an enlarged high aspect ratio prolate shape. In the “feathery” coatings, these intra-columnar pores are represented by a single USAXS population due to their extremely small dimensions (see Figure 5.21b right). In this case, the dimensions of the prolate shaped cross-section of these pores remains constant along their complete length.

In all three analyzed coatings, the growth prolate shaped sections of the intra-columnar pores accounted in the cross-section oriented perpendicular to the axis of the substrate rotation, and the obliquely oriented intra-columnar pores in the parallel cross-section exhibit the highest volume fractions, respectively. This configuration improves the isolating capabilities of the
coatings by their occupancy within the primary columns and orientation oblique to the flux of heat.

6.4 USAXS analysis of the influence of ageing on the anisotropic characteristics of the porosity in three EB-PVD PYSZ TBCs

Ageing of the EB-PVD TBCs at 1100°C for 100h induces morphological changes driven by the reduction of the surface energy, i.e. surface area. As mentioned in Section 6.1, bonding necks form along the periphery of neighboring individual primary columns, stabilizing the gaps between them. Additional bonding necks are created at the contact points between feather-arms, breaking up the enlarged section of the attached voids. The enlarged cross-section of intra-columnar pores breaks up into groups of low aspect ratio pores. All these events exhibit a specific influence on the created spatial and geometrical characteristics of the porosity in the manufactured EB-PVD PYSZ TBCs.

6.4.1 Inter-columnar gaps

During ageing of the EB-PVD coatings, some particular alterations in the distribution of the inter-columnar pores take place. Inter-columnar pores of all coatings, except those determined in the parallel direction of “feathery” coatings, exhibit a size distribution represented by two USAXS void populations. This configuration indicates the stabilization of fine and coarse sections of the inter-columnar gaps by the formed sintering bridges principally at the bottom (see Fig. 5.14 to Fig. 5.16) and middle region (see Fig. 5.23 to Fig. 5.25) of the coatings, respectively. Another aspect of the ageing effect on these features is the smoothness of the feather-arm tips located at the periphery of the primary columns. Then, the increase or reduction of the volume fraction is regulated by the interrelation between the closure effect of the bonding necks and the smoothness effect of the peripheral surface area by the reduction of the aspect ratio of the feather-arms. In the case of “feathery” coatings, the section of the primary columns enclosed in the cross-section oriented parallel to the axis of substrate rotation is tightly compacted. Then, the smoothness effect of the extremely irregular section of the inter-columnar gaps in the cross-section oriented parallel to the axis of substrate rotation clearly dominates the close-up effect between the columns. This configuration produces a uniform width of the gaps after ageing.

The width of inter-columnar gaps in the three analyzed coatings slightly decreases after ageing. The exception is the gaps enclosed in the parallel direction of the “coarse” coatings. The smoothness effect dominates the closure of the gaps, once the sintering bridges stabilize the separation between primary columns during ageing. Moreover, changes in the volume fraction of inter-columnar gaps are directly associated with these competing phenomena.

6.4.2 Voids between feather-arms

High temperature ageing of all EB-PVD coatings activates the sintering process. This thermal activated phenomenon induces the closure of the fine section of the triangular cross-section of the voids between feather arms, and the coarsening of fine sectioned voids in both analyzed directions perpendicular and parallel to the axis of substrate rotation. The remaining external open sections exhibit lower aspect ratios and lengths than those in as-coated conditions. Thus, after ageing, the volume fraction of the remaining enlarged voids between feather-arms considered by the USAXS analysis is established by the closure of the fine section of these voids, and the creation of coarse voids by the opening (coarsening) effect between non-contacting fine voids. Moreover, the averaged orientation of the voids between feather-arms
changes to slight higher azimuthal angles (see values in Table 5.2 to Table 5.7) and a larger distribution (broader scattering intensity peaks in aniso-scans polar figures in Fig. 5.13) in both analyzed directions perpendicular and parallel to the axis of substrate rotation. The change in orientation of these voids is related to the change in the considered section of these features by the USAXS analysis. The exterior section, which exhibits an irregular shape in as-coated conditions, is now the only section considered for the analysis of these features after ageing.

### 6.4.3 Intra-columnar pores

Sintering phenomenon activated during the ageing process produces important microstructural changes in the intra-columnar pores as described in Section 6.1. Two dominating populations of low aspect ratio pores (spheres) were detected in the cross-sections oriented parallel and perpendicular to the axis of substrate rotation by the USAXS analysis in all analyzed coatings after the ageing process (see Fig. 5.23 to Fig. 5.25). In the parallel direction, the break-up process of the cross-section of enlarged oblate shaped pores located between the “banana” shaped elements is the dominating effect. In the perpendicular direction, the fine prolate section of the high aspect-ratio intra-columnar pores breaks up into low aspect ratio pores, whereas the oblate coarse region evolves into coarser low aspect ratio pores. Then, the two formed intra-columnar pores groups are composed of arrays of coarse low-aspect-ratio coarse pores, and fine pores located intermittently between these arrays of coarse pores.

### 6.5 SANS-BET analysis of the influence of process parameters and ageing on the microstructure of EB-PVD PYSZ TBCs

#### 6.5.1 EB-PVD PYSZ TBCs in as-coated conditions

The BET analysis of the EB-PVD coatings exhibits principally the differences in the surface of the voids between feather-arms created at the periphery of the primary columns (see Fig. 5.8). Similar deduction of the origin of the BET surface area in EB-PVD TBCs is presented by Fritscher et al. [140]. This analysis method showed that “fine” and “feathery” coatings contain the highest surface area. “Fine” coatings are comprised of very fine primary columns (see Table 5.1) containing short voids between feather-arms, which are regularly interconnected to the intra-columnar pores. This configuration is accomplished by the created large “banana” shaped elements after each low rotation speed, which comprises the total length of the feather-arms. The low substrate temperature enhances the irregularity of the deposited and diffused mass, creating an interconnected configuration (see Figure 6.13). Even tough, the created feather-arms are short as observed in the Fig. 5.1, the elevated number of primary columns per volume unit of the coating gives this configuration the characteristic of containing a high surface area value. Conversely, “feathery” coatings are comprised by conical primary columns (see Table 5.1). These features exhibit extremely deep and numerous feather arms at the periphery of the primary columns (see Fig. 5.1). Since these two coatings were deposited at the same substrate temperature, differences in the columnar microstructures between these two coatings are influenced principally by the rotation speed during the deposition process. As observed in Fig. 5.1, the columnar widths are alike in the bottom region (see Table 5.1), whereas the inter-columnar spacing is more compact in the fine coatings. Thus, the shadowing effect between the primary columns tips, rather than the nucleation process, seems to be the principal factor affecting the growth process of the primary columns and their porosities. Moreover, “intermediate” coatings display a slight higher BET surface area than “parallel” and “coarse” coatings. “Intermediate” coatings exhibit intermediary values of the primary column diameters (see Table 5.1). Their
Discussion

The microstructure exhibits a relatively deep and homogeneous distribution of feather arms along the primary columns periphery. Moreover, “coarse” and “parallel” coatings were deposited at the same substrate temperature. Thus, differences in the columnar structure between “coarse” and “parallel” are influenced by the shadowing between the primary columns tips. “Coarse” coatings exhibit broad primary columns (see Table 5.1 and Fig. 5.1). The deepness of their feather arms related to the primary column diameter is low. In addition, due to the low number of primary columns per volume unit of coating, these exhibit the lowest BET surface area. In the case of “parallel” coatings, the primary columns display diameters similar to those observed in the “intermediate” coatings (see Table 5.1 and Fig. 5.1). Nevertheless, since the deepness of the feather arms is low, these coatings exhibit a low BET surface area (see Figure 6.14).

