

Synthesis of Crystalline Tool Coatings Based on Al_2O_3 Using High Speed PVD

Parisa Aghdam Tönnißen

April 2026

Schriftenreihe Oberflächentechnik, Band 86

Hrsg.: Prof. Dr.-Ing. K. Bobzin

Partner im
LABORATORIUM
FÜGETECHNIK
OBERFLÄCHENTECHNIK



Synthesis of Crystalline Tool Coatings Based on Al_2O_3 Using High Speed PVD

**Synthese kristalliner Werkzeugbeschichtungen auf Al_2O_3 -Basis mittels
High-Speed-PVD**

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen
Hochschule Aachen zur Erlangung des akademischen Grades einer Doktorin der
Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Parisa Aghdam Tönnißen, geb. Hassanzadegan Aghdam

Berichter/in: Univ.-Prof. Dr.-Ing. Kirsten Bobzin
apl. Prof. Dr. rer. nat. Rainer Cremer

Tag der mündlichen Prüfung: 18. Dezember 2025

„Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek online verfügbar.“

Schriftenreihe Oberflächentechnik

Band 86

Parisa Aghdam Tönnißen

**Synthesis of Crystalline Tool Coatings
Based on Al_2O_3 Using High Speed PVD**

Shaker Verlag
Düren 2026

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: D 82 (Diss. RWTH Aachen University, 2025)

Copyright Shaker Verlag 2026

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

Print-ISBN	978-3-8191-0700-9
PDF-ISBN	978-3-8191-0646-0
ISSN	1864-0796
eISSN	2944-5736

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren
Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9
Internet: www.shaker.de • e-mail: info@shaker.de

Acknowledgements

My foremost gratitude goes to Prof. Kirsten Bobzin for providing me with the opportunity to pursue my doctoral studies at the Surface Engineering Institute (IOT) at RWTH Aachen University. I would also like to extend my sincere thanks to Prof. Rainer Cremer for serving as the second reviewer and to Prof. Christian Hopmann for chairing the examination committee.

This dissertation is based on research findings obtained from two research projects “Investigation of High-Speed PVD Technology Concerning the Deposition of α -Al-O+X and Al-Ti-O+X Coatings for Die Casting of High-Melting Steel Alloys”, BO 1979/42-3, and “Research on the High-Temperature Synthesis of Al_2O_3 and ZTA Coatings Using HS-PVD”, BO 1979/105-1. I am deeply grateful to the German Research Foundation (DFG) for financially supporting these research projects.

I would also like to thank all current and former colleagues and staff members at IOT who contributed to this work, whether through scientific discussions, technical assistance, or administrative support. This includes my students, whose reliability and dedication were essential for the successful execution of experiments. I am particularly thankful to the former and current chief engineers and team leaders, Dr. Tobias Brögelmann, Dr. Christian Kalscheuer, and Max Philipp Möbius, for their guidance and mentorship. For the many constructive discussions and scientific exchanges, I am especially grateful to Dr. Muhammad Tayyab, Dr. Lidong Zhao, and Katja Radermacher. I also sincerely appreciate Dr. Tiancheng Liang and Dr. Tobias Brögelmann for their valuable feedback on my dissertation, which provided important insights and significantly improved the quality of this work.

I am especially grateful to my office colleagues Jessica Borowy, Marta Miranda Marti and Stefanie Cirakman for the supportive and friendly working environment. The stimulating conversations, shared challenges, and moments of laughter made this journey not only productive but also truly enjoyable. Particular gratitude is extended to Thomas Offermann and Lore Stalpers, who were always by my side when facing technical challenges, offering their expertise, reliability, and readiness to help.

My deepest gratitude goes to my family and especially to my parents. Their unconditional love, endless encouragement, and unwavering belief in me have been the foundation of everything I

Acknowledgements

have achieved. They have supported me in every possible way and have always inspired me to pursue my goals with determination and integrity. This accomplishment would not have been possible without their sacrifices and constant support. I am also deeply thankful to my only brother Parsa, whose encouragement and confidence, both in moments of challenge and celebration, have meant more to me than words can express.

Finally, I would like to thank my beloved husband Nicklas for his patience, understanding, and steadfast support throughout this journey. His encouragement during challenging times, his confidence in my abilities, and his continuous motivation have been my greatest source of strength. I am profoundly grateful to share this achievement with him.

Zusammenfassung

Steigende Anforderungen an höhere Produktivität in der Fertigung führen zu komplexen Beanspruchungen von Werkzeugen wie Hartmetallen in der Zerspanung oder Warmarbeitsstählen für Ur- und Umformwerkzeuge. Dabei überlagern sich mechanische, chemische und thermische Belastungen. Hartstoffschichten wie Al_2O_3 verlängern durch ihre hohe Warmhärte, Oxidations- und Verschleißbeständigkeit die Standzeit von Werkzeugen und sind in der Zerspanung etabliert. Industriell erfolgt deren Abscheidung auf Zerspanwerkzeuge fast ausschließlich durch chemische Gasphasenabscheidung (CVD) bei Substrattemperaturen von $T_s > 800^\circ\text{C}$. Dies schränkt jedoch die Anwendung auf Warmarbeitsstählen ein. Die physikalische Gasphasenabscheidung (PVD) könnte eine Alternative bieten, scheitert jedoch bislang an der industriellen Umsetzung kristalliner Al_2O_3 -Schichten. Gründe hierfür sind die prozessbedingte Targetvergiftung in sauerstoffhaltigen Prozessen sowie die Bildung überwiegend amorpher Phasen bei $T_s < 700^\circ\text{C}$.

Diese Arbeit untersucht kristalline $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ -Hartstoffschichten mit hohem Aluminiumanteil $x_{\text{Al}} > 70$ At.-% als potenzielle Lösung für Warmarbeitsstähle. Die Synthese erfolgt mittels High-Speed-PVD (HS-PVD), das sich durch reduzierte Empfindlichkeit gegenüber Targetvergiftung und stabile reaktive Prozesse sogar bei $T_s > 800^\circ\text{C}$ auszeichnet, und sich somit als Alternative zu CVD- Al_2O_3 auf Hartmetallwerkzeugen anbietet. Das Leistungspotenzial wird anhand von $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ -beschichtetem X40CrMoV5-1-Stahl in Kontakt mit 100Cr6-Schmelze zur Bewertung der Diffusions- und Stahlanhaftung für Formwerkzeuge untersucht. Zudem wird beim Drehbearbeitung von C45+N mit Al_2O_3 -beschichteten WC-Co-Werkzeugen das Verschleißverhalten erforscht. Die Al_2O_3 -beschichteten Hartmetalle zeigen eine hohe Phasenstabilität bis $T = 1.200^\circ\text{C}$ und deutliche Standzeiterhöhung, insbesondere beim Einsatz geeigneter nitridischer Haftvermittler wie TiAlN . Trotz thermisch induzierter Zugspannungen infolge hoher Substrattemperatur von $T_s \approx 850^\circ\text{C}$ können durch Prozessanpassungen Druckeigenspannungen in Al_2O_3 -Beschichtungen erzielt werden, was gegenüber den typischen Zugeigenspannungen in CVD- Al_2O_3 für die Zerspanung vorteilhaft ist. Die Ergebnisse belegen das Potenzial von HS-PVD zur Herstellung oxidischer Hartstoffschichten für Hochtemperaturanwendungen wie das Ur- und Umformen von Stahl sowie zur Leistungssteigerung von Hartmetallen in der Zerspanung.

Abstract

Increasing demand for higher productivity in manufacturing processes results in complex stress collectives on tools, such as cemented carbides used in cutting applications and hot work steels employed in primary shaping and forming operations. These tools experience a combination of mechanical, chemical, and thermal stresses. Hard coatings like Al_2O_3 are well-established in cutting applications due to their excellent hot hardness, oxidation, and wear resistance, which significantly extend tool life. Industrially, these coatings are almost exclusively deposited via chemical vapor deposition (CVD) at substrate temperatures above $T_s > 800^\circ\text{C}$, limiting their applicability on hot work steels due to thermal sensitivity. Moreover, industrial breakthroughs of Al_2O_3 coatings through Physical Vapor Deposition (PVD) techniques remain unresolved. Key challenges include target poisoning in oxygen-containing reactive processes and the predominance of amorphous phases in coatings synthesized at low substrate temperatures $T_s < 700^\circ\text{C}$.

This work investigates crystalline $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ hard coatings as a potential solution for hot work steels. The higher aluminum content $x_{\text{Al}} > 70$ at.-% than previously analyzed in the state of the research, promotes higher thermal stability. The coatings are synthesized using High Speed PVD (HS-PVD), a technology characterized by reduced sensitivity to target poisoning and stable reactive processing even at $T_s > 800^\circ\text{C}$. Thus, it offers a promising alternative to CVD in cutting applications. The performance potential is evaluated through immersion tests of $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ coated X40CrMoV5-1 steel in molten 100Cr6 steel, assessing diffusion and adhesion behavior relevant to forming tool applications. Furthermore, cutting performance of Al_2O_3 coated WC-Co tools at $T_s \approx 850^\circ\text{C}$ in turning operation of C45+N is studied. Using process parameter optimization Al_2O_3 coatings with compressive residual stresses are deposited by HS-PVD even at $T_s \approx 850^\circ\text{C}$. These compressive stresses increase cutting performance over the tensile stresses usually found in CVD Al_2O_3 . Al_2O_3 coated cemented carbides in this study reveal phase stability up to $T = 1,200^\circ\text{C}$, and significant increase in service life particularly when combined with nitride-based interlayers such as TiAlN in turning operations. The results demonstrate the potential of these oxide-based coatings synthesized by HS-PVD under high temperature conditions for manufacturing processes, including the hot forming of steels and as a possible alternative to CVD Al_2O_3 in enhancing the performance of cemented carbides in machining operations.

Table of contents

1	Introduction	1
2	State of the art	3
2.1	Fundamental of physical vapor deposition	3
2.2	High Speed physical vapor deposition	6
2.2.1	Hollow cathode discharge	6
2.2.2	Gas flow sputtering	9
2.3	Al ₂ O ₃ coatings in manufacturing processes	10
2.4	TiAlN and AlCrN systems as an interlayer for Al ₂ O ₃	13
2.5	Properties and synthesis of Al ₂ O ₃ coatings	16
2.6	Approaches to synthesize crystalline Al ₂ O ₃ coatings by PVD at $T_s < 700\text{ }^{\circ}\text{C}$	17
2.6.1	(Al,Cr) ₂ O ₃ solid solution coatings	20
2.6.2	Intermediate conclusion of modification of Al ₂ O ₃ with Cr	26
2.7	High temperature $T_s \geq 700\text{ }^{\circ}\text{C}$ synthesis of Al ₂ O ₃ coatings	27
2.8	Conclusions derived from the state of the art	29
3	Research approaches and solutions	32
4	Coating deposition and fundamental analysis methods	35
4.1	HS-PVD prototype machine	35
4.2	Analysis methods of fundamental coating properties	38
5	Synthesis of (Al,Cr)₂O₃ coatings at $T_s \approx 550\text{ }^{\circ}\text{C}$	40
5.1	Influence of chromium content on the coating properties of (Al,Cr) ₂ O ₃	41
5.2	Selection of a suitable interlayer from the AlCrN system	45
5.2.1	Process parameters for deposition of (Al,Cr _L)N interlayer	45
5.2.2	Coating properties of (Al,Cr _L)N interlayer	46
5.2.3	Analysis of (Al,Cr _L)N/X40CrMoV5-1 compound adhesion strength	49
5.3	(Al,Cr) ₂ O ₃ thickness adjustment to enhance adhesion strength	52
5.3.1	Deposition parameters of (Al,Cr _L)N/(Al,Cr _L) ₂ O ₃ system on hot work steel	52
5.3.2	Influence of oxide functional layer thickness on the coating and compound adhesion properties of (Al,Cr _L)N/(Al,Cr _L) ₂ O ₃	53
5.4	Residual stresses in HS-PVD coatings	56
5.4.1	Analysis of residual stress by XRD using $\sin^2\psi$ method	56
5.4.2	Correlation of residual stress with coating and adhesion properties	57
5.4.3	Intermediate conclusion of residual stress in HS-PVD coatings	62

5.5	High temperature properties depending on Cr content	62
5.5.1	Al-rich (Al,Cr _L)N/(Al,Cr _L) ₂ O ₃ coating	64
5.5.2	Cr-rich (Al,Cr _H)N/(Al,Cr _H) ₂ O ₃ coating	73
5.6	Intermediate conclusion of effect of Cr content on high temperature properties	75
6	Behavior of the coated hot work steel in contact with molten 100Cr6 steel	77
6.1	Coating and preparation of hot work steel pins for immersion tests	77
6.2	Performance comparison between coated and uncoated pins in immersion tests	78
6.3	Intermediate conclusions of immersion tests in 100Cr6 melt	83
7	High temperature $T_s > 700$ °C PVD process of Al₂O₃ system	84
7.1	Effect of O ₂ gas flow on properties of coatings deposited at $T_s \approx 780$ °C	84
7.1.1	Phase stability by in situ HT-XRD in vacuum and atmosphere	88
7.1.2	High temperature nanoindentation (HT-NI)	94
7.1.3	Intermediate conclusion of high temperature properties of pure Al ₂ O ₃	97
7.2	Effect of process parameters on properties of coatings deposited at $T_s \approx 850$ °C	98
7.2.1	Properties of coatings deposited at $T_s \approx 850$ °C	98
7.2.2	Residual stress of coatings deposited at $T_s \approx 850$ °C	102
7.2.3	Intermediate conclusion to the coatings deposited at $T_s \approx 850$ °C	103
8	Performance in dry turning operation	105
8.1	Process parameters and procedure for cutting tests	105
8.2	Coating and adhesion strength properties	107
8.3	Cutting behavior of coated tools in turning of C45+N steel	109
8.4	Intermediate conclusion of performance in turning operation	118
9	Summary and future perspectives	119
10	Literature	I
11	Appendix	XI

Table of figures

Figure 2.1: Schematic of glow discharge with a planar cathode after [MP15]	7
Figure 2.2: Illustration of HS-PVD principle.....	9
Figure 2.3: Hardness of AlCrN coatings against Al content and structure based on [KKS02].....	15
Figure 2.4: Phase diagram of the binary Al_2O_3 - Cr_2O_3 system [BKS05]	21
Figure 2.5: Classification of hard materials in the bonding triangle based on [HS95]	22
Figure 4.1: a) Schematic representation of HS-PVD in the top view, b) substrate table, and c) a target plate with 30 target segments	35
Figure 4.2: Integration of ceramic insulation materials in HS-PVD coating unit a) initial state, b-c) after integration	37
Figure 4.3: Implementation of substrate desk rotation system in HS-PVD	38
Figure 4.4: Indentation values considered in this work and schematic illustration of force displacement curve according to DIN EN ISO 14577	39
Figure 5.1: Target configurations for the $(\text{Al,Cr})_2\text{O}_3$ coatings.....	40
Figure 5.2: Effect of Cr content on morphology and topography of $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c]	42
Figure 5.3: Analysis of phase composition depending on Cr content in $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c].....	43
Figure 5.4: Indentation hardness H_{IT} and indentation modulus E_{IT} of the $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c].....	44
Figure 5.5: Rockwell imprints of the $(\text{Al,Cr})_2\text{O}_3$ coatings	45
Figure 5.6: Fracture cross-sectional SEM micrographs of $(\text{Al,Cr}_L)\text{N}$ coated X40CrMoV5-1 [BKM+23]	47
Figure 5.7: Phase analysis of $(\text{Al,Cr}_L)\text{N}$ interlayers deposited with different parameters [BKM+23]	48
Figure 5.8: Box plots of indentation hardness H_{IT} and indentation modulus E_{IT} of $(\text{Al,Cr}_L)\text{N}$ interlayers [BKM+23]	49
Figure 5.9: Rockwell imprints of $(\text{Al,Cr}_L)\text{N}$ coatings on X40CrMoV5-1 steel [BKM+23].....	50
Figure 5.10: Scratch tracks of monolayer $(\text{Al,Cr}_L)\text{N}$ coating with $t_i = 30$ min and graded $(\text{Al,Cr}_L)\text{N}$ coating with $U_B = -125$ V [BKM+23]	51
Figure 5.11: SEM cross-section images of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings deposited by a) $t_f = 60$ min and b) $t_f = 90$ min [BKM+23].....	53

Table of figures

Figure 5.12: CLSM images of Rockwell imprints of samples coated by a) $t_f = 60$ min and b) $t_f = 90$ min [BKM+23]	54
Figure 5.13: CLSM images of scratch tracks with a) $t_f = 60$ min and b) $t_f = 90$ min [BKM+23]	55
Figure 5.14: Morphology of coatings on WC-Co and X40CrMoV5-1 substrates [BKM+24b]	58
Figure 5.15: CLSM micrographs of a) Rockwell indentation imprints and b) scratch tracks on oxide/WC-Co compounds [BKM+24b]	60
Figure 5.16: XRD patterns of coatings on both substrate materials [BKM+24b]	61
Figure 5.17: Residual stress state on different substrates via XRD [BKM+24b]	62
Figure 5.18: SEM micrographs of a) as-deposited state and annealed samples for $t_{vac.} = 1$ h at b) $T_{vac.} = 1,000$ °C and c) $T_{vac.} = 1,200$ °C [BKM+23]	65
Figure 5.19: Effect of annealing in vacuum on the phase composition of $(Al,Cr_L)N/(Al,Cr_L)_2O_3$ coatings [BKM+23]	66
Figure 5.20: Box plot of a) indentation hardness H_{IT} , b) indentation modulus E_{IT} and c) force displacement curves of $(Al,Cr_L)N/(Al,Cr_L)_2O_3$ coating before and after annealing [BKM+23]	68
Figure 5.21: Elementary diffusion behavior a) before and b) after annealing $T_{vac.} = 1,000$ °C in vacuum [BKM+23]	69
Figure 5.22: EDX mappings after annealing $T_{vac.} = 1,200$ °C in vacuum [BKM+23]	70
Figure 5.23: EDX line scans of the coated samples before and after annealing test in vacuum	71
Figure 5.24: Compound adhesion strength after annealing tests a) Rockwell b) scratch tests	72
Figure 5.25: Effect of annealing for $t_{vac.} = 1$ h on $(Al,Cr_H)N/(Al,Cr_H)_2O_3$ [BKM+24c]	73
Figure 5.26: Diffusion behavior of $(Al,Cr_H)N/(Al,Cr_H)_2O_3$ [BKM+24c]	75
Figure 6.1: a) Schematic illustration of a coated pin, b) coated pin with delamination, c) coated pin without delamination, d) detailed image of coating delamination, and e) detailed image of completely coated pin edge	78
Figure 6.2: Experimental set up of immersion tests	79
Figure 6.3: SEM cross-sectional images of a) uncoated and b) coated pin after immersion test in 100Cr6 melt steel for $t_{imm.} = 3$ s	80
Figure 6.4: a) Coated pin after $t_{imm.} = 3$ s of the immersion, b) after embedding, c) SEM cross-sectional micrograph, and d) detailed SEM micrograph	81
Figure 6.5: EDX mappings of coated pins after immersion tests in 100Cr6 melt	82

Figure 7.1:	Fractured cross-sectional SEM micrographs of Al_2O_3 coatings deposited at a) $T_s \approx 550^\circ\text{C}$ and at b-c) $T_s \approx 780^\circ\text{C}$ [BKH22]	86
Figure 7.2:	Effect of substrate temperature and oxygen gas flow on phase composition of Al_2O_3 coatings [BKH22].....	86
Figure 7.3:	H_{IT} and E_{IT} of Al_2O_3 coatings deposited under different conditions [BKH22].....	87
Figure 7.4:	Inside of High temperature chamber of XRD equipment	88
Figure 7.5:	Temperature-time progressing diagram during HT XRD	89
Figure 7.6:	HT-XRD results in vacuum for Al_2O_3 coating deposited at $T_s \approx 780^\circ\text{C}$ with $Q_{O_2} = 80$ sccm [BKM+24a]	90
Figure 7.7:	HT-XRD results in vacuum for Al_2O_3 coating deposited at $T_s \approx 780^\circ\text{C}$ by $Q_{O_2} = 120$ sccm [BKM+24a].....	91
Figure 7.8:	HT-XRD results in atmosphere for Al_2O_3 coating deposited at $T_s \approx 780^\circ\text{C}$ by $Q_{O_2} = 120$ sccm [BKM+24a].....	92
Figure 7.9:	Morphology of the Al_2O_3 coatings deposited by $Q_{O_2} = 80$ sccm, a) as-deposited, b) after HT-XRD in vacuum, and Al_2O_3 coatings deposited by $Q_{O_2} = 120$ sccm, c) as-deposited, d) after HT-XRD in vacuum and e) in atmosphere [BKM+24a]	93
Figure 7.10:	Illustration of nanoindentation with xSol high temperature stage.....	95
Figure 7.11:	HT-NI results of Al_2O_3 coatings deposited at $T_s \approx 780^\circ\text{C}$ [BKM+24a]	96
Figure 7.12:	Morphology and topography of Al_2O_3 coatings deposited under different conditions	99
Figure 7.13:	XRD results of Al_2O_3 coatings deposited at a) $T_s \approx 850^\circ\text{C}$, comparison of detailed XRD patterns deposited at b) $T_s \approx 850^\circ\text{C}$ and c) $T_s \approx 780^\circ\text{C}$ with $U_B = -125$ V and $Q_{O_2} = 120$ sccm.....	100
Figure 7.14:	Cross-sectional STEM micrographs in a) BF, b-c) DF, and d) SAED pattern	101
Figure 7.15:	SEM cross-section of Al_2O_3 coating deposited at $T_s \approx 850^\circ\text{C}$ with $U_B = -125$ V and $Q_{O_2} = 80$ sccm in detailed at coating/substrate interface.....	104
Figure 8.1:	a) Illustration of CC800/9 SinOx, b) TiAl48 plugged target and c) substrates	106
Figure 8.2:	Morphology of a) Al_2O_3 and b) TiAlN and c) TiAlN/ Al_2O_3 coating on WC-Co substrate.....	108
Figure 8.3:	CLSM images of Rockwell imprints on a) Al_2O_3 and b) TiAlN and c) TiAlN/ Al_2O_3 coated CNMA tools	109
Figure 8.4:	Schematic illustration of the turning process and b) VB_{max} on the flank face	110
Figure 8.5:	Maximum flank wear land width of VB_{max} of coated cutting tools as a function of the cutting time t_c for $v_c = 120$ m/min	111

Table of figures

Figure 8.6: Light microscopic images of the flank and rake face of the a) Al_2O_3 , b) TiAlN and c) TiAlN/ Al_2O_3 coated tools under $v_c = 120$ m/min over the tool service life	112
Figure 8.7: Maximum flank wear land width of VB_{max} of TiAlN/ Al_2O_3 and TiAlN coated tools as a function of the cutting time t_c for $v_c = 200$ m/min	113
Figure 8.8: Wear on flank and rake face of TiAlN and TiAlN/ Al_2O_3 coated tools over tool service life under $v_c = 200$ m/min	115
Figure 8.9: SEM images and EDX mappings on rake face of TiAlN/ Al_2O_3 coated tools under a cutting speed of $v_c = 120$ m/min a) and b) $v_c = 200$ m/min	116
Figure 8.10: SEM image and EDX mappings on flank face of TiAlN/ Al_2O_3 coated tool under a cutting speed of $v_c = 200$ m/min	117
Figure 11.1: SEM-images before and after annealing in in atmosphere for $t = 1$ h	XI
Figure 11.2: XRD results after annealing in atmosphere for $t = 1$ h	XI
Figure 11.3: Indentation values of coatings after annealing in atmosphere for $t = 60$ min	XII
Figure 11.4: Al_2O_3 coated sample after HT-XRD in atmosphere	XII

List of tables

Table 5.1:	Coating process parameters of the ternary (Al,Cr) ₂ O ₃ system	41
Table 5.2:	Chemical composition of the (Al,Cr) ₂ O ₃ coatings.....	42
Table 5.3:	Coating process parameters of (Al,Cr _L)N interlayer	46
Table 5.4:	Nanoindentation values of (Al,Cr _L)N interlayers.....	48
Table 5.5:	Critical normal loads $L_{c1} - L_{c3}$ of (Al,Cr _L)N interlayers on X40CrMov5-1 steel	51
Table 5.6:	Process parameters of (Al,Cr _L)N/(Al,Cr _L) ₂ O ₃ system	52
Table 5.7:	Coating properties of (Al,Cr _L)N/(Al,Cr _L) ₂ O ₃ system in as-deposited state	54
Table 5.8:	Nanoindentation values of oxide coatings on different substrates	59
Table 5.9:	Coating parameters of (Al,Cr _H)N/(Al,Cr _H) ₂ O ₃ system deposited in dc mode.....	63
Table 5.10:	Effect of annealing on indentation values of (Al,Cr _H)N _g /(Al,Cr _H) ₂ O ₃ coating	74
Table 7.1:	Process parameters of Al ₂ O ₃ coatings deposited at $T_s \approx 780$ °C in dc mode.....	85
Table 7.2:	Effect of annealing during HT-XRD on indentation values	94
Table 7.3:	Parameters of coating process at $T_s \approx 850$ °C.....	98
Table 7.4:	Nanoindentation values of Al ₂ O ₃ coatings deposited at $T_s \approx 850$ °C.....	102
Table 7.5:	Residual stress in Al ₂ O ₃ coatings deposited at $T_s \approx 850$ °C analyzed using XRD.....	103
Table 8.1:	Process parameters of Al ₂ O ₃ coatings deposited for cutting tests	105
Table 8.2:	Process parameters for the deposition of TiAlN by CC800/9 SinOx	107
Table 8.3:	Indentation values of Al ₂ O ₃ , TiAlN and TiAlN/Al ₂ O ₃ coatings on WC-Co substrate.....	109

List of abbreviations

AIP	Arc Ion Plating
BF	Bright-field
ccp	cubic close-packed
CLSM	Confocal Laser Scanning Microscopy
CVD	Chemical Vapor Deposition
dc	Direct Current
dcMS	Direct Current Magnetron Sputtering
DF	Dark-field
DFG	German Research Foundation (GER. Deutsche Forschungsgemeinschaft, DFG)
DIN	German Institute for Standardisation (GRE. Deutsches Institut für Normung)
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray Spectroscopy
EPMA	Electron Probe Microanalysis
FIB	Focused Ion Beam
FWHM	Full Width at Half Maximum
GFE	Central Facility for Electron Microscopy
GFS	Gas Flow Sputtering
GI	Grazing Incidence
HCD	Hollow Cathode Discharge
hcp	hexagonal close-packed
HF	Adhesion Class
HPPMS	High-Power Pulsed Magnetron Sputtering
HS-PVD	High-Speed Physical Vapor Deposition
HT-NI	High-Temperature Nanoindentation
HT-PVD	High Temperature Physical Vapor Deposition
HT-XRD	High Temperature X-ray Diffraction
IFW	Institute of Production Engineering and Machine Tools
IOT	Institute for Surface Engineering
mf	Medium Frequency
mfMS	Medium Frequency Magnetron Sputtering
MS	Magnetron Sputtering
MT-CVD	Moderate Temperature Chemical Vapor Deposition

NI	Nanoindentation
PVD	Physical Vapor Deposition
rfMS	Radio Frequency Magnetron Sputtering
RT	Room Temperature
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGO	Thermally Grown Oxide
XAES	X-ray Induced Auger Electron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

List of formula symbols

a_p	Cutting depth
A_{Target}	Target area
ds/dt	Deposition rate
dT/dt	Heating rate
d_{plug}	Plug diameter
d_{target}	Target distance
$d_{Thermo.}$	Thermocouple distance
E	Modulus of elasticity
E_{IT}	Indentation modulus
f	Frequency
F_{max}	Indentation force
F_N	Normal force
F_{NI}	Nanoindentation force
h	Height
H	Hardness
H_{IT}	Indentation hardness
h_{IT}	Indentation depth
I	Current
I_B	Bias current
l	Lenght
L_c	Critical normal load
p	Pressure
P_C	Cathode power
Q_{Ar}	Argon gas flow
Q_{Kr}	Krypton gas flow
Q_{O2}	Oxygen gas flow
r	Radius
Ra	Average line roughness
s	Thickness of coating
s_t	Functional layer thickness
T	Temperature
t	Time

T_{anneal}	Annealing temperature
t_c	Cutting time
$t_{coat.}$	Coating time
t_{etch}	Etching time
t_f	Functional layer deposition time
T_H	Heating temperature
t_{hold}	Holding time
T_{HT-NI}	High temperature nanoindentation temperature
t_i	Interlayer deposition time
t_{imm}	Immersion time
t_{NI}	Nanoindentation time
t_{off}	Pulse off time
t_{on}	Pulse on time
T_s	Substrate temperature
T_{vac}	Vacuum temperature
t_{vac}	Annealing time in vacuum
U	Voltage
U_B	Substrate bias voltage
U_C	Cathode voltage
VB_{max}	Maximum flank wear land width
w	Width
W_{el}	Elastic work
W_{pl}	Plastic work
x_{Cr}	Atomic amount of chromium
$x_{(element)}$	Content of element
α	Coefficient of thermal expansion
σ	Residual stress
γ	Rake angle
ε	Lattice strain
η_{el}	Elastic work percentage
θ	Diffraction angle XRD
λ	Wavelength
μ	Mass attenuation coefficient

List of formula symbols

v_c	Cutting speed
ν	Poisson ratio
v_s	Sliding velocity
ρ	Density
τ_{max}	Maximum penetration depth XRD
ω	Incoming angle XRD
ω_{table}	Table rotation speed
$\varnothing$	Diameter

1 Introduction

Manufacturing processes are increasingly focused on achieving high productivity. This rise in productivity often results in complex stress collectives on tool materials. The mechanical, chemical, and thermal loads usually overlap under such conditions. Consequently, tools reach the end of their service life more quickly. One approach to extending tool life is the application of thin protective coatings. Tools used in primary shaping, forming, and cutting are the main application areas for oxide coatings. Due to its excellent wear resistance, hot hardness, and chemical inertness, Al_2O_3 is a promising coating material for further increasing the service life of production tools under such complex stress collectives.

Although nitride and diamond-like carbon (DLC) coatings have become industrially established in many processes, Al_2O_3 coatings synthesized by physical vapor deposition (PVD) have yet to achieve industrial breakthroughs despite their potential advantages. The possibility of lower substrate temperatures $T_s < 600^\circ\text{C}$ in PVD processes enables coating of temperature sensitive tool materials such as hot work tool steel, which is used in primary shaping and forming tools. However, the lower crystallinity of binary Al_2O_3 coatings deposited by PVD at these low temperatures reduces their thermal stability. Modifying binary Al_2O_3 coatings with Cr facilitates the synthesis of crystalline $(\text{Al,Cr})_2\text{O}_3$ solid solutions at lower substrate temperatures $T_s < 600^\circ\text{C}$ through PVD. However, challenges such as phase transformation and thermal instability, addressed in [KLJ+12], persist particularly in coatings with high chromium content $x_{\text{Cr}} \geq 30$ at.-% in the metal portion. Coatings with high aluminum content $x_{\text{Al}} > 70$ at.-% remain largely unexplored despite their potential advantages in enhancing thermal stability. Furthermore, a thermally stable interlayer system is required not only for the adhesion strength enhancement of $(\text{Al,Cr})_2\text{O}_3$ on the hot work steel, but also to prevent issues such as thermal instability and porosity, observed in [BBK+19] for the selected metallic AlCr interlayer.

Crystalline Al_2O_3 coatings synthesized by chemical vapor deposition (CVD) are established as a benchmark for cutting operations. Cemented carbide tools with CVD- Al_2O_3 are still among the best-selling products for turning operations. The drawbacks of CVD processes for cutting tools include thermal cracks, tensile stress formation, and tool embrittlement. Moreover, the high process temperature required to deposit CVD coatings limits the choice of suitable substrate materials. Besides the problems mentioned in cemented carbide cutting tools, there are even more problems for forming tools, where we most likely deal with steel dies that require

an additional heat treatment after the CVD process. These drawbacks of CVD processes have increased interest in synthesizing crystalline Al_2O_3 at high temperatures $T > 700^\circ\text{C}$ by PVD. However, existing research in this context is limited and has primarily focused on fundamental investigations such as phase formation. The high-temperature properties, residual stress states, and machining performance of Al_2O_3 coatings deposited by PVD at $T > 700^\circ\text{C}$ leave significant knowledge gaps. Challenges such as process instability due to target poisoning, deposition of reproducible coatings with the desired stoichiometry, and a narrow process window addressed in literature can be a reason for these limited studies.

