Moulding Materials with Tailored Coefficient of Thermal Expansion for Glass Forming

S. Fries, S. Herzog, D. P. Wilhelm, T. Grunwald, Chr. Broeckmann

Precision forming is an efficient process for producing aspherical lenses. Various optical glasses can be used. The wide range of optical glasses requires an adjustment of the thermal expansion coefficient of the moulding tool. Currently, tungsten carbide and silicon carbide are used as moulding materials, providing stability at high temperatures and high heat conductivity values. Unfortunately, thermal expansion of these hard materials is lower than $5 \cdot 10^{-6}$ 1/K, which leads to defects after cooling. A new material concept is developed to overcome the limitations in thermal expansion. Using MAX-phase composites allows a tailored coefficient of thermal expansion for the intended application.

Precision Glass Moulding

In Precision Glass Moulding (PGM), precision optics, which are conventionally produced in a streamlined iterative grinding and polishing process, are manufactured in just one process step without any post-processing. In this process, a glass blank is formed under temperature and force between two moulding tools with the target geometry's negative shape. This comparably short process chain offers excellent potential compared to conventional optics production, which increases economic efficiency in the production of precision optics and thus reduces production costs. Similarly, a scaling approach (wafer-level moulding) in PGM allows several precision optics to be manufactured in just one process step, which increases the cost-effectiveness of the manufacturing process and helps to meet the increasing global demand for cost-effective precision optics in the future. Precision optics are currently used in various industries, such as medical, laser, camera, and sensor technology. In medical technology, for example, precision optics are installed in endoscopes, which dominantly determine the imaging quality [1]. These endoscope lenses are made from K-VC89 glass, for example.

Fig. 1 shows the process sequence for PGM in a schematic diagram. In the beginning, a glass blank is positioned on the lower "insert" in the process chamber. Once the glass blank has been positioned, the process chamber closes. The process chamber is closed via a quartz glass cylinder to enable a high vacuum atmosphere inside the process chamber. This vacuum is necessary to protect the components in the process chamber from the damaging influence of

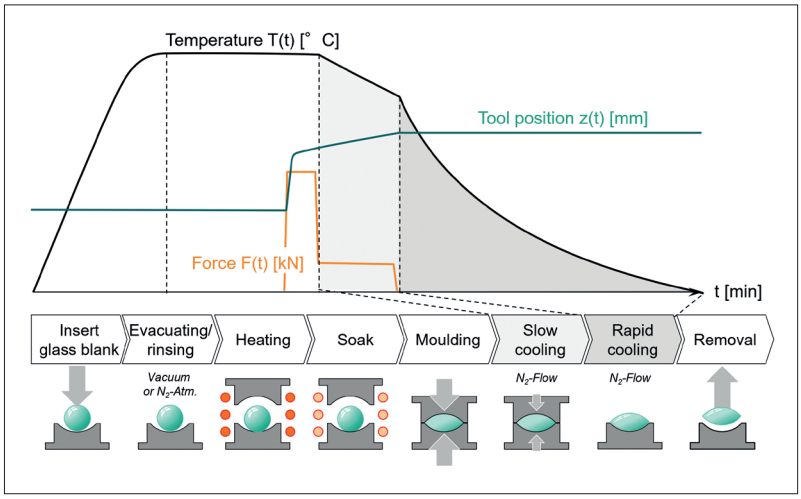


Fig. 1 Process sequence for precision glass moulding

Sofia Fries
Institute of Applied Powder Metallurgy and Ceramics (IAPK) at RWTH Aachen e. V.
52064 Aachen, Germany

Simone Herzog, Christoph Broeckmann
Institute for Materials Application in Mechanical Engineering (IWM)
RWTH Aachen University
52064 Aachen, Germany

Dennis Patrick Wilhelm, T. Grunwald
Laboratory for Machine Tools and Production Engineering (WZL) of RWTH Aachen University, Campus Boulevard 30
52074 Aachen, Germany