Taking into account the process parameters utilized for the manufacture of all five EB-PVD coatings (see Table 4.3), it is evident that the substrate temperature is the principal factor controlling the measured BET surface area. Under the influence of the shadowing effect between primary columns tips due to the rotation of the substrates, the substrate temperature governs the nucleation process of the primary columns and the surface diffusion at the growing surfaces during the deposition of vapor. Consequently, the nucleation and subsistence of the feather-arms directly depends on the surface diffusion activated by the utilized substrate temperature.

![Figure 6.13](image1.png)

**Figure 6.13:** SEM micrographs of cross-sections oriented in the direction perpendicular (a) and parallel (b) to the axis of substrate rotation of the “fine” EB-PVD coatings in as-coated conditions.

![Figure 6.14](image2.png)

**Figure 6.14:** SEM micrographs of cross-sections oriented in the direction perpendicular (a) and parallel (b) to the axis of substrate rotation of the “parallel” EB-PVD coatings in as-coated conditions.

Moreover, the anisotropic distribution of the intra-columnar pores can be analyzed via SANS (Porod surface area). The resulting Porod surface area during the SANS measurements emerges by the interfaces between individual pores and solid bulk PYSZ material. Differences in the intensities of the Porod constant (\(P_c\)) at different angle values represent the orientation of corresponding pore regions containing a high surface fraction, which is directly related
with the aspect-ratio of these features. The schematic shown in Fig. 6.15 displays the contribution of each pore to the intensity of the Porod constant is exhibited in the polar figures at angles perpendicular to their main open dimensions. The distribution of the pores orientation controls the sharpness of the resulting peaks.

**Figure 6.15**: Schematic representation of the polar distribution of the SANS-Porod surface area corresponding to the shape and orientation of the scattering pores.

**Fig. 6.16** shows the arrays of “cut-shaped” intra-columnar pores oriented perpendicular to the axis of substrate rotation within the columns, which are the principal contributors to the intensity and orientation of the overall surface area in the horizontal axis (0-180°) (see Fig. 5.6). These features are created in the middle volume of the primary columns (Zone 1) and oriented perpendicular to the axis of substrate rotation. Top view micrographs of all coatings exhibit these “cut-shaped” features in the top surface of the individual columns (see Fig. 5.1 right). Their orientation is parallel to the plane of vapor incidence created through the rotation movement during the vapor deposition process (see Fig. 2.12). Intra-columnar pores in Zone 2 and Zone 3 are distributed within the primary columns around this core of “cut-shaped” pores (see Fig. 6.16), contributing to the intensity of the Porod constant at angles perpendicular to their main open dimensions in Fig. 5.6. The height of the surface area’s polar distribution (90-270°) is originated by the surface area from fine inter-columnar pores created in the Zone 2, and oriented parallel to the voids between feather-arms. Porod constant intensities at intermediate angles are originated principally by the fine intra-columnar pores oriented parallel to voids between feather-arms in the Zone 3.

**Figure 6.16**: Schematic representation and SEM micrograph from the cross-section of the primary columns top view showing the pores arrays accountable for the shape and intensity of the measured Porod constant polar curves: (orange) “cut-shaped” intra-columnar gaps, and (yellow) fine intra-columnar pores parallel to voids between feather-arms.
Fig. 6.17 shows the detailed top view of the shape and distribution of the fine intra-columnar pores within Zone 1 (left) and Zone 2 (right). Fine “cut-shaped” intra-columnar pores are clearly observable at the micrographs taken from the middle region of the primary columns (Zone 1) (see Fig. 6.17a). Higher intensity of the Porod surface area corresponding to these features is enhanced due to their high aspect ratio and low misalignment. Moreover, aligned intra-columnar pores parallel to the voids between feather-arms in the Zone 2 and Zone 3 exhibit lower aspect ratio shapes and a orientation distribution all around the axial center of the primary column axis (see Fig. 6.17b).

Figure 6.17: SEM micrograph from the cross-sections of the top view of primary columns showing the pores arrays accountable for the shape and intensity of the measured Porod constant polar curves: (a) “cut-shaped” intra-columnar gaps within Zone 1, and (b) fine intra-columnar pores parallel to voids between feather-arms within Zone 3. Schematic figures and arrows show the shape approximation of the pores and their location within the cross-section of the primary columns, respectively.

6.5.2 EB-PVD PYSZ TBCs after ageing

After the applied ageing conditions at 1100°C for 1h and 100h, the interrelation between the BET surface area of the different coatings previously observed in as-coated conditions disappears (see Fig. 5.8). After ageing conditions, the surface area values depend on the remaining open section of the feather arms, and obviously on the number of primary columns per volume unit of the coating. Since the manufactured coatings exhibit different configuration of number of primary columns and dimensioning of the feather-arms, the BET surface area reduction takes place during ageing differently in each of the analyzed coatings.

Graphs shown in Fig. 5.8 indicate that “feathery” coatings display the highest surface area reduction, which takes place non-parallel to the other analyzed coatings. In this case, the voids between feather arms contained in these coatings exhibit an extremely fine cross-section and a high aspect-ratio in as-coated conditions. This configuration encloses extremely high driving force energy for sintering phenomenon to occur, inducing the break-up of a considerable large segment of the cross-section of such fine features, and the reduction of the aspect ratio of the remaining voids (see Fig. 5.25). The subsequent occurrence of these two effects induced the observable large surface area reduction. In the case of “fine” coatings containing voids between feather arms with a low aspect ratio, the exhibited surface area reduction is controlled solely by the mass transfer between the convex to concave sections without a break-up of the voids cross section, and the closure of the interconnection to the intra-columnar pores (see Fig. 6.18). Moreover, “coarse” and “parallel” coatings exhibit the lowest surface area reduction after ageing. The porosity is created in these coatings under the
influence of mass diffusion at the high substrate temperatures (~ 1000°C) utilized during the coating deposition. Then pores display a quasi stabilized surface area and shape configuration, which remains almost unchangeable at the applied ageing temperature (1100°C). Thus, the reduction of the aspect ratio effect is considered as the principal factor dominating the surface area reduction of the intra-columnar pores in these “coarse” (see Fig. 5.24) and “parallel” (see Fig. 6.19) coatings. “Intermediate” coatings display a surface reduction pattern which corresponds to an intermediary kinetic state of the created voids between feather arms compared with the other manufactured coatings. This configuration is achieved principally by the used intermediary substrate temperature (~ 950°C) during the deposition of the coatings, which slightly enhances the reduction of the surface area by the activation of the surface mass diffusion (see Fig. 5.23). Especially in these coatings, the BET surface area seems to remains almost unalterable after ageing 1100°C/1h. Nevertheless, this effect is accountable within the uncertainties of the BET method (± 5%).

Figure 6.18: SEM micrographs of cross-sections oriented in the direction perpendicular (a) and parallel (b) to the axis of substrate rotation of the “fine” EB-PVD coatings after ageing at 1100°C/100h.