The studies of alumina coatings synthesized by PVD emphasize the necessity of a deposition technique to overcome the existing limitations of conventional PVD processes. High speed PVD (HS-PVD) used in this dissertation is a special process variant of PVD technology. It works based on the principle of hollow cathode gas flow sputtering (GFS). Two characteristic properties can describe GFS. A hollow cathode glow discharge prevents the migration of gas ions from the electric field in front of the cathodes, enhancing the plasma ionization. HS-PVD can be a potential solution to enhance the deposition rate while maintaining process stability in a reactive process. The reason is the separation of the reactive gas inlet from the target surface as well as convective particle transport, reducing the target poisoning.

This work addresses the research gaps in synthesizing $(\text{Al,Cr})_2\text{O}_3$ coatings with high aluminum content $x_{\text{Al}} > 70$ at.-% in the metal portion. The investigations focus on finding a suitable high-temperature stable interlayer and analyzing the effect of reduced Cr content on performance at high temperatures. The hot work tool steel X40CrMoV5-1 coated with HS-PVD will be examined under harsh conditions in contact with molten steel 100Cr6 in immersion tests for the first time. The basic aspects regarding the adhesion of molten steel to $(\text{Al,Cr})_2\text{O}_3$ coatings and the chemical and structural stability of the coatings will be investigated. In addition, this work aims to contribute to the limited research into the high-temperature $T > 700^\circ\text{C}$ synthesis of Al_2O_3 coatings using PVD for cemented carbide tools in cutting applications. The specific characteristics of HS-PVD, which reduce the target poisoning, have an advantage in enabling stable reactive oxide processes at such high deposition temperatures. Moreover, it will be investigated whether the compressive residual stresses in HS-PVD coatings can be achieved despite thermally induced tensile residual stresses. The cemented carbide tools coated with Al_2O_3 by HS-PVD will be examined in turning tests that focus on cutting applications.

2 State of the art

This chapter begins by introducing the fundamentals of PVD technology. The High Speed PVD process, used for coating development and application in this dissertation, is presented along with its advantages over conventional PVD technologies. The underlying principles of this technology are explained, focusing on hollow cathode discharge and gas flow sputtering. Furthermore, this dissertation reviews the properties, application areas, and synthesis technologies of aluminum-based oxide coatings that are used for wear protection. The focus is on tools used in manufacturing technology, particularly primary forming and cutting tools. The challenges associated with synthesizing alumina coatings at lower substrate temperatures $T_s < 700\text{ }^{\circ}\text{C}$ and high temperatures $T_s \geq 700\text{ }^{\circ}\text{C}$ by PVD are discussed.

2.1 Fundamental of physical vapor deposition

Physical vapor deposition (PVD) techniques rank among the commonly utilized coating deposition technologies. In accordance with DIN 8580, they are classified under the fifth main group of manufacturing processes, “coating”, within its eighth subgroup 5.8, “coating from the gaseous or vaporous state (vacuum coating)”. The following fundamentals of PVD technology are gathered mainly from [Bob13], in addition to the literature cited.

PVD is vacuum-based coating technology in which the coating material is deposited onto a substrate via thermal or kinetic energy through the gas phase. The coating process occurs in a fine or high vacuum with pressures of $10^{-4}\text{ Pa} \leq p \leq 10\text{ Pa}$. PVD methods allow for the synthesis of coatings with thicknesses s varying from a few nanometers to several micrometers, typically less than $s = 10\text{ }\mu\text{m}$. Depending on the energy supply, PVD processes are classified as sputtering or thermal evaporation. The PVD process is divided into three phases. The first phase involves using high energy to change the solid coating material, known as the “target,” into the gas phase. The coating particles are transported via the gas phase to the coating substrate in the second phase. These particles then condense on the substrate’s surface, enabling coating formation and growth in the third phase.

The film growth in the third phase is determined by both the incoming particles’ characteristics and the substrate surface’s nature. When atoms reach a solid surface, they may either bounce off immediately or transfer enough energy to become temporarily attached as adatoms. Over time, more atoms adhere to these adatoms, leading to the formation of small clusters. Once

these clusters exceed a critical size, they continue to grow into crystallites through heterogeneous nucleation on the substrate. Subsequently, thin films can be formed by crystallite merge and expansion.

A negative bias voltage is usually applied to the substrates in PVD processes. This negative voltage accelerates the positively charged particles towards the substrate, enhancing adatom mobility and increasing particle bombardment of the substrate. Consequently, the bias voltage can influence the kinetic energy of film-forming particles, thereby impacting coating properties such as morphology and residual stress. Moreover, the kinetic energy of the arriving particles impacts how strongly they bond to the substrate. The mass, chemical composition, impact rate, and angle of the incoming particles are the other factors influencing the coating properties. The substrate also plays a crucial role by influencing film formation through its surface roughness, chemical composition, and temperature. The substrate temperature in PVD processes is usually in the range of $100\text{ }^{\circ}\text{C} \leq T_s \leq 600\text{ }^{\circ}\text{C}$. This allows the coating of temperature sensitive substrate materials, such as hardened steel, at temperatures below their annealing temperatures. As a result, the coating process does not result in an undesirable drop in the substrate's hardness. In addition, lower process temperatures reduce the risk of thermal distortion or dimensional change of complex tools, which is critical in precision applications such as die casting [Nog11].

The morphology of PVD coatings is influenced by several factors, including the specific PVD technique employed, process parameters, chemical composition, and coating architecture. In a monolayer coating architecture, where the chemical composition remains uniform across the coating thickness, a columnar morphology is typically observed. As the diameter of the columns increases with increasing layer thickness, the compressive residual stress generally rises. This limits the maximum coating thickness for monolayers having dense morphology. Furthermore, this aspect challenges conventional PVD processes such as magnetron sputtering and arc PVD for deposition of monolayer coatings with a thickness of $s \geq 10\text{ }\mu\text{m}$. The process of re-nucleation during coating growth results in a dense, fine-crystalline morphology. However, this change reduces compressive residual stress, enabling the thickness of the coating to be increased, particularly in multilayer coating architecture.

Nitride, oxide, oxynitride, and carbide coating systems can be synthesized using reactive gases such as N_2 , O_2 and C_2H_2 in a reactive PVD process. One of the cost-effective power supplies with

simple process control used in PVD technology is the direct current (dc) source. This is mostly used in magnetron sputtering (MS), which is known as direct current magnetron sputtering (dcMS). In a conventional dcMS discharge, the cathode is kept at a constant negative voltage. A phenomenon that may occur in a reactive PVD process is the formation of non-conductive layers on targets, known as "target poisoning". Target poisoning leads to consequent arcing, process instability, reduction of deposition rate, and in worst case, the complete process breakdown. The reduction of target poisoning is particularly relevant to synthesizing the oxide coating systems addressed in this dissertation.

The insulating layer on the target's surface acts as a capacitor, where the target serves as one conductor and the plasma as the other conductor. Since direct current cannot pass through a capacitor, this leads to two major issues, described in the following [Sel98]:

1. Since ion current is essential for sputtering, areas covered by the insulating film receive no ion bombardment. This prevents further material removal, resulting in additional growth of the insulating layer on the target.
2. If the parasitic capacitor cannot fully charge to the applied voltage, dielectric breakdown may occur, causing a sudden release of charge carriers. This increases local current density, potentially leading to arcing, which introduces unwanted particulate contamination.

Preventing target poisoning is one of the critical factors for the success of reactive PVD processes and one of the challenges, especially in the deposition of oxide coating systems from metallic targets. One approach that has been used to reduce target poisoning is the use of pulsed dc power supplies, developed during the late 1980s [Smi95]. Over time, these evolved into medium frequency (mf) and high power pulsed magnetron sputtering (HPPMS) technologies. The effectiveness of pulsed power supplies in eliminating target poisoning is based on fundamental physical principles. By employing pulsed power supplies, the applied voltage is periodically reversed or switched off at intervals. This allows charge buildup to dissipate as electrons in the plasma neutralize the insulating areas during the negative pulse phase. A further development of mfMS is HPPMS technology. Hereby, pulses with on time of $40 \mu\text{s} \leq t_{on} \leq 200 \mu\text{s}$ and frequencies in the range of $500 \text{ Hz} \leq f \leq 4,000 \text{ Hz}$ are used [CTS+04]. HPPMS enhances the ionization of the target material due to its high power density, enabling the efficient removal of even difficult-to-sputter materials.

Although pulsed technologies offer significant advantages in reactive sputtering processes, certain challenges persist. Pulsed power supplies require more complex control mechanisms and are often associated with higher costs. Additionally, efficiency losses in power transmission can occur, especially if the pulses are too short or excessively intense. Another major drawback of pulsed power supplies is their generally lower deposition rate compared to dc power supplies. This not only limits their suitability for applications requiring thick coatings $s > 15 \mu\text{m}$ but also affects overall production efficiency in batch processes, where achieving high productivity is essential for industrial competitiveness. Studies in [SCC+04] have shown that for HPPMS, the deposition rate for reactive sputtering of alumina is approximately three times lower than for conventional dc sputtering.

Further challenges arise when depositing highly insulating materials, such as oxide coatings, using this technique. These include:

1. Extensive process optimization: Achieving a stable process requires significant effort in optimizing deposition parameters before a coating with the desired stoichiometry can be reproducibly synthesized.
2. Continuous monitoring and adjustments: To obtain stoichiometric coatings while maintaining a high deposition rate, constant monitoring and fine-tuning of process parameters are essential.
3. Limited process window: To create a reactive sputtering process that is stable in the long-term, has less arcing, and does not significantly affect the deposition rate, a narrow process window is often utilized.

2.2 High Speed physical vapor deposition

HS-PVD is a special variant of the PVD process and belongs to the sputtering techniques family. This coating technology is based on a combination of hollow cathode discharge (HCD) and gas flow sputtering (GFS). This chapter provides a detailed discussion of this process, presenting the specific characteristics of HCD and GFS.

2.2.1 Hollow cathode discharge

In this subchapter, the fundamentals are gathered from the works of [LL05], [MP15] and the literature cited. The development of hollow cathode technology has evolved significantly over time, driven by advancements in vacuum discharge research and thin film deposition

techniques. The term “hollow cathode discharge” typically refers to plasma within a cathode that has a cavity-like geometry. A glow discharge with a planar cathode, which is typical in conventional PVD processes, is shown schematically in Figure 2.1.

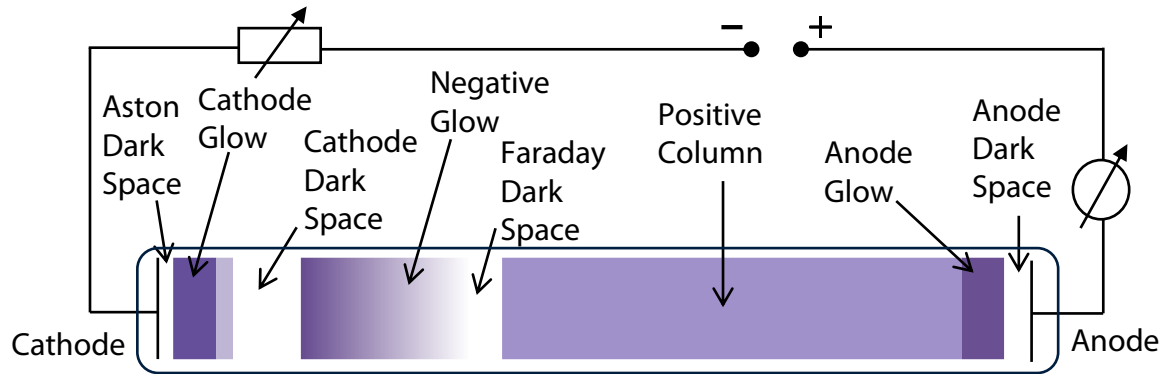


Figure 2.1: Schematic of glow discharge with a planar cathode after [MP15]

Hereby, the potential applied between the cathode and the anode produces a non-uniform electric field between the parallel electrodes. The difference in electron and ion mobility is responsible for this strong electric field at the cathode and less close to the anode. The cathode sheath, which is the region connecting the cathode to the bulk plasma or negative glow region, contains three different regions, as described in the following:

1. Aston dark space: This area is characterized by minimal visible light emission in front of the cathode, with an electric field that decreases linearly from the cathode to the negative glow region. Electrons in this area do not have enough energy for gas ionization.
2. Cathode glow: The electrons emitted from cathodes possess sufficient energy to excite the neutral gas and atoms sputtered off the cathode surface.
3. Cathode dark space: This region accounts for most of the drop in voltage between the cathode and negative glow region, which is also referred to cathode fall. This voltage drop results from gas ionization. The emitted electrons from the cathode are accelerated away from the cathode through the cathode fall.

The negative glow region is the brightest part of the discharge, with a sharp boundary at the cathode dark space but a more diffuse transition into the Faraday dark space. This area consists of a high density of electrons with high energy, extending up to several tens of electron volts.

Gas ionization takes place in the negative glow region through collisions between the accelerated electrons and gas atoms or molecules. The gas ions are accelerated toward the cathode in the cathode fall region. When they collide with the cathode surface, they release secondary electrons, which then contribute to the ionization process. The discharge is maintained by secondary electron emission from the cathode. The energetic secondary electrons provide the ionization required to maintain the discharge.

At the end of the negative glow, the electrons have lost most of their energy. This leads to a reduced chance of excitation and ionization, marking the beginning of the Faraday dark region. The Faraday dark space is typically short and exhibits a slight increase in the electric field before transitioning into the positive column, where the field remains low and uniform. The electrons, which are responsible for most of the current in the positive column, are prevented from reaching the cathode.

The fundamental characteristics of planar glow discharge, as previously explained, are crucial for analyzing the modifications introduced by hollow cathode geometries. By the 1970s, the vacuum coating industry began exploring hollow cathode discharges for coating deposition. The hollow cathode can have either a circular or linear geometry. Hereby, the focus is on the linear source that is used in the HS-PVD coating unit for this dissertation.

The hollow cathode with a linear geometry consists of two plates positioned at a specific distance from each other. The zones of the glow discharge on both sides overlap due to the position of the two cathodes standing opposite each other. As a result, the negative glow light of the hollow cathode discharge is largely enclosed by the cathode surface. This arrangement reduces gas ions from escaping the electric field in front of the cathodes. Due to this, the loss of ions, caused by recombination, can be reduced in a hollow cathode. Therefore, no magnetic field is required to trap electrons in front of the targets, as in MS. As A. Günter-Schulze already described in 1923, one of the positive characteristics of hollow cathode discharge is known as the “pendulum effect” [Gün23]. Due to the parallel arrangement of the cathodes, the electrons that enter the negative glow region are slowed down by the other cathode side because of similar charges and are accelerated to the opposite side. These electrons are trapped inside a hollow cathode and have a pendulum movement, which increases the total distance each electron travels. As a result, electrons have many more chances to collide with gas atoms which leads to

a greater probability of ionization. The hollow cathode effect typically depends on specific discharge conditions, including the parameters of the external circuit, gas pressure, and the geometric dimensions of the hollow cathode [FVC+17].

2.2.2 Gas flow sputtering

The principle of GFS in this subchapter is discussed based on the publications of Ishii. The GFS has been addressed since 1988 in studies of Ishii et. al., in which they examined GFS for sputtering of Cu [IHT88]. The sputtering source in GFS is a hollow cathode, which can be either a cylindrical target or two planar target plates. The principle of the GFS or HS-PVD process, as applied in this dissertation, is schematically illustrated in Figure 2.2.

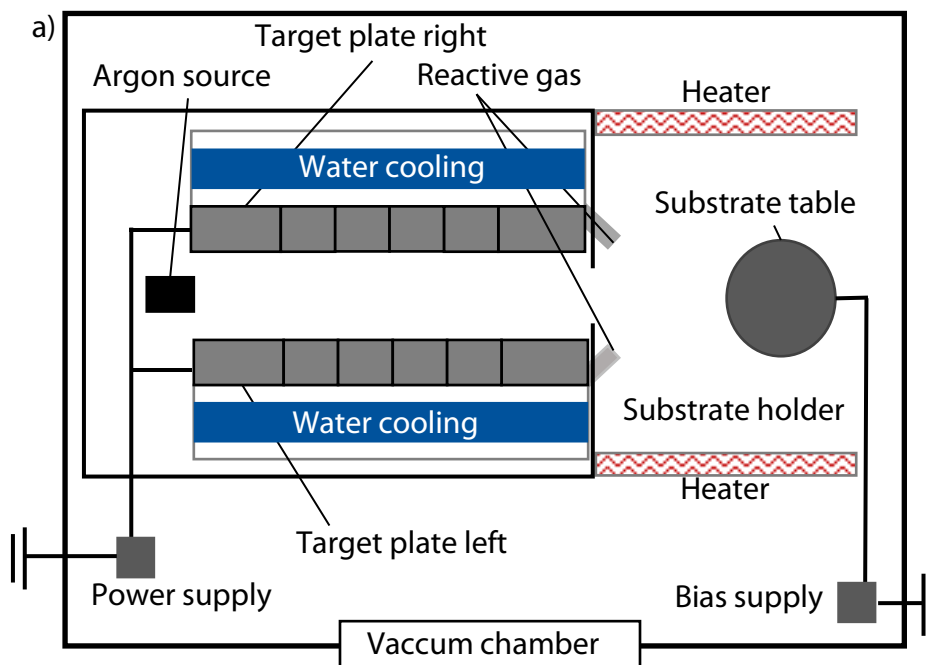


Figure 2.2: Illustration of HS-PVD principle

The process gas flows through the hollow cathode, which consists of two target plates positioned at a specific distance of $d_{\text{target}} \approx 2$ cm from each other. Noble gases, such as argon in the case of HS-PVD, are usually used as process gases. A sufficiently high negative voltage is applied to the hollow cathode, igniting a glow discharge between the two parallel cathode plates and initiating plasma formation. The electrons emitted from the target ionize the process gas and generate positive ions. The positive gas ions accelerate toward the negatively charged targets. This bombardment causes sputtering of the material from the target surfaces. Unlike the MS process,

no magnetic field is required to trap electrons in front of the targets. The target arrangement in HS-PVD reduces the escape of gas ions and electrons from the electric field near the cathodes and acts effectively as a trap.

Another characteristic of this process compared to arc PVD and MS is the convective transport of the sputtered particles to the substrate. This is achieved by a directed inert gas flow through the hollow cathode. Moreover, the process gas flow can be up to 15 times higher than in conventional PVD processes [JW93], leading to a process pressure in the fine vacuum range, $1 \text{ Pa} \leq p \leq 100 \text{ Pa}$, rather than the high vacuum range of conventional PVD, $10^{-4} \text{ Pa} \leq p \leq 10 \text{ Pa}$ [Bob13]. A negative bias voltage is applied to the substrate, which is positioned in front of the hollow cathode. The positively charged particles are accelerated towards the substrate with enhanced kinetic energy, resulting in a denser coating morphology. Moreover, reactive gases are supplied outside of the hollow cathode. This eliminates target poisoning compared to conventional PVD processes, where the entire target surface is directly exposed to reactive gases. All the characteristics mentioned in the HS-PVD process can influence the residual stress in the growing coating. However, the specific effects of these characteristics remain to be thoroughly investigated.

2.3 Al₂O₃ coatings in manufacturing processes

According to DIN 8580, manufacturing processes are categorized into six main groups. Tools used in the first three groups, such as primary shaping (GER. Urformen), forming (GER. Umformen), and cutting (GER. Trennen), are the main application areas for oxide coatings. Primary shaping involves creating solid bodies from formless materials and cutting produces components by the local separation of material.

Primary shaping and forming

The high pressure die casting (HPDC) is regarded as highly sustainable due to the significant amount of material processed in the final product. HPDC is particularly resource-efficient for high production volumes and automation, and it is well-established in the industry for low-melting alloys like aluminum and magnesium. The tools used in HPDC are made from alloyed hot work tool steels, with the most common types being Cr- and Mo-containing steels such as X38CrMoV5-1 and X40CrMoV5-1 [MC25]. Die casting of high-melting alloys places enormous demands on the tool material. The high melting temperatures of steel alloys expose

the tools to severe thermal fatigue, oxidation, and adhesion of molten metals, causing conventional hot work tool steels to reach their performance limits. In comparison to hot work steel tools, ceramic dies are expensive, particularly when the mold geometry is complex. Moreover, ceramic casting tools have a strong tendency to fail especially when thermal cycling is combined with mechanical forces. Currently, no industrially viable solutions exist for HPDC of high-melting alloys like steel materials. Consequently, several studies have suggested that using metallic dies with a coating capable of withstanding harsh conditions during the primary shaping and forming of steel alloys may be viable [LHK+01]. Semi-solid metal (SSM) processing is driven by significant technological potential. This process involves forming in the semi-solid state between the solidus and the liquidus. Consequently, SSM forming is conducted at lower temperatures than HPDC. This significantly reduces thermal loads on tools, while a relatively low viscosity of the semi-solid material is obtained. Another advantage is reduced shrinkage due to the high solid fraction, $x_{solid} = 40\%$ [HK09]. Flemings and his group first discovered this process in the early 1970s [FBB+78]. Thereby, tools made from X40CrMoV5-1 were used for SSM die casting of 34CrNiMo6 steel. The lock-up time after injection of SSM metal to the die could be adjusted in range of $0\text{ s} < t < 30\text{ s}$. After injection tools were cooled for $t_{Injec.} \approx 5\text{ s}$. The maximum production rate of 40 components per hour could be reached. However, the semi-solid forming of high-melting steel alloys has not yet achieved industrial applicability. This is due to technological challenges, primarily due to the higher processing temperatures required compared to the SSM forming of low-melting alloys. The temperature range for steel alloys depends on the selected material and varies in the range of $1,250\text{ }^{\circ}\text{C} < T < 1,500\text{ }^{\circ}\text{C}$ [HK09].

Among steel alloys, X210CrW12 and 100Cr6 have emerged as particularly suitable for semi-solid processing. Their broad semi-solid regimes make them ideal candidates for detailed investigations into phase formation during processing, leading to extensive studies. The investigations in [LHK+01] compared uncoated and coated high-melting molybdenum-alloy dies in the semi-solid forming of steel. Different oxide-based coatings such as Al_2O_3 , ZrO_2 , and MgAl_2O_4 were tested. The coated dies, regardless of the coating system, showed higher oxidation resistance than the uncoated ones after producing 10 steel components. The uncoated tool was not feasible since it strongly sublimates in the SSM forming of 100Cr6. Moreover, it was found that these short-term investigations were insufficient to distinguish the effect of coating systems. The authors assumed that the coating system might influence the dies'

performance after long-term testing. Overall, the study demonstrated the potential of oxide-based coating systems for application in semi-solid steel forming.

Among various coating systems, crystalline Al_2O_3 coatings offer excellent thermal stability, oxidation resistance, and anti-adhesive properties, making them particularly promising for die casting and forming applications. Studies in [KSA+04] investigated Al_2O_3 coatings regarding their performance in the semi-solid forging of 100Cr6 steel with tool materials made from X38CrMoV5-1 hot work steel. The tool exhibited significant mechanical and corrosive damage after eight test cycles. Furthermore, Al_2O_3 coatings synthesized by PVD were examined on X38CrMoV5-1 dies in semi-solid forging tests of X210CrW12 steel [BBI08]. An investigation of the Al_2O_3 coated tool, after 33 forming cycles, revealed that the coating remained intact and stable. In [BLM06b], steel upsetting model tests were conducted on Al_2O_3 coated molybdenum-based plates. After 50 tests, the coated plates showed only minimal marks of iron adhesion, and no coating delamination was observed.

Cutting

Turning is a machining process classified under the “cutting” category and is further categorized under machining with geometrically defined cutting edges in DIN 8580. Coated carbide tools are established for machining with a geometrically defined cutting edge. Approximately 85 % of all cemented carbide tools used in turning operations are coated with wear-resistant hard coatings [NN14]. Depending on process conditions and material combinations, the tools are subjected to crater wear, flank wear, and notch wear, which result from abrasion, adhesion, diffusion, or oxidation. Additionally, chipping can occur due to cohesive substrate failure. One of the main focuses of coating used in cutting applications is wear protection against abrasion and adhesion. The temperature at the cutting edge determines the wear mechanisms affecting the tool during machining [Klo18]. While abrasion and adhesion dominate at lower cutting temperatures, tool wear at higher temperatures is primarily caused by diffusion and oxidation in addition to abrasion. As cutting temperatures rise, research priorities shift toward high-temperature properties of coated tools, especially oxidation resistance and diffusion barrier functionality. Effective abrasion protection at high temperatures can be achieved when the coatings possess sufficient high-temperature strength. Due to these properties, cemented carbides with CVD- Al_2O_3 are still one of the best-selling products for turning operations [Bob17]. However, due to its predominantly ionic bonding,

Al_2O_3 has a low tendency to adhere to metals. This characteristic presents a disadvantage when Al_2O_3 coatings are deposited directly on metallic substrates. This material incompatibility leads to reduced adhesion, which makes the deposition of a suitable interlayer necessary. Therefore, the next subchapter 2.4 deals with the interlayer systems studied in this context so far. Subsequently, subchapter 2.5 provides a more detailed explanation of the properties and synthesis methods of Al_2O_3 coatings.

2.4 TiAlN and AlCrN systems as an interlayer for Al_2O_3

The first PVD coating used in the industry was TiN [Mat85]. Compared to the TiN coating used on cutting tools, the TiAlN system has higher hardness. The addition of Al to the cubic crystal structure of TiN leads to solid solution strengthening. Moreover, passive layers of Al_2O_3 form on top of the TiAlN coating which makes TiAlN considerably more oxidation resistant than TiN coatings. Therefore, TiAlN was considered in several studies as interlayer for the alumina coatings deposited by PVD. Within the DFG project BO 1979/3 “Nanocrystalline $\gamma\text{-Al}_2\text{O}_3$ coatings: Fundamental investigations on synthesis, structure and machining properties” studies were conducted on synthesizing $\gamma\text{-Al}_2\text{O}_3$ coatings using MS at IOT in Aachen, Germany. Hereby, to improve adhesion of $\gamma\text{-Al}_2\text{O}_3$ on the cemented carbide substrate, the $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ interlayer was employed [BBR+10]. To provide high hardness and oxidation resistance, the high Al content in $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ was considered. The transition from $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ to $\gamma\text{-Al}_2\text{O}_3$ was conducted in different ways: a direct and sharp transition from $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ to $\gamma\text{-Al}_2\text{O}_3$ or with a graded transition zone. During coating process within the transition zone, a continuous reduction in the $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ and a uniform increase in the amount of $\gamma\text{-Al}_2\text{O}_3$ were conducted. After annealing for $t = 1$ h at $T = 1,200$ °C in vacuum, the $(\text{Ti}_{37}\text{Al}_{63})\text{N}$, containing cubic c-TiN and c-AlN, transforms into c-TiN and hexagonal h-AlN in both variations. It can be concluded that the c-AlN is not phase stable at $T = 1,200$ °C. Moreover, the thickness of the $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ interlayer increases, explained by formation of h-AlN with a higher average volume than c-AlN.

After annealing tests in the atmosphere, the formation of $\alpha\text{-Al}_2\text{O}_3$ begins at $T = 900$ °C and is influenced by the choice of transition zone between the $(\text{Ti}_{37}\text{Al}_{63})\text{N}$ interlayer and $\gamma\text{-Al}_2\text{O}_3$. After annealing in the atmosphere at $T = 1,000$ °C, a higher content of $\alpha\text{-Al}_2\text{O}_3$ is observed for coatings with graded transition zone compared to coatings with a direct transition. The non-graded TiAlN/ $\gamma\text{-Al}_2\text{O}_3$ coating still possess much γ -phase [BBR+10]. Furthermore, the compound adhesion strength analysis using scratch test exhibits higher critical loads for graded

(Ti₃₇Al₆₃)N/ γ -Al₂O₃ compared to coatings with direct transition from (Ti₃₇Al₆₃)N to γ -Al₂O₃ before and after annealing tests at $T = 900\text{ }^{\circ}\text{C}$ in ambient air [Ewe12].

Due to their outstanding wear, adhesion, and oxidation resistance at high temperatures, AlCrN hard coatings also have established wear protection as coatings for tools. Compared to the binary c-CrN coating, the ternary AlCrN coating with a cubic structure exhibits increased hardness while having a lower indentation modulus [Hol84]. The influence of two different interlayer systems, (Ti₃₇Al₆₃)N and (Al₄₀Cr₆₀)N, on the thermal stability of γ -Al₂O₃ was the focus of further investigations within the DFG project BO 1979/3 at IOT, Aachen [BBM+11]. The graded (Ti₃₇Al₆₃)N/ γ -Al₂O₃ and (Al₄₀Cr₆₀)N/ γ -Al₂O₃ coated cemented carbide substrates were investigated after annealing tests for $t = 1\text{ h}$ in atmosphere at $T = 900\text{ }^{\circ}\text{C}$ and $T = 1,000\text{ }^{\circ}\text{C}$. (Ti₃₇Al₆₃)N/ γ -Al₂O₃ developed α -Al₂O₃ and TiO₂ after annealing at $T = 1,000\text{ }^{\circ}\text{C}$, while (Al₄₀Cr₆₀)N/ γ -Al₂O₃ stayed stable and no α -Al₂O₃ or Cr₂O₃ was formed.

It was shown that the oxidation resistance of the γ -Al₂O₃ can be increased by choosing the more stable (Al₄₀Cr₆₀)N interlayer. However, the oxidation resistance was limited to $T = 1,000\text{ }^{\circ}\text{C}$, as the (Al₄₀Cr₆₀)N/ γ -Al₂O₃ coating was destroyed at higher temperatures and no further analysis was possible. Despite higher oxidation resistance, scratch tests after annealing tests showed a lower critical force for (Al₄₀Cr₆₀)N/ γ -Al₂O₃ coated samples compared to (Ti₃₇Al₆₃)N/ γ -Al₂O₃. When depositing γ -Al₂O₃ on (Al₄₀Cr₆₀)N interlayer, the problem of the oxidized CrN in form of Cr₂O₃ arises. The thermally grown oxide (TGO) in form of Cr₂O₃ was observed in the transition zone between (Al₄₀Cr₆₀)N and γ -Al₂O₃. The lower adhesion strength after the annealing tests of (Al₄₀Cr₆₀)N/ γ -Al₂O₃ can be attributed to the TGO layer. Moreover, the cutting performance of (Ti₃₇Al₆₃)N/ γ -Al₂O₃ and (Al₄₀Cr₆₀)N/ γ -Al₂O₃ coated cemented carbide tools in milling operations of X6CrNiMoTi17-12-2 was investigated in [Ewe12]. Despite higher oxidation resistance of (Al₄₀Cr₆₀)N/ γ -Al₂O₃, (Ti₃₇Al₆₃)N/ γ -Al₂O₃ coated tools exhibit higher wear resistance than (Al₄₀Cr₆₀)N/ γ -Al₂O₃ coated tools, affecting both the flank face and crater wear [Ewe12]. Overall, the results suggest that TiAlN is a more suitable interlayer for γ -Al₂O₃ in cutting applications, particularly where the operating temperature typically does not exceed $T = 800\text{ }^{\circ}\text{C}$. In contrast, for primary forming and shaping processes of steel alloys, the operating temperatures typically can vary in range of $1,250\text{ }^{\circ}\text{C} < T < 1,500\text{ }^{\circ}\text{C}$, the AlCrN interlayer with cubic structure shows limitations due to its restricted oxidation resistance up to $T = 1,000\text{ }^{\circ}\text{C}$.

At an Al content of $x_{Al} > 60$ at.-% exclusively considering metallic elements, AlCrN reveals a crystal structure change from a pure cubic to a mixed-phase structure of cubic and hexagonal (h). The phase transformation into a hexagonal crystal structure, however, leads to a reduction in hardness. Research works in [KKS02] showed that the hardness of AlCrN coatings with a cubic structure, deposited by arc ion plating (AIP), is enhanced by increasing aluminum content. However, in AlCrN coatings with a hexagonal structure, hardness reduces with increasing aluminum content, as shown in Figure 2.3.