Corresponding author: Sofia Fries
E-mail: s.fries@iwm.rwth-aachen.de

Keywords: MAX phases, moulding materials, composite, FAST

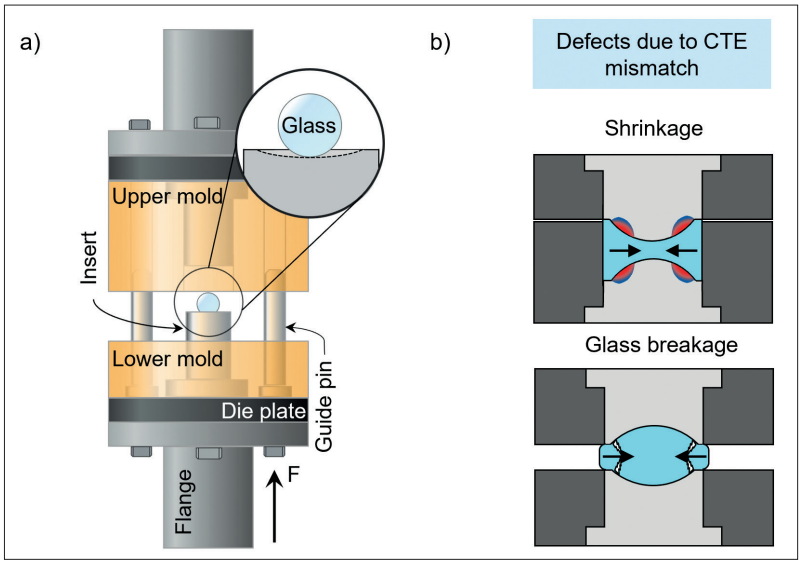


Fig. 2 Exemplary mould design precision forming (a) and defects due to mismatch in coefficient of thermal expansion (b)

oxygen (O_2), which leads to oxidation and thus, high-temperature corrosion. In order to ensure better heat conduction and to displace oxygen, the process chamber is subsequently flooded with the inert gas nitrogen (N_2). The nitrogen is channeled through cavities in the die plate. In the following process step, the inside of the chamber is heated in a controlled manner using concentric infrared (IR) radiators.

A temperature homogenization phase begins as soon as the target temperature is reached. For this, the temperature is kept constant so that all temperature gradients inside the process undercut a specified threshold. Once homogenisation is complete, the actual forming of the glass begins. The forming process is initiated by the mould halves drifting towards each other. Precisely fitted "guide pins" ensure the concentric accuracy of the upper and the lower insert, which determines the eccentricity error of the moulded optic (Fig. 2 a). The linear movement of the tools is force- and displacement-controlled, which influences the final geometry of the optics. Two cooling phases are carried out in the last two process steps. The cooling rate is controlled via the inert gas volume flow and the reheating of the IR emitters.

In the first phase, cooling is carried out gradually. During this phase, the mould halves remain in contact with the glass. At the start of the second cooling phase, the mould halves drift apart, and rapid cooling of the glass begins. Once the moulds and the glass have cooled down, the finished optics can be removed.

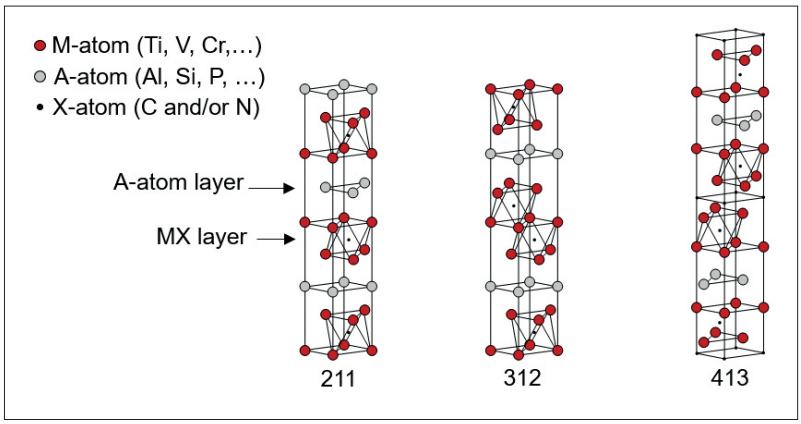


Fig. 3 Crystallographic structure of MAX-phases. M_6X-Octaeder and A-atoms form alternating layer coefficient of thermal expansion