Furthermore, the sintering phenomenon of isolated intra-columnar pores induces a shape evolution toward low surface area geometry and the collimation between neighboring pores during their shape change. SANS analysis demonstrates that the corresponding surface area of intra-columnar pores abruptly decreases and a narrower distribution of the preferential orientation of the pores is achieved (narrow intensity peaks). The effect of sintering on the surface area distribution is clearly different on each analyzed coating as shown in polar figures shown in Fig. 5.7a and Fig. 5.7b.
Arrays of pores created by the collimation between “cut-shaped” intra-columnar pores and their subsequent shape evolution enhance the emergence of an intensity peak oriented parallel to the horizontal (0-180°) and perpendicular (90-270°) to the rotation axis as shown in Fig. 6.20. The correlation of the evolved “cut-shaped” pores observed in Fig. 6.17 demonstrate the preferential orientation of these features in the direction parallel to the axis of substrate rotation. Additionally, the shape evolution of pores originated by the break up of fine section of voids between feather-arms features located in the Zone 3 (see Fig. 6.16) originates the peaks oriented intermediately to perpendicular and parallel to axis of substrate rotation since these are parallel to the periphery of the columns (see Fig. 5.7). Following the same principle, the pores in Zone 2 also contribute to the peaks oriented parallel to the vertical axis (90-270°). This configuration is created by the related orientation of the polyhedral section achieved by such features during the ageing of the coatings as observable in “parallel” and “coarse” coatings aged at 1100°C for 100h (see Fig. 6.20). Intra-columnar pores achieve a polyhedral shape with their composing edges oriented perpendicular to the surface area peaks displayed in the Porod constant polar figures (see Fig. 6.20).

![Figure 6.20](image)

**Figure 6.20**: SEM micrograph cross-sections of the top view of primary columns of “coarse” (top) and “parallel” coatings (bottom) after ageing at 1100°C/100h, showing the pore arrays accountable for the shape and intensity of the measured Porod constant polar curves: (a) and (c) “cut-shaped” intra-columnar gaps within Zone 1, and (b) and (d) fine intra-columnar pores parallel to voids between feather arms within Zone 3. Figures and arrows show the shape approximation of the pores and their location within the cross section of the primary columns, respectively.

The intensity of the peaks and the abrupt or smooth decay of the Porod constant curves at zones between maximum peaks are directly related to the aspect-ratio of the corresponding pores as shown in Fig. 6.15, and the number of similar oriented pores and their polydispersity. Longer ageing of the EB-PVD coatings for 100 hours at 1100°C diminishes the surface area of the intra-columnar pores. This effect is mainly attributed to the shape evolution toward
lower aspect ratio shapes and the creation of new pores during the collimation process between neighboring features. The stability of formed peaks maxima in the Porod polar figures indicates the stability of the attained polyhedral shape of the intra-columnar pores and the achieved orientation of their edges during ageing. Sintering studies in Section 6.1 exhibit the right-angled equilibrium shape of intra-columnar pores achieved after similar ageing process.

The isotropic or preferred distribution of the Porod surface area of the analyzed coatings is related to the interrelation between the mentioned spatial and geometrical characteristics of the pores containing random and non-random oriented edges. According to the Porod surface distribution in Fig. 5.7b the “feathery” and “fine” coatings still exhibit the highest intra-columnar pore surface area. SEM micrographs in Fig. 5.23 and Fig. 6.17 indicate that the pores resulting from the thermal evolution of the coarse section of the “cut-shaped” pores are the principal contributors to the peak oriented parallel to the 0-180° axis. Specifically in the “fine” coatings, these resulting pores are misaligned from this horizontal axis, which correspond to the misaligned peak resulting form the SANS analysis in as-coated conditions (see Fig. 5.6). Moreover, the surface area distribution of “intermediate” coatings is created by a quasi-perfectly random distribution of the faceted edges of the intra-columnar pores, whereas “parallel” pores contain a higher number of faceted intra-columnar pores with their longest edges oriented parallel to the axis of substrate rotation (see Fig. 6.20). The surface area peaks corresponding to the “coarse” coatings indicate the preferential orientation of the intra-columnar pores in the directions perpendicular and parallel to the axis of substrate rotation, with additional pores oriented in intermediate angles.

Due to the relative low temperature and short time utilized for the ageing of the coatings, the shape of intra-columnar pores are still in the evolving process to reach their equilibrium Wulff shape. Then the resulting orientation, size and shape of the pores is still determined by the original characteristics of these features created during the deposition process. Choi et al. [224] demonstrate that internal cavities in Sapphire smaller than 100 nm reach the equilibrium Wulff shape after ageing at 1600°C/50h.

### 6.6 Thermal conductivity of EB-PVD PYSZ TBCs

Considering the pores as thermal insulators (i.e. insignificant radiation and convection contribution), all types of pores in EB-PVD PYSZ TBCs will contribute to the reduction of the thermal conductivity according to their effectiveness by interrupting the flow of phonons through the coating. The influence of the pores on the thermal conductivity is related to their size, volume fraction, orientation, shape, and spatial distribution. According to the kinetic theory of gases, fine pore dimensions increase the Knudsen number, which consequently restricts the energy exchange of gas molecules within the pore surfaces due to molecule-molecule collisions. Then, the pore changes its capacity from conducting medium to insulator.

Volume fraction of pores influences directly the insulating capacity of the coatings (see Fig. 6.21). Higher volume fraction of the pores corresponds to a higher amount of isolating media within a solid material diminishing the capacity of the heat to flow. Thermal conductivity of EB-PVD coatings exhibits a quasi-linear relation to the bulk density. Similar results on EB-PVD PYSZ coatings were reported by Schulz et al. [102] and Jang et al. [215]. In this case, the values of the bulk density consider the volume of the open (inter-columnar gaps and voids between feather-arms), and closed porosity (intra-columnar pores) in the EB-PVD coatings. Then, the differences in the thermal conductivity in relation to the bulk density of the analyzed EB-PVD coatings indicate the additional influence of the spatial and geometrical characteristics of all these pores on the overall thermal conductivity. Thermal conductivity values of “intermediate”, “fine” and “parallel” coatings are similar, despite the clear
differences in their bulk density. Moreover, the thermal conductivity of “feathery” and “coarse” coatings exhibit clear differences related to the coatings containing slight dissimilar bulk density values. The factors corresponding to inter-columnar gaps \((k_{\text{coat}} / k_{\text{col}})\) in the non-interacting approximation (see Table 5.10) indicate the almost constant effect of their spatial and geometrical characteristics on the thermal conductivity of “feathery”, “intermediate” and “coarse” EB-PVD coatings. This fact indicates that the differences in the thermal conductivity of the analyzed coatings rely in the spatial and geometrical characteristics of the pores within the primary columns.

The orientation of the pores with respect to the heat flux enhances or restricts the influence of variations in their volume fraction. Narrow low volume fraction gaps oriented perpendicular to the heat flux will effectively restrict the heat flux through the coatings than higher volume fraction parallel wide gaps. Furthermore, the shape of the pores affects directly the surface area fraction of the cross-section through which the phonons should flow. Finally, the distribution of the pores within the cross-section along the coating thickness determines the local statistically representative heat flux density. The thermal diffusivity values measured with the LFA method represent the thermal conductivity corresponding to this averaged flux density through the Eq. 2.1.

**Figure 6.21**: Thermal conductivity values as function of density of the manufactured EB-PVD PYSZ TBCs in as-coated conditions.

The different pore kinds in EB-PVD coatings influence the overall thermal conductivity in accordance to their specific spatial and geometrical characteristics. Inter-columnar gaps between primary columns contain their mean open dimension (length) parallel to the heat flux (parallel to the primary column axis). Thus, significant changes in the volume fraction of such features influence only slightly the overall thermal conductivity of the coatings. Voids between feather-arms exhibit an orientation inclined to the heat flux. The influence of such features on the overall thermal conductivity is principally related to their inclination angle, the deepness of the occupied cross-section toward the column core, and the volume fraction. Finally, intra-columnar pores occupy the highest region within the cross-section of the individual primary columns. Their distribution in the columns cross-section and their orientation inclined to the heat flux give these features the capacity to induce a great influence on the overall thermal conductivity of EB-PVD TBCs according to their volume fraction.