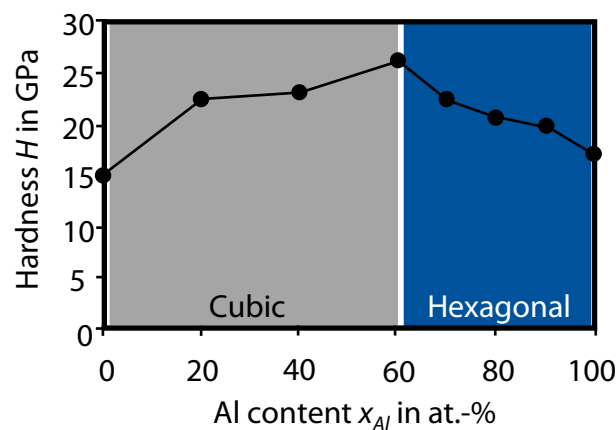


Figure 2.3: Hardness of AlCrN coatings against Al content and structure based on [KKS02]

The critical value of the transition to the mixed phase h-AlN and c-AlN also depends slightly on the deposition technique and parameters. Studies in [BBT13] investigated the effect of deposition technology on the phase formation of AlCrN coatings. Hereby, AlCrN coatings with $5 \text{ at.-%} \leq x_{Al} \leq 77 \text{ at.-%}$ in metallic portion were deposited using three different technologies of dcMS, mfMS and HPPMS. Formation of h-AlN was found in $(\text{Al}_{50}\text{Cr}_{50})\text{N}$ coatings deposited by HPPMS. However, in $(\text{Al}_{58}\text{Cr}_{42})\text{N}$ and $(\text{Al}_{59}\text{Cr}_{41})\text{N}$ coatings, deposited by dcMS and mfMS respectively, just c-AlN was detected. The $(\text{Al}_{60}\text{Cr}_{40})\text{N}$ coatings were also deposited by HPPMS using other process parameters in studies of [BKM+25]. Compared to studies in [BBT13], the $(\text{Al}_{60}\text{Cr}_{40})\text{N}$ coatings were deposited in a cubic structure, despite having higher Al content. These results show that not only the Al content in coatings but also the deposition technology and the process parameters affect the phase structure of AlN.

The h-AlN phase is thermally more stable than the cubic phase. As a result, the phase transition from c-AlN to h-AlN happens at high temperatures. In [RDH+05], the phase stability of AlCrN coatings with different cubic and hexagonal structures was investigated by annealing tests in an

argon atmosphere at temperatures between $600\text{ }^{\circ}\text{C} < T < 1,300\text{ }^{\circ}\text{C}$. No phase transformation occurred in coatings with the h-AlN, as they were already in their thermodynamically stable state. Therefore, c-AlCrN would not be a suitable interlayer for semi solid shaping and forming of steel alloys, as failure could occur because of spinodal phase separation at the high temperatures involved in such applications.

2.5 Properties and synthesis of Al_2O_3 coatings

Al_2O_3 is among the most widely used coating materials in applications requiring high wear resistance and hardness at elevated temperatures $T \geq 800\text{ }^{\circ}\text{C}$. Al_2O_3 is also known for its chemical stability, owing to its predominantly ionic atomic bonding. However, the hot hardness and thermal stability of Al_2O_3 coating depend on the phase structure [ÅSF+04].

Al_2O_3 is a polymorph material found in numerous metastable forms besides the thermodynamically stable α - Al_2O_3 , also known as corundum [LB98]. The transition phases η , γ , χ , δ , κ , and θ are categorized into two main groups based on their crystal structures: cubic close-packed (ccp) and hexagonal close-packed (hcp). The oxygen anions reside in the lattice spaces, and the aluminum cations are distributed in the interstitial spaces, depending on the specific phase [LB98]. Alumina polymorphs have different properties and applications in many fields of engineering. They can be synthesized with many techniques, and more than one polymorph can coexist at the same temperature. The α , γ , κ , and θ phases of Al_2O_3 are the most relevant phases for technical applications, with the rhombohedral α -phase being the most thermodynamically stable form. The phase transformation often proceeds via several intermediate stages, typically in the order $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$. The phase transformation usually begins at temperatures about $T \approx 900\text{ }^{\circ}\text{C}$, whereby complete formation of the α -phase is only observed in the range of $1,100\text{ }^{\circ}\text{C} \leq T \leq 1,140\text{ }^{\circ}\text{C}$. The stable α -phase possesses a hcp structure, a high modulus of elasticity of $E \approx 440\text{ GPa}$, and a hardness of around $H \approx 22\text{ GPa}$ [ZHF+96].

CVD is established to synthesize pure crystalline Al_2O_3 coatings at high substrate temperatures of $T_s > 1000\text{ }^{\circ}\text{C}$. However, the choice of materials is severely limited at such high substrate temperatures. In contrast, substrate temperatures in the range of $400\text{ }^{\circ}\text{C} < T_s < 700\text{ }^{\circ}\text{C}$ using PVD processes enable coating temperature sensitive materials, such as hot work tool steel. However, these lower temperatures result in lower crystallinity of the Al_2O_3 coatings deposited by PVD. Differences arise depending on the initial structure, the coating deposition technology,

and the annealing conditions. For example, studies in [ESS+09] showed that from amorphous magnetron-sputtered Al_2O_3 coatings, γ -phase is formed at a temperature of $T \approx 1,000^\circ\text{C}$. Both α - and δ -phases were found beside the γ -phase from a temperature of $T \approx 1,025^\circ\text{C}$. In contrast, Al_2O_3 coatings with predominantly crystalline γ -phases in as-deposited state showed no intermediate phase transformations, indicating a direct γ - to α -phase transformation at $T \approx 1,080^\circ\text{C}$. The Al_2O_3 coatings were synthesized using radio frequency reactive magnetron sputtering (rfMS) from Al_2O_3 targets, as shown in studies of [CN91]. Coatings consisted of crystalline γ -phase in an amorphous matrix. The transformation from γ - to α -phase was observed in the coatings annealed at $T \approx 1,200^\circ\text{C}$ for two hours.

When reviewing the approaches for synthesizing crystalline Al_2O_3 coatings using PVD, two primary routes become apparent as the focus of most researchers. These routes primarily differ in substrate temperature during coating and can be categorized into low temperature approaches, $400^\circ\text{C} < T_s < 700^\circ\text{C}$, and synthesis at high temperatures $700^\circ\text{C} \leq T_s < 850^\circ\text{C}$. These two approaches are closely linked to the substrate materials used in application fields in which Al_2O_3 coatings are utilized. In the following chapters, a detailed examination of both approaches will be presented, along with a review of the existing literature.

2.6 Approaches to synthesize crystalline Al_2O_3 coatings by PVD at $T_s < 700^\circ\text{C}$

As discussed in subchapter 2.3, tool materials made from hardened hot work steel play a crucial role in manufacturing processes such as HPDC and SSM forming of low-melting alloys. However, the manufacturing process of high-melting steel alloys is not industrially established. Although numerous research efforts, detailed in subchapter 2.3, focused on extending the lifespan of hot work steel dies using Al_2O_3 coatings applied via PVD, no substantial industrial advancements have been realized. Although nitride tool coatings are well-established in machining applications, only a few manufacturers offer tools with PVD alumina coatings. The first Al_2O_3 coated tool by PVD was patented by Sandvik in 2004 [SKF+98]. In 2005, Walter AG presented tiger Tec Silver Al_2O_3 tool coating deposited by PVD for turning operations in Exposition Mondiale de la Machine Outil (EMO) in Hanover¹. Moreover, Walter still offers

¹ WALTER präsentiert Weltneuheit zur EMO, (2005) Zerspanungstechnik.de, <https://www.zerspanungstechnik.de/blog/2005/08/03/walter-praesentiert-weltneuheit-zur-emo/>

PVD alumina coating for turning with indexable inserts² and thread milling with indexable inserts³. One possible explanation for the restricted industrial adoption could be that the Al_2O_3 coatings explored so far in these applications have not demonstrated sufficient stability in such harsh operating conditions. One reason for the thermal instability of these coatings could be the low substrate temperatures $T_s < 700\text{ °C}$, which leads to synthesizing Al_2O_3 coatings with predominantly amorphous phases. These amorphous structures are generally less resistant to mechanical and thermal stresses than their crystalline ones, thus limiting the life span of the coated tools.

Pulsed Plasma

The use of pulsed plasma is one of the most widely studied and discussed approaches in the literature for synthesizing and stabilizing pure crystalline Al_2O_3 at moderate temperatures. This approach focuses on the use of highly ionized PVD processes, such as Arc PVD, mf bipolar pulsed MS, and HPPMS. The underlying principle is the characteristic high degree of ionization in these techniques, along with the associated high energy of plasma species, which facilitates increased ion energy. Arc PVD has primarily been investigated combined with the effect of substrate bias voltage for the deposition of crystalline Al_2O_3 at moderate temperatures. While the formation of the crystalline phases was observed at $T_s = 600\text{ °C}$ and a bias voltage of $U_B = -200\text{ V}$ in [BKM+03], TEM analyses also revealed the presence of a high content of amorphous phases. In contrast, a lower bias voltage promoted the synthesis of the α -phase, as observed in studies of [ZH97]. Consequently, this relationship remains unresolved and not fully understood.

A key motivation for investigating pulsed plasma processes in mfMS and HPPMS was their potential to enable the deposition of nanocrystalline stable $\gamma\text{-Al}_2\text{O}_3$ coatings at lower substrate temperatures $T_s < 700\text{ °C}$. This approach was also investigated in the completed German Research Foundation project BO1979/3-2 on “Nanocrystalline $\gamma\text{-Al}_2\text{O}_3$ Coatings” at Surface Engineering Institute (IOT) of RWTH Aachen University. The studies hereby focused on the

² Produktionskatalog (2021),
https://elibrary.walter-tools.com/frontend/getcatalog.do?catalogId=682901&lang=de-de&searchquery=Al2O3#page_1

³ Alles, was das Gewindefräsen braucht (2024),
https://elibrary.walter-tools.com/frontend/getcatalog.do?catalogId=921263&lang=de-de&searchquery=Al2O3#page_120

deposition of crystalline $\gamma\text{-Al}_2\text{O}_3$ coatings using mfMS. Within this project, the high temperature properties of $\gamma\text{-Al}_2\text{O}_3$ coatings deposited by mfMS were studied [BBR+10]. The TiAlN interlayer was employed to improve adhesion of $\gamma\text{-Al}_2\text{O}_3$ on the cemented carbide substrate. XRD results confirmed that the γ -phase remains stable after annealing in vacuum at $T = 1,200^\circ\text{C}$, while annealing in ambient air led to α -phase transformation. A significant morphological change occurred also at $T = 1,000^\circ\text{C}$ in ambient air. Moreover, the indentation hardness reduced from $H_{IT} \approx 17$ GPa to $H_{IT} \approx 11$ GPa, while the indentation modulus increased from $E_{IT} \approx 260$ GPa to $E_{IT} \approx 310$ GPa. Furthermore, cutting performance of such coated tools using mfMS was the focus of research in [FSK+10]. Hereby, turning tests of X5CrNi18-10 steel workpiece were performed with coated cemented carbide tools. The performance of TiAlN coated tools was compared to TiAlN/ $\gamma\text{-Al}_2\text{O}_3$. Both coatings had a similar thickness. The $\gamma\text{-Al}_2\text{O}_3$ coatings with a thickness of $s = 2\ \mu\text{m}$ were deposited on a TiAlN interlayer with $s = 4\ \mu\text{m}$. After a cutting time of $t_c = 13$ min, coated tools reached a maximal flank wear land width of $VB_{max} = 300\ \mu\text{m}$, while TiAlN after $t_c = 8$ min. In [EMW+10], Al_2O_3 coatings with amorphous and γ -phases were deposited at $T_s \approx 640^\circ\text{C}$ using mfMS on Si substrates. After annealing tests, phase transformation sequences were found, ending in the formation of the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$. Thereby, SEM analysis of the coating morphology showed the formation of thermal cracks after annealing tests. In [BBK+18b], a significantly higher oxidation resistance of HPPMS coated cemented carbide inserts compared to the mfMS (Ti,Al)N/ $\gamma\text{-Al}_2\text{O}_3$ was reported. After an annealing test at $T = 900^\circ\text{C}$ in atmosphere, the HPPMS coated variant exhibited slightly higher indentation hardness compared to the mfMS variant.

Modification of binary Al_2O_3 using Si and Cr

In the 21st century, research interest has grown in modifying the binary Al_2O_3 coatings deposited by PVD with stabilizing elements such as Si and Cr. The aim was to enhance the thermal stability of Al_2O_3 coatings, deposited at $T_s < 700^\circ\text{C}$. The influence of Si on the thermal stability of Al_2O_3 coatings deposited in a bipolar pulsed mode by MS was analyzed in [BBM+13]. The Al_2O_3 coatings with and without Si modification were deposited on a TiAlN interlayer as an adhesion layer. Differential scanning calorimetry (DSC) measurements showed that modification of Al_2O_3 coatings with Si increased the stability of γ -phase, as the transformation of γ - to α -phase is retarded to temperatures above $T = 1,200^\circ\text{C}$. In contrast, the α -phase was formed in Al_2O_3 coatings without Si at lower temperatures of $T = 1,100^\circ\text{C}$. However, X-ray

Diffraction (XRD) measurements indicated that adding Si-content of $x_{Si} = 4$ at.-%, led to a high amount of amorphous phase in the as-deposited Al_2O_3 coating. This resulted in a decrease in indentation hardness of as-deposited coatings from $H_{IT} = 18$ GPa to $H_{IT} = 10$ GPa. Moreover, after annealing in air at $T = 1,250$ °C for one hour, both α -phase and θ -phase were detected. After annealing at $T = 1,300$ °C, α -phase was only observed in modified coatings.

2.6.1 $(Al,Cr)_2O_3$ solid solution coatings

In the 21st century, research interest has grown in modifying the PVD binary Al-O coatings with Cr. The motivation was to find an alternative to α - Al_2O_3 synthesized by CVD and widespread substrate materials that can be coated to steel substrates. This subchapter outlines the fundamental physical principles that motivate the development of $(Al,Cr)_2O_3$ solid solution coatings using PVD techniques. Particular focus is placed on the role of Cr in stabilizing the corundum structure at lower deposition temperatures. Furthermore, based on the current state of research, the extent to which this concept has been successfully realized will be critically discussed.

Fundamental backgrounds

The phase diagram of the binary Al_2O_3 - Cr_2O_3 system under the thermodynamic equilibrium state is shown in Figure 2.4. Based on this phase diagram, a small region of $(Al,Cr)_2O_3$ of solid solution with a corundum structure, α - $(Al,Cr)_2O_3$, is formed under the thermodynamic equilibrium state. This solid solution between Al_2O_3 and Cr_2O_3 exists above a critical temperature of $T \approx 1,300$ °C for all compositions [BKS05]. As already shown in [ALH+99], α - Cr_2O_3 with corundum structure crystallizes at lower deposition temperatures, 300 °C $\leq T \leq 500$ °C, than α - Al_2O_3 . This can be explained by the lower standard formation enthalpy of Cr_2O_3 , $\Delta H^\circ_{Cr_2O_3} = 1,164$ kJ/mol, than that of α - Al_2O_3 with $\Delta H^\circ_{Cr_2O_3} = 1,690$ kJ/mol [Bar95]. Furthermore, it exhibits comparable lattice parameters to α - Al_2O_3 . PVD technology enables deposition beyond thermodynamic equilibrium, allowing for the synthesis of metastable phases at lower temperatures than those required under thermodynamic equilibrium conditions. Studies in [Saa64] demonstrated that the co-deposition of two oxide materials can result in the formation of solid-solution hard coatings.

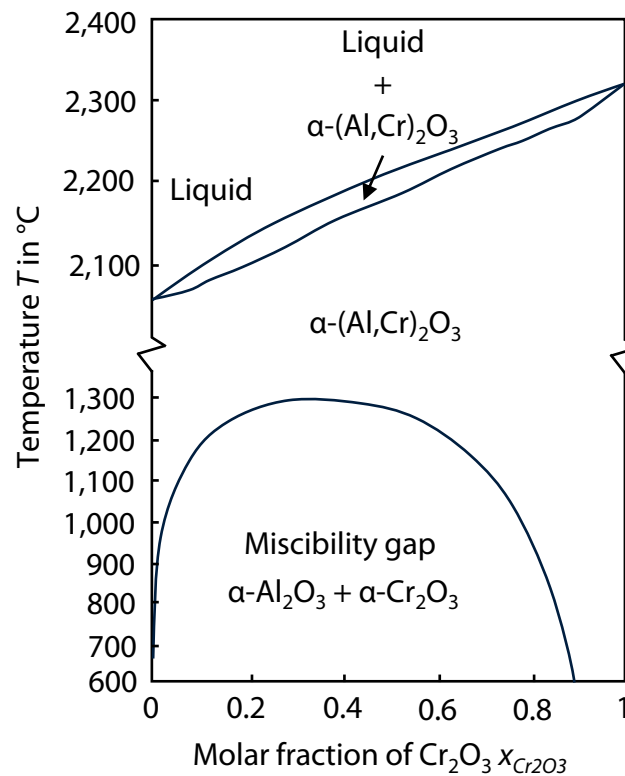


Figure 2.4: Phase diagram of the binary Al_2O_3 - Cr_2O_3 system [BKS05]

Adding Cr to Al_2O_3 results in lattice distortions, while Cr^{3+} ions substitute for Al^{3+} , having differences in ionic radii. Chromium has a larger ionic radius $r_{\text{Cr}^{3+}} = 0.63 \text{ \AA}$ compared to aluminum with $r_{\text{Al}^{3+}} = 0.51 \text{ \AA}$ [Ahr52]. Thereby, classical solid solution strengthening can enhance hardness. With all these physical backgrounds, researchers aimed to modify alumina with Cr to synthesize $(\text{Al,Cr})_2\text{O}_3$ with a corundum structure at temperatures lower than $T \approx 1,300 \text{ }^\circ\text{C}$ using PVD. The distortion of the $(\text{Al,Cr})_2\text{O}_3$ solid solution is attributed not only to the difference in the ionic radii of Al^{3+} and Cr^{3+} but also to the variation in their bonding characteristics. The classical “Holleck triangle” is shown in Figure 2.5. Holleck classifies hard coating materials based on their chemical bonding character, dividing them into metallic, covalent, or ionic groups [Hol90]. Coatings with metallic bonding are characterized by high adhesion strength on the metallic substrate materials and high toughness. Ionic groups are chemically more stable and therefore have a low tendency to react. They are more brittle and possess high oxidation resistance. Covalent bonding, on the other hand, primarily enhances hardness. The difference in electronegativity between the two elements determines whether a bond is more ionic or covalent. The larger the difference, the more ionic the bond tends to be. The electronegativity difference is slightly larger for Al–O than for Cr–O. Therefore, the Al–O

bond is generally more ionic than the Cr–O bond. The mixed ionic and covalent bonds in $(\text{Al,Cr})_2\text{O}_3$ solid solutions provide a promising balance between thermal stability, chemical resistance, and hardness, according to the “Holleck triangle”. These properties make them particularly attractive as protective coatings used in high-temperature applications, where wear resistance, thermal stability, and oxidation protection are critical.

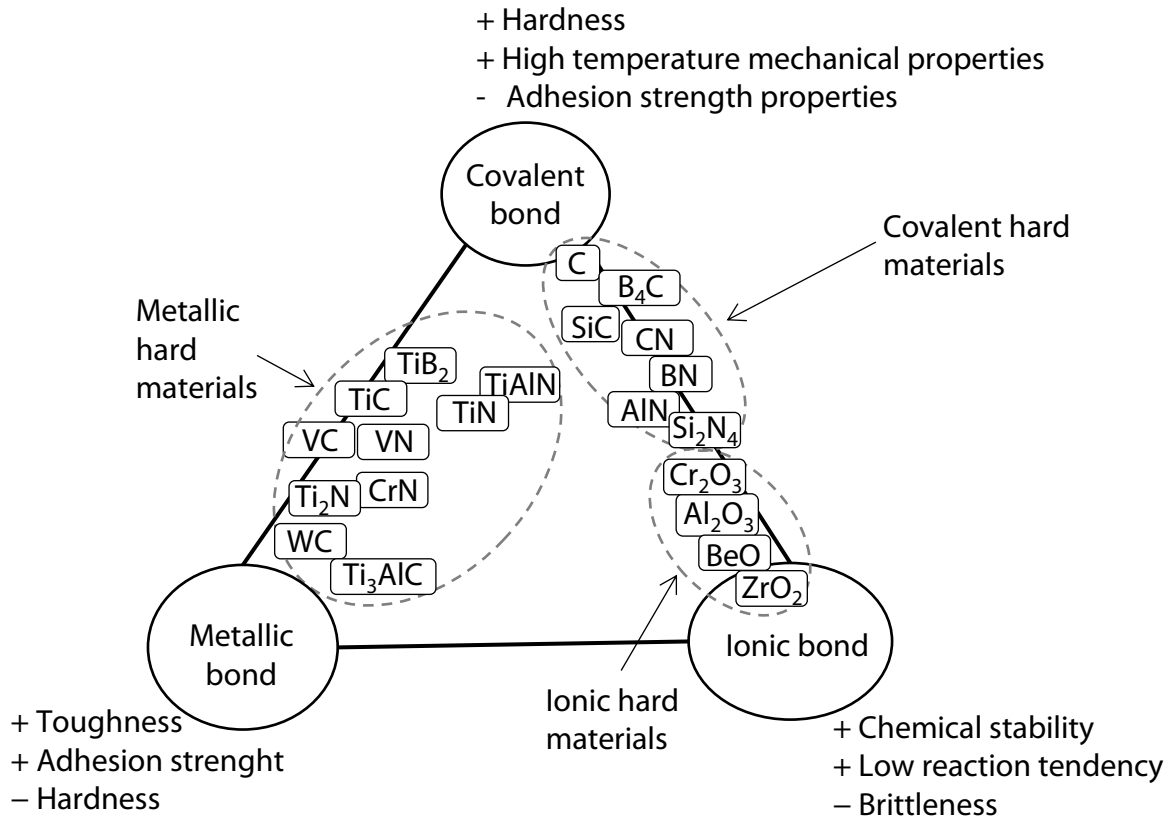


Figure 2.5: Classification of hard materials in the bonding triangle based on [HS95]

Impact of Cr content on properties of $(\text{Al,Cr})_2\text{O}_3$

For the low-temperature deposition of $(\text{Al,Cr})_2\text{O}_3$ solid solutions, conventional PVD processes, predominantly arc PVD and MS have been addressed in the literature so far. The effect of the Cr content on the coating properties of $(\text{Al,Cr})_2\text{O}_3$, especially the phase formation, was the focus of several studies. These studies aimed to synthesize $(\text{Al,Cr})_2\text{O}_3$ with a corundum structure. In [DRK+17], the $(\text{Al,Cr})_2\text{O}_3$ coatings with different Cr contents x_{Cr} in the metallic portion, $40 \text{ at.-%} \leq x_{\text{Cr}} \leq 80 \text{ at.-%}$, were deposited by arc PVD. The low-Cr containing $(\text{Al,Cr})_2\text{O}_3$ coatings with $x_{\text{Cr}} \approx 40 \text{ at.-%}$ were synthesized in metastable cubic $(\text{Al,Cr})_2\text{O}_3$ phases at

$T = 450\text{ }^{\circ}\text{C}$. The high-Cr containing $(\text{Al,Cr})_2\text{O}_3$ coatings with $x_{\text{Cr}} \approx 80\text{ at.}\%$ directly crystallized with corundum $(\text{Al,Cr})_2\text{O}_3$.

The same results were already observed for arc PVD deposited $(\text{Cr,Al})_2\text{O}_3$ coatings consisting of minimum $x_{\text{Cr}} \approx 36\text{ at.}\%$ in [KSG+12]. The XRD analysis revealed that the formation of cubic $(\text{Cr,Al})_2\text{O}_3$ and corundum $(\text{Cr,Al})_2\text{O}_3$ depends on the Al and Cr content and the O_2 reactive gas flow. Increasing O_2 gas flow in the process promotes the growth of the α -phase, especially with increasing Cr content. In contrast, increasing the Al content and reducing O_2 gas flows tend to form the cubic phase. The wear behavior of coated cemented carbide inserts in the turning test showed that the coated tools with the cubic phase had a similar wear behavior to the corundum ones. Moreover, lower flank wear was observed for inserts with increasing Al content in the coating.

In [DSL+10], $(\text{Al,Cr})_2\text{O}_3$ coatings with $29\text{ at.}\% \leq x_{\text{Cr}} \leq 75\text{ at.}\%$ in metallic portion, deposited via reactive MS, were analyzed regarding their microstructure. The transmission electron microscopy (TEM) analysis showed that the Al-rich $(\text{Al}_{64}\text{Cr}_{36})_2\text{O}_3$ coating exhibits a smaller grain size, $d_{\text{grain}} \approx 27\text{ nm}$, compared to the $(\text{Al}_{33}\text{Cr}_{67})_2\text{O}_3$ coating with larger grain sizes of $d_{\text{grain}} \approx 44\text{ nm}$. A shift to larger diffraction angles and lower peak intensities were also observed in XRD results as the chromium content decreased in the coatings. The lattice constant decreased with increasing aluminum content due to the smaller ionic radius of Al^{3+} compared to Cr^{3+} . Additionally, the (012) peak disappeared at higher aluminum contents. The authors suggest that this may be attributed to a reduction in grain size or the possible formation of an amorphous phase in the coatings.

Witthaut et al. investigated the $(\text{Al,Cr})_2\text{O}_3$ coating with $57\text{ at.}\% < x_{\text{Cr}} < 74\text{ at.}\%$ in metallic portion, deposited using reactive MS at a substrate temperature of $T_s = 500\text{ }^{\circ}\text{C}$ [WCR+00]. The investigations focused on analyzing the chemical bonding states by X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES). The results showed that the bonding character of oxygen in $(\text{Al,Cr})_2\text{O}_3$ solid solutions was strongly influenced by variations in the Cr:Al ratio. The results showed that increasing the Al content in the coatings changes the bonding state characteristic of oxygen towards reduced conductivity. This reduced electrical conductivity indicates a shift toward a more ionic character. According to the “Holleck triangle”, a higher degree of ionic bonding correlates with greater chemical

stability. Therefore, it can be assumed that increasing the Al content in $(\text{Al,Cr})_2\text{O}_3$ coatings enhances their oxidation resistance, as the bonding character becomes more ionic.

The phase stability behavior of the $(\text{Al,Cr})_2\text{O}_3$ solid solution coatings was also the focus of several studies. In [KLJ+12], the $(\text{Al}_{32}\text{Cr}_{68})_2\text{O}_3$ coatings deposited by reactive MS remained in a face-centered cubic structure after annealing at temperatures up to $T = 700\text{ }^\circ\text{C}$ for $t = 8\text{ h}$. However, a phase transformation to the corundum structure was observed at $T \geq 900\text{ }^\circ\text{C}$ with annealing for $t = 2\text{ h}$ in ambient air.

The deposition of $(\text{Cr,Al})_2\text{O}_3$ coatings using arc PVD presents additional challenges, particularly concerning droplet formation, which affects thermal stability. Droplet formation is a known issue in the arc PVD process and is normally undesired in the coatings. In [EPL+13] $(\text{Al}_{50}\text{Cr}_{50})_2\text{O}_3$ coatings synthesized via arc PVD exhibited a multiphase composition, predominantly consisting of a corundum structure alongside a cubic solid solution. Moreover, the existence of an amorphous phase was confirmed by selected area electron diffraction (SAED). After an annealing test conducted for $t = 2\text{ h}$ at $T = 1,050\text{ }^\circ\text{C}$, XRD results showed the formation of $\alpha\text{-Al}_2\text{O}_3$. DSC analysis confirmed that the α -phase crystallized from initially amorphous, Al-rich droplets. These microstructural changes were analyzed by TEM, which indicated the presence of thermal cracks and voids. These were likely caused by volume changes associated with phase transformations.

Over the past decade, HS-PVD technology has been employed beyond conventional PVD processes such as MS and arc PVD to synthesize $(\text{Cr,Al})_2\text{O}_3$ coatings. The technological characteristics of HS-PVD discussed in chapter 2.2 enable the synthesis of oxide coatings such as $(\text{Cr,Al})_2\text{O}_3$ with high thicknesses $s \geq 10\text{ }\mu\text{m}$ while ensuring stability in reactive oxide processes. Within the German Research Foundation (GER. Deutsche Forschungsgemeinschaft, DFG) project BO 1979/42-1 “Investigation of high speed PVD technology concerning the deposition of $\alpha\text{-Al-O+X}$ and Al-Ti-O+X coatings for die casting of high melting steel alloys” research works were conducted on synthesizing $(\text{Cr,Al})_2\text{O}_3$ coatings using HS-PVD at Surface Engineering Institute (IOT) in Aachen, Germany. In [BBK+18a], $(\text{Cr}_{87}\text{Al}_{13})_2\text{O}_3$ coatings with a metallic AlCr interlayer were deposited on cemented carbide substrates using HS-PVD at substrate temperatures of $500\text{ }^\circ\text{C} \leq T_s \leq 850\text{ }^\circ\text{C}$ and an oxygen gas flow of $Q_{\text{O}_2} = 300\text{ sccm}$. A maximum deposition rate of $ds/dt \approx 38.8\text{ }\mu\text{m/h}$ was achieved under a static substrate mode. The

substrate temperatures $T_s \leq 547$ °C led to the deposition of amorphous coatings, whereas crystalline coatings were deposited at $T_s \geq 597$ °C. However, morphology analysis showed that high substrate temperatures $T_s \geq 728$ °C led to porosity inside the metallic AlCr interlayer. It was assumed that the porosity resulted in brittle failure and lower coating adhesion strength to the cemented carbide substrate. Deposition of the crystalline $(\text{Cr}_{87}\text{Al}_{13})_2\text{O}_3$ coatings at $T_s \leq 547$ °C was not possible, which could be due to the high oxygen gas flow $Q_{\text{O}_2} = 300$ sccm chosen in this study. As the authors mentioned, process instability with a gas flow $Q_{\text{O}_2} = 300$ sccm resulted from target poisoning. Even the coating time had to be significantly reduced for processes with higher temperatures, as the process was unstable. This effect led not only to a reduced deposition rate but also to a drop in the crystallinity of deposited oxide coatings in [BBK+18a].

In another study at IOT, the Cr content was increased to $x_{\text{Cr}} \approx 29$ at.-%, and oxygen gas flow was reduced to $Q_{\text{O}_2} = 80$ sccm compared to their previous studies. Thereby, the crystalline $(\text{Al}_{71}\text{Cr}_{29})_2\text{O}_3$ coatings were deposited on X40CrMoV5-1 substrates at $T_s \approx 570$ °C using HS-PVD [BBK+19]. The high-temperature behavior of crystalline $(\text{Al}_{71}\text{Cr}_{29})_2\text{O}_3$ coated X40CrMoV5-1 substrates was the focus in this case. For this purpose, the coated samples were annealed in vacuum at $T = 600$ °C, $T = 800$ °C, $T = 1,000$ °C, and $T = 1,300$ °C for one hour. However, due to the interlayer's thermally induced dissolution after annealing tests, it was shown that the pure metallic AlCr interlayer is unsuitable for high-temperature applications. Moreover, oxygen was detected in the interlayer after the annealing test at $T = 600$ °C, due to the formation of oxide bonds inside the interlayer. Furthermore, the formation of an Al-rich zone at the top of the $(\text{Al,Cr})_2\text{O}_3$ coating was observed. This inhomogeneity in morphology and chemical composition led to a significant reduction in the indentation hardness H_{IT} of the coatings after annealing at high temperatures. The chromium content $x_{\text{Cr}} = 29$ at.-% of the coatings in [BBK+19] seems to be still too high, which led to the mentioned issues under the high temperature range analyzed in this study. Moreover, the evaluation of the previous findings also shows that a suitable interlayer is necessary not only to enhance the adhesion strength of $(\text{Al,Cr})_2\text{O}_3$ coating on metallic substrate but also to enhance the oxidation resistance for high temperature applications.

2.6.2 Intermediate conclusion of modification of Al_2O_3 with Cr

One of the promising approaches to enhance the durability of hot work steel tools is the application of Al_2O_3 -based coatings synthesized by PVD. Research has demonstrated that the co-deposition of Al and Cr oxides leads to solid solution strengthening, influencing the microstructure, phase formation, and mechanical properties of the $(\text{Al,Cr})_2\text{O}_3$ coatings. The ability to deposit crystalline $(\text{Al,Cr})_2\text{O}_3$ coatings at lower substrate temperatures of $T_s < 600^\circ\text{C}$ avoids an undesired drop in the hardness of the annealed and hardened hot work steel substrate materials.

Based on the current state of the art, it is evident that while significant progress has been made in the synthesis of crystalline $(\text{Al,Cr})_2\text{O}_3$ coatings at lower substrate temperatures $T_s \leq 600^\circ\text{C}$ using PVD, these coatings do not achieve the industrial breakthrough as known for CVD Al_2O_3 . These have so far failed due to their lower high temperature properties. From a fundamental standpoint, the modification of Cr into Al_2O_3 aims primarily to facilitate the formation of the corundum structure at lower deposition temperatures due to Cr_2O_3 's lower standard formation enthalpy and structural similarity to $\alpha\text{-Al}_2\text{O}_3$. Therefore, most existing studies focused on Cr-rich $(\text{Al,Cr})_2\text{O}_3$, typically exceeding $x_{\text{Cr}} \approx 29$ at.-% in the metallic fraction to achieve corundum structure. However, this approach was not fully successful because of their low thermal stability.