Drawbacks of current moulding materials

This description is idealised for the case that the glass to be formed has the same thermal expansion behaviour as the tools. Tungsten carbide (WC) is predominantly used as the moulding material, silicon carbide (SiC) is also used in isolated cases. These materials are characterised by high temperature resistance, hardness and thermal conductivity. At 4,3–5,0 · 10^{-6} 1/K and 3,3–4,5 · 10^{-6} 1/K respectively, the Coefficient of Thermal Expansion (CTE) of WC and SiC are significantly lower than the CTE of industrially used, formable glasses in the range of 7–13 · 10^{-6} 1/K. The glass K-VC89, mentioned in the example of endoscope optics, has a linearized CTE of 8,4 · 10^{-6} 1/K (50–500 °C). As a result, the glass shrinks by a larger margin than the mould during cooling, which specifies the target geometry of the optics (Fig. 2 b). This deviation leads to an unwanted deviation in the shape of the lens, which must be compensated.

The compensation takes place in the mould construction. The geometric shape of the tools is adapted so that the glass has the target geometry despite the higher shrinkage after moulding and cooling. The development of the adapted tool design is usually realised by iterative forming of the glass with tools of the target geometry and subsequent measurement of the optics. The measured deviation is then transferred to the mould design and a further iteration is carried out. This is repeated until the optics meet the specifications. Another method for determining the compensated mould design is the use of a Finite Element Simulation. In this simulation, a model of the process is generated which uses the material characteristics of the glass and the moulds to calculate an adapted mould design. Both methods involve a great deal of effort and reduce the cost-effectiveness of the PGM. By matching both the tool and glass CTE values, the tool compensation step can be avoided or reduced in complexity. As thermal expansion of optical glasses is in a wide range, a material with a tailored thermal coefficient is needed for the application.

New material concepts

At RWTH Aachen University, a new material concept is developed to overcome thermal expansion limitations. The so-called MAX-

phases reinforced with SiC are promising candidates for moulding materials for glass forming. The MAX-phases' synthesis and properties have been scientists' focus since the 2000s. The term MAX phase is derived from the chemical formula $M_{n+1}AX_n$ of such a compound. M stands for a transition metal from group 3 to 6 in the periodic table, A for an element from group 13 to 16, and X for carbon, nitrogen, or both [2]. Fig. 3 shows the crystallographic structure of the MAX-phases with alternating near-close-packed M layers and pure group-A element layers, respectively. Small X-atoms are found in the octahedral sites of M-atoms. Due to its layered structure, this material class has a unique combination of properties. From one side, they are elastically stiff and thermally conductive. On the other hand, they resist thermal shock and are both damage tolerant and easy to machine. The CTE of MAX phase materials is 7,2–13 · 10^{-6} 1/K, which is in the range of most optical glasses [3].

One of the best characterised MAX phases is Ti_3SiC_2. Synthesis of Ti_3SiC_2 is widely investigated and this material is commercially available as a powder. Tab. 1 compares the mechanical properties of the MAX phase material Ti_3SiC_2 and WC, which is currently used as mould material. The low hardness presumably makes the pure Ti_3SiC_2 unsuitable as a moulding material. Nevertheless, the CTE for Ti_3SiC_2 is 9,1 · 10^{-6} 1/K and is therefore almost twice as high as the CTE for WC [4]. By adding of a carbide phase like TiC or SiC, the CTE of the composite is reduced. However, the compression strength and elongation to fracture are increased [5]. Despite the unique combination of material properties and numerous suggested application possibilities, MAX-Phases could neither establish as mechanically machinable alternative for structural ceramics [6] nor as a substitute for nickel-based alloys [2]. One of the few industrial applications is the dry drilling of concrete, where the MAX phase serves as a binding matrix for diamond particles [4, 7]. In this paper, the authors introduce the promising new application of MAX phase composites as a tool for PGM.

In Fig. 4, material properties relevant for precision forming are depicted. The spider diagram shows, how suitable the material is for the application. First, the geometry and surface quality are important. Fracture toughness, hardness and Young's modulus are relevant to the cutting and polishing strategy. For the glass moulding process, higher thermal conductivity ensures homogeneous temperature distribution in the mould. The Vickers hardness correlates with the wear resistance. CTE is relevant for the complexity and precision of the lens geometry. Tungsten carbide has exceptional high values for hardness, thermal conductivity, and Young's modulus. During precision forming, glass has a consistency like honey, so that lower pressures compared to for example metal sheet forming are required. This reduces the significance of the hardness values for the glass forming application. To summarise, a wide range of properties can be covered by MAX phase composites depending on the intended carbide content (light blue area).