Graphs in Fig. 5.26 show clear differences in the thermal conductivities of the five analyzed EB-PVD coatings in as-coated conditions. Generally, coatings manufactured at low temperatures (850°C) exhibit lower thermal conductivity values than those deposited at higher
temperatures (1000°C). However, it seems that there is a strong interrelation between the temperature and rotation speed. Rotation speed and substrate temperature are principally accountable for the number, size and shape of the created porosity through the shadowing effect and the activation of mass diffusion, respectively. Thus, since the middle region of the cross-section is the zone largely exposed to the vapor phase, it is the most dense volume region within the primary columns. This phenomenon is specially enhanced by the deposition of the coatings at higher temperatures. The vapor deposition is accumulatively restricted toward the edge of the primary columns due to the reduction of the time that these regions are in contact with the vapor flux during the “sunrise-sunset” period (angle of vapor incidence < 180°) [15]. Thus, pores created within this edge region exhibit wider and sharper cross-sections. This effect influences the distribution of the porosity within the primary columns.

The flat slopes of the graphs in Fig. 5.26 exhibit the independence of the thermal conductivity to the measuring temperature of the analyzed coatings, except for “coarse” coatings. This insensitivity of the thermal conductivity to variations of the temperature is normally attributed to the presence of Y3+solute ions and O2- vacancies in the meta-stable tetragonal structure that scatter the phonons flowing through the solid material [40, 112]. However, the flat slope of the thermal conductivity curve changes into a T-1 (T is the temperature of the specimen) slope behavior at low temperature values after ageing, which is typical for the Debye temperature behavior (see Fig. 5.28). Under these aged conditions, the thermal conductivity is diminished by Umklapp processes between flowing phonons by increasing the measuring temperatures until the Debye temperature is reached. The mean free path wavelength of the phonons reaches values similar to the inter-ionic distances at this point. Therefore, the thermal conductivity remains unchangeable at higher measuring temperatures. Since the chemical composition and crystalline structure of the EB-PVD coatings remain constant, these observed changes in the curves slope should be influenced by other factors. Thermal diffusivity and specific heat coefficient are the two factors influencing the relation thermal conductivity - temperature of solid materials. Since the specific heat coefficient is principally dependent on the chemical composition, it seems that the thermal diffusivity is the factor inducing the observed slope changes of the thermal conductivities after ageing.

USAXS and SANS analysis have demonstrated that the internal microstructure of EB-PBD coatings exhibit high-surface-area, nano-sized, distributed pores in equilibrium with the solid PYSZ material. Under these conditions, a considerable fraction of the overall ions comprising the primary columns is located directly in contact with the free surface area of the different pore types. These ions vibrate differently to the ions in equilibrium within the solid material. Thus, an accumulative slight scattering effect is induced by each of these surface ions into the phonons flowing through the solid material. Then, a scattering effect is induced. Since the ageing of the coatings induces a reduction of the free surface area, the scattering effect diminishes in relation with the decrease of the free surface area, and a curve with a T-1 slope behavior appears.

Furthermore, the slight increase in the thermal conductivity values at temperatures above 800°C during the LFA measurements of all coatings in as-coated conditions indicates the activation of the mass diffusion (see Fig. 5.29). This behavior agrees with the analysis of the activation of sintering in “intermediate” EB-PVD coatings in Section 6.1. Furthermore, Fig. 5.27 shows that the thermal conductivity values of the EB-PVD coatings in as-coated conditions during the heating and cooling processes by the LFA measurements are different. This effect indicates that an irreversible phenomenon like sintering took place during the heating phase at temperatures higher than 800°C. Sintering induces important microstructural changes in the previously equilibrated pores-solid configuration resulting during the coating process as discussed in Section 6.1. Thus, the insulating effect of orientation and high surface area cross-section of the remaining pores almost vanishes after ageing. It is clear that the
“coarse” and “parallel” EB-PVD coatings with the lowest total porosity volume fraction exhibit the highest thermal conductivity values after ageing (see Table 5.1 and Fig. 5.28). Considering that the volume fraction of the overall porosity remains almost unchanged after ageing according to the Archimedes density measurements and the thermal conductivity graphs in Fig. 5.26 and Fig. 5.28, it is clear that the aspect ratio and orientation of the pores influences directly the effect of the volume fraction on the thermal conductivity of EB-PVD coatings. Moreover, this effect is responsible for the differences in the thermal conductivity increase after ageing at 1100°C/1h for “coarse” and “feathery” coatings. As shown in Table 5.8a, the thermal conductivity of “feathery” coatings is principally governed by the high aspect ratio nano-sized intra-columnar pores, which, after ageing, evolve into low-aspect-ratio pores. Due the enlarged shape and nano size, these pores contain a high energy (driving force) to reach low-aspect-ratio configurations at 1100°C/1h ageing. In the case of “coarse” coatings, the thermal conductivity is principally influenced by the fine voids between feather-arms as shown in Table 5.8a. Ageing of these coatings will induce only a slight increase in the thermal conductivity due to their less effectiveness as insulators and their larger size that affect s the surface energy driving the surface area reduction at the applied ageing conditions.

The surface area of intra-columnar pores in the direction perpendicular to the heat flux after ageing (see Fig. 5.7) follow an interrelated trend to the thermal conductivities of the coatings shown in Fig. 5.28, especially after ageing at 1100°C/1h. EB-PVD coatings containing a higher surface area exhibit lower thermal conductivity values, and vice versa. The morphological changes of the pores modify the distribution of the regions occupied by the voids between feather-arms and intra-columnar pores, and the shape/orientation of these features within the primary columns. Fine sections of voids between feather-arms break up into arrays of intra-columnar pores with low-aspect-ratio shapes. Thus, the surface area determined by SANS after ageing corresponds principally to the intra-columnar pores that mainly influence the thermal conductivity of the EB-PVD coatings after ageing.

6.6.1 “Intermediate” morphology

“Intermediate” EB-PVD coatings display one of the highest total porosity values and an intermediary conical shape of the primary columns as shown in Table 5.1. The factors in Table 5.8a indicate that the oblate-shaped fine section of the voids between feather-arms measured in the cross-section oriented perpendicular to the axis of substrate rotation, and prolate-shaped intra-columnar pores measured in both directions are the principal pores reducing the thermal conductivity through the primary columns. The influence of the geometric and orientation characteristics of these features is enhanced by their high aspect ratio, high volume fraction and small azimuthal angle in these coatings in as-coated conditions. Thermal conductivity values reported by Jang et al. [116] show that EB-PVD PYSZ coatings (~ 300 μm thickness) manufactured at 950°C/10 rpm conditions exhibit similar values to those obtained for “intermediate” coatings (950°C/12 rpm) in this work. After ageing, the achieved reduction of the thermal conductivity through these mentioned characteristics disappears due to changes in the shape of the pores into low-aspect-ratio geometry. Under these conditions, (a) the volume fraction, and (b) the partially-regular distribution of the pores are the principal factor governing the thermal conductivity of the aged primary columns. The influence of inter-columnar gaps on the overall thermal conductivity of these coatings remains unaltered. This effect results from the consistence of the randomly-formed sintering bridges during ageing, which stabilize the opening dimensions of these features.
6.6.2 “Coarse” morphology

“Coarse” EB-PVD coatings exhibit the lowest total porosity and a pronounced conical shape of the primary columns (see Table 5.1). According to the factors in Table 5.8a, the oblate-shaped fine voids between feather-arms, and the enlarged prolate-shaped intra-columnar pores determined in the cross-section oriented in the direction perpendicular to the axis of substrate rotation are the principal factors determining the thermal conductivity of these coatings. Again the high aspect ratio, volume fraction and small azimuthal angle are the principal aspects of these features enhancing their influence on the overall thermal conductivity of these coatings. Investigations on EB-PVD PYSZ TBCs by Jang et al. [225] exhibit comparable thermal conductivity and overall porosity values for coatings (~ 300 μm thickness) manufactured at conditions (950°C/5 rpm) similar to these “coarse” coatings (1000°C/3 rpm). Ageing these coatings induce changes in the morphology of the pores similarly to “intermediate” coatings. Then, the thermal conductivity in the primary columns is only governed by the volume fraction of the remaining low-aspect-ratio pores and an irregular distribution of the pores within the primary columns due to the low substrate rotation. Similar to the “intermediate” coatings, the influence of the inter-columnar gaps on the thermal conductivity of the coating remains constant due to the stability of their open dimensions after ageing.