Such high Cr content, $x_{\text{Cr}} \geq 29$ at.-%, may lead to notable lattice distortions due to the larger ionic radius of Cr^{3+} compared to Al^{3+} . This can result in increased internal stress, grain coarsening, or the formation of metastable or even amorphous phases, particularly under PVD conditions far from thermodynamic equilibrium, which were partially addressed in the previous studies. Moreover, as seen in the “Holleck triangle”, increasing Cr content can shift the bonding character toward more covalent behavior, potentially reducing the ionic contribution associated with reduced chemical stability and oxidation resistance.

Limited research has explored the synthesis and high-temperature properties of $(\text{Al,Cr})_2\text{O}_3$ coatings with lower Cr content $x_{\text{Cr}} < 29$ at.-%. However, a lower Cr content may also enhance the ionic character of the bonding, reduce structural inhomogeneities, and ultimately improve oxidation resistance. This background motivates the present work to investigate Al-rich $(\text{Al,Cr})_2\text{O}_3$ coatings, despite most prior studies focusing on Cr-rich compositions.

Moreover, an additional focus in this work is placed on enhancing the adhesion strength properties of $(\text{Al,Cr})_2\text{O}_3$ coatings on hot work steel substrates by introducing an AlCrN interlayer system, which is more oxidation resistant than metallic AlCr. The deposition of a multilayer system by a HS-PVD coating unit with just one hollow cathode is only possible with same compositions of the individual layers in relation to the metallic components. Therefore, Al-rich $(\text{Al,Cr})_2\text{O}_3$ with an Al-rich AlCrN interlayer can be deposited by HS-PVD in a batch process. With the backgrounds discussed in subchapter 2.4, AlCrN has higher oxidation resistance than TiAlN. Moreover, the results in literature emphasize promising oxidation resistance of AlCrN coatings, based on the phase composition. Considering the high application temperatures $T > 1,200^\circ\text{C}$ in HPDC, Al-rich AlCrN with hexagonal structure has potential as an interlayer system for $(\text{Al,Cr})_2\text{O}_3$, compared to c-AlCrN.

2.7 High temperature $T_s \geq 700^\circ\text{C}$ synthesis of Al_2O_3 coatings

As outlined in [Bob17], Al_2O_3 coatings deposited by CVD have been utilized for cutting tools since 1979. The first patented Al_2O_3 coatings primarily focused on direct deposition onto cemented carbide substrates without an interlayer [Hal73]. To enhance the compound adhesion strength, interlayers such as TiCN and TiC were later introduced to enhance the performance of Al_2O_3 coated cemented carbide tools by CVD. In 1990, Walter introduced TiCN/ Al_2O_3 multilayer coatings deposited by moderate temperature CVD (MTCVD) [Küb91]. Another approach to enhance coating performance involved reducing roughness by refining the microstructure through substrate temperatures of $T_s < 900^\circ\text{C}$ by MTCVD. This approach is particularly advantageous for finishing machining processes, where a higher surface quality of the machined workpiece is required. Lower coating roughness contributes to improved finishing quality. Recent trends focus on controlled texture [MAA+17] and fine-crystalline coatings [WWŠ+24] to enhance the wear performance of CVD Al_2O_3 coated tools. However, thermal cracks usually form in CVD coatings due to the development of tensile stresses during cooling to room temperature [GST+19]. Compared to CVD coatings, PVD coatings are usually characterized by compressive residual stress, which results in increased fatigue resistance as also observed in [BLT05]. Milling tests in [SQG96] showed that the compressive residual stress in PVD coatings led to delayed initiation of crack formation and propagation compared to CVD coated tools. This led to an increase in the performance of cutting tools. Moreover, when the compressive residual stress in coatings was eliminated through heat treatment at $T = 850^\circ\text{C}$, the tendency for edge chipping increased significantly. Compared to CVD, PVD coatings have

no chlorine impurities caused by AlCl_3 precursors, and edge blunting can be avoided, allowing tools to maintain sharp cutting edges [BLM+06a]. In [BBM+21], it was demonstrated that compressive residual stresses in PVD coatings can be adjusted and controlled using process parameters such as substrate bias voltage. A compressive residual stress state in a range of $-3 \text{ GPa} \leq \sigma \leq -2 \text{ GPa}$ led to the highest resistance against crack formation, resulting in the best cutting performance. However, compressive residual stresses out of this range resulted in increased abrasive wear. This residual stress adjustment can enhance the performance of cutting tools and represents a significant advantage of PVD technology.

In contrast to the numerous studies, addressed in subchapter 2.5, on the synthesis of PVD Al_2O_3 at temperatures $T_s < 700 \text{ }^\circ\text{C}$, only a few studies address the synthesis of Al_2O_3 by means of high-temperature PVD processes at $T_s \geq 700 \text{ }^\circ\text{C}$. In the 1990s, researchers had already attempted to synthesize Al_2O_3 at such high temperatures. The motivation was to achieve coatings consisting of lower undesired amorphous phases as well as to synthesize the α -phase. The PVD processes that have so far been used to synthesize Al_2O_3 at $T_s \geq 700 \text{ }^\circ\text{C}$ include MS and arc PVD. Zywitzki et al. synthesized multiphase coatings consisting of γ - and α - Al_2O_3 using dual-cathode MS at substrate temperatures between $680 \text{ }^\circ\text{C} \leq T_s \leq 770 \text{ }^\circ\text{C}$ [ZHF+96]. In [BKR+99], Al_2O_3 coatings were deposited by a reactive arc process at $200 \text{ }^\circ\text{C} \leq T_s \leq 800 \text{ }^\circ\text{C}$. The effect of substrate temperature on coating properties and high-temperature properties was studied. Al_2O_3 coatings deposited at $600 \text{ }^\circ\text{C} \leq T_s \leq 800 \text{ }^\circ\text{C}$ were thermally stable under vacuum annealing at $T = 1,000 \text{ }^\circ\text{C}$, whereas crack formation was observed in coatings deposited at lower substrate temperatures of $200 \text{ }^\circ\text{C} \leq T_s \leq 500 \text{ }^\circ\text{C}$. The synthesis of pure crystalline Al_2O_3 using an arc PVD process was detected without bias voltage at $T_s \approx 800 \text{ }^\circ\text{C}$ [BKM+03]. The Al_2O_3 coating, with a thickness of $s \approx 900 \text{ nm}$, was deposited using a laboratory-scale arc PVD machine, achieving a deposition rate of $ds/dt \approx 720 \text{ nm/h}$. Since industrial PVD coating units are neither designed nor capable of operating at such high substrate temperatures, studies on the synthesis of Al_2O_3 using HT-PVD processes are until now absent.

Intermediate conclusion of the synthesis of pure Al_2O_3

The deposition of Al_2O_3 coatings at higher process temperatures of $700 \text{ }^\circ\text{C} \leq T_s \leq 900 \text{ }^\circ\text{C}$ using PVD technology offers great potential for achieving pure crystalline coatings. However, industrial PVD systems are generally not engineered for substrate temperatures above $T_s \geq 700 \text{ }^\circ\text{C}$, as such conditions are typically achievable only in specialized laboratory reactors

findable in literature. However, laboratory-scale setups cannot provide the coating uniformity, throughput, and process stability required for reliable tool coating. Moreover, the coating thickness of only a few hundred nanometers reported in [BKM+03] indicates severe target poisoning. Even if industrial PVD systems could operate at such elevated temperatures, target poisoning would still significantly impact process stability and coating quality. Higher process temperatures lead to a faster reaction of the reactive gases with the metallic target. The higher the process temperature, the greater the process instability and target poisoning, whereby a stable process would be possible within a narrow process parameter range. Due to this, the adjustment of the coating properties is only possible in a narrow process window, which makes it difficult to further develop coatings and adapt them to the fields of application. Low coating thicknesses of only a few hundred nanometers, reduced process stability, and reproducibility are also other issues of HT-PVD processes. To overcome these limitations, alternative PVD technologies beyond arc and magnetron sputtering should be considered. HS-PVD based on hollow cathode gas flow sputtering, is a promising approach, as it effectively eliminates target poisoning and allows stable high-temperature coating deposition. Furthermore, HS-PVD technology provides a unique advantage by enabling processing at elevated substrate temperatures of $T_s > 700\text{ }^{\circ}\text{C}$, which are otherwise inaccessible with industrial PVD equipment.

Moreover, the studies to date mainly focus on phase formation analysis. In the case of HT-synthesized Al_2O_3 coatings by PVD, the investigation of the high temperature coating properties, the residual stress state, and cutting performance in machining applications are not considered. In addition, a lack of knowledge about the HT-PVD process and a narrow process window makes it difficult to assess the influence of process parameter variations on coating properties and the interactions between them.

2.8 Conclusions derived from the state of the art

Reviewing state-of-the-art research and technologies in PVD processes for oxide coatings highlights key challenges and developments. Despite the synthesis of $\gamma\text{-Al}_2\text{O}_3$ in the mentioned literature at $T_s < 700\text{ }^{\circ}\text{C}$, the Al_2O_3 coatings synthesized by PVD have not achieved the same industrial establishment as nitride coatings. As shown in [Ewe12], target poisoning can reduce process stability, reproducibility, and deposition rate. The consequences are uneconomical process control in the synthesis of Al_2O_3 coatings and lower coating thickness, which argue against their use as protection coatings. Only a few tool manufacturers currently offer PVD

Al_2O_3 coatings for machining applications, whereas nitride-based coatings are far more widespread in the industry. The slower industrial adoption of PVD Al_2O_3 coatings has also been influenced by patent strategies, which have historically restricted broader commercialization and widespread implementation.

Modifying the binary Al_2O_3 coatings with Cr in $(\text{Al,Cr})_2\text{O}_3$ coatings can synthesize crystalline structures at lower substrate temperatures $T_s \leq 600^\circ\text{C}$. The formation of $(\text{Al,Cr})_2\text{O}_3$ solid solutions enhances thermal stability without reducing the indentation hardness, as observed in Si-modified Al_2O_3 coatings. These properties make $(\text{Al,Cr})_2\text{O}_3$ coatings more promising than Si-modified Al_2O_3 coatings. However, their coating properties are influenced by variations in Cr:Al ratios. So far, issues such as phase transformation, interlayer instability, and porosity formation remain critical challenges that are addressed for $(\text{Al,Cr})_2\text{O}_3$ coatings with high chromium content $x_{\text{Cr}} \geq 25$ at.-%. These issues negatively affect the coating adhesion and performance at elevated temperatures. Future research is needed regarding interlayer design and analysis of the high temperature properties of $(\text{Al,Cr})_2\text{O}_3$ containing lower Cr content $x_{\text{Cr}} < 25$ at.-% to enhance coating durability and industrial applicability.

In contrast, the synthesis of crystalline pure Al_2O_3 coatings requires high substrate temperatures $T_s \geq 800^\circ\text{C}$, conventionally achieved via CVD for cutting applications. The drawbacks of CVD, such as thermal cracks, tensile stress formation, and tool embrittlement, have led to increased interest in PVD alternatives. PVD coatings offer advantages such as compressive residual stress, absence of chlorine impurities, and better edge sharpness, making them attractive for cutting tool applications. The deposition of Al_2O_3 at $T_s \geq 800^\circ\text{C}$ on cemented carbide tools using PVD offers potential advantages for achieving fine and pure crystalline coatings in cutting applications. Existing research in this field is very limited and has primarily focused on phase formation rather than high temperature properties, residual stress states, or practical machining performance, leaving significant knowledge gaps. Moreover, target poisoning negatively affects deposition rates and process stability in conventional PVD processes such as MS and arc PVD. This challenge necessitates precise process optimization and monitoring to ensure reproducible coatings with the desired stoichiometry. Although pulsed sputtering techniques like mfMS and HPPMS have been applied to improve the deposition of oxide coatings in reactive PVD processes, issues such as process instability, a narrow process window, and reduced deposition rates continue to limit their industrial adoption and scalability. Overall, the studies of Al_2O_3

and $(\text{Al,Cr})_2\text{O}_3$ coatings using conventional PVD processes emphasize the necessity of a deposition technique to overcome existing process limitations. Characteristics of HS-PVD indicate the potential to maintain process stability at elevated temperatures without the cost of reduced deposition rate. However, further research is needed to fully understand the influence of HS-PVD on residual stress states and high temperature coating properties.

3 Research approaches and solutions

This work is based on two research hypotheses. These focus on synthesizing crystalline hard Al_2O_3 coatings using HS-PVD on two different tool materials, such as temperature sensitive hot-work steel X40CrMoV5-1 and cemented carbide WC-Co, used in manufacturing processes.

Hypothesis 1: Cr-modified Al_2O_3 coatings with a Cr content lower than $x_{\text{Cr}} \approx 29$ at.-% produced by HS-PVD at low substrate temperature $T_s \approx 550$ °C are qualified for protecting hot work steel X40CrMoV5-1, considering the primary shaping and forming application of high-temperature melting alloys. Four research questions are formulated, to verify this hypothesis. The research findings of this dissertation, presented in chapters 5 and 6 answer the following four questions.

1. Can crystalline $(\text{Al,Cr})_2\text{O}_3$ coatings with chromium content of $x_{\text{Cr}} = 8$ at.-%, $x_{\text{Cr}} = 12$ at.-% and $x_{\text{Cr}} = 22$ at.-% be synthesized at $T_s \approx 550$ °C?

The $(\text{Al,Cr})_2\text{O}_3$ coatings with different chromium contents are deposited on X40CrMoV5-1 by HS-PVD. Their phase composition, morphology, indentation hardness, and modulus are analyzed and compared in subchapter 5.1.

2. Can h-AlCrN interlayer, already in its thermodynamically stable state, enhance the adhesion strength of $(\text{Al,Cr})_2\text{O}_3$ coatings on X40CrMoV5-1, depending on its thickness and architecture?

In subchapter 5.2, adhesion properties of different AlCrN interlayers are investigated by scratch tests and Rockwell indentation tests. Hereby, the influence of interlayer thickness s_i , architecture, and substrate bias voltage U_B was investigated. To analyze the adhesion strength between substrate and interlayer, deposition of the functional $(\text{Al,Cr})_2\text{O}_3$ coating is initially omitted. Furthermore, AlCrN/ $(\text{Al,Cr})_2\text{O}_3$ coatings are produced in subchapter 5.3. Hereby, the thickness of the functional $(\text{Al,Cr})_2\text{O}_3$ layer s_f varied to enhance the adhesion strength properties. In this dissertation, for the first time, the residual stresses in HS-PVD coatings are studied and presented in chapter 5.4, to understand further the correlation between HS-PVD coating and adhesion strength properties.

3. Can the reduction of Cr content from $x_{Cr} = 28$ at.-% to $x_{Cr} = 15$ at.-% and the deposition of an h-AlCrN interlayer enhance the high temperature properties of AlCrN/(Al,Cr)₂O₃ coated hot work steel up to $T = 1,200$ °C?

In subchapter 5.5 annealing tests in vacuum and in the atmosphere at $T = 800$ °C, $T = 900$ °C, $T = 1,000$ °C and $T_{vac.} = 1,200$ °C are performed on AlCrN/(Al,Cr)₂O₃ coated samples. Post-annealing analyses are conducted on diffusion behavior, morphology changes, indentation hardness, and indentation modulus.

4. Does diffusion and adhesion occur at the interface between AlCrN/(Al,Cr)₂O₃ coating and molten 100Cr6 steel?

Chapter 6 evaluates the interaction of these coatings with molten 100Cr6 steel, focusing on diffusion, oxidation, and adhesion behavior through immersion tests. Coated and uncoated X40CrMoV5-1 samples are analyzed regarding metal-physical corrosion and the tendency to adhere to steel in the liquid and semisolid state under different immersion times.

Hypothesis 2: Compressive residual stress containing crystalline Al₂O₃ coatings synthesized via HS-PVD at $T_s \approx 850$ °C possess the required mechanical and thermal stability for application on cemented carbide tools in turning operations. This hypothesis is validated in chapter 7 and chapter 8, addressing the following research questions:

1. How do elevated temperatures $T > 700$ °C affect the Al₂O₃ coating properties deposited with different oxygen gas flows at $T_s \approx 780$ °C?

In subchapter 7.1, the effect of oxygen gas flow on the properties of Al₂O₃ coatings in both as-deposited and high temperature conditions are explored. The high temperature XRD (HT-XRD) is conducted to analyze the phase transformations up to $T = 1,200$ °C in vacuum and atmosphere. Moreover, high temperature nanoindentation (HT-NI) tests at $T_{HT-NI} = 650$ °C and $T_{HT-NI} = 750$ °C are applied to analyze the indentation hardness and modulus directly at these elevated temperatures.

2. Can adjusting bias voltage and gas pressure still synthesize crystalline Al_2O_3 coatings with compressive residual stress even at higher substrate temperature $T_s \approx 850^\circ\text{C}$ by HS-PVD?

Three Al_2O_3 coatings are deposited on cemented carbide substrates under varying bias voltages and oxygen gas flow conditions at $T_s \approx 850^\circ\text{C}$. Residual stress in these coatings is analyzed, and its impact on coating properties is discussed in subchapter 7.2.

3. What cutting time can cemented carbide tools coated with Al_2O_3 at $T_s \approx 850^\circ\text{C}$ using HS-PVD achieve in dry turning operation of C45+N steel under industrial cutting parameters before reaching a defined failure criterion?

In chapter 8, cemented carbide coated tools undergo turning tests on C45+N workpieces to evaluate Al_2O_3 operating behavior and achievable cutting time t_c before reaching a maximum flank wear width of $VB_{max} \approx 100\ \mu\text{m}$. Cutting experiments are carried out at the Institute of Production Engineering and Machine Tools (IFW) of Leibniz University Hannover in Germany. The cutting tests are conducted using parameters in the lower range of industrial applications to verify the performance of HS-PVD coatings. TiAlN coated tools using a mfMS industrial coating at IOT is considered as a reference. As discussed in subchapter 2.4, previous studies at IOT show that the deposition of the TiAlN interlayer enhances the adhesion of Al_2O_3 coating on cemented carbide. AlCrN is not considered, due to the high substrate temperatures up to $T_s \approx 850^\circ\text{C}$, promoting the formation of Cr_2O_3 and negatively reduce the adhesion strength of Al_2O_3 . Therefore, additional tools are coated with TiAlN/ Al_2O_3 and subjected to machining tests. The cutting edges of the tested tools are then analyzed in terms of their machining behavior and compared with those of the Al_2O_3 and TiAlN coated tools.

4 Coating deposition and fundamental analysis methods

In the following, the HS-PVD coating unit used and its modifications carried out in the scope of this dissertation are explained. Furthermore, fundamental characterization methods of coating properties are presented. Since these investigations were carried out consistently for each coating variant in this thesis, they are presented here. The further development-relevant characterization methods are introduced accordingly directly before their results.

4.1 HS-PVD prototype machine

The coatings in this work were deposited using the HS-PVD machine at IOT. The HS-PVD coating unit is schematically illustrated in Figure 4.1 a).

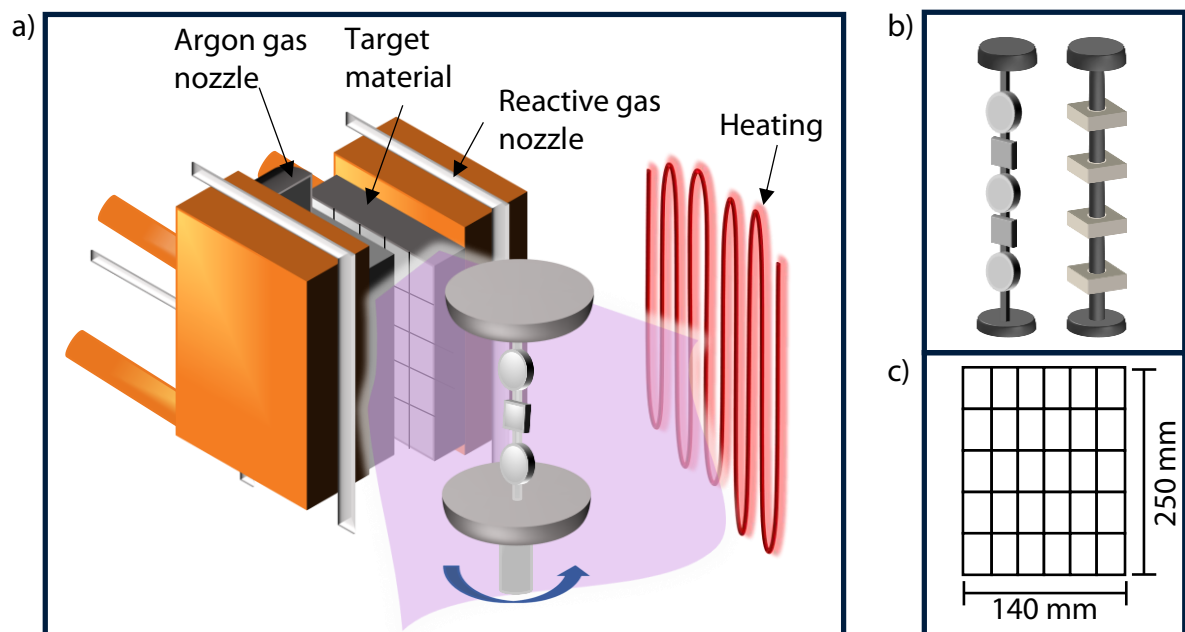


Figure 4.1: a) Schematic representation of HS-PVD in the top view, b) substrate table, and c) a target plate with 30 target segments

The two target plates that form the hollow cathode are positioned at a fixed distance of $d_{\text{target}} = 20 \text{ mm}$, without any variability. When the power supply is activated, the ionization of the argon process gas, introduced between the two target plates, generates a glow discharge and produces plasma that facilitates the sputtering of the metallic target materials. Reactive gases such as oxygen and nitrogen are injected through gas nozzles in front of the hollow cathode. Recently, a power supply MP2-100, MAGPULS GmbH, Sinzheim, Germany, was installed and integrated with the HS-PVD device. In addition to pulsed modes, the new power supply enabled

a more stable reactive process in direct current (DC) mode. A gas control system can adjust the reactive and process gas flows. The cooling of the chamber, the cathodes, and the power supplies is ensured by several water-cooling circuits. Two heaters are in the coating chamber at the right and left sides of the substrate table. The temperature of these heaters can be regulated by the heater power and measured using thermocouples. The substrate temperature in the working chamber can be read out using a thermocouple positioned beside the substrate table at a distance of $d_{Thermo.} \approx 8$ mm from the substrate. The tools and flat samples are fixed to substrate holders on the substrate table during the coating process, as depicted in Figure 4.1 b). The sputter target plate at each side with a length of $l = 250$ mm and width of $w = 140$ mm is comprised of 30 individual target segments, as shown in Figure 4.1 c). The hollow cathode setup in HS-PVD imposes a limitation when attempting to deposit multilayer coatings composed of different metallic elements. For instance, deposition of bilayer coating with a top layer of specific element combination and an interlayer with other elements is not feasible within the same process batch. This limits the flexibility in material selection for multilayer architectures.

The HS-PVD coating unit is a prototype machine. Therefore, it is continuously developed and optimized at IOT through several projects to meet the evolving process requirements. In previous research projects at the IOT, numerous adjustments have already been implemented to advance the machine. These developments can be summarized as follows:

- Reduction of vacuum pump wear through the installation of a water-cooled baffle grid before the vacuum pump intake to reduce particle load.
- Optimization of the vacuum system by a high-throughput vacuum fore pump to restore original evacuation time and pressure conditions.
- Stabilization of bias voltage by redesigning bias contacts with electrically insulated, temperature-resistant spring contacts to ensure consistent plasma.
- Minimizing carbon contamination with encapsulating heating elements and insulation components with temperature-resistant metal sheets.

The insulation components and heaters in the coatings chamber were made of graphite, as shown in Figure 4.2 a). Despite the shielding of the heaters with metal plates, the carbon contamination caused by the graphite insulation components was not significantly reduced. The deposition of Al_2O_3 coatings via HS-PVD at $T_s > 700$ °C was one of the approaches in this

study. Such high substrate temperatures up to $T_s \approx 850$ °C and the oxygen-containing reactive process further intensified the reaction of the graphite insulation with plasma species during the coating process. Another solution in this work involves replacing insulation components. A ceramic material from SCHUPP Industriekeramik GmbH, Aachen, Germany, was integrated into the HS-PVD coating unit. As insulation constituted a significant portion of the components in the coating chamber, as shown in Figure 4.2 b), and the hollow cathode housing, Figure 4.2 c), its replacement successfully eliminated carbon contamination in the coating.

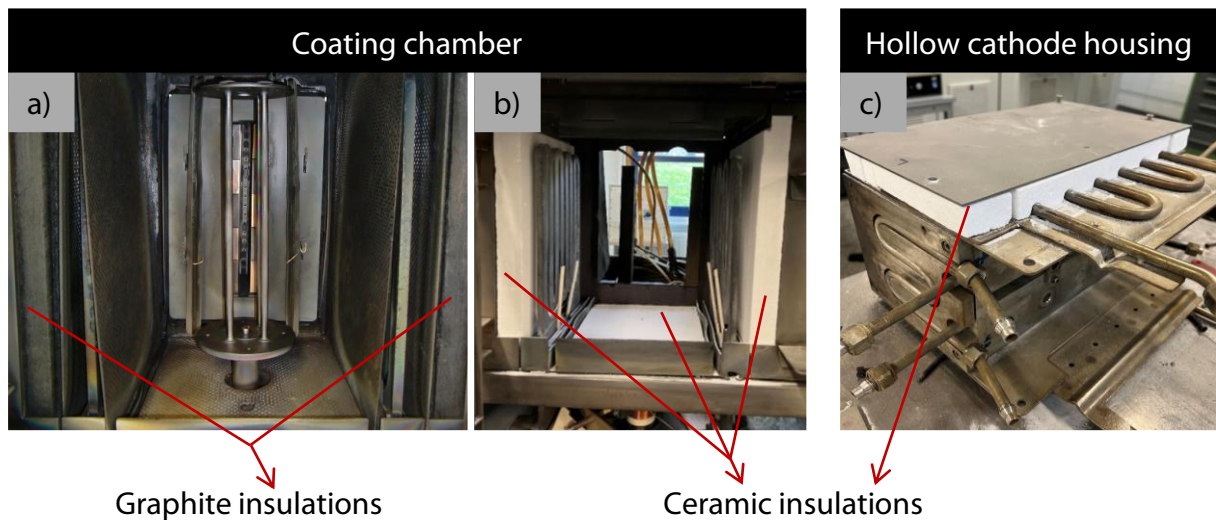


Figure 4.2: Integration of ceramic insulation materials in HS-PVD coating unit a) initial state, b-c) after integration

Another measure was developing an automatic substrate rotation device. Previously, substrate rotation was manual, causing inhomogeneous coating deposition and a time-consuming process. The system now integrates an adjustable substrate table rotation using a motor and gearbox, enabling single-fold rotation, as shown in Figure 4.3.

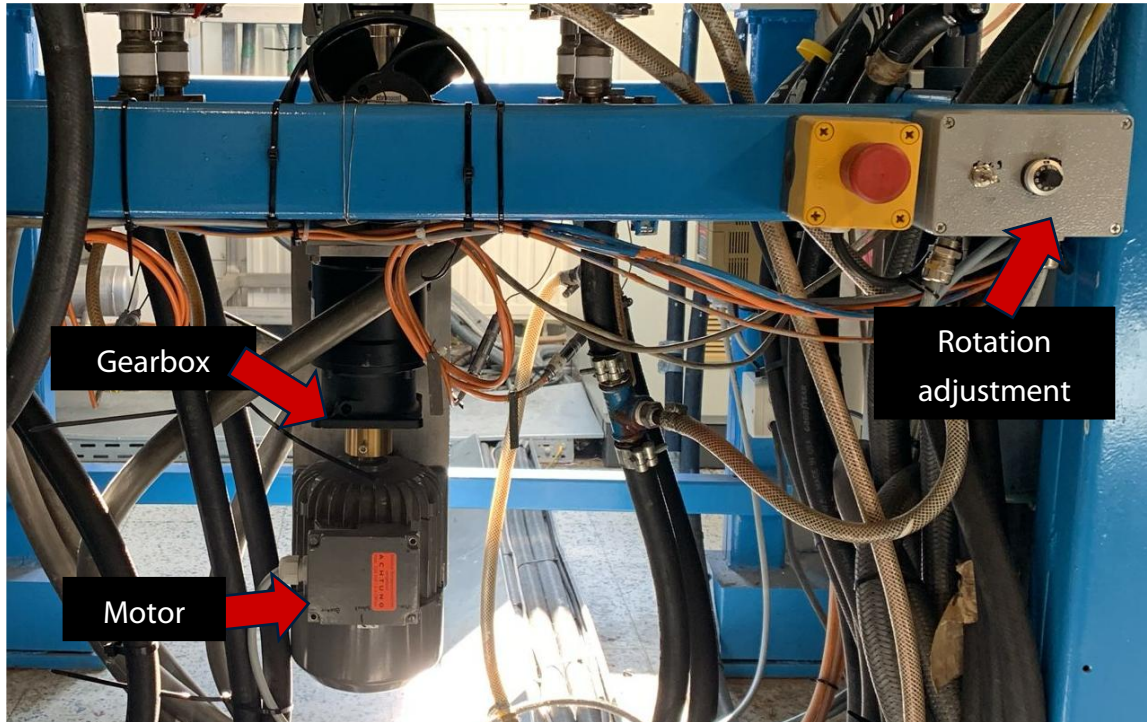


Figure 4.3: Implementation of substrate desk rotation system in HS-PVD

4.2 Analysis methods of fundamental coating properties

Coating morphology and thickness were determined using scanning electron microscopy (SEM) analyses on fracture cross-sections of coated substrates. The investigations were performed using SEM DSM982 Gemini, Carl Zeiss GmbH, Jena, Germany. Furthermore, the Cr:Al ratio of the coatings was measured at GFE by energy dispersive X-ray spectroscopy (EDX). Coatings were further analyzed by electron probe microanalysis (EPMA) with a JEOL JXA-8530F microprobe equipped with a Schottky field emission cathode. These three analyses were conducted at the Central Facility for Electron Microscopy (GFE) at RWTH Aachen University. Line roughness measurements were conducted using confocal laser scanning microscopy (CLSM). The average line roughness R_a of the coatings was obtained under DIN EN ISO 4287 utilizing a VK-X210 microscope manufactured by Keyence Corporation in Osaka, Japan. The coatings were investigated in terms of phase composition and crystal orientation using grazing incidence (GI) XRD 3003, GE Energy Germany GmbH, Ratingen, Germany. The XRD measurements were carried out using Cu-K α radiation, wavelength $\lambda = 0.1540598$ nm, $U = 40$ kV, $I = 40$ mA, diffraction angle $20^\circ \leq 2\theta \leq 80^\circ$, and incoming angle $\omega = 3^\circ$.

To investigate the indentation hardness, H_{IT} and indentation modulus E_{IT} , nanoindentation measurements were carried out according to DIN EN ISO 14577 with a TriboIndenter TI 950,

Bruker Corporation, Billerica, Massachusetts, USA. An indentation force of $F_{max} = 10$ mN was applied, and the indentation depth was kept below 10 % of the coating thickness. Thereby, the indentation force was linearly increased and decreased over the timespan of $t_{NI} = 5$ s and for a holding time of $t_{hold} = 3$ s. Subsequently, the results were evaluated according to Oliver and Pharr [PO92]. For this purpose, constant Poisson's ratios of $\nu = 0.23$ and $\nu = 0.25$ were assumed for the oxide and nitride coatings, respectively. By averaging the results of a minimum of 20 indents on each coating, the values of the indentation hardness H_{IT} and indentation modulus E_{IT} were determined. To avoid the impact of coating roughness on the results, the coatings were polished to an average line roughness $Ra \approx 0.02$ μm before nanoindentation measurements. Furthermore, the elastic work W_{el} and plastic work W_{pl} were obtained by integrating the force–displacement curves, and the elastic work percentage η_{el} was determined, Figure 4.4. The area under the unloading section of the force–displacement curve represents the elastic work W_{el} , while W_{pl} corresponds to the area under the loading section minus W_{el} .