Tab. 1 Properties of Ti_3SiC_2 [4] and WC [10]

Property	Ti_3SiC_2	WC
Coefficient of thermal expansion, CTE [10^{-6} 1/K]	9,1 · 10^{-6} (RT – 1000 °C)	4,9 (RT – 600 °C)
Young's modulus [GPa]	343	696
Fracture toughness, KIC [MPa $m^{1/2}$]	4,5–7,2	4–6
Vickers hardness [HV]	100–165	2200

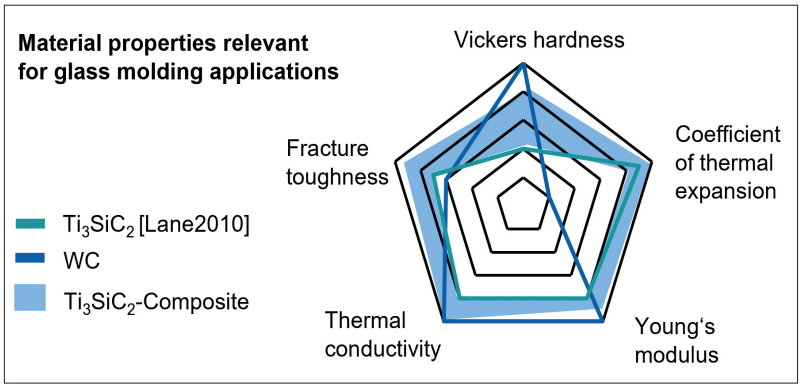


Fig. 4 Material properties relevant for glass moulding applications – values for currently used tungsten carbide tools are compared to MAX-phase material Ti_3SiC_2 [11] and its possible composites

Feasibility study

Field-Assisted Sintering Technology (FAST) is used to produce dense MAX phase composites. In the FAST process, an electric current is passed through the powder under pressure, and the powder is heated by Joule heat. The heating rates of up to 1000 K/min and holding times of a few minutes enable densification without significant grain coarsening. The quasi-static pressure during the FAST process reinforces the densification mechanisms, such as lattice diffusion, and also activates plastic deformation and grain boundary sliding [8]. The possible parameters for the microstructure design are therefore the starting powders, their preparation, and the FAST process parameters. The particle size and the selected starting materials are decisive for the sintering activity and the reactions that take place. Varying the dwell time at sintering temperature makes it possible to produce a fine-grained or coarse-grained microstructure [9].

In the first feasibility study at the IAPK at RWTH Aachen University, Ti_3SiC_2 powder was mixed with milled silicon carbide and sintered using field-assisted sintering technology. In Fig. 5, a fully dense MAX compos-