6.6.3 “Feathery” morphology

“Feathery” EB-PVD coatings display a slightly higher total porosity values than “intermediate” coatings, and an intermediary conical shape of the primary columns as shown in Table 5.1. Their lowest thermal conductivity values in as-coated conditions is governed principally by the oblate-shaped large voids between feather-arms determined in both directions, the prolate-shaped intra-columnar pores determined in the cross-section oriented in the direction perpendicular to the axis of substrate rotation, and by the fine oblate shaped intra-columnar pores identified in the cross section oriented parallel to the axis of substrate rotation (see Table 5.8a). In this case, the thermal conductivity decrease is influenced mainly by the low azimuthal angle and length of the voids between feather-arms within the core of the primary columns, and the fine section and high volume fraction of the intra-columnar pores. Similar low thermal conductivity and overall porosity values were reported by Jang et al. [225] for EB-PVD PYSZ TBCs (~ 300 μm thickness) manufactured at 950°C/20 rpm. Similar to “coarse” and “intermediate” coatings, fine section of voids between feather-arms and intra-columnar pores evolve into low-aspect-ratio pores during ageing. Since the distribution of the remaining pores within the columns is uniformly distributed, the possibility that the pores interrupt the flux of phonons through the cross-section of the columns is higher. The influence of the intra-columnar gaps on the thermal conductivity remains unaltered due to their stability during ageing.

6.6.4 “Fine” and “parallel” morphologies

“Fine” and “parallel” EB-PVD coatings display intermediate thermal conductivity values in as-coated conditions as shown in Fig. 5.26. “Fine” coatings exhibit lower thermal conductivity values than those of “parallel” coatings, which can be primarily correlated to their higher total porosity volume fraction than “parallel” coatings (see Table 5.1). After ageing at 1100°C/100h, “parallel” coatings exhibit a significant increase in thermal conductivity, whereas “fine” coatings show a moderate thermal conductivity increase (87% and 65% respectively, measured at 200°C) (see Figure 5.3.1-4). SEM micrographs in Figure 6.13 and Figure 6.14 show the shape and distribution of the pores within “fine” and “parallel”
Discussion

EB-PVD coatings, respectively. “Fine” coatings exhibit a homogeneous distribution of the pores across the primary columns cross-section, whereas “parallel” coatings display a compact region in the middle of the primary columns core. Thus, the volume fraction and distribution of the pores is the factor influencing the differences in the thermal conductivity values between these coatings.

6.7 Comparison of morphological effects on the thermal conductivity of EB-PVD PYSZ TBCs

EB-PVD process parameters such as substrate temperature and rotation speed are considered as key factors controlling the spatial and geometrical characteristics of the created porosity, and, consequently, the overall thermal conductivity of the manufactured coatings. Rotation speed influences principally the shadowing effect between neighboring columns, which is principally accountable for the size and shape of the formed intra-columnar pores, voids between feather-arms and inter-columnar gaps within the EB-PVD TBCs. Moreover, substrate temperature influences the number of nucleated primary columns, and the activation and dominance of surface mass diffusion that also governs the dimensions of the created pores. A similar hypothesis is formulated by Cho et al. [88], who applied a Monte Carlo simulation to determine the factors affecting the growth process of EB-PVD coatings deposited on rotating substrates. Mass diffusion phenomenon binds the created “banana” shaped elements, closing the corresponding coupled pores in form of inter-columnar pores and voids between feather-arms. The distribution of the pores within primary columns is mainly affected by the period of time that each section of the growing surface is exposed to the vapor phase, and the diffusion of the attached atoms to reduce the created surface area.

According to the thermal conductivities of the different pore-group domains given in Table 5.8a for the “intermediate”, “coarse” and “feathery” EB-PVD coatings in as-coated conditions, it is likely that the inter-columnar gaps barely contribute to reducing the thermal conductivity due to their orientation parallel to the heat flux (less than 10%). Furthermore, the effectiveness of the voids between feather-arms to reduce the thermal conductivity (thermal conductivity factor, \(k_{fa}/k_{ia}\)) is primarily determined by the stereometric characteristics of the fine section of these voids. The deep fine sections interrupt the phonon flux by inserting oblique discontinuities (slices) deep within the column’s core, which exhibit different orientations at the directions perpendicular and parallel to the axis of substrate rotation. Such features reach a different depth in each microstructure determined by the dominance of surface diffusion (substrate temperature), and the shadowing “sunrise-sunset” effect of the neighboring column tips (rotation speed).

Furthermore, according to the SEM micrographs, intra-columnar pores occupy the largest region of the primary columns cross-section. Variations in the spatial and geometrical characteristics of these features have a significant influence on the overall thermal conductivity of the coatings. Prolate-like shaped “sperm-cell” intra-columnar pores represent one of the principal barriers governing the reduction of the thermal conductivity of the columns due to their higher volume fraction, high aspect ratio, low azimuthal angle, and a uniform distribution in the cross-section area of the primary columns (see Table 5.8). Additionally, intra-columnar pores oriented parallel to the voids between feather-arms, observed in the cross-section oriented parallel to the axis of substrate rotation, induce an additional reduction of the thermal conductivity as shown in the Table 5.8. These features exhibit a high surface area configuration due to their oblate-like shape, and a high volume fraction. Such characteristics compensate their reduced influence on the thermal conductivity due to their slightly higher azimuthal angles and location near the edges of the primary columns. This theory is supported by the distribution of these features in the SEM
micrographs (see Fig. 5.19 to Fig. 5.21), and is confirmed by the agreement between the modeled and experimental thermal conductivity values and their interrelation for the three microstructures in the as-coated state (see Table 5.10).