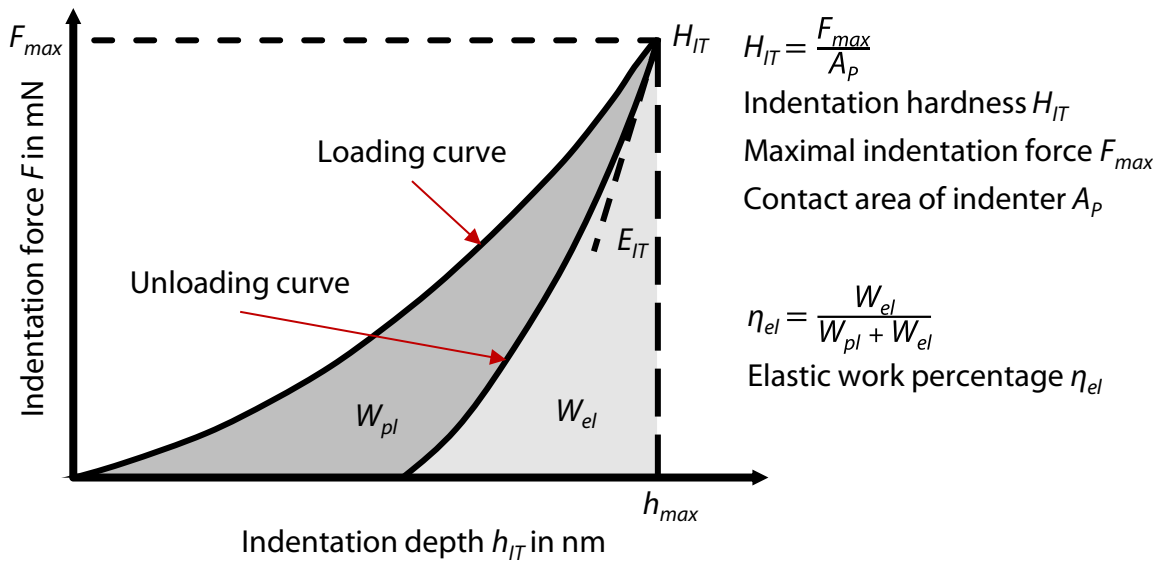


Figure 4.4: Indentation values considered in this work and schematic illustration of force displacement curve according to DIN EN ISO 14577

5 Synthesis of (Al,Cr)₂O₃ coatings at $T_s \approx 550$ °C

In previous work at IOT, a (Al₇₁Cr₂₉)₂O₃ coating system with a crystalline structure has been successfully deposited at $T_s \approx 570$ °C. The process window for the synthesis of this coating system, established in [BBK+19], was the basis of coating development in this dissertation. However, in the investigations presented here, the bias voltage was increased from $U_B = -75$ V to $U_B = -175$ V to reduce surface roughness by refining morphology. An approach to enhance the high temperature properties of the coatings in this dissertation is to reduce the chromium content to $x_{Cr} < 29$ at.-%. Moreover, an AlCrN interlayer was developed to enhance the adhesion strength of the coatings on the X40CrMoV5-1 substrate and to increase the high temperature stability.

To investigate the influence of Cr content on phase formation, three (Al,Cr)₂O₃ coatings with $x_{Cr} < 29$ at.-% were synthesized. The hardened and annealed hot work tool steel X40CrMoV5-1, with a hardness of $H = (54 \pm 2)$ HRC was used as substrate material. The coatings were deposited at a substrate temperature of $T_s \approx 550$ °C, enabling the coating of substrate materials such as hot working steel X40CrMoV5-1 without exceeding the annealing temperature of $T_{anneal.} \approx 560$ °C. The cylindrical samples with a diameter of $\varnothing = 25$ mm and a width of $h = 8$ mm were prepared using grinding, lapping, and polishing processes. The substrate surface was polished with a 3 µm water-based diamond suspension, revealing an average line roughness of $Ra \approx 0.01$ µm after polishing. Three target configurations (TC) were employed, as presented in Figure 5.1. The coating systems with a low, medium and high content of Cr named as, (AlCr_L)₂O₃, (AlCr_M)₂O₃ and (AlCr_H)₂O₃ were deposited using TCL, TCM, and TCH, respectively. TCL exhibited the lowest number of Cr segments, whereby TCH with 10 segments had the highest number. Hereby, Al targets with a purity of 99.5 % and Cr targets with a purity of 99.95 % were used.

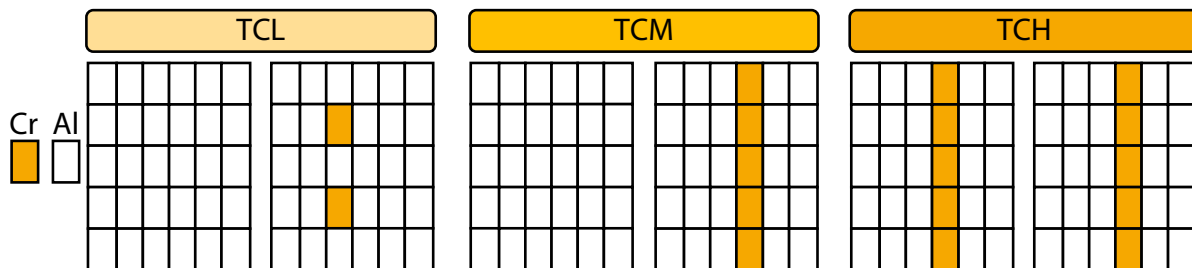


Figure 5.1: Target configurations for the (Al,Cr)₂O₃ coatings

The coating process was carried out in a direct current mode and without any rotation of the substrates. Prior to argon plasma etching, the substrates were heated up to a substrate temperature of $T_s \approx 550$ °C. The substrate temperature was measured using a thermocouple, as described in subchapter 4.1. The etching process was carried out with a bias voltage of $U_B = -450$ V and an argon gas flow of $Q_{Ar} = 9,000$ sccm for a duration of $t_{etch.} = 25$ min. The process window determined in the previous works at IOT in [BBK+19] forms the basis for the development of the process window of (Al,Cr)₂O₃ coatings in this work. The process parameters were kept constant for the three coating systems and are summarized in Table 5.1.

Table 5.1: Coating process parameters of the ternary (Al,Cr)₂O₃ system

Process ID	4475	4521	4524
Coating	(AlCr _L) ₂ O ₃	(AlCr _M) ₂ O ₃	(AlCr _H) ₂ O ₃
Target configuration	TCL	TCM	TCH
Cathode power P_C in kW	6	6	6
Cathode current I_C in A	15	15	15
Bias voltage U_B in V	-175	-175	-175
Bias current I_B in A	3	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000	8,000
O ₂ gas flow Q_{O_2} in sccm	80	80	80
Pressure p in Pa	33.4	33.4	33.4
Heater temperature T_H in °C	640 ± 10	640 ± 10	640 ± 10
Substrate temperature T_s in °C	550 ± 15	550 ± 15	550 ± 15
Rotation speed ω_{Table} in rpm	-	-	-
Coating time $t_{coat.}$ in min	60	60	60

5.1 Influence of chromium content on the coating properties of (Al,Cr)₂O₃

EDX analysis was used to determine the variation of the chemical composition in the (Al,Cr)₂O₃ system. The ratio of aluminum and chromium was calculated. The results of the EDX analysis are shown in Table 5.2. The results show a clear correlation between the number of chromium targets and the chromium content of the coating. This changes from $x_{Cr} = 8.4$ at. % for TCL to $x_{Cr} = 21.7$ at. % for TCH. Since the aim is to produce coatings with a chromium content of $x_{Cr} < 29$ at.-%, all three target configurations fulfill this requirement and will be investigated further.

Table 5.2: Chemical composition of the $(\text{Al,Cr})_2\text{O}_3$ coatings

Target configuration	Coating system	Al in at. %	Cr in at. %	Al:Cr in -
TCL	$(\text{Al,Cr}_L)_2\text{O}_3$	91.6 ± 0.4	8.4 ± 0.4	10.9
TCM	$(\text{Al,Cr}_M)_2\text{O}_3$	88.4 ± 0.2	11.6 ± 0.2	7.6
TCH	$(\text{Al,Cr}_H)_2\text{O}_3$	78.3 ± 0.1	21.7 ± 0.1	3.6

The influence of the chromium content on the coating morphology and topography is illustrated in Figure 5.2. The coating thickness increases with increasing chromium content. This is attributed to the higher sputtering rate of Cr compared to Al. Furthermore, all coatings exhibit a dense columnar morphology that differs in detail. The $(\text{Al,Cr}_L)_2\text{O}_3$ coating shows less columnar morphology than $(\text{Al,Cr}_H)_2\text{O}_3$ in SEM cross-section images. However, the columns of $(\text{Al,Cr}_H)_2\text{O}_3$ are thinner, as detectable in topography images. Moreover, increasing the bias voltage successfully led to a reduction of coating roughness compared to previous coatings, where the mean roughness Ra was measured in the range of $0.3 \mu\text{m} \leq Ra \leq 1.5 \mu\text{m}$ [BBK+18a].

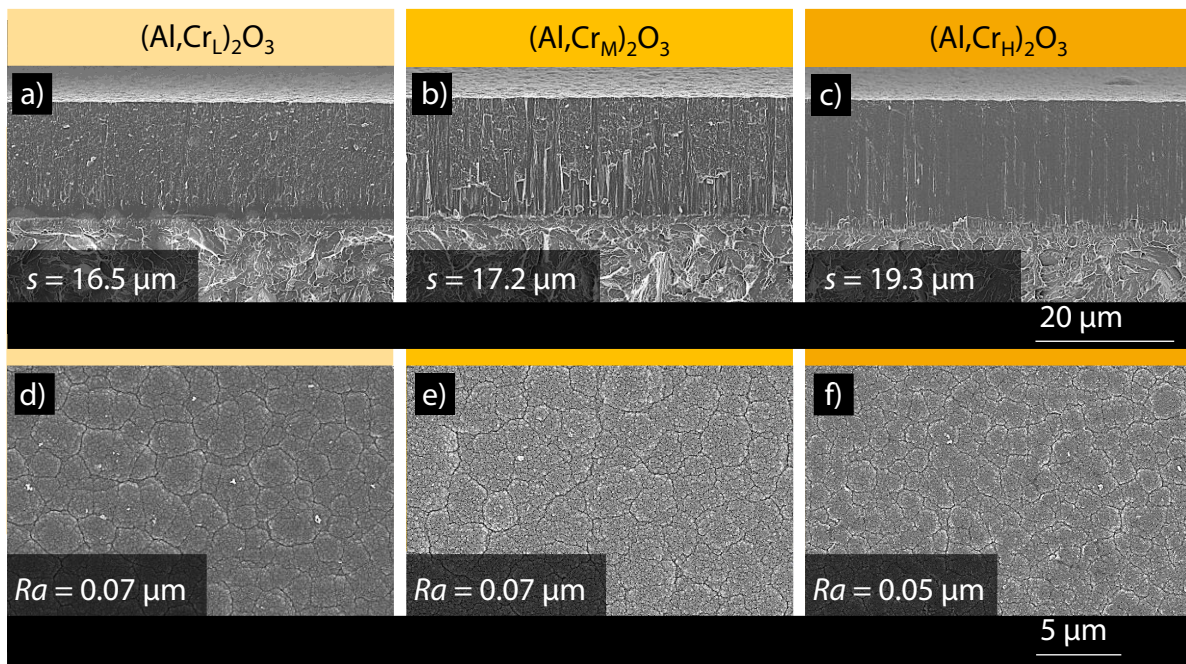


Figure 5.2: Effect of Cr content on morphology and topography of $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c]

The phase composition of the $(\text{Al,Cr})_2\text{O}_3$ coatings with varying chromium content was determined using XRD. The diffractograms are compared in Figure 5.3. The phase composition is independent of the analyzed chromium content in the coating. The peaks can be assigned to

$\gamma\text{-Al}_2\text{O}_3$, whereby the orientation (400) is preferably formed. It can be observed that the peak intensity at (400) decreases with an increase in the Cr content. This could be explained by microstructure refinement. Considering the refinement of the coating morphology in Figure 5.2, it is assumed that the reduction in grain size with increasing Cr content is the reason for the different peaks. However, deeper microstructure analysis such as TEM is required to verify this assumption.

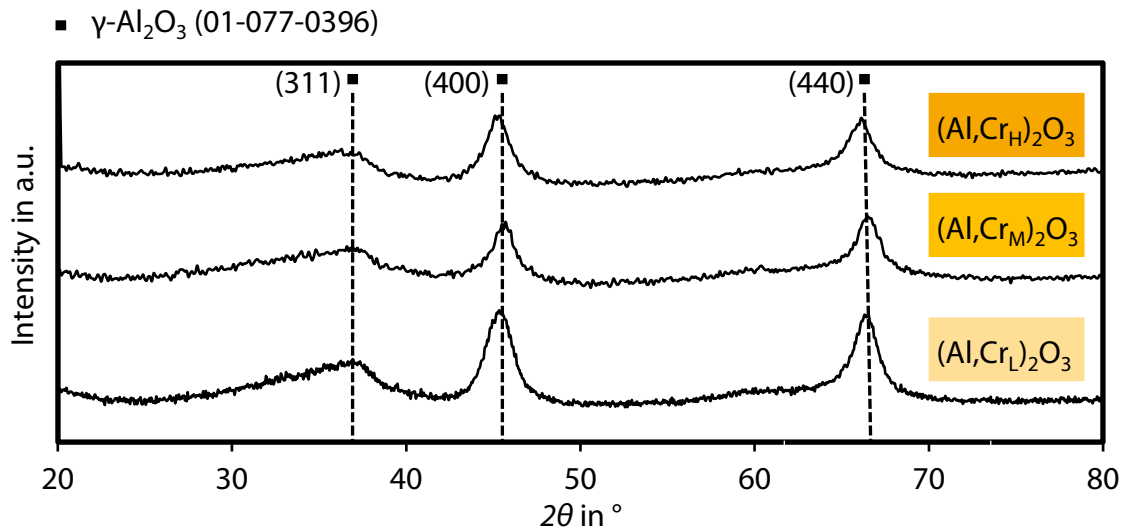


Figure 5.3: Analysis of phase composition depending on Cr content in $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c]

Figure 5.4 shows the indentation hardness H_{IT} and indentation modulus E_{IT} determined by nanoindentation for the $(\text{Al,Cr})_2\text{O}_3$ coatings. The indentation hardnesses and indentation moduli are comparable for the $(\text{Al,Cr}_\text{L})_2\text{O}_3$ and $(\text{Al,Cr}_\text{M})_2\text{O}_3$ coating systems. In contrast, these properties are significantly increased for the $(\text{Al,Cr}_\text{H})_2\text{O}_3$ coating system. Despite sharing the same crystalline phase, this behavior is likely influenced by several factors, including solid solution hardening, lattice distortions, and a finer microstructure. Chromium has a larger ionic radius compared to aluminum.

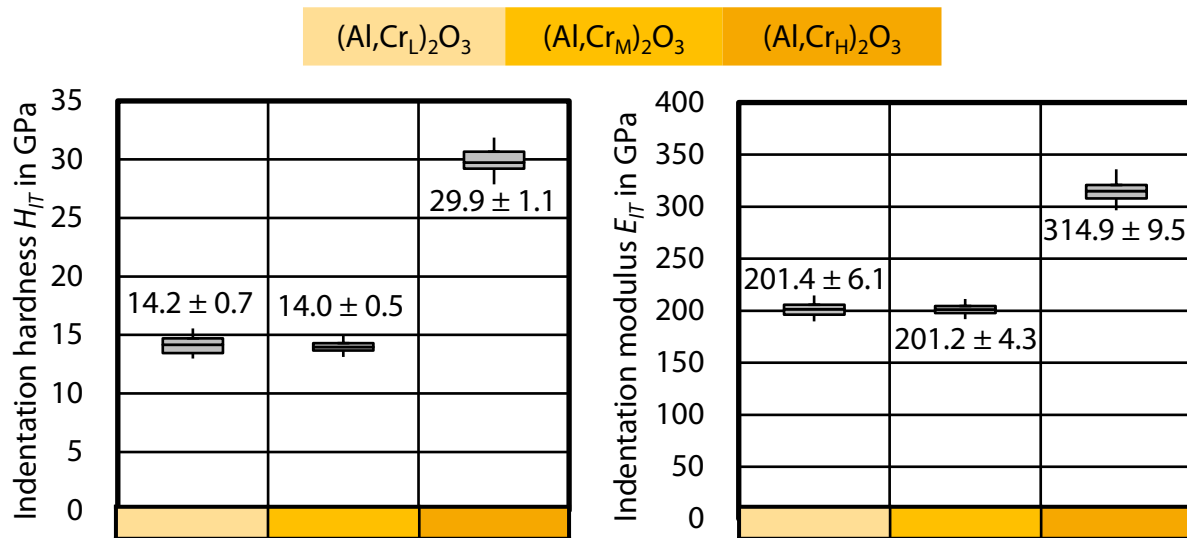


Figure 5.4: Indentation hardness H_{IT} and indentation modulus E_{IT} of the $(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+24c]

This could lead to lattice distortions. These lattice distortions cause solid solution hardening, as the alumina lattice becomes stiffer and more resistant to deformation due to the high chromium content. Moreover, the nanoindentation results correlate with the observations from the coating morphology, whereby a morphology refinement is detected for $(\text{Al,Cr}_H)_2\text{O}_3$. The fine and dense $(\text{Al,Cr}_H)_2\text{O}_3$ coating morphology could result in a significantly higher indentation hardness H_{IT} and a higher indentation modulus E_{IT} .

Adhesion strength properties of $(\text{Al,Cr})_2\text{O}_3$ coatings on hot work steel

Rockwell indentation tests were conducted to determine the adhesion strength to the steel substrate. The Rockwell indentation tests in this dissertation were all carried out in accordance with DIN 4856. Thereby, a Rockwell tip was indented perpendicular to the surface with a normal force of $F = 588.4\text{ N}$ using a Rockwell tester HP100, KNUTH Machine Tools GmbH, Wasbek, Germany. The crack formations and spalling at the edge of the Rockwell imprint were investigated by confocal laser scanning microscopy (CLSM). The Rockwell imprint images taken with CLSM were normally compared with the characteristic defects of the individual adhesion classes (HF) described in DIN 4856. A classification of the appropriate adhesive strength groups from HF 1 to HF 6 is not valid since the thickness of $(\text{Al,Cr})_2\text{O}_3$ coatings exceeds the thickness limitation of $s = 10\text{ }\mu\text{m}$ as defined in DIN 4856. Therefore, the adhesion strength of $(\text{Al,Cr})_2\text{O}_3$ coatings on X40CrMoV5-1 substrate was qualitatively investigated using the Rockwell indentation test, as presented in Figure 5.5. All coatings show a poor adhesion

strength on the substrate, as significant delamination is visible around the imprints. This indicates the necessity of a suitable interlayer to increase the adhesion strength of these compounds. The Rockwell imprint images taken with CLSM were compared with the characteristic defects of the individual adhesion classes (*HF*) described in DIN 4856

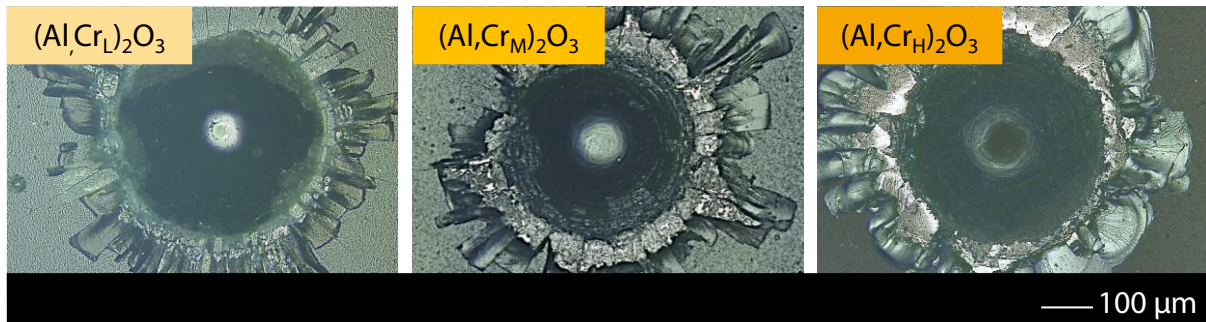


Figure 5.5: Rockwell imprints of the $(\text{Al,Cr})_2\text{O}_3$ coatings

5.2 Selection of a suitable interlayer from the AlCrN system

As explained in subchapter 4.1, the HS-PVD used in this study contains one hollow cathode, resulting in a limitation to deposit bilayer coating with a top layer of specific element combination and an interlayer with other elements within the same process batch. Therefore, the Al:Cr ratio of each layer cannot be chosen freely, as the change in target configuration within a batch is not possible. The effect of the AlCrN interlayer system on compound adhesion between the hot work steel X40CrMoV5-1 substrate and $(\text{Al,Cr})_2\text{O}_3$ coating was investigated. Thereby, the developments were first carried out for $(\text{Al,Cr}_L)_2\text{O}_3$, which has the lowest Cr content and deposited with target configuration TCL. Various $(\text{Al,Cr}_L)\text{N}$ interlayer systems were considered. Hereby, the influence of interlayers with different thicknesses s_i , architectures as well as bias voltages U_B were investigated. To analyze the adhesion strength between substrate and interlayer, deposition of the functional $(\text{Al,Cr}_L)_2\text{O}_3$ layer is initially omitted.

5.2.1 Process parameters for deposition of $(\text{Al,Cr}_L)\text{N}$ interlayer

Interlayers with varying thicknesses s_i , architectures, and bias voltages were deposited in a dc mode using target configuration TCL. The effect of the thickness of AlCrN interlayer on adhesion strength was obtained by varying the coating time t_i . A minimum coating time of $t_i = 20$ min was selected to obtain a thickness similar to that of the metallic AlCr interlayer used in previous studies [BBK+19]. An interval of $\Delta t_i = 10$ min was chosen to increase the coating thickness. All three AlCrN interlayers were deposited using a monolayer architecture.

Moreover, two graded AlCrN interlayers were deposited at different bias voltages. The graded coating architecture was formed using a gradient increase of the nitrogen gas flow Q_{N_2} . This results in a uniform transition of properties from the metallic substrate to the ceramic interlayer. Furthermore, it may assist in controlling residual stress within the coating. The process parameters for the five AlCrN coatings are listed in Table 5.3. Before the coating deposition, the substrates were prepared and subjected to an argon plasma etching as described in chapter 5.

Table 5.3: Coating process parameters of $(\text{Al,Cr}_L)\text{N}$ interlayer

Process ID	Monolayer architecture			Graded architecture	
	4488	4489	4490	4491	4492
Target configuration	TCL	TCL	TCL	TCL	TCL
Cathode power P_C in kW	6	6	6	6	6
Cathode current I_C in A	15	15	15	15	15
Bias voltage U_B in V	-125	-125	-125	-125	-150
Bias current I_B in A	3	3	3	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000	8,000	8,000	8,000
N_2 gas flow Q_{N_2} in sccm	800	800	800	0-800	0-800
Pressure p in Pa	33.9	33.9	33.9	33.7-33.9	33.7-33.9
Heater temperature T_H in $^\circ\text{C}$	640 ± 10	640 ± 10	640 ± 10	640 ± 10	640 ± 10
Substrate temperature T_s in $^\circ\text{C}$	550 ± 15	550 ± 15	550 ± 15	550 ± 15	550 ± 15
Rotation speed ω_{Table} in rpm	-	-	-	-	-
Interlayer coating time t_i in min	20	30	40	20	20

5.2.2 Coating properties of $(\text{Al,Cr}_L)\text{N}$ interlayer

The $(\text{Al,Cr}_L)\text{N}$ interlayers were analyzed by EDX to determine the chemical composition. The coatings consist of $x_{\text{Al}} = (95 \pm 1)$ at.-% and $x_{\text{Cr}} = (5 \pm 1)$ at.-%. SEM cross-sectional micrographs of the coatings are illustrated in Figure 5.6. The fine columnar morphology remains constant and demonstrates no changes regarding the coating time. The interlayers with nitrogen gradation in the process also showed a thickness comparable to monolayer coatings. A dense, fine columnar morphology can be observed, whereby no significant influence of the substrate bias voltage U_B on the morphology is visible.

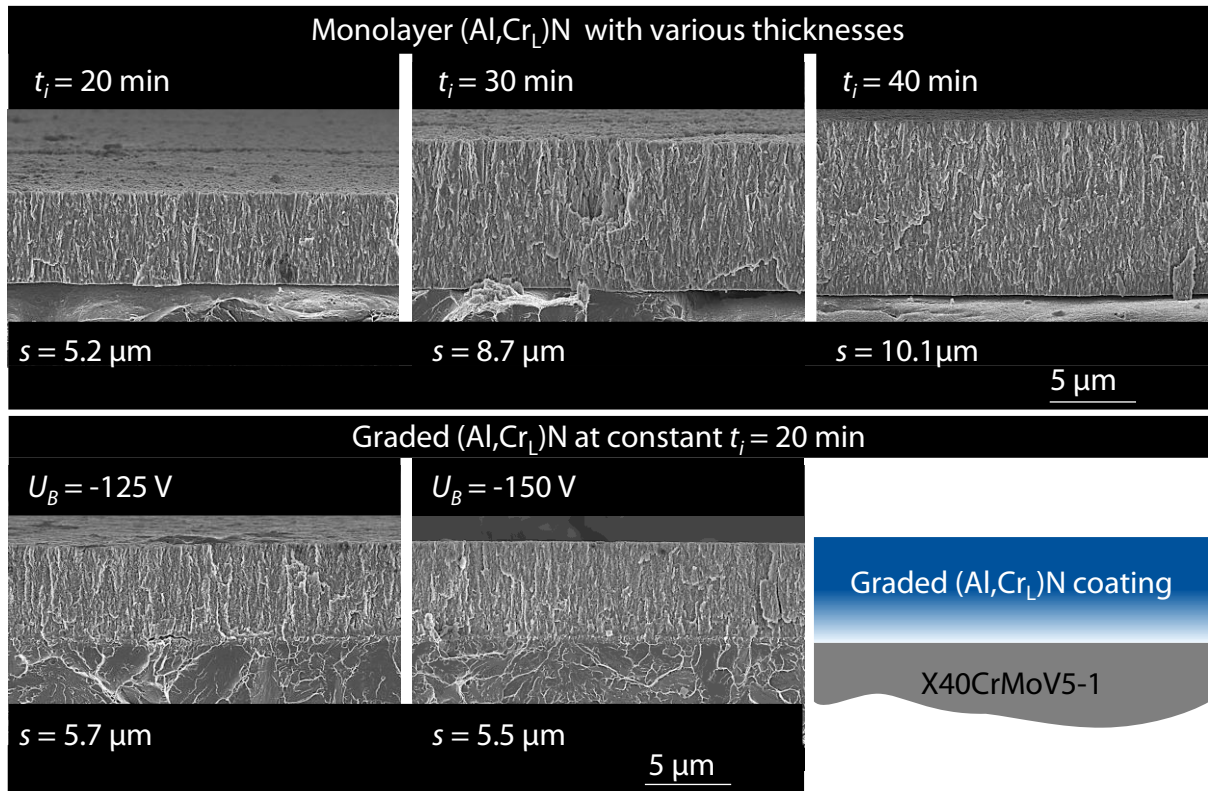


Figure 5.6: Fracture cross-sectional SEM micrographs of $(\text{Al,Cr})_L\text{N}$ coated X40CrMoV5-1 [BKM+23]

XRD diffractograms of $(\text{Al,Cr})_L\text{N}$ interlayers are shown in Figure 5.7. The results exhibit coatings consisting of the same phase composition of h-AlN and c-CrN. The AlN phase in a hexagonal structure is detected, attributed to the high Al content $x_{\text{Al}} \approx 95$ at.-% in the coatings, as discussed in subchapter 2.4.

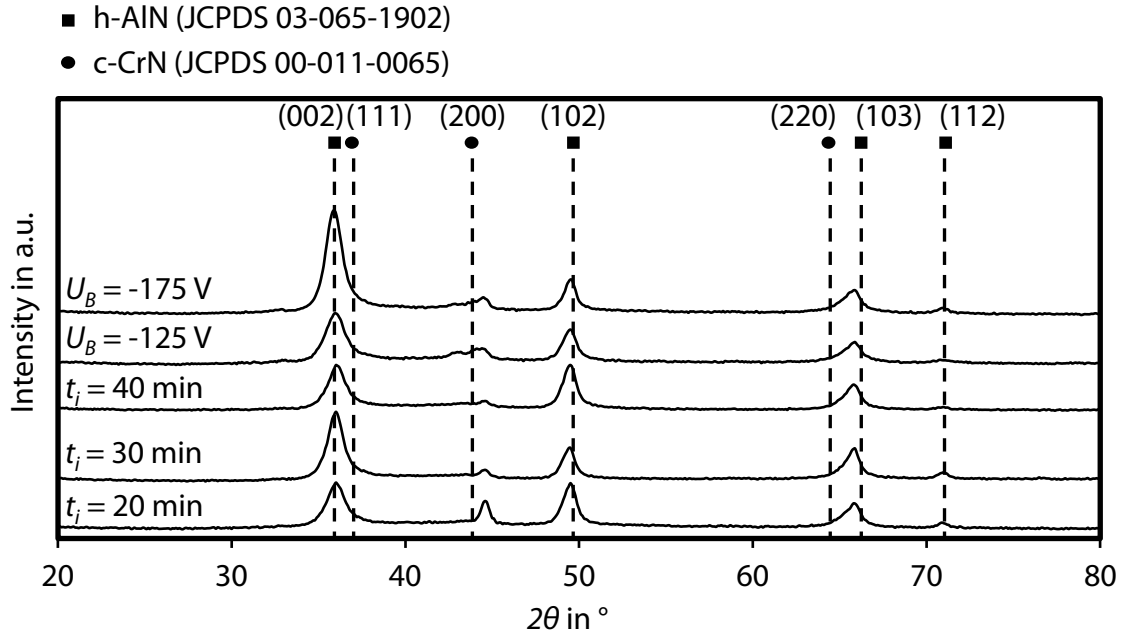


Figure 5.7: Phase analysis of (Al,Cr_L)N interlayers deposited with different parameters [BKM+23]

The indentation hardness, indentation modulus, and elastic work percentage η_{el} of (Al,Cr_L)N are listed in Table 5.4. The indentation hardness and indentation modulus are also presented in box plots in Figure 5.8 for better comparability.

Table 5.4: Nanoindentation values of (Al,Cr_L)N interlayers

Architecture	Monolayer			Gradation	
Parameters	$t_i = 20$ min	$t_i = 30$ min	$t_i = 40$ min	$U_B = -125$ V	$U_B = -175$ V
H_{IT} in GPa	8.3 ± 0.4	8.7 ± 0.4	8.5 ± 0.5	10.2 ± 0.5	10.5 ± 0.4
E_{IT} in GPa	154.0 ± 5.3	148.2 ± 4.9	144.6 ± 4.7	207.0 ± 11.9	170.4 ± 30.1
η_{el} in %	40	42	42	45	45

The coating thickness does not significantly affect the indentation values of monolayer (Al,Cr_L)N. However, these interlayers indicate a lower elastic work percentage than those with graded architecture. Moreover, increased substrate bias voltage influences neither the indentation values nor the elastic work percentage of interlayers with graded architecture. Furthermore, coatings with a graded architecture have a slightly higher indentation hardness and modulus than the monolayer coatings, as shown in Figure 5.8.

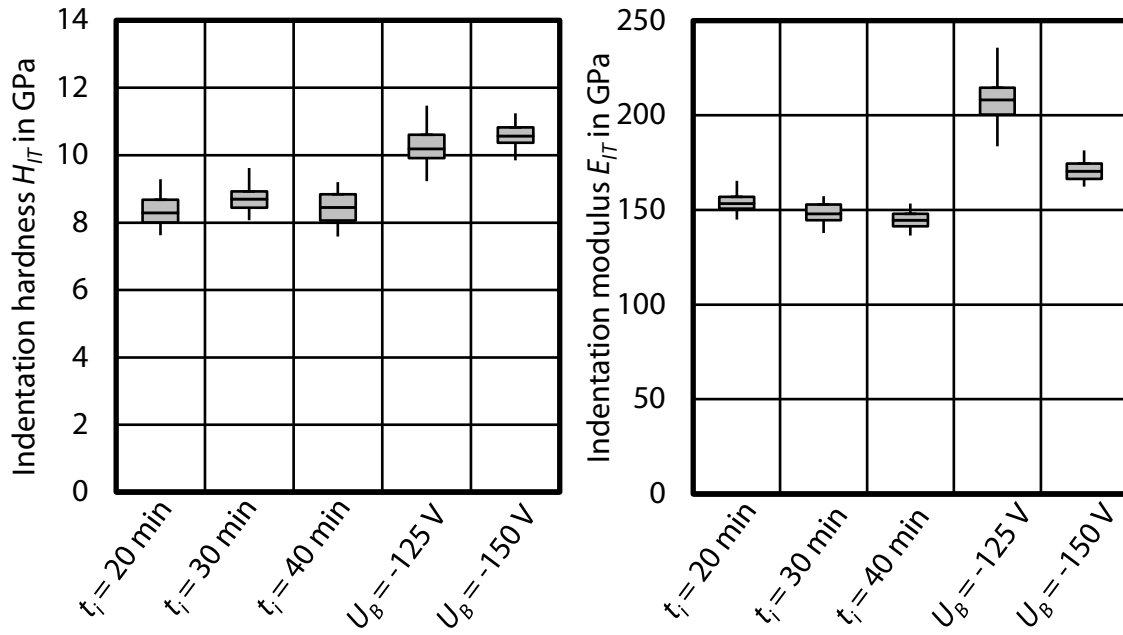


Figure 5.8: Box plots of indentation hardness H_{IT} and indentation modulus E_{IT} of $(\text{Al,Cr})_L\text{N}$ interlayers [BKM+23]

5.2.3 Analysis of $(\text{Al,Cr})_L\text{N}/\text{X40CrMoV5-1}$ compound adhesion strength

Rockwell indentation and scratch tests were conducted to determine the interlayer with the highest adhesion strength to the steel substrate. The Rockwell indentation tests were carried out in accordance with DIN 4856, as described in subchapter 5.1. Furthermore, a scratch tester HPG 200/2, Gesellschaft für Fertigungstechnik und Entwicklung Schmalkalden e.V., Schmalkalden, Germany, was used to analyze the adhesion strength of the coating/substrate compound under sliding load. A conical diamond with Rockwell C geometry was scratched over the coating surface at a constant normal force, at a sliding velocity $v_s = 10 \text{ mm/min}$, and over a distance of $x_{\text{Scratch}} = 4 \text{ mm}$. The normal force F_N was increased in increments of $\Delta F_N = 5 \text{ N}$. The scratch tracks were evaluated using CLSM. The critical normal loads L_{c1} - L_{c3} were determined according to DIN EN ISO 20502.