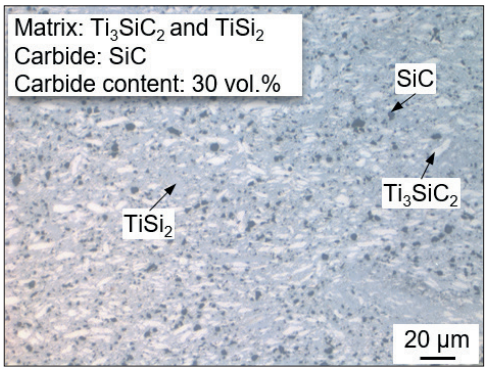


Fig. 5 Light optical micrograph of a MAX phase composite

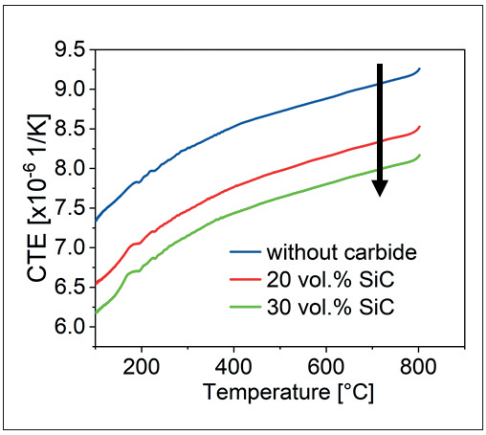


Fig. 6 Coefficient of thermal expansion for pure Ti_3SiC_2 and its composites

ite containing 30 vol.-% carbide is shown. Silicon carbide grains (dark grey) are about 0,3 µm and are homogeneously distributed in a matrix consisting of Ti_3SiC_2 and $TiSi_2$. The coefficient of thermal expansion for the composite depends on the carbide content. As shown in Fig. 6, a clear trend is present. For the relevant temperature range between RT and 500 °C, a CTE of $8{,}7 \cdot 10^{-6}$ 1/K is measured without any carbide addition. By adding 20 vol.-% and 30 vol.-% of SiC, CTE values are reduced to $7{,}9 \cdot 10^{-6}$ 1/K and $7{,}6 \cdot 10^{-6}$ 1/K, respectively. So, the MAX phase composites produced fulfil the requirement of the adjustable coefficient of thermal expansion.

However, as shown in Fig. 4, the mould material must also fulfil other characteristic parameters. Therefore, the thermal conductivity of the composites was determined. At 500 °C, a value of 28 W/m · K was measured without carbide addition. After carbide addition, the thermal conductivity increased. As 20 vol.-% carbide was added, a slight increase to 29,5 W/m · K was achieved. By adding 30 vol.-% silicon carbide, a significant rise in thermal conductivity to 31,8 W/m · K was achieved. Since a homogeneous temperature distribution is essential, the higher thermal conductivity benefits the precision glass moulding process. Higher thermal conductivity reduces the time for temperature homogenisation and so the overall process time. Vickers hardness is another property that is significantly influenced by the addition of carbides. In our study, a mean hardness value of 590 HV20 was measured without carbide addition. A substantial increase in Vickers hardness to 1200 HV20 is found due to carbide addition. However, no clear trend is visible by adding 20 vol.-% and 30 vol.-% SiC, respectively.

In summary, the investigated MAX phase composites made of Ti_3SiC_2 and SiC meet the moulding material requirements for precision glass moulding. A variable CTE from $7{,}6 \cdot 10^{-6}$ 1/K to $8{,}7 \cdot 10^{-6}$ 1/K between RT–500 °C and the thermal conductivity of 28–31,8 W/m · K provide a basis for further developments. In further studies, the preparation of glass moulds will be focused. The polishing strategy for this new composite will be investigated next.

Acknowledgment

This work is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 506535305.

References

[1] INGENERIC GmbH: Customized aspheres, toric lenses, and free-form optics. URL: https://ingeneric.com/wp-content/uploads/2023/06/INGENERIC_Aspheres_2023.pdf.

[2] Barsoum, M.W.: The MN+1AXN phases: A new class of solids: Thermodynamically stable nanolaminates. In: Progress in Solid State Chemistry **28** (2000) [1] 201–281

[3] Sun, Z.M.: Progress in research and development on MAX phases: a family of layered ternary compounds. In: Int. Mater. Rev. **56** (2011) [3] 143–166

[4] Barsoum, M.W.: MAX Phases. Properties of machinable ternary carbides and nitrides. Weinheim 2013

[5] Radovic, M.; et al.: Effect of temperature, strain rate and grain size on the mechanical response of Ti_3SiC_2 in tension. In: Acta Materialia **50** (2002) [6] 1297–1306

[6] Barsoum, M.W.; El-Raghy, T.: Synthesis and characterization of a remarkable ceramic: Ti 3 SiC 2. In: J. Amer. Ceram. Soc. **79** (1996) [7] 1953–1956

[7] Prikhna, T.A.; et.al.: Studies of the oxidation stability, mechanical characteristics of materials based on MAX phases of the Ti-Al-(C, N) systems, and of the possibility of their use as tool bonds and materials for polishing. In: J. of Superhard Mater. **36** (2014) [1] 9–17

[8] Guillon, O.; et al.: Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments. In: Adv. Engin. Mater. **16** (2014) [7] 830–849

[9] El-Raghy, T.; Barsoum, M.W.: Processing and mechanical properties of Ti_3SiC_2: I, Reaction path and microstructure evolution. In: J. Amer. Ceram. Soc. **82** (1999) [10] 2849–2854

[10] Sarin, V.K. (ed.): Comprehensive hard materials. Amsterdam 2014

[11] Lane, N.J.; Vogel, S.C.; Barsoum, M.W.: High-temperature neutron diffraction and the temperature-dependent crystal structures of the MAX phases Ti_3SiC_2 and Ti_3GeC_2. In: Physical Rev. **B 82** (2010) [17]