Furthermore, during the ageing process significant thermally-induced changes occur principally at the voids between feather-arm and intra-columnar pores. Changes into shapes with lower aspect ratios clearly indicate the sintering effect, which controls the surface area reduction of the pores. This effect is evident in the aspect ratio USAXS-modeled values of these pores after the ageing process. Fine section of the pyramidal cross-section of voids between feather-arms created in as-coated conditions disappears completely by breaking up into arrays of low aspect ratio pores. Coarse section of these voids evolves into isolated lower aspect ratio openings at the edge of the primary columns. Feather-arm features bound together through the previously formed contact points, leaving broader but shorter gaps between the feather-arm openings. High-aspect-ratio prolate-shaped intra-columnar pores (fine “banana” shaped pores) connecting the two rows of pores created by each rotation phase break-up and evolve into low-aspect-ratio pores. Consequently, a different equilibrium configuration of the pores results from the sintering process, altering the effectiveness of the pores in interrupting the heat transfer through the coatings. Considering the changes in the thermal conductivity of the coatings after heat-treatment at 1100°C/100h (see Table 5.10 and Fig. 5.28) and their morphological changes (see Fig. 5.23 to Fig. 5.25), it is evident that the changes in the fine section of voids between feather-arms, and the prolate-like shaped and oblate-like intra-columnar pores aligned behind these features toward the core of primary columns are the principal effects accountable for the drastic thermal conductivity increase in EB-PVD TBCs. The disappearance of heat-flux hindering paths (shape and distribution of the pores) by the formation of collimated isotropic features facilitate heat transfer through the primary columns. The insulating effect of the orientation and aspect ratio by increasing the surface area cross-section decreases abruptly after ageing. The only effect of low aspect ratio pores on the thermal conductivity of the primary columns is principally related to their volume fraction and distribution. This agrees well with the consideration of Lu et al. [122] and Cernuschi et al. [142], proving that spheres together with cylinders and plates oriented parallel to the heat flux yield the lowest effect on the reduction of the thermal conductivity.
7 Conclusions

Thermal barrier coatings (TBCs) deposited on the metallic turbine blades are considered as a viable additional method to the air cooling system to increase the inlet temperature in the turbine of aero engines without reducing the efficiency of this rotating component. The implementation of TBCs would give these machines the capability to improve the energy exchange, and consequently, the efficient use of fuel energy resources. This development represents an important economic and environmental aspect for society due to the impact of the air transportation of people and goods around the world by this medium.

Electron-Beam Physical Vapor Deposition method (EB-PVD) is currently the most accurate manufacturing process that produces light-weight coatings with an efficient combination of thermo-mechanical properties required for the high-temperature cyclic in-service life conditions in aero-engine turbines. The columnar structure of these coatings is primarily composed of individual primary columns separated by inter-columnar gaps. This configuration gives these coatings the capability to compensate the stresses produced by the differences in the thermal expansion coefficient with the formed TGO, and the metallic bond and substrate, during thermal cyclic conditions. Moreover, the individual primary columns are composed of a fixed configuration of solid material and voids between feather-arms formed at the edges of the primary columns, and enlarged intra-columnar pores in the core of the primary columns.

This work demonstrates that the columnar microstructure, the local configuration of the solid material, and the porosity within the primary columns can be modified by altering process parameters such as substrate rotation speed and substrate temperature. These morphological changes consequently induce alterations in the thermal conductivity values of the manufactured coatings. The operating mechanisms leading to the differences are analyzed and the circumstances for their occurrence are discussed.

Five EB-PVD coatings were manufactured by varying these two mentioned parameters. Significant differences in the morphological and thermal characteristics between the five manufactured EB-PVD PYSZ TBCs were determined. It was observed that rotation speed influences mainly the shadowing effect between neighboring columns, which is principally accountable for the number, size and shape of the created intra-columnar gaps, voids between feather-arms, and, consequently, inter-columnar pores within the EB-PVD TBCs. The substrate temperature influences the number of nucleated primary columns, and the activation of surface mass diffusion, which governs the nucleation and persistency of the growth process of the pores within the primary columns. Moreover, rotation of the substrates during the coating process alters the interrelation between the different zones of the Movchan’s diagram along the temperature axis. Increasing the temperature from 0.38 Tm to 0.43 Tm produces different microstructural changes at different rotation speeds. At low rotation speed, the microstructure changes from Zone 1 to the corresponding high-temperature limit of Zone 2, whereas the microstructure seems to remain unaltered among the limits of Zone 1 and the neighboring low-temperature region of the Zone 2 at high rotation speed.

The microstructure of EB-PVD coatings manufactured under conventional rotation conditions exhibits a strong anisotropic character. A qualitative analysis of the anisotropy of the primary columns and inter-columnar gaps has been done in the past solely by visual observations based on SEM micrographs. In this work, a detailed quantitative analysis of this anisotropic configuration was achieved by the combination of sophisticated measuring techniques such as USAXS, SANS, and SEM micrographs analysis. The results indicate that all pores (inter-columnar gaps, voids between feather-arms, and intra-columnar pores) comprise a strong anisotropic configuration at the cross-sections oriented in the directions perpendicular and parallel to the axis of substrate rotation. The anisotropic distribution of the porosity in the EB-
PVD coatings is mainly related to the changes of the vapor incidence angle at the different regions of the primary columns due to the rotating conditions and influenced by the substrate temperature during the coating process. The middle region of the primary columns is exposed to the vapor phase along a 180° “sunrise-sunset” period, whereas the contact of the vapor toward the edges accumulatively limited by the shape of the ridges of the neighboring columns.

USAXS analysis (measuring and modeling) accurately describes the anisotropic character of the porosity of EB-PVD coatings. It demonstrates that inter-columnar gaps exhibit higher volume factions, and in some coatings higher dimensions in the direction perpendicular to the axis of substrate rotation compared to the parallel direction. Voids between feather-arms display clear differences in their orientation and depth within the core of the primary columns in the directions perpendicular and parallel to the axis of substrate rotation. Three groups of intra-columnar pores were identified. “Sperm-cell”-shaped pores are visible at the cross-section oriented in the direction perpendicular to the axis of substrate rotation and oblate- and prolate-shaped pores near the periphery of the primary columns in the parallel direction, whereas “cut-shaped” pores are observable in the middle region of the cross-section oriented in the direction parallel to the axis of substrate rotation.

The “sperm-cell” shaped pores and oblate/prolate pores are created due to the nano-shadowing of the multiple nucleation and growth of “banana” shaped features during the rotation of the substrates (“sunrise-sunset” periods). These pores nucleate between the edges of the “banana” shaped features formed during the last material deposited in each rotation movement. Then, they grow between the individual features in accordance to the rotation speed and substrate temperature, which govern their length and thickness, respectively. The second “cut-shaped” pores are also created at the edges of the “banana” shaped features but oriented in the direction parallel to the axis of the substrate rotation. The pores are also originated due to the rotation movement of the substrate and the inefficient deposition of the vaporized phase at the beginning and the end of the “sunrise-sunset” periods. The rotation movement creates a time dependence of the quantity of available vaporized material for deposition, which is lower at the beginning-end of each period. The length of these pores is dependent of the rotation speed, and their thickness is influenced by the substrate temperature (activation of mass diffusion).

The quantitative USAXS and SANS analysis reveals important microstructural differences in the porosity enclosed in EB-PVD coatings, which are originated mainly from changes in the kinetic of the condensation process during the vapor deposition. These variations are principally influenced by the alteration of the rotation speed and temperature of the substrate. Furthermore, the activation of thermal-induced processes like sintering induces additional morphological changes to the manufactured EB-PVD coatings during ageing of these materials. Moreover, the USAXS characterization of the porosity corresponds well with the measured thermal conductivity for three of the analyzed EB-PVD coatings according to the applied non-interacting approximation based on Maxwell’s modeling. The approximation indicates that the oblate/prolate shaped intra-columnar pores measured at the cross section oriented parallel to the axis of substrate rotation, and the deepest region of the voids between feather-arms and the “sperm-cell” intra-columnar pores measured at the section perpendicular to the axis of substrate rotation are the principal contributors to the thermal isolating capability of the EB-PVD PYSZ TBCs. According to the cross-sections observed in the SEM micrographs, the intra-columnar pores occupy the largest region of the primary columns volume. Then, it is expected that these features influence the conductance of heat through the primary columns. The inter-columnar gaps induce only a slight influence on the thermal conductivity of these coatings.
Although SANS analysis of the intra-columnar pores exhibits a high surface area fraction of the “cut-shaped” intra-columnar pores, the non-interacting thermal conductivity approximation indicates that the first “sperm-cell” intra-columnar pores and the oblate/prolate shaped intra-columnar pores are the principal closed pores governing the thermal conductivity of the coatings. These later pores exhibit an oblique orientation related to the heat flux, whereas the “cut-shaped” ones are oriented parallel to the heat flux.