Figure 5.9 reveals the CLSM images of the Rockwell imprints of interlayers on X40CrMoV5-1 steel substrate. The coated samples with a monolayer architecture and different thicknesses show similar adhesive failures with diverse spalling at the imprint edge and are classified as *HF 5*. This illustrates that the change in coating thickness has no significant effect on the adhesion strength of monolayer $(\text{Al,Cr})_L\text{N}$ coatings to the substrate. The graded $(\text{Al,Cr})_L\text{N}$ coated sample with $U_B = -125 \text{ V}$ exhibits the highest adhesion strength *HF 1* since no obvious

spalling or cracks have been observed. However, by increasing the substrate bias voltage to $U_B = -150\text{ V}$ the compound adhesion strength was reduced to $HF\ 3$. An increase in substrate bias raises the kinetic energy of the ions, potentially causing lattice defects and the implantation of process gases, as described in [Dav93]. Consequently, this may elevate compressive residual stress, reducing compound adhesion.

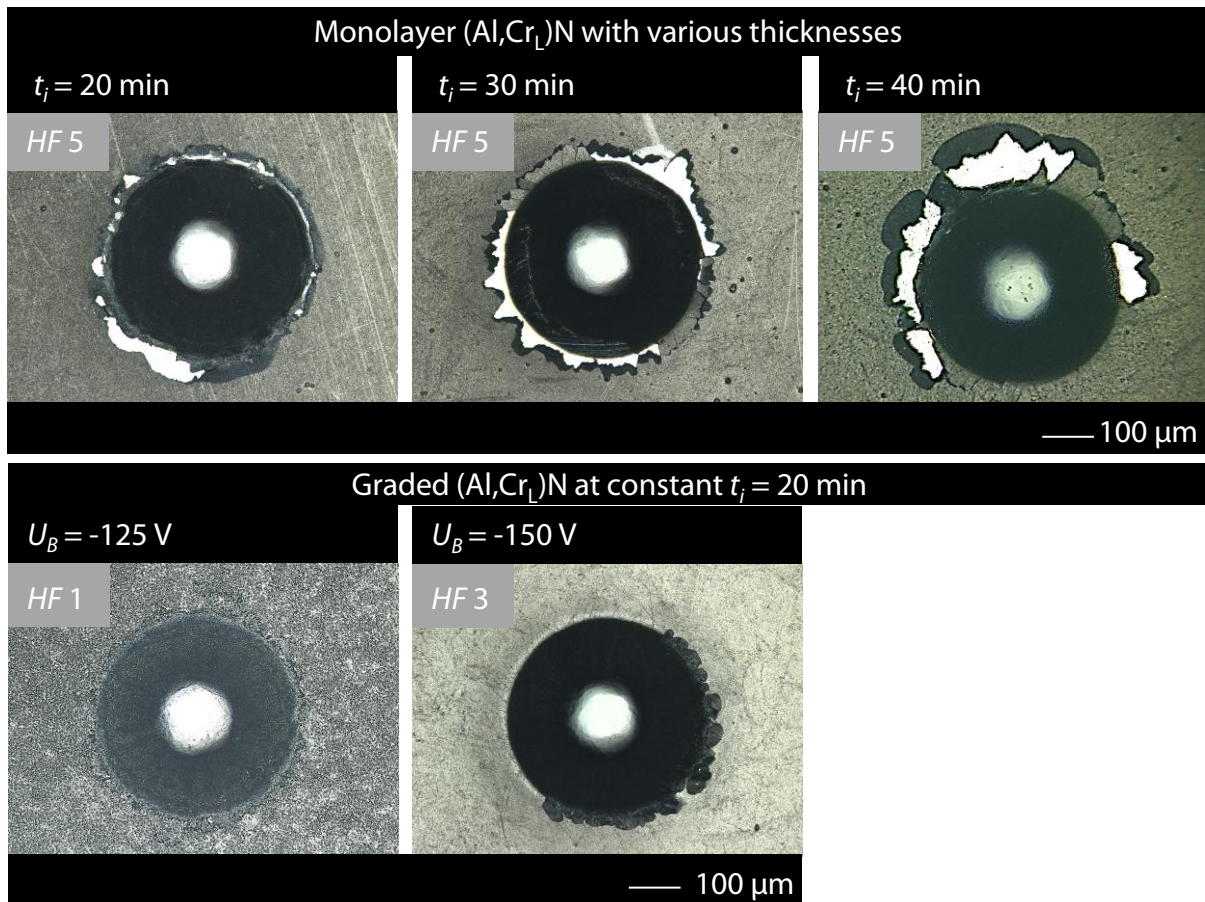


Figure 5.9: Rockwell imprints of $(\text{Al,Cr}_L)\text{N}$ coatings on X40CrMoV5-1 steel [BKM+23]

Figure 5.10 exemplarily displays the scratch test results of monolayer $(\text{Al,Cr}_L)\text{N}/\text{X40CrMoV5-1}$ compound with $t_i = 30\text{ min}$ and the graded $(\text{Al,Cr}_L)\text{N}/\text{X40CrMoV5-1}$ compound with $U_B = -125\text{ V}$. Critical normal loads L_{c1} - L_{c3} of all $(\text{Al,Cr}_L)\text{N}$ coated samples are listed in Table 5.5.

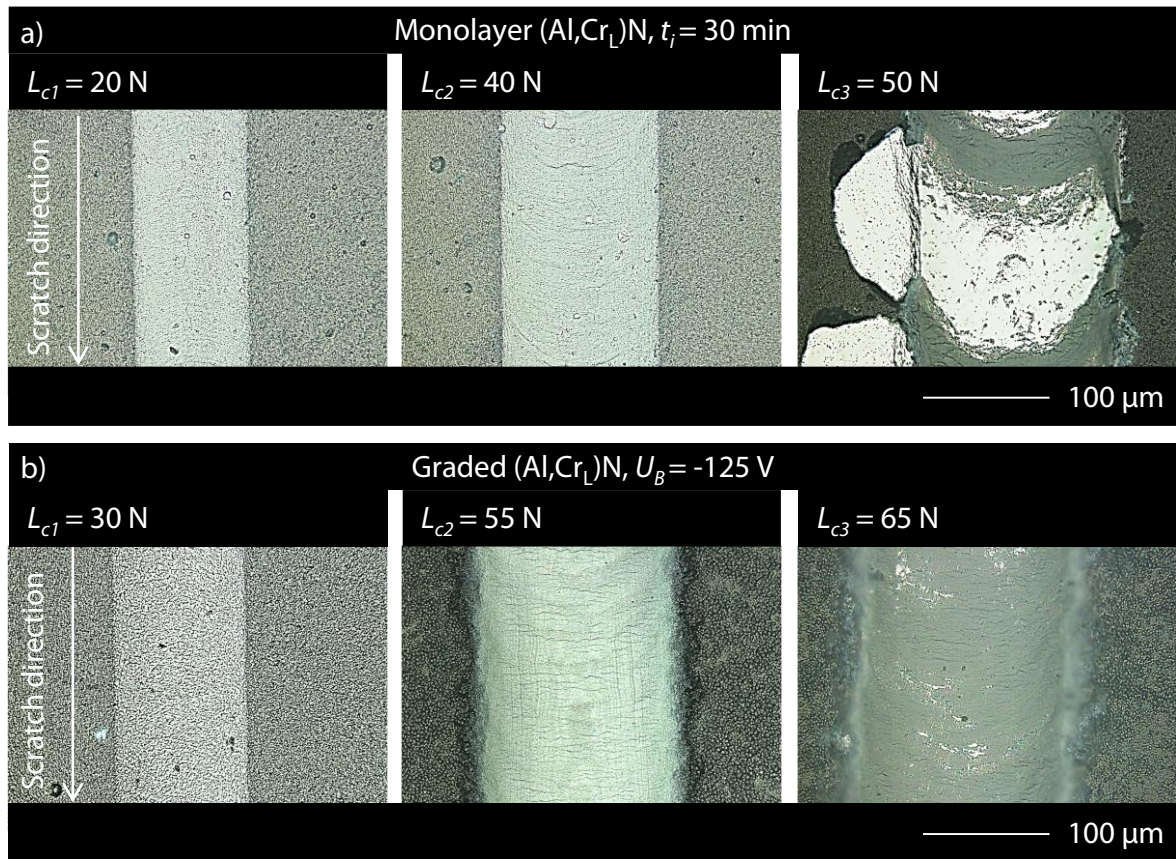


Figure 5.10: Scratch tracks of monolayer $(\text{Al,Cr}_L)\text{N}$ coating with $t_i = 30$ min and graded $(\text{Al,Cr}_L)\text{N}$ coating with $U_B = -125$ V [BKM+23]

The results reveal the same critical normal loads $L_{c1} = 20$ N, $L_{c2} = 40$ N, and $L_{c3} = 50$ N for monolayer $(\text{Al,Cr}_L)\text{N}$ coatings. Using graded architecture, the critical normal loads are enhanced. In contrast, increasing the bias voltage to $U_B = -150$ V reduces the compound adhesion strength, as observed in the Rockwell tests shown in Figure 5.9. The graded $(\text{Al,Cr}_L)\text{N}$ coating deposited by $U_B = -125$ V exhibits the highest adhesion strength on the substrate. Due to its promising adhesion behavior, this interlayer is chosen to be deposited in the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ system for further investigation.

Table 5.5: Critical normal loads $L_{c1} - L_{c3}$ of $(\text{Al,Cr}_L)\text{N}$ interlayers on X40CrMov5-1 steel

Coating	Monolayer architecture			Graded architecture	
	$t_i = 20$ min	$t_i = 30$ min	$t_i = 40$ min	$U_B = -125$ V	$U_B = -150$ V
L_{c1} in N	20	20	20	30	30
L_{c2} in N	40	40	40	55	40
L_{c3} in N	50	50	50	65	50

5.3 (Al,Cr)₂O₃ thickness adjustment to enhance adhesion strength

In the next step, (Al,Cr_L)N/(Al,Cr_L)₂O₃ coatings were deposited on X40CrMoV5-1 substrate using TCL. The aim was to reach an adhesion strength in the Rockwell indentation test, showing no coating delamination at the Rockwell imprint edge. For this purpose, the production and results of two AlCrN/(Al,Cr)₂O₃ variants with different oxide functional layer thicknesses s_f are presented in this subchapter.

5.3.1 Deposition parameters of (Al,Cr_L)N/(Al,Cr_L)₂O₃ system on hot work steel

The two (Al,Cr_L)N/(Al,Cr_L)₂O₃ coating variants were deposited in dc mode and without substrate rotation by HS-PVD using the target configuration TC2. Therefore, in the following these coatings were named as (Al,Cr_L)N/(Al,Cr_L)₂O₃. The coating time of functional layer t_f was varied in two coating processes to analyze the effect of functional layer thickness s_f on the adhesion strength, Table 5.6. The graded (Al,Cr_L)N interlayer with the highest adhesion strength in subchapter 5.2.3 was chosen.

Table 5.6: Process parameters of (Al,Cr_L)N/(Al,Cr_L)₂O₃ system

Coating step	Interlayer	Functional layer	
Process parameters	(Al,Cr _L)N	(Al,Cr _L) ₂ O ₃	
Process ID		4534	4535
Target configuration	TCL	TCL	TCL
Cathode power P_C in kW	6	6	6
Cathode current I_C in V	15	15	15
Bias voltage U_B in V	-125	-175	-175
Bias current I_B in A	3	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000	8,000
O ₂ gas flow Q_{O_2} in sccm	-	80	80
N ₂ gas flow Q_{N_2} in sccm	0-800	-	-
Pressure p in Pa	33.7-33.9	33.4	33.4
Heater temperature T_H in °C	640 ± 10	640 ± 10	640 ± 10
Substrate temperature T_s in °C	550 ± 15	550 ± 15	550 ± 15
Rotation speed ω_{Table} in rpm	-	-	-
Interlayer/functional layer t_f/t_i coating time in min	20	60	90

The scratch and Rockwell indentation tests were performed as described in subchapter 5.2.3. The aim was to choose the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ variation with the highest adhesion strength on X40CrMoV5-1 substrate for further analysis at high temperatures. Since the total coating thickness s_t exceeds the allowed range in used DIN norms of the Rockwell and scratch tests, the imprints were qualified and not quantified to $HF1-5$ and $L_{C1}-L_{C3}$, respectively.

5.3.2 Influence of oxide functional layer thickness on the coating and compound adhesion properties of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$

Figure 5.11 shows the SEM images of the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings in an as-deposited state. The interlayer thickness s_i and the thickness of functional oxide layer s_f are also added in Figure 5.11. The coatings demonstrate dense and columnar morphologies. The oxide functional layer shows a promising bonding to the graded interlayer. Moreover, $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings also exhibit strong bonding at the interface to the substrate regardless of the total coating thickness.

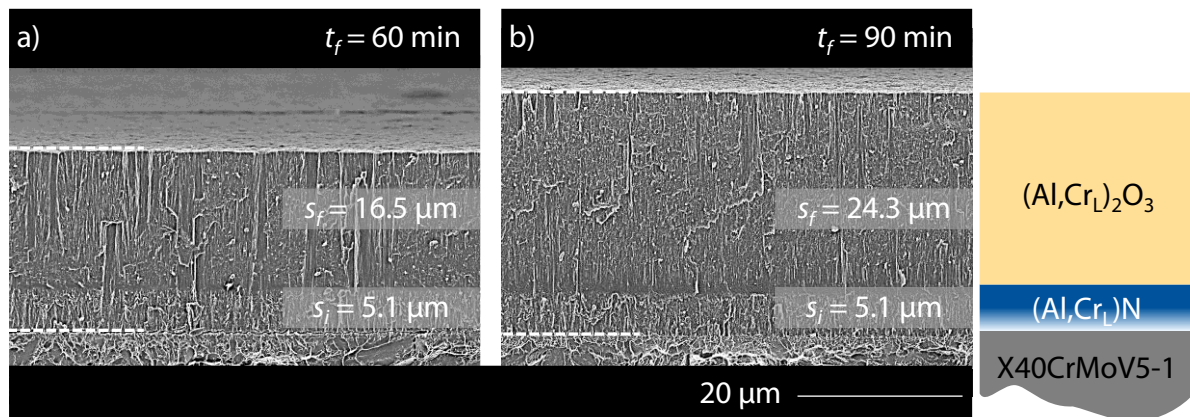


Figure 5.11: SEM cross-section images of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings deposited by

a) $t_f = 60$ min and b) $t_f = 90$ min [BKM+23]

The coating indentation hardness, indentation modulus, elastic work percentage, and average line roughness Ra of both coating variants are listed in Table 5.7. The metallic element contents, analyzed by EDX, are also given in Table 5.7. The coatings demonstrate comparable properties regarding chemical composition and indentation values. However, a slight increase in roughness is visible with increasing thickness. Compared to $(\text{Al,Cr}_L)_2\text{O}_3$ coatings without interlayer in Table 5.2, $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings show a slight increase in Cr content. This can be attributed to the additional interlayer deposition step. During this step, Al exhibits a

higher tendency to react with the reactive gas than Cr, leading to more pronounced target poisoning of the Al target. As a result, the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings contain a higher Cr content than the single layer $(\text{Al,Cr}_L)_2\text{O}_3$ coatings. This hypothesis is discussed by EDX line scans, shown in subchapter 5.5.1.

Table 5.7: Coating properties of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ system in as-deposited state

Coating	$t_f = 60 \text{ min}$	$t_f = 90 \text{ min}$
H_{IT} in GPa	15.2 ± 0.7	14.1 ± 0.6
E_{IT} in GPa	218.9 ± 6.3	209.1 ± 5.4
η_{el} in %	49	48
x_{Al} in at.-%	88 ± 0	86 ± 1
x_{Cr} in at.-%	12 ± 0	14 ± 1
Ra in μm	0.05	0.07

The adhesion strength between the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings and X40CrMoV5-1 was qualitatively investigated using the Rockwell indentation test, as presented in Figure 5.12. A adhesion classification in groups of HF 1 to HF 6 is again not valid since the thickness of coatings exceeds the thickness limitation of $s = 10 \mu\text{m}$ as defined in DIN 4856. However, comparing the kind and severity of the observed failures allowed for a qualitative evaluation of the compound adhesion.

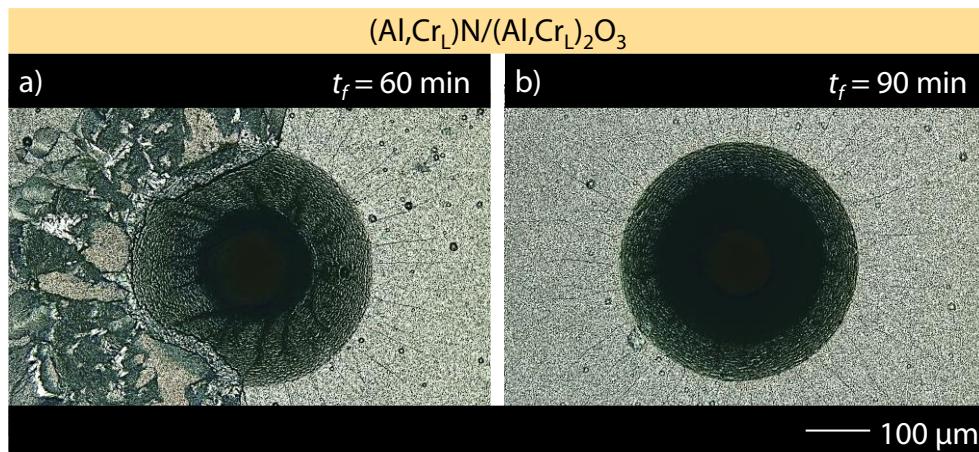


Figure 5.12: CLSM images of Rockwell imprints of samples coated by a) $t_f = 60 \text{ min}$ and b) $t_f = 90 \text{ min}$ [BKM+23]

Coated samples with a thinner functional layer show several delamination at the edge of the Rockwell imprint. In contrast, with increasing thickness of the functional layer higher adhesion strength is visible, since no obvious spalling has been observed.

Moreover, scratch tests following DIN EN ISO 20502 were carried out to evaluate the coating adhesion on steel X40CrMoV5-1. However, a classification to L_{C1-C3} is not carried out, since the coating thickness is $s_f > 20\ \mu\text{m}$. Instead, the applied normal forces are given to compare the adhesion strength behavior of the coated samples in Figure 5.13.

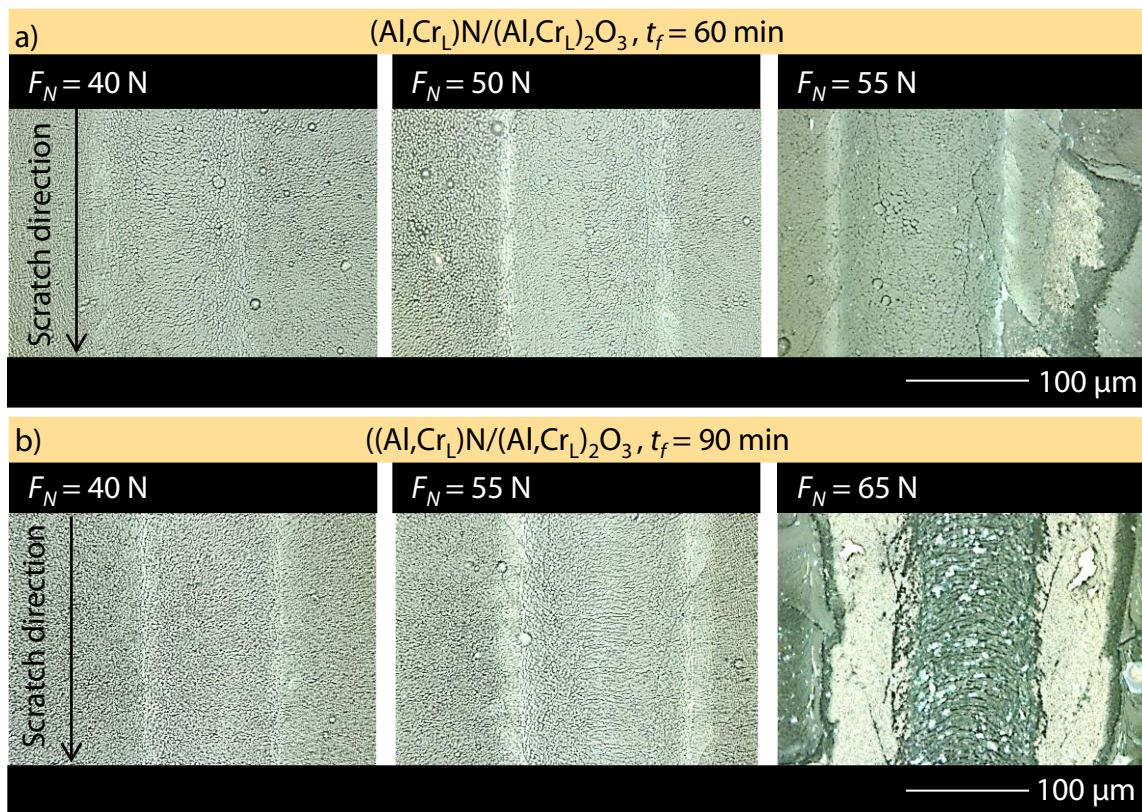


Figure 5.13: CLSM images of scratch tracks with a) $t_f = 60\text{ min}$ and b) $t_f = 90\text{ min}$ [BKM+23]

Under a normal force of $F_N = 55\text{ N}$, the scratch track reveals spallation at the edge of the scratch track for $t_f = 60\text{ min}$, as can be seen in Figure 5.13 a). In contrast, the scratch track of $t_f = 90\text{ min}$ demonstrates just cracks and no spallation is visible under the same condition, as shown in Figure 5.13 b). The results show that the functional layer thickness also affects the compound adhesion of $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ coatings on the substrate under dynamic loading. Analogous to Rockwell indentation tests, coated samples with higher thickness also demonstrate higher

compound adhesion in scratch tests. It can be assumed that the increase of s_f positively influences the compound adhesion. As other coating properties of both samples are almost comparable, this observation may be the result of the varied residual stress state in the coatings due to the thickness differences. This aspect will be discussed in chapter 5.4. Despite a high coating thickness of up to $s_t \approx 30\ \mu\text{m}$, the coatings show a high adhesion strength to the X40CrMoV5-1 hot work steel.

5.4 Residual stresses in HS-PVD coatings

In the following chapter, the residual stress state in $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings deposited using HS-PVD is investigated. The analysis of compound adhesion strength in subchapter 5.3 shows enhanced adhesion strength with increasing coating thickness on the X40CrMoV5-1 substrate. The coating properties, such as chemical composition, morphology, and indentation hardness, are comparable and independent of coating thickness, as presented in subchapter 5.3. It is assumed that the process-specific properties of HS-PVD described in subchapter 2.2 could affect residual stress. In this context, the residual stress in coatings with different thicknesses was examined. Additionally, different substrates were used to determine whether this effect could be observed independently of substrate material. The $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coated X40CrMoV5-1 and WC-Co were analyzed. Coatings were deposited in the same process batch with the identical coating parameters from Table 5.6. The following investigations focused on the correlations of coating properties, adhesion strength, and residual stress.

5.4.1 Analysis of residual stress by XRD using $\sin^2\psi$ method

Residual stress measurements of the coatings were performed by application of the $\sin^2\psi$ -method on a General Electric diffractometer type Seifert XRD 3003 ETA, equipped with Co-K α radiation. These measurements were conducted at the Institute of Production Engineering and Machine Tools (IFW), Leibniz Universität Hannover, Germany. A peak of (440) for oxide coatings deposited on steel substrates and a peak of (400) for oxide coatings deposited on WC-Co substrates were measured. These peaks selected for residual stress measurements are chosen to avoid overlapping with those of the X40CrMoV5-1 and WC-Co substrate. A total of 15 scans were measured per azimuth direction $\Phi = 0^\circ$ and $\Phi = 90^\circ$. The residual stress was analyzed using the software “RAYFLEX Analyze” by Seifert. The residual stress was determined in the X-ray analysis based on the lattice strain. Based on Hooke's law [Ryc84], these lattice strains ε are proportional to the existing residual stresses σ . The proportionality constant here

is the modulus of elasticity E . The quantities in the equation of Hooke's law are tensors. Assuming that the coating is an elastically isotropic material, the elastic behavior can be simplified by S_I and $\frac{1}{2}S_2$. The values S_I and $\frac{1}{2}S_2$ are then calculated respectively by Equation 5.1 and Equation 5.2, from the indentation moduli analyzed using the nanoindentation and Poisson's ratio.

$$\frac{1}{2}S_2 = \frac{(1+\nu)}{E} \quad \text{Equation 5.1}$$

$$S_I = -\left(\frac{\nu}{E}\right) \quad \text{Equation 5.2}$$

S_I, S_2 : First and second X-ray elastic constant

E : Modulus of elasticity

ν : Poisson's ratio

The indentation modulus E_{IT} were measured using nanoindentation as described in chapter 4.2. Subsequently, the residual stresses were calculated using the relationship between the elastic behavior and the lattice strain. The calculated maximum penetration depth τ_{max} , based on the X-ray Mass Attenuation coefficient μ of the used Co-K α radiation, was determined using Equation 5.3 [STS+09]:

$$\tau_{max} = \frac{1}{2\mu} \cdot \sin\theta \quad \text{Equation 5.3}$$

Maximum penetration depth of $\tau_{max,440} = 17.0 \mu\text{m}$ and $\tau_{max,400} = 12.9 \mu\text{m}$ were determined. The density of the coating $\rho = 3.65 \text{ g/cm}^3$ was calculated. The density is usually determined experimentally, but there is also the possibility of estimating the density based on crystallographic data, as discussed in [Sim13].

5.4.2 Correlation of residual stress with coating and adhesion properties

The morphology of the coatings is illustrated in Figure 5.14. SEM cross-sectional images illustrate a fine columnar morphology of coatings deposited on both substrate materials. A gap in coating/WC-Co interface is visible, indicating a poor bonding of (Al,Cr_L)N interlayer to the WC-Co substrate. This was to be expected, as the focus of adhesion enhancement in

subchapter 5.2 was on the steel X40CrMoV5-1 substrate and not on the WC-Co. The coatings deposited on the WC-Co substrates are thinner than those deposited on the steel substrate. Since the deposition time was the same and substrates were coated in the same coating batch, the observed differences in coating thickness suggest that substrate material may influence the coating growth rate. In this case, the coating growth rate is higher for coatings deposited on X40CrMoV5-1 substrate.

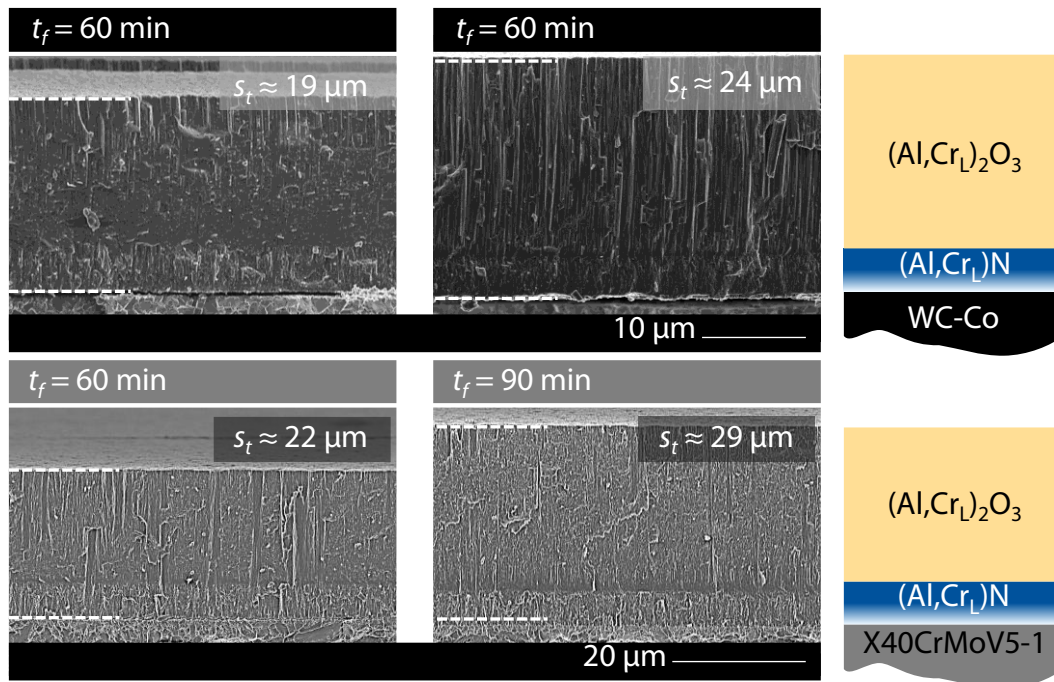


Figure 5.14: Morphology of coatings on WC-Co and X40CrMoV5-1 substrates [BKM+24b]

No significant change in indentation hardness H_{IT} is determined by increasing the coating thickness on both substrate materials, Table 5.8. However, a higher percentage of elastic work as well as a higher indentation hardness and modulus is measured on the WC-Co substrate compared to the steel substrate. Coatings deposited on WC-Co show a slight increase of the indentation modulus E_{IT} and elastic work percentage η_{IT} as the coating thickness increases. However, these values stay comparable for coatings deposited on the steel substrate when the thickness is increased.

Table 5.8: Nanoindentation values of oxide coatings on different substrates

Substrate material	WC-Co		X40CrMoV5-1	
Functional coating time t_f	60 min	90 min	60 min	90 min
H_{IT} in GPa	21 ± 1	22 ± 1	15.2 ± 0.7	14.1 ± 0.6
E_{IT} in GPa	247 ± 9	261 ± 7	218.9 ± 6.3	209.1 ± 5.4
η_{el} in %	57	63	49	48

The compound adhesion strength of the oxide coatings with different thicknesses on the WC-Co substrate was analyzed using Rockwell indentation and scratch tests. The CLSM micrographs are illustrated in Figure 5.15. The adhesion strength classifications HF 1 – HF 6 are not valid, since coating thicknesses of $s > 10$ μm are not included in DIN 4856. A qualitative evaluation of the Rockwell imprints was performed in this case. For the sample with a lower coating thickness, a complete delamination of the coating from the substrate can be observed around the Rockwell imprint. In comparison, the sample with a higher coating thickness shows cohesive failure at the edge of the Rockwell imprint. A complete delamination of the coating from the substrate was not found in this case.