Furthermore, ageing induces important additional morphological and thermal conductivity changes in the five manufactured EB-PVD coatings. According to the analysis of the surface area reduction, the thermally-activated mass diffusion mechanism responsible for such morphological changes is surface diffusion. This mass diffusion mechanism activates at temperatures \( \geq 900 \, ^\circ\text{C} \). The break-up and evolvement processes (sinterability) occurring within the cross-sections of the created pore groups are influenced by the shape and orientation of these features after the deposition of the coating. High-aspect ratio pores contain a high propensity to sintering due to the created large Laplace stresses between the concave and convex regions of the pore. Moreover, disorientation induces a coalescence effect between neighboring pores during the shape evolvement process. Then, EB-PVD coatings containing porosity with high sinterability configurations like “feathery” coatings exhibit an abrupt surface area reduction and the appearance of different sized pores in their cross-sections during ageing. The thermal conductivity of such coatings change accordingly to the surface area reduction, i.e. abruptly.

Sintering bridges created at the contact points between primary columns stabilize the width of the intra-columnar gaps. The fine section of voids between feather-arms breaks into low aspect ratio voids, whereas the coarse exterior section evolves to low-aspect ratio open gaps. Similarly, all the elongated “sperm-cell” intra-columnar located in the perpendicular direction, and “cut-shaped” and oblate/prolate shaped intra-columnar pores located in the parallel direction evolve also into low-aspect-ratio shapes. The achieved low-aspect-ratio geometry exhibits a noticeably lower effect on the reduction of the thermal conductivity of the EB-PVD PYSZ TBCs. The quasi-equilibrated shape of closed intra-columnar pores is composed of faceted surfaces. This phenomenon is clearly demonstrated by STEM micrographs and validated by the SANS analysis. This configuration indicates the anisotropic character of the surfaces composing the equilibrated Wulff shape, which was not observed in this work due to the low temperature ageing applied.

This work gives the basis for the understanding of the microstructural features (pores and solid material) and their equilibrated configurations in EB-PVD PYSZ TBCs manufactured under rotating conditions at different process parameters and aged at temperatures similar to those achieved at in-service conditions. The investigated manufacturing conditions are directly applicable for the deposition of EB-PVD coatings. Nevertheless, the thermo-cyclic resistance of the manufactured coatings must be characterized.
References


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Appendix

Appendix A
Formulae for thermal conductivity modeling

Appendix B
USAXS model fitting of aniso-scans - I(Q) curves
Appendix A1

Gas-Phase Conductivity

The conductivity of the gas phase within pores differs that in free space, $k_g \sim 0.027 \text{ W(m-K)}^{-1}$. From the kinetic theory of gases at pressure $p$ and temperature $T$ by [226, 227]

$$k_p = k_g \left( 1 + \frac{4\eta}{\eta + 1} \frac{2 - \alpha_a}{\alpha_a} \frac{K_n}{\text{Pr}} \right)^{-1}$$

Eq. (A1-1)

where $\eta \equiv C_p/C_v$ is the specific heat ratio, $\alpha_a$ the accommodation coefficient (unity for TBCs [227]), $\text{Pr}$ the Prandtl number, $K_n = \Lambda/d_w$ the Knudsen number, and $\Lambda$ the mean free path length of gas molecules. The kinetic theory of gases gives

$$k_g = (1.66\eta - 0.92) \left( \frac{p^2}{m_g k_B T} \right)^{\frac{1}{2}} \frac{\Lambda}{N_A/C_v}$$

Eq. (A1-2a)

$$\Lambda = \frac{k_B T}{2^{\frac{1}{2}} \pi d_g^2 p}$$

Eq. (A1-2b)

where $k_B$ is the Boltzmann constant, $d_g$ and $m_g$ the diameter and mass of the gas molecules, and $N_A$ the Avogadros number. By substitution of Eq. A1-2a into Eq. A1-2b:

$$k_g = \frac{1.66\eta - 0.92}{\pi d_g^2 N_A/C_v} \left( \frac{k_B T}{2m_g} \right)^{\frac{1}{2}}$$

Eq. (A1-3)

Note that

$$k_p = \frac{k_g}{1 + C_1 T/t \cdot p}$$

Eq. (A1-4)

Where $C_1 = 2.5 \times 10^{-5}$ Pa(m/K) for air, and $t$ is the inclusion thickness.

When $K_n << 1$, the gas behaves as a continuum, but, when $K_n >> 1$, the energy exchange between the molecules and the pore surface is largely restricted by collisions between molecules in the pore. Thus, when the pore is sufficiently thin, the gas conductivity across its section decreases by increasing the temperature and decreasing the pressure (Fig. A1).

For the case of voids between feather arms with $t \sim 120$ nm, and intra-columnar pores with $t \sim 20$ nm relevant to EB-PVD TBCs, this analysis show that at atmospheric pressure the pore conductivity in both cases is negligible.

![Figure A1: Normalized pore conductivity as a function of the pore width.](image-url)
Appendix A2

**Distribution of pores shapes and orientations**

For spherical pores having a constant aspect ratio, $\gamma$, but distributed orientation

\[
\frac{\bar{k}}{k_s} = 1 - \int_0^{\pi/2} \int_0^{\pi/2} HP_1(\varphi, \theta) d\varphi \cdot d\theta
\]  
(Eq. A2-1)

where $P_1$ is the probability density function characterizing the orientations. The influence function $H$ is given by Eq. 2.4.3-2, with

\[
n = \cos \theta \cdot \sin \varphi_1 + \sin \theta \cdot \sin \varphi_2 + \cos \varphi_3
\]  
(Eq. A2-2)

where $e_i$ (i = 1, 2, 3) are the unit vectors along the Cartesian coordinates $x_i$.

Furthermore, for pores aligned in a specific orientation $x$, but having a distributed aspect ratio, $P_2(\gamma)$, then

\[
\frac{\bar{k}_x}{k_s} = 1 - \int_0^1 H_x(\gamma) P_2(\gamma) d\gamma
\]  
(Eq. A2-3)

Where $H_x$ is the x-component of $H$. 


Appendix A3

Determination of the \( Hi \) tensor

For the analysis of the \( Hi \) tensor, we consider an insulating ellipsoidal inclusion \((k_*=0)\) with a volume \( V^* \) embedded within a reference volume \( V \) of an infinite three-dimensional solid having isotropic thermal conductivity \( k_0 \) \(^{(128)}\). The dimensioning of the inclusion is described by its semi axes \( a_1, a_2, \) and \( a_3 \) parallel to the coordinates \( x_1, x_2, \) and \( x_3, \) and the unite vector \( l, m, \) and \( n \) along them, respectively. During the heat conduction through such configuration (Fig. A3-1), the change of the heat flux vector (per volume \( V \)) \( \Delta \mathbf{Q} \) due to the inclusion is a linear function of the field temperature gradient \( \mathbf{G}^0 \):

\[
\Delta \mathbf{Q} = H \cdot \mathbf{G}^0
\]  

(Eq. A3-1)

where the second range tensor \( H \) is a function of the inclusion shape and conductivity.

The expression for the tensor \( H \) as an ellipsoidal form inclusion in closed form in terms of standard elliptic integrals is as follows:

\[
H = \frac{V^*}{V} (k_* - k_0) \left( A_1 l l + A_2 m m + A_3 n n \right) \]  

(Eq. A3-2)

where \( V^* = (4\pi/3)a_1a_2a_3 \) is the ellipsoidal inclusion volume. The coefficients \( A_1, A_2, \) and \( A_3 \) have the form:

\[
A_i = \left[ 1 + \frac{k_* - k_0}{k_0} J_i \right], \quad i = 1, 2, 3
\]  

(Eq. A3-3)

where the geometrical factor \( J_i \) is given by

\[
J_i = \frac{a_ia_2a_3}{2} \int_0^\infty \frac{du}{(a_i^2 + u)(a_i^2 + u) + (a_j^2 + u) + (a_k^2 + u)}
\]  

(Eq. A3-4)

The coefficients \( A_i \) in the tensor \( H \) reflect both the geometry and conductivity of the inclusion. Thus, in the case of an insulating inclusion \((k_* = 0)\), the coefficients \( A_i \) is influenced purely by geometrical factors.

In the case of a spheroid with \( a_1 = a_2 = a \), and \( n \) as the unit vector along the spheroids axis of symmetry

\[
H = \frac{V^*}{V} (k_* - k_0) \left[ \left( 1 + \frac{k_* - k_0}{k_0} F(\gamma) \right)^{-1} (I - nn) + \left( 1 + \frac{k_* - k_0}{k_0} (1 - 2F(\gamma)) \right)^{-1} (nn) \right]
\]  

(Eq. A3-5)
where $\gamma = a/a_3$ is the aspect ratio of the spheroid and $I = e_1 e_1 + e_2 e_2 + e_3 e_3$ is the unit tensor. The shape function $F(\gamma)$ for the analysed ellipsoids is given by:

$$F(\gamma) = \frac{1 - g(\gamma)}{2(1 - \gamma^2)} \quad \text{(Eq. A3-6)}$$

For oblate shape ellipsoid

$$g(\gamma) = \frac{\gamma^2}{\sqrt{\gamma^2 - 1}} \arctan \sqrt{\gamma^2 - 1} \quad \text{(Eq. A3-7)}$$

For prolate shape ellipsoid

$$g(\gamma) = \frac{\gamma^2}{\sqrt{1 - \gamma^2}} \ln \frac{1 + \sqrt{1 - \gamma^2}}{1 - \sqrt{1 - \gamma^2}} \quad \text{(Eq. A3-8)}$$

For a sphere $F(\gamma) = 1/3$. In the limit of $\gamma \to 0$ (penny-shaped inclusion) $F(\gamma) \to 1/2$, whereas for $\gamma \to \infty$ (cylinder) $F(\gamma) \to \pi/4\gamma$.

In the case of a thin oblate spheroidal inclusion ($\gamma >> 1$):

$$H = \frac{V^*}{V} (k_* - k_0) \left( 1 + \frac{k_* - k_0}{k_0} \frac{\pi}{4\gamma} \right)^{-1} (I - nn) + \left( 1 + \frac{k_* - k_0}{k_0} \left( 1 - \frac{\pi}{2\gamma} \right) \right)^{-1} (nn) \quad \text{(Eq. A3-9)}$$

In the case of a strongly prolate shape ($\gamma << 1$):

$$H = \frac{V^*}{V} (k_* - k_0) \left[ \left( 1 + \frac{k_* - k_0}{2k_0} \left( 1 + 2\gamma - \gamma^2 \ln \frac{2}{\gamma} \right) \right)^{-1} (I - nn) + \left( 1 + \frac{k_* - k_0}{k_0} \left( \gamma^2 \ln \frac{2}{\gamma} - \gamma^2 \right) \right)^{-1} (nn) \right] \quad \text{(Eq. A3-10)}$$
Appendix A4

Thermal flux in a solid material containing aligned, spatial and size distributed inclusions

In this case, the pores have fixed orientation and aspect ratio but arbitrary distribution in size and space. Flat pores oriented perpendicularly to the heat flux (in this case $z$-axis) with $k \equiv k_z$ have a substantial effect on the thermal conductivity, but minimal in the transverse direction. Consequently, the effect of flat pores inclined at an angle $w$ to the horizontal axis (Fig. A4-1) on the overall thermal conductivity can be calculated through the coordinate transformation

$$ k = k_z \sin^2 w + k_z \cos^2 w $$

(Eq. A4-1)

For insulating flat pores $d/\ell << 1$ oriented perpendicular to the $z$-axis:

$$ \frac{k_r}{k_z} = 1 - \Phi $$

(Eq. A4-2)

$$ \frac{k_z}{k_z} = 1 - \frac{8}{3} \Phi_N, \quad \text{where} \quad \Phi_N = \frac{3}{4\pi} \frac{d}{\ell} \Phi $$

(Eq. A4-3)

For insulating cylindrical pores oriented perpendicular to the $z$-axis:

$$ \frac{k_r}{k_z} = 1 - \Phi $$

(Eq. A4-4)

$$ \frac{k_z}{k_z} = 1 - 2\Phi $$

(Eq. A4-5)

Figure A4-1: Schematic of aligned, flat spheroidal pores (a). Thermal conductivity of the pores oriented perpendicular to the heat flux at various aspect ratios
Appendix B1

USAXS model fitting (specimens in as coated conditions)

(a)

(b)

Q = 0.00020

Q = 0.00068

Q = 0.00149

Q = 0.00348

Q = 0.01285

Appendix B1.1: USAXS-mapping method of the direction perpendicular to axis substrate rotation in intermediate coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 42° (red), and 82° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B1.2: USAXS-mapping method of the direction parallel to axis substrate rotation in intermediate coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 56° (red), and 86° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B1.3: USAXS-mapping method of the direction perpendicular to axis substrate rotation in coarse coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, Q measured at 0 ° (black), 54 ° (red), and 88 ° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B1.4: USAXS-mapping method of the direction parallel to axis substrate rotation in coarse coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, $Q$ measured at 0° (black), 63° (red), and 96° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different $Q$ values.
Appendix B1.5: USAXS-mapping method of the direction perpendicular to axis substrate rotation in feathery coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 42° (red), and 90° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B1.6: USAXS-mapping method of the direction parallel to axis substrate rotation in feathery coatings in as coated conditions: (a) scattering intensities as function of the scattering vector, \( Q \) measured at 0° (black), 60° (red), and 90° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different \( Q \) values.
Appendix B2

USAXS model fitting (specimens after 1100°C for 100hrs ageing)

(a)

(b)

Appendix B2.1: USAXS-mapping method of the direction perpendicular to axis substrate rotation in intermediate coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 45° (red), and 84° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B2.2: USAXS-mapping method of the direction parallel to axis substrate rotation in intermediate coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 61° (red), and 87° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B2.3: USAXS-mapping method of the direction perpendicular to axis substrate rotation in coarse coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 54° (red), and 92° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Appendix B2.4: USAXS-mapping method of the direction parallel to axis substrate rotation in coarse coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, $Q$ measured at 0° (black), 68° (red), and 98° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different $Q$ values.
Appendix B2.5: USAXS-mapping method of the direction perpendicular to axis substrate rotation in feathery coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 52° (red), and 88° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
Continuation …

(a)

Appendix B2.6: USAXS-mapping method of the direction parallel to axis substrate rotation in feathery coatings after aged conditions at 1100 °C for 100 hours: (a) scattering intensities as function of the scattering vector, Q measured at 0° (black), 60° (red), and 90° (green) azimuthal angles; and (b) measured (black) and fitted (red) aniso-scans curves at different Q values.
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