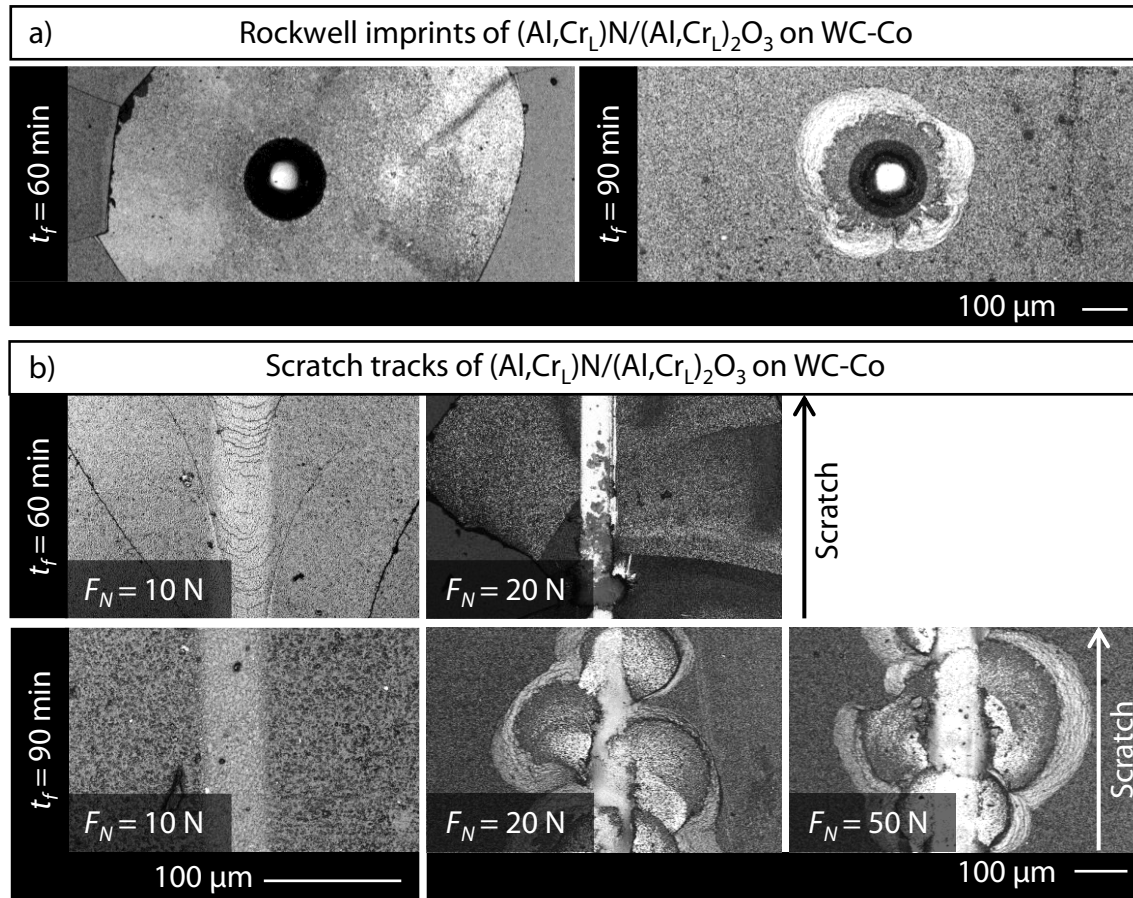


Figure 5.15: CLSM micrographs of a) Rockwell indentation imprints and b) scratch tracks on oxide/WC-Co compounds [BKM+24b]

For the scratch test results, the classification L_{C1-C3} is not valid because of the high thickness $s > 20\ \mu\text{m}$ of the investigated coatings. At a normal scratch force of $F_N = 10$ N, cracks are found at the edge of the scratch track for the sample with a lower coating thickness. In contrast, only plastic deformation is observed for the samples with a higher thickness. Under a normal scratch force of $F_N = 20$ N, a wider area with coating delamination is found for the samples with a lower thickness compared to a higher thickness. Under a higher normal force of $F_N = 50$ N, a large area of exposed substrate due to coating delamination is not observed for samples with higher thickness. Overall, the results of the compound analysis show a low adhesion strength of the oxide coating on the WC-Co substrate. However, coatings with higher thickness exhibit less severe failure compared to thinner coatings. The same behavior was also observed for these coatings deposited on the steel substrate as discussed before in subchapter 5.3.

The residual stress analysis of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings on both substrate materials was performed using XRD. The XRD patterns are shown in Figure 5.16. The coating peaks refer to $\gamma\text{-Al}_2\text{O}_3$ and are marked as dashed lines. The WC-Co and X40CrMoV5-1 substrate peaks are labeled as “s” in the diagram. The peak (440) is considered for the analysis of residual stresses of oxide coatings on the steel substrate. As evident from the XRD patterns, this peak is at the same position as the WC-Co substrate peak. Therefore, the peak (400) is considered for the analysis of residual stresses of coatings deposited on the WC-Co substrate.

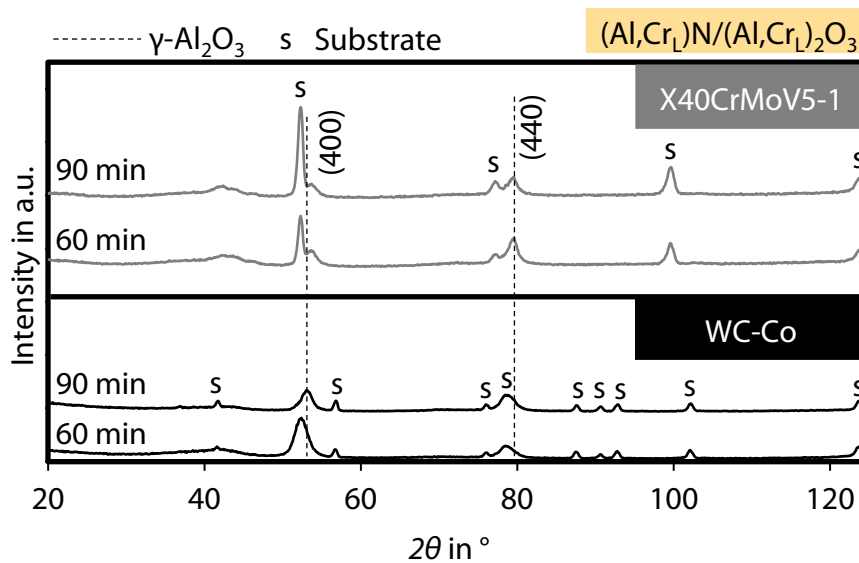


Figure 5.16: XRD patterns of coatings on both substrate materials [BKM+24b]

The coatings depict compressive residual stress, as shown in Figure 5.17. With higher coating thickness a reduction in the compressive residual stress is visible, irrespective of the substrate material. Moreover, significantly higher compressive residual stress is measured for the coatings deposited on WC-Co. The significant reduction in compressive stress observed for thicker coatings on WC-Co compared to steel can be attributed to differences in plastic deformation behavior, substrate stiffness, and stress distribution mechanisms, as also discussed in [SBK+18]. The WC-Co substrate's higher yield strength and stiffness limit plastic deformation, leading to a higher initial stress buildup in coatings. Thicker coatings on hot work steel experience stress relaxation due to plastic deformation in the substrate interface, which could lead to a minimal change in residual stress between thin and thick coatings. In contrast, WC-Co's higher yield strength limits plastic deformation, resulting in more pronounced differences.

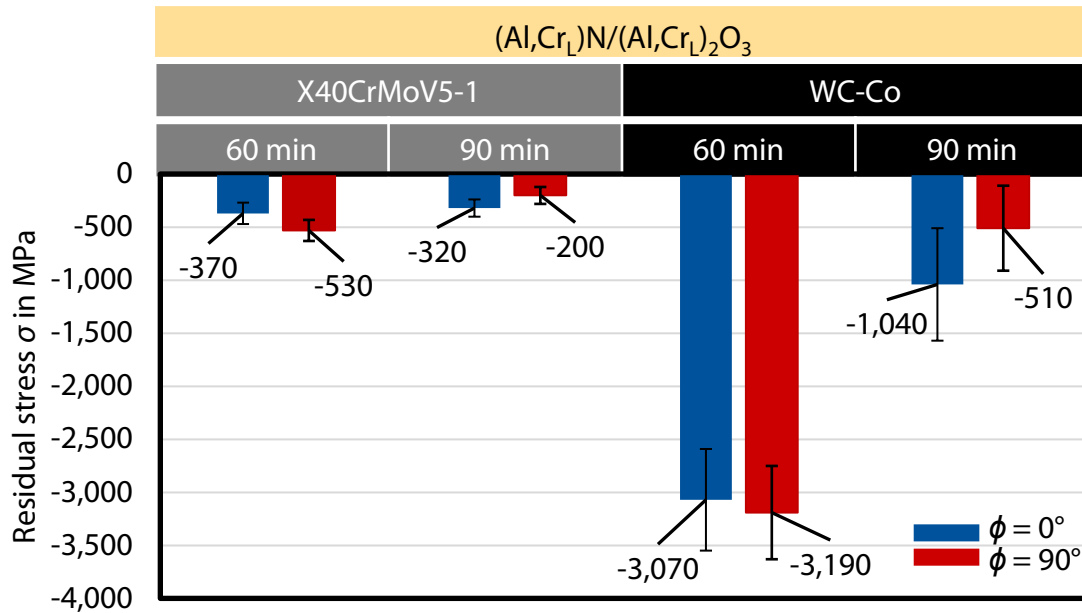


Figure 5.17: Residual stress state on different substrates via XRD [BKM+24b]

5.4.3 Intermediate conclusion of residual stress in HS-PVD coatings

Residual stress measurements via XRD confirm the presence of compressive residual stress in the thick HS-PVD coatings with total thickness up to $s_t \approx 29 \mu\text{m}$. An increase in coating thickness leads to a reduction in compressive residual stress irrespective of substrate material. Moreover, coatings show different adhesion strength to substrate depending on the substrate material. Since the coating morphology, chemical composition and indentation values are almost comparable, this observation indicates the dominant effect of residual states on compound adhesion properties. Moreover, significantly higher compressive residual stress is observed in coatings on WC-Co compared to X40CrMoV5-1. As the morphology and chemical composition of the coatings deposited on both substrates are comparable, the higher indentation hardness and modulus on WC-Co can be attributed to the higher compressive residual stress. The reduced adhesion strength of the coatings on WC-Co can be explained by the higher indentation hardness and modulus results from the higher compressive residual stress on WC-Co compared to X40CrMoV5-1.

5.5 High temperature properties depending on Cr content

To analyze the effect of chromium content on the properties of $(\text{Al,Cr})_2\text{O}_3$ coatings with an AlCrN interlayer under high temperatures $T \geq 1,000^\circ\text{C}$, two coating variants were chosen. The Beside the $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coatings, deposited using the TCL with the lowest target content, $(\text{Al,Cr}_H)\text{N}/(\text{Al,Cr}_H)_2\text{O}_3$ coatings were deposited by TCH with the highest number of Cr

target. The (Al,Cr_L)N/(Al,Cr_L)₂O₃ coating with thicker functional layer was selected for further investigations by annealing tests due to its higher compound adhesion strength on steel substrate, as shown in subchapter 5.3. Since the (Al,Cr_H)₂O₃ system exhibits the highest indentation hardness, which could be beneficial for wear resistance, its high temperature properties are also important to investigate. A nitride (Al,Cr_H)N interlayer was also deposited as an adhesion layer for the functional oxide coating. The coating parameters were comparable to the (Al,Cr_L)N/(Al,Cr_L)₂O₃ system and listed in Table 5.9.

Table 5.9: Coating parameters of (Al,Cr_H)N/(Al,Cr_H)₂O₃ system deposited in dc mode

Process ID	4692	
Coating step	Interlayer	Functional layer
Process parameters	(Al,Cr _H)N	(Al,Cr _H) ₂ O ₃
Target configuration	TCH	TCH
Cathode power P_C in kW	6	6
Cathode current I_C in V	15	15
Bias voltage U_B in V	-125	-175
Bias current I_B in A	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000
O ₂ gas flow Q_{O_2} in sccm	-	80
N ₂ gas flow Q_{N_2} in sccm	0-800	-
Pressure p in Pa	33.7-33.9	33.4
Heater temperature T_H in °C	640 ± 10	640 ± 10
Substrate temperature T_s in °C	550 ± 15	550 ± 15
Rotation speed ω_{Table} in rpm	-	-
Interlayer/functional layer t_f/t_i coating time in min	20	90

High temperature behavior was investigated by annealing tests in vacuum at $T_{vac.} = 1,000$ °C and $T_{vac.} = 1,200$ °C for $t_{vac.} = 1$ h in a high vacuum furnace, PVA TePla AG, Wetztenberg, Germany. Considering the addressed application of coatings in this study, during primary shaping processes such as HPDC, the mold is actively cooled, however the coating surface is in direct contact with the molten steel. Due to the high temperatures in addressed application, these such high temperatures were considered to analyze the behaviors of coatings. After loading the vacuum furnace with coated samples, the chamber was evacuated until a base pressure of $p = 5 \cdot 10^{-6}$ mbar was reached. Subsequently, the samples were heated up to the desired

temperature with a heating rate of $dT/dt \approx 7$ °C/min. Once the desired annealing temperature was attained, the temperature was kept constant for $t_{vac.} = 1$ h. During the annealing period the pressure inside the furnace was kept lower than $p \leq 5 \cdot 10^{-5}$ mbar. Finally, the annealed sample was cooled down in vacuum slowly, with a cooling rate of $dT/dt \approx 4$ °C/min. After annealing tests, the coated samples were embedded in epoxy resin, so that cross-sections of the annealed samples could be investigated by SEM. Moreover, elemental mappings with EDX were carried out to examine the diffusion behavior. For this purpose, a Phenom XL SEM, Thermo Fisher Scientific, Waltham, USA, with an EDX detector was utilized. Thereby, the diffusion behavior of Al, Cr, N, and O was the focus of EDX mappings after the annealing tests. Moreover, annealing tests in atmosphere were conducted at $T_{atm.} = 800$ °C and $T_{vac.} = 900$ °C and $T_{atm.} = 1,000$ °C for $t_{vac.} = 1$ h. The annealing tests in atmosphere were carried out by RTH 52 16S, Nabertherm GmbH, Germany. The results of the annealing tests are discussed separately for AlCrN/(Al,Cr)₂O₃ coatings named as Al-rich (Al,Cr_L)N/(Al,Cr_L)₂O₃ and (Al,Cr_H)N/(Al,Cr_H)₂O₃ coating considered as Cr-rich in the following two subchapters.

5.5.1 Al-rich (Al,Cr_L)N/(Al,Cr_L)₂O₃ coating

The chemical composition of the functional layer analyzed. The elemental content of $x_{Al} \approx 33$ at.-%, $x_{Cr} \approx 6$ at.-%, and $x_O \approx 61$ at.-% is determined by EPMA in the as-deposited state. Considering the metallic elements, the coatings show $x_{Al} \approx 85$ at.-% and $x_{Cr} \approx 15$ at.-%, representing the EDX analysis in Table 5.7. The SEM micrographs of polished and embedded samples in an as-deposited state and after annealing tests in vacuum are shown in Figure 5.18.

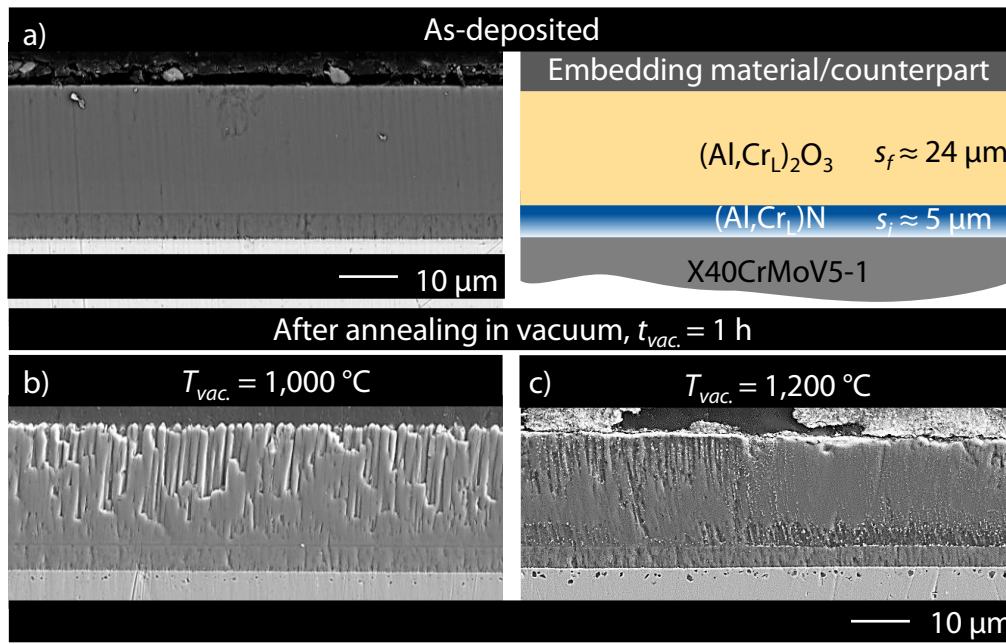


Figure 5.18: SEM micrographs of a) as-deposited state and annealed samples for $t_{vac.} = 1$ h at b) $T_{vac.} = 1,000^\circ\text{C}$ and c) $T_{vac.} = 1,200^\circ\text{C}$ [BKM+23]

In Figure 5.18 a), the dense columnar structure in the as-deposited state is not as clearly visible as in the fractural cross-section images in Figure 5.18 b) due to the polished cross-sections prepared after embedding. However, the initial columnar structure is visible for both samples after annealing tests in vacuum for $t_{vac.} = 1$ h at $T_{vac.} = 1,000^\circ\text{C}$ and $T_{vac.} = 1,200^\circ\text{C}$ in Figure 5.18 b-c). In addition, smooth areas can also be detected in the coating zone, which again results from sample polishing preparation before SEM analyses. In the outer region of the functional layer, widening and separation of columns are visible after annealing at $T_{vac.} = 1,000^\circ\text{C}$, Figure 5.18 b). This is attributed to the phase transformations during annealing. In atmosphere, the widening and separation of columns are a free path for oxygen diffusion at high temperatures. The oxidation protection of the substrate can be limited by this morphology change. However, neither within the $(\text{Al,Cr})_2\text{O}_3$ functional layer nor within the AlCrN interlayer, defects such as pores and crack formations can be observed. The functional layer also shows a promising bonding to the interlayer after annealing tests up to $T_{vac.} = 1,200^\circ\text{C}$. The thickness change and separation of the interlayer into different zones after annealing under the same conditions cannot be determined, unlike the metallic AlCr interlayer in prior studies [BBK+19]. Figure 5.19 shows the phase composition of the coating before and after annealing in vacuum for $t_{vac.} = 1$ h.

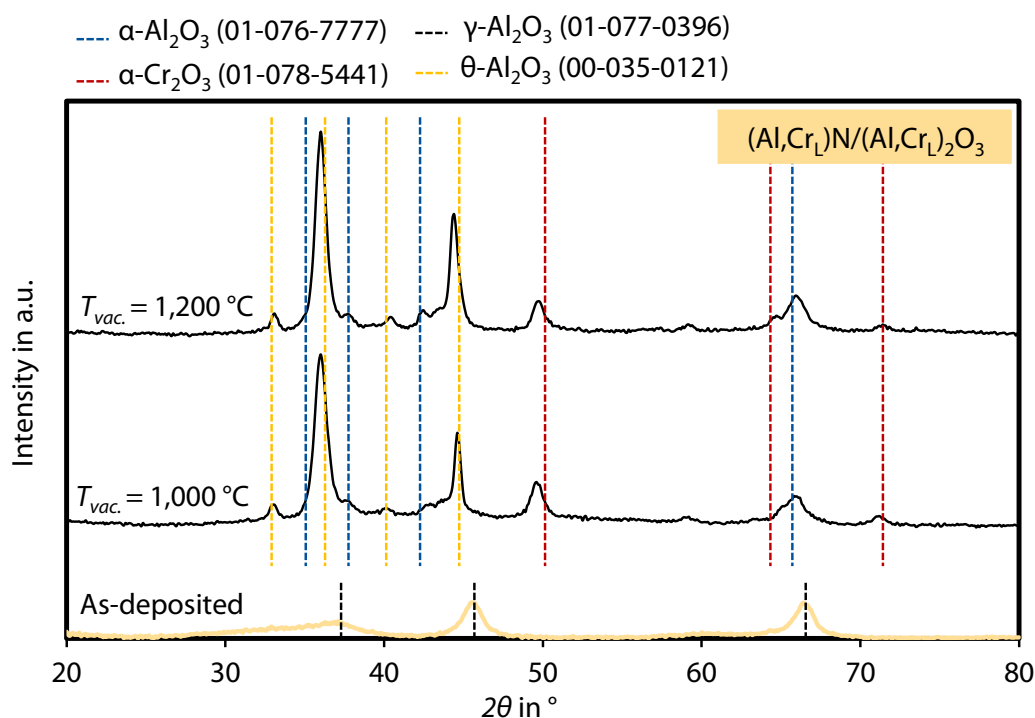


Figure 5.19: Effect of annealing in vacuum on the phase composition of $(\text{Al,Cr})\text{N}/(\text{Al,Cr})_2\text{O}_3$ coatings [BKM+23]

In the as-deposited state, peaks are assigned to $\gamma\text{-Al}_2\text{O}_3$. After annealing at $T_{\text{vac.}} = 1,000^\circ\text{C}$, the characteristic peaks of $\alpha\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ are visible, whereas no γ -phase can be detected. This indicates a complete phase transformation of $\gamma\text{-Al}_2\text{O}_3$ during annealing at $T_{\text{vac.}} = 1,000^\circ\text{C}$. The absence of a crystalline Cr_xO_y phase in the as-deposited state suggests that Cr is bonded in an amorphous phase. In contrast, additional peaks are detected after annealing, which are assigned to crystalline $\alpha\text{-Cr}_2\text{O}_3$. The formation of α - and $\theta\text{-Al}_2\text{O}_3$ is associated with densification and volume shrinkage due to their higher crystallographic density compared to the γ -phase. This is consistent with the observed columnar widening and separation in the outer regions of the functional layer, as shown in Figure 5.18 b). By increasing the annealing temperature to $T_{\text{vac.}} = 1,200^\circ\text{C}$, additional peaks are not observed. This indicates the stability of the preformed crystalline Cr_2O_3 and Al_2O_3 phases. However, the intensity of the peaks slightly increases after annealing at $T_{\text{vac.}} = 1,200^\circ\text{C}$. The SEM cross-sections of the annealed samples in Figure 5.18 show that despite the phase transformation, no visible defects such as cracks or delamination owing to thermally induced stress can be determined.

The nanoindentation values after annealing tests in vacuum are presented as box plots in Figure 5.20 a-b). After annealing at $T_{vac.} = 1,000$ °C in vacuum an indentation hardness of $H_{IT} = (18.7 \pm 1.3)$ GPa and an indentation modulus of $E_{IT} = (220.9 \pm 11.5)$ GPa were measured. Thereby, a significant increase compared to the as-deposited state, with $H_{IT} = (14.1 \pm 0.6)$ GPa and $E_{IT} = (209.1 \pm 5.4)$ GPa, is noticeable. This enhancement is likely due to the formation of additional crystalline phases in the coating after annealing, as confirmed by the phase analysis, shown in Figure 5.19. In addition, thermally induced sintering and volume shrinkage associated with phase transformations may also contribute to the enhanced indentation values. In contrast, annealing at higher temperature of $T_{vac.} = 1,200$ °C resulted in comparable values to the as-deposited state, as depicted in Figure 5.20 a-b). A possible explanation for this could be grain growth in the coating after annealing, as also observed in [YSS19]. Grain growth may exert a dominant influence, reducing hardness values despite the presence of more crystalline phases. Another possible reason for the reduced hardness could be microcracks in the microstructure that are not detectable by SEM-images in Figure 5.18 b).

While the elastic work percentage of $\eta_{el} = 50$ % remains constant after the annealing at $T_{vac.} = 1,200$ °C, it increases slightly to $\eta_{el} = 54$ % at $T_{vac.} = 1,000$ °C. Moreover, load-displacement curves indicate homogeneous development during loading and unloading for annealed samples, Figure 5.20 c). Hereby, no visible fluctuating development of the load-displacement curves can be noticed, unlike the behavior observed in (Al₇₁Cr₂₉)₂O₃ coatings after annealing already at $T_{vac.} = 600$ °C in previous works [BBK+19]. SEM cross-sections in Figure 5.18 show that the functional layer and interlayer exhibit no inhomogeneities within the morphology after annealing at high temperatures up to $T_{vac.} = 1,200$ °C.

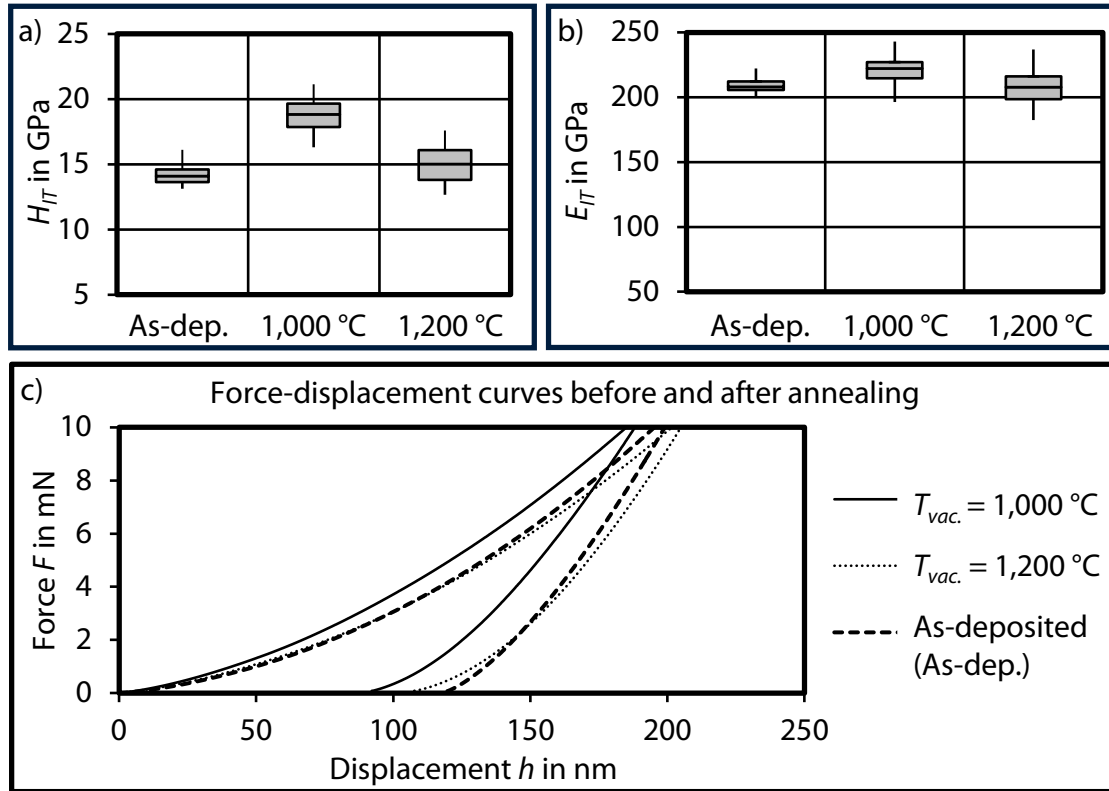


Figure 5.20: Box plot of a) indentation hardness H_{IT} , b) indentation modulus E_{IT} and c) force displacement curves of $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coating before and after annealing [BKM+23]

The element distribution is analyzed by EDX mappings to investigate the elemental diffusion behavior, particularly concerning the AlCrN interlayer as well as thermally induced changes of the chemical composition after annealing. Figure 5.21 a-b) depicts the corresponding EDX mapping results in an as-deposited state and after annealing at $T_{vac.} = 1,000^\circ\text{C}$ in vacuum. To identify the substrate and various coating regions, a cross-sectional SEM image is presented in Figure 5.21. Concerning the elementary distribution in as-deposited and after annealing at $T_{vac.} = 1,000^\circ\text{C}$, no iron diffusion from the steel substrate into the interlayer or functional layer is observed after annealing. A homogeneous distribution of Al and Cr is evident within both the top layer and the interlayer. Additionally, chromium, as an alloying element, is uniformly distributed throughout the steel substrate. Considering the aluminum content, minimal diffusion of Al into the substrate is indicated by a red zone in the peripheral area adjacent to the interlayer. Despite this, Al remains still homogeneously distributed in the interlayer, with no Al-deficient regions observed.

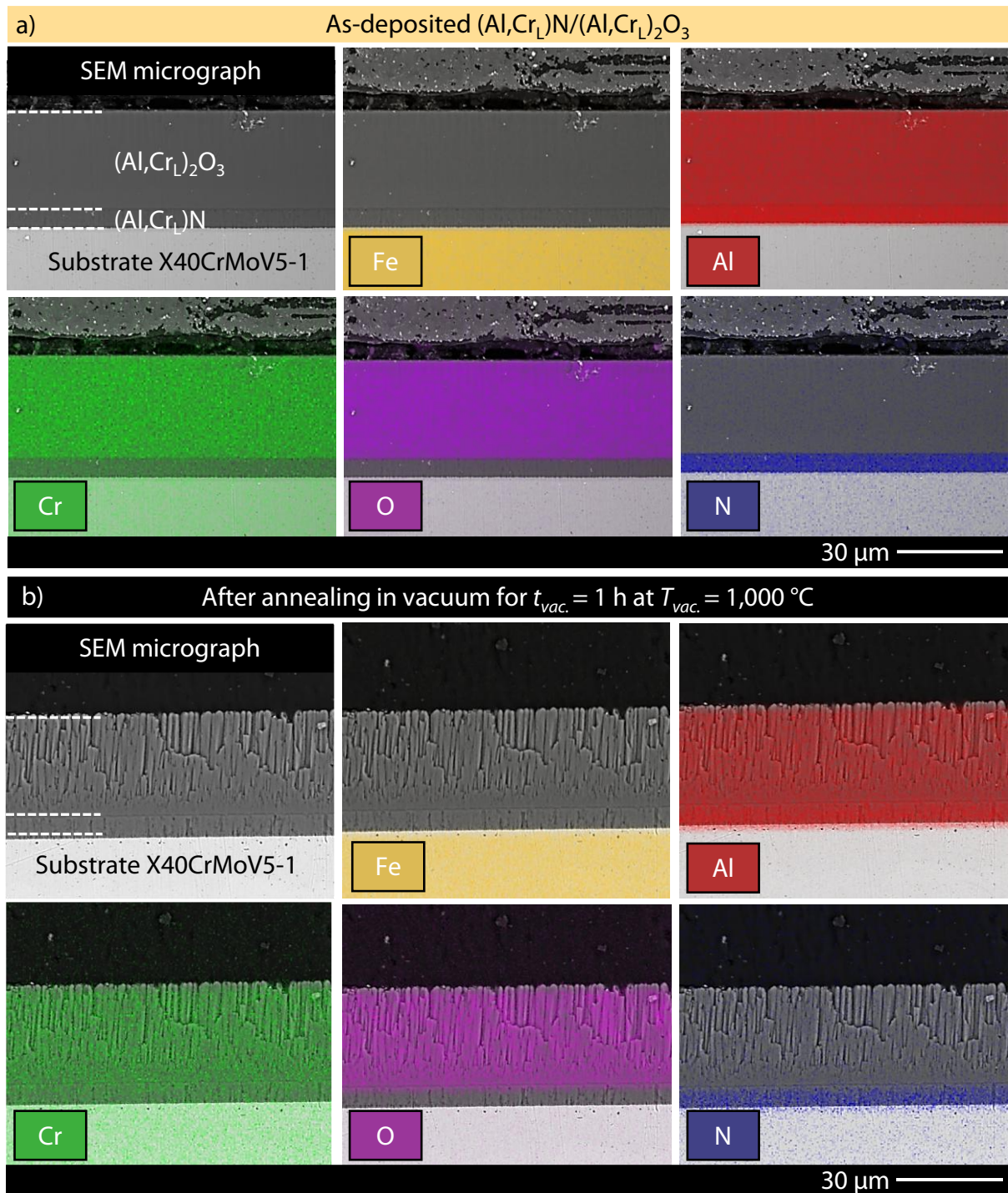


Figure 5.21: Elementary diffusion behavior a) before and b) after annealing $T_{vac.} = 1,000^\circ\text{C}$ in vacuum [BKM+23]

Similarly, oxygen is uniformly distributed in the functional layer. However, oxygen is detected in the interlayer, suggesting the diffusion of oxygen into the interlayer. EDX mapping further reveals a homogeneous distribution of nitrogen within the interlayer. Nitrogen is also detected

in the substrate, which is attributed to diffusion processes. Despite these findings, no chemical separation of the interlayer into distinct zones is observed after annealing at $T_{vac.} = 1,000^\circ\text{C}$.

Similar investigations were conducted on a coated sample annealed in vacuum at $T_{vac.} = 1,200^\circ\text{C}$. The corresponding EDX mappings are illustrated in Figure 5.22. As seen in the sample annealed at $T_{vac.} = 1,000^\circ\text{C}$, a uniform distribution of Al and Cr is also retained in the functional layer and interlayer at $T_{vac.} = 1,200^\circ\text{C}$. No Al- or Cr-enriched layers, as reported in [BBK+19] are observed for the $(\text{Al,Cr})_2\text{O}_3$ functional layer in this study.

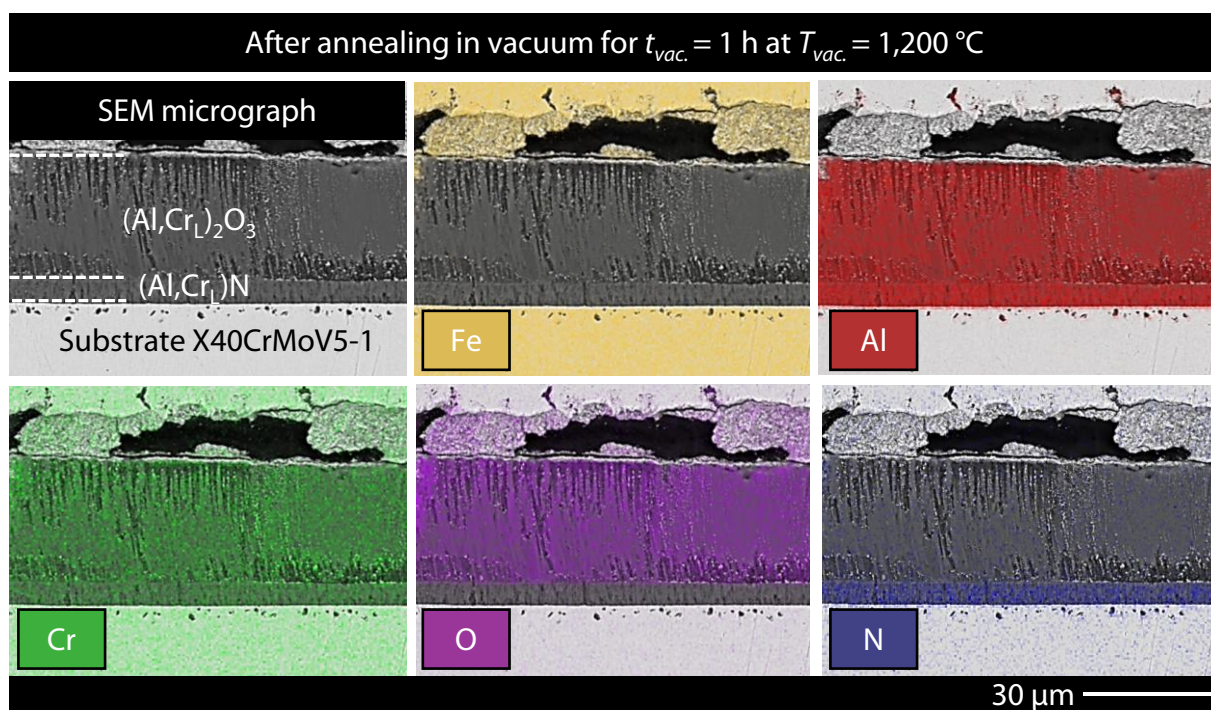


Figure 5.22: EDX mappings after annealing $T_{vac.} = 1,200^\circ\text{C}$ in vacuum [BKM+23]

The Al-rich zone previously detected in the substrate disappears after annealing at $T_{vac.} = 1,200^\circ\text{C}$. Moreover, the interlayer shows no oxygen. Oxygen is instead evenly distributed throughout the functional layer. Similarly, nitrogen shows an almost uniform distribution within the interlayer zone. Even under high thermal load, both layers remain well-bonded to the substrate. Moreover, small voids in substrate are visible. The reason of void's formation in substrate is not clear. Moreover, EDX line scans are conducted on the same samples before and after annealing, as shown in Figure 5.23.

Concerning the chemical composition in as-deposited and after annealing tests, no iron diffusion from the steel substrate into the interlayer or functional layer is observed. This is within good agreement with EDX mappings. Therefore, the voids in substrate cannot be related to the iron diffusion towards coating. EDX line scan shows that the Al content reduces slightly from interlayer to top layer in as-deposited state. This can confirm the hypothesis, discussed in subchapter 5.3.2, regarding the increased Cr content in $\text{AlCrN}/(\text{Al,Cr})_2\text{O}_3$ compared to monolayer $(\text{Al,Cr})_2\text{O}_3$ coatings. In addition, a decrease in the Al content within the interlayer can be observed. The Al content homogenizes in the interlayer after the annealing tests. No significant interdiffusion of Fe and Al between the coating and substrate can be detected.

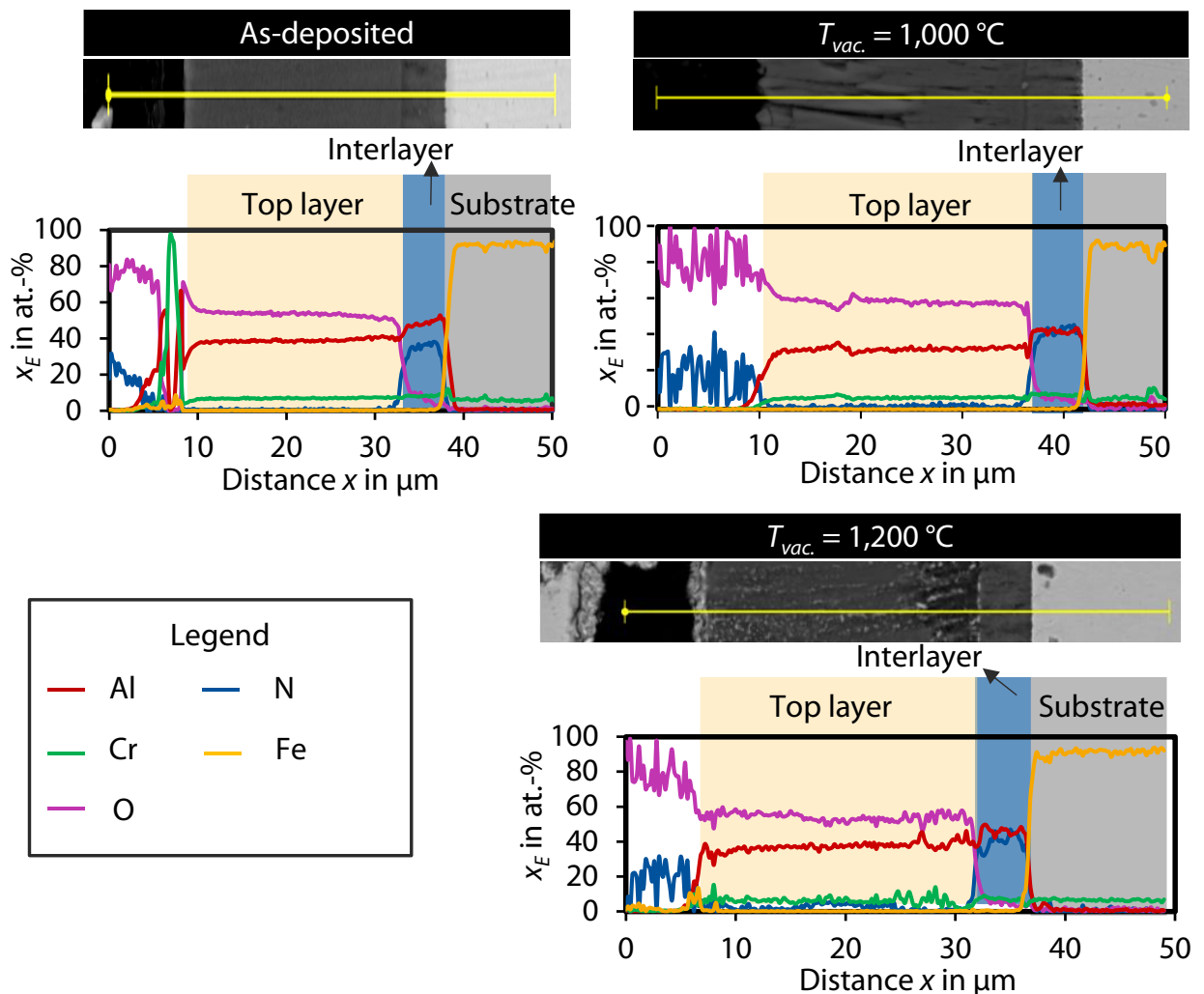


Figure 5.23: EDX line scans of the coated samples before and after annealing test in vacuum

Compound adhesion strength properties

The adhesion strength between the Al-rich $(\text{Al,Cr}_L)\text{N}/(\text{Al,Cr}_L)_2\text{O}_3$ coating and the X40CrMoV5-1 substrate was also investigated after annealing in a vacuum using Rockwell indentation and scratch test. The results are shown as an example in Figure 5.24. The substrate material tempered to a hardness of $H \approx 53$ HRC becomes softer after annealing tests in vacuum, $H \approx 43$ HRC, comparing the Rockwell indentations before and after annealing, Figure 5.24 a). Nevertheless, the results of the Rockwell indentation test after annealing at $T_{vac.} = 1,000^\circ\text{C}$ in vacuum only shows cohesive failure at the edge of the Rockwell imprints, without large-scale delamination of the coating from the substrate or adhesive failure. The results of the scratch test after annealing at $T_{vac.} = 1,200^\circ\text{C}$ in vacuum are shown as an example in Figure 5.24 b). These also exhibit substrate exposure in the scratch track at normal force of $F_N = 80$ N. compared to the as-deposited state with $F_N = 65$ N, Figure 5.13 b).

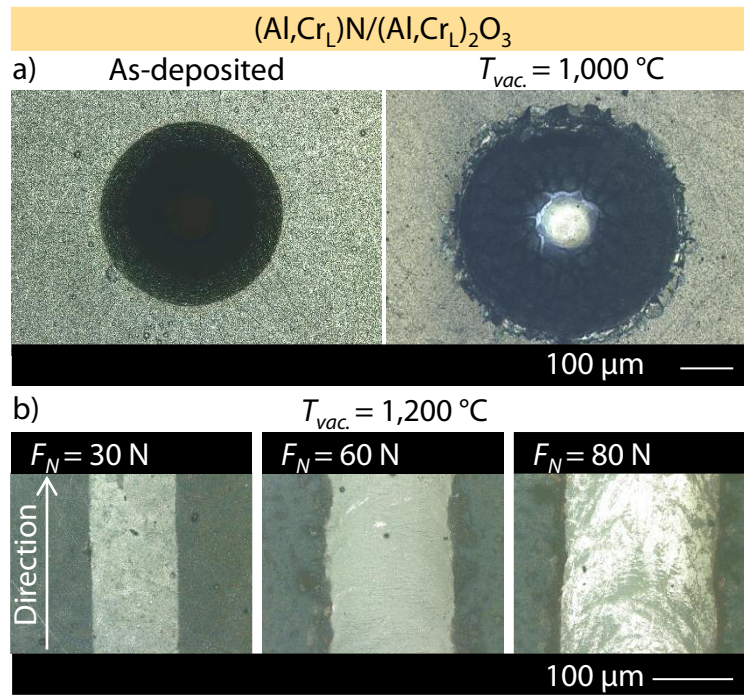


Figure 5.24: Compound adhesion strength after annealing tests a) Rockwell b) scratch tests

After annealing tests for $t_{vac.} = 1$ h in atmosphere at $T_{atm.} = 1,000^\circ\text{C}$, Al-rich coatings are delaminated. The samples annealed in atmosphere reveal comparable results as samples in as-deposited state, regarding phase composition and indentation values up to $T_{atm.} = 900^\circ\text{C}$. The SEM cross-sectional images exhibit only small differences, shown in Figure 11.1 in Appendix. The XRD results indicate almost identical spectra. The phase composition in

Figure 11.2 as well as indentation hardness and modulus, Figure 11.3, show no significant change.

5.5.2 Cr-rich $(\text{Al,Cr}_\text{H})\text{N}/(\text{Al,Cr}_\text{H})_2\text{O}_3$ coating

The chemical composition of the functional layer was analyzed by EPMA. The elemental content of $x_{\text{Al}} \approx 28$ at.-%, $x_{\text{Cr}} \approx 11$ at.-%, and $x_{\text{O}} \approx 61$ at.-% was determined. Considering the metallic elements, the coatings show $x_{\text{Al}} \approx 72$ at.-% and $x_{\text{Cr}} \approx 28$ at.-%, analyzed by EDX. As observed for $(\text{Al,Cr}_\text{L})\text{N}/(\text{Al,Cr}_\text{L})_2\text{O}_3$ coating, a reduction of Al content in $(\text{Al,Cr}_\text{H})\text{N}/(\text{Al,Cr}_\text{H})_2\text{O}_3$ compared to monolayer $(\text{Al,Cr}_\text{H})_2\text{O}_3$ coating in subchapter 5.1 is visible. In following the effect of high temperature on Cr-rich coatings were presented and discussed.

After the annealing tests for $t_{\text{vac.}} = 1$ h in vacuum at $T_{\text{vac.}} = 1,000^\circ\text{C}$, Cr-rich coatings are delaminated. Therefore, annealing tests are conducted at a lower temperature of $T_{\text{vac.}} = 800^\circ\text{C}$ in vacuum and the annealing tests in atmosphere are excluded. The phase transformation in the $(\text{Al,Cr}_\text{H})\text{N}/(\text{Al,Cr}_\text{H})_2\text{O}_3$ coating are analyzed by XRD and are shown in Figure 5.25. A comparison of the XRD diffractograms for the as-deposited state and the annealed sample in vacuum at $T_{\text{vac.}} = 800^\circ\text{C}$ shows no significant differences. The XRD results reveal the presence of the $\gamma\text{-Al}_2\text{O}_3$, with no evidence of crystalline chromium phases. The peak positions remain unchanged. However, a slight reduction in peak intensity can be attributed to the different samples needed for the annealing tests.

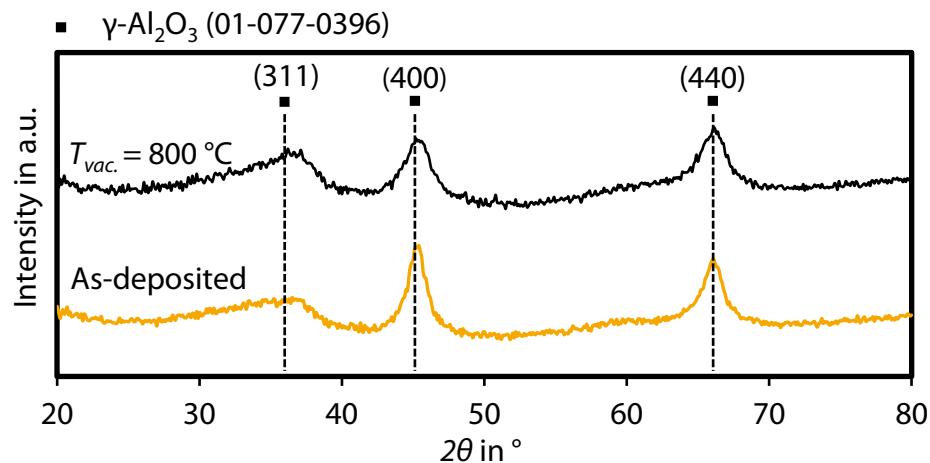


Figure 5.25: Effect of annealing for $t_{\text{vac.}} = 1$ h on $(\text{Al,Cr}_\text{H})\text{N}/(\text{Al,Cr}_\text{H})_2\text{O}_3$ [BKM+24c]

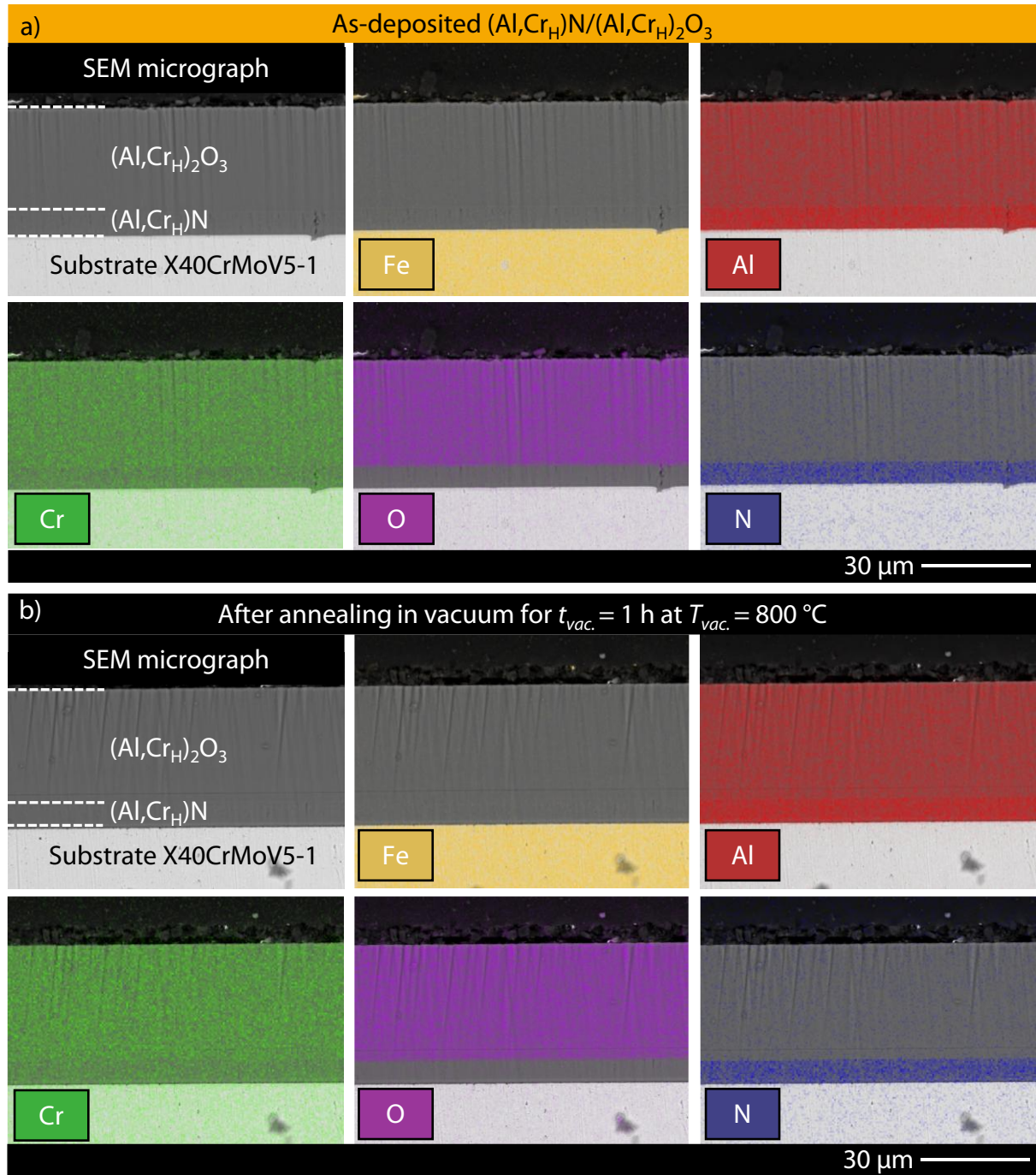
The indentation hardness H_{IT} and indentation modulus E_{IT} determined by nanoindentation on a polished coating surface before and after annealing in vacuum are listed in Table 5.10. The slight increase in indentation values after annealing $T_{vac.} = 800$ °C for $t_{vac.} = 1$ h in vacuum can be explained by the different samples used for annealing tests.

Table 5.10: Effect of annealing on indentation values of (Al,Cr_H)N_g/(Al,Cr_H)₂O₃ coating

Sample state	As-deposited	Annealed at $T_{vac.} = 800$ °C
H_{IT} in GPa	22.1 ± 1.8	24.8 ± 1.1
E_{IT} in GPa	272.3 ± 9.9	286.5 ± 10.5

Figure 5.26 a-b) shows cross-sections analyzed using SEM to determine structural changes in the coating before and after annealing at $T_{vac.} = 800$ °C in vacuum. The dense structure of the coating can be seen in the SEM cross-sections. Defects are visible neither within the (Al₇₈Cr₂₂)₂O₃ functional layer nor within the interlayer. Instead, the coating appears very dense, with closely aligned columns. The bond between the functional layer and interlayer as well as between interlayer and substrate reveals no significant defects.

The EDX mappings of coated sample in an as-deposited state and after annealing for $t_{vac.} = 1$ h and at $T_{vac.} = 800$ °C are also illustrated in Figure 5.26 a-b). In the area of the substrate material, mainly iron and chromium can be detected, as is expected from the composition of the hot work tool steel. In the interface between the functional layer and the substrate there is a zone in which only Cr, Al and N can be detected, which is assigned to the interlayer. Furthermore, no additional layers with Al or Cr enrichment can be detected as formed in the metallic AlCr interlayer after annealing in studies of [BBK+19], which can show the more suitability of the ceramic AlCrN interlayer up to $T_{vac.} = 800$ °C. In contrast to the metallic AlCr interlayer in [BBK+19], no oxygen is detected in the area of the interlayer in Figure 5.26 b), indicating that oxygen diffusion into interlayer can be excluded. A homogeneous distribution of the elements Cr, Al and O can be observed in the functional layer before and after annealing tests.

Figure 5.26: Diffusion behavior of $(\text{Al,Cr}_H)_N/(\text{Al,Cr}_H)_2\text{O}_3$ [BKM+24c]

5.6 Intermediate conclusion of effect of Cr content on high temperature properties

To investigate the influence of Cr doping on $(\text{Al,Cr})_2\text{O}_3$ coatings deposited by HS-PVD, three variations are investigated, each with $x_{Cr} < 30 \text{ at.}\%$. For the $(\text{Al,Cr})_2\text{O}_3$ coatings with different Cr content, all coating systems exhibit a dense morphology without voids or cracks. The higher Cr content results in a denser and thicker $(\text{Al,Cr})_2\text{O}_3$ coating. Changing the Cr content in

monolayer $(\text{Al,Cr})_2\text{O}_3$ coating from $x_{\text{Cr}} \approx 8$ at.-% to $x_{\text{Cr}} \approx 12$ at.-% and $x_{\text{Cr}} \approx 22$ at.-% shows no effect on the phase composition.

The selected ceramic AlCrN interlayer with h-AlN is more phase stable than c-AlN, and therefore a more promising candidate for addressed applications such as HPDC of steel alloys. Through comparison with the AlCr interlayer used in a previous study [BBK+19], a thermally induced dissolution of the AlCrN interlayer is not observed in this study. Thus, AlCrN reveals a better diffusion barrier to prevent interdiffusion compared to AlCr interlayer. Basically, AlCrN coatings with a h-AlN phase are unsuitable as tool coatings for wear protection, due to its lower indentation hardness and modulus than cubic one. However, they appear to be appropriate as interlayers in this case, due to their higher phase stability compared to cubic ones.

Furthermore, annealing tests up to $T_{\text{vac.}} = 1,200^\circ\text{C}$ are performed in vacuum for $t_{\text{vac.}} = 1$ h to evaluate the interdiffusion behavior in vacuum and phase stability of AlCrN/ $(\text{Al,Cr})_2\text{O}_3$ coatings with $x_{\text{Cr}} \approx 15$ at.-% and $x_{\text{Cr}} \approx 28$ at.-%. Despite phase transformations, no spallation and crack formations are observed for AlCrN/ $(\text{Al,Cr})_2\text{O}_3$ coating system with $x_{\text{Cr}} \approx 15$ at.-% after annealing test up to $T_{\text{vac.}} = 1,200^\circ\text{C}$. Annealing tests in atmosphere confirm the oxidation resistance in ambient air of this coating up to $T_{\text{atm.}} = 900^\circ\text{C}$. While previous studies in [Wel20] reported an increase in indentation hardness and modulus after annealing in atmosphere up to $T_{\text{atm.}} = 800^\circ\text{C}$, the results in this study exhibit comparable indentation values after annealing at temperatures up to $T_{\text{atm.}} = 900^\circ\text{C}$. In this context, the high Al content of $x_{\text{Al}} = 85$ at.-% can be decisive. Based on these results, the Al-rich $(\text{Al,Cr}_\text{L})\text{N}/(\text{Al,Cr}_\text{L})_2\text{O}_3$ variant deposited by HS-PVD has been selected for further investigations under harsher conditions in immersion tests in molten steel 100Cr6.

6 Behavior of the coated hot work steel in contact with molten 100Cr6 steel

The interactions between coatings and molten steel have not yet been extensively studied, resulting in a significant knowledge gap. Therefore, the fundamental investigation of failure mechanisms and adhesion behavior is of central importance. For the first time, immersion tests were carried out to evaluate the HS-PVD coated hot work steel substrates in contact with molten steel 100Cr6. The aim is to evaluate the behavior of Al-rich $(\text{Al}, \text{Cr}_L)\text{N}/(\text{Al}, \text{Cr}_L)_2\text{O}_3$ coatings in contact with molten steel, focusing on their metal-physical corrosion and adhesion tendency.

6.1 Coating and preparation of hot work steel pins for immersion tests

Immersion tests were carried out with $(\text{Al}, \text{Cr}_L)\text{N}/(\text{Al}, \text{Cr}_L)_2\text{O}_3$ system with $x_{\text{Cr}} \approx 15$ at.-%, which had previously demonstrated promising high temperature performance in annealing tests. The substrates for immersion tests were prepared as pins from hardened and annealed hot work tool steel X40CrMoV5-1, with a hardness of $H = (54 \pm 2)$ HRC. The pins had a diameter of $d_{\text{pin}} = 14$ mm and a length of $L_{\text{pin}} = 40$ mm. The surface of the pins was polished to a roughness of $Ra \approx 0.01$ μm before the coating process. These pins were coated in the HS-PVD coating machine using the process windows defined for the $(\text{Al}, \text{Cr}_L)\text{N}/(\text{Al}, \text{Cr}_L)_2\text{O}_3$ system with a functional layer coating time $t_f = 90$ min, as described in Table 5.6. The pins were coated in one-fold rotation with a rotation speed of $\omega_{\text{Table}} = 7$ rpm to ensure a homogeneous coating thickness distribution.

Figure 6.1 a) shows the schematic representation of the coated and uncoated regions of the cylindrical test pins used in the immersion tests. The uncoated region at the base is due to the pin holder used during the coating process. Initial coating attempts led to incomplete coverage and edge delamination due to rapid cooling immediately after the coating deposition process, as shown in Figure 6.1 b). The delaminated areas, highlighted in yellow, are attributed to thermal stress, as depicted in Figure 6.1 b). A magnified view in Figure 6.1 d) shows the coating delamination at the edge more clearly. This issue was resolved by implementing a controlled cooling protocol, whereby the temperature was reduced incrementally by $T = 150$ °C steps to minimize thermal stress. This optimized process resulted in uniform and defect-free coatings on the pins, as shown in Figure 6.1 c). The yellow-highlighted region demonstrates complete coating coverage, and a magnified view in Figure 6.1 e) shows a uniform and intact coating at

the edges. The optimized pins are now suitable for extensive immersion testing to investigate their resistance to metallurgical corrosion and adhesion behavior in 100Cr6 steel melt.

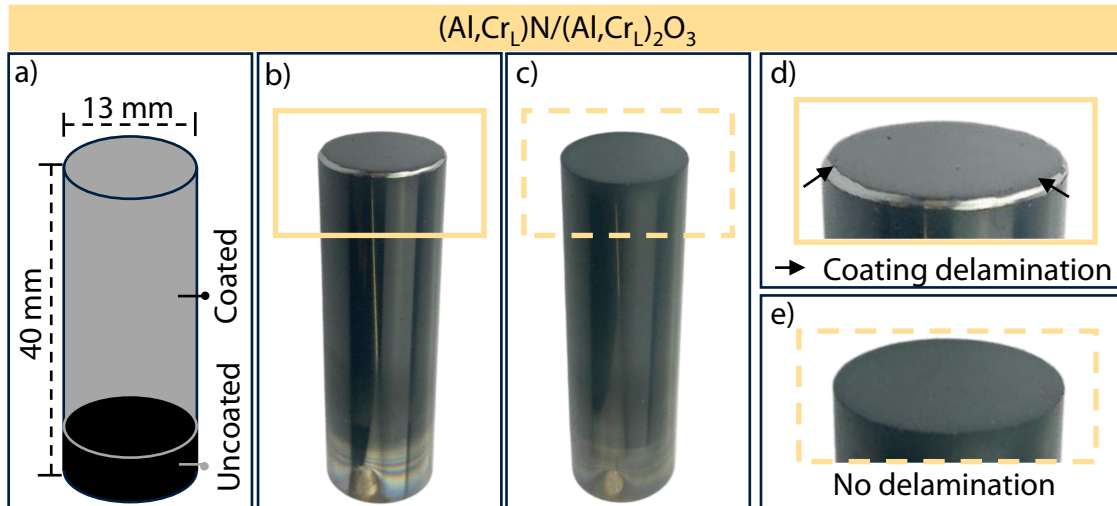


Figure 6.1: a) Schematic illustration of a coated pin, b) coated pin with delamination, c) coated pin without delamination, d) detailed image of coating delamination, and e) detailed image of completely coated pin edge

6.2 Performance comparison between coated and uncoated pins in immersion tests

The widely used construction of 100Cr6 steel was selected in this work as the melt for the immersion tests. This steel has been chosen in several studies for investigations in the primary SMM processing, as discussed in subchapter 2.3. A middle-frequency induction heating unit from iew Induktive Erwärmungsanlagen GmbH, Gumpoldskirchen, Austria, was utilized for the immersion tests. The setup for the immersion tests is shown in Figure 6.2. The 100Cr6 steel was inductively heated in a melting crucible until a homogeneous melt was formed. Since the pins were not cooled, there was a risk of them being inductively melted. Therefore, the induction unit had to be switched off before immersing the pins to prevent the pins from melting. The pre-tests demonstrated that the molten metal solidified within approximately 20 seconds after the induction furnace was turned off. Immediately after the induction unit was switched off, the pins were introduced into the melt. Pins were first immersed in the melt for $t_{imm.} = 3$ s, where the melt was still liquid, considering the HPDC application. Subsequently, the immersion time was increased to $t_{imm.} = 10$ s. The mixture of solid and liquid states, resulting from solidification during this period, nears the state of semi-solid metal forming application.

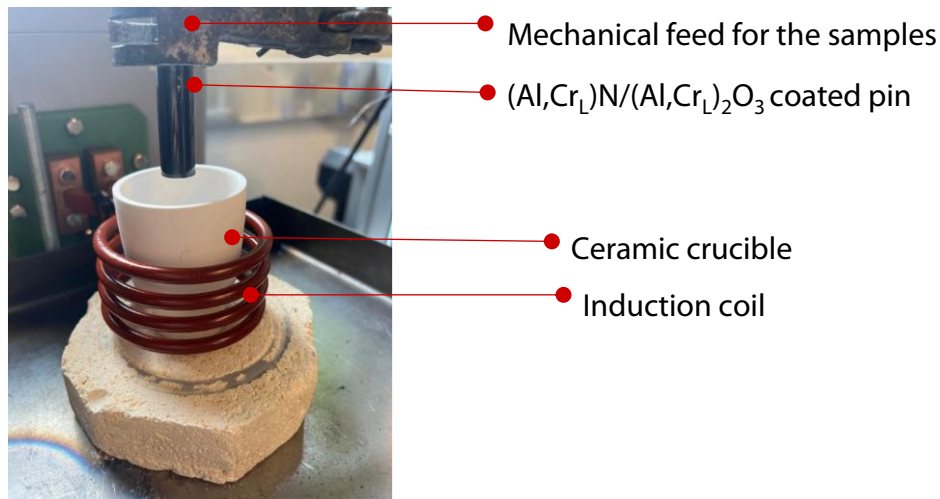


Figure 6.2: Experimental set up of immersion tests

The immersion tests were repeated twice. An uncoated pin was first immersed in molten steel to compare it with the coated pin. Strong adhesion of the molten steel to the uncoated pins is observed after only $t_{imm.} = 3$ s. In cross-sectional SEM investigations, the boundary between the original pin surface and the melt is difficult to identify, as shown in Figure 6.3 a). Moreover, the boundary is not as straight and homogeneous as expected, which can be attributed to additional metal-physical interactions such as the melting of the X40CrMoV5-1 pin on the surface. On the other hand, during the cross-section preparation, the melt separated from the coated pin due to the low adhesion tendency. The cross-section of this (Al,Cr_L)N/(Al,Cr_L)₂O₃ coated pin after the immersion test in 100Cr6 melt for $t_{imm.} = 3$ s is shown in Figure 6.3 b). A dense coating morphology can be seen in the cross-section. No coating defects such as cracks or pores can be observed within the coating. The bond between coating and interlayer as well as between interlayer and substrate shows no defects.

As mentioned earlier, the pins were coated using a one-fold rotation mode. Even with rotation, only a small reduction in the deposition rate is observed, with $ds/dt \approx 27 \mu\text{m/h}$ for the coated pins versus $ds/dt \approx 29 \mu\text{m/h}$ for coatings applied without rotation, as illustrated in Figure 5.11 b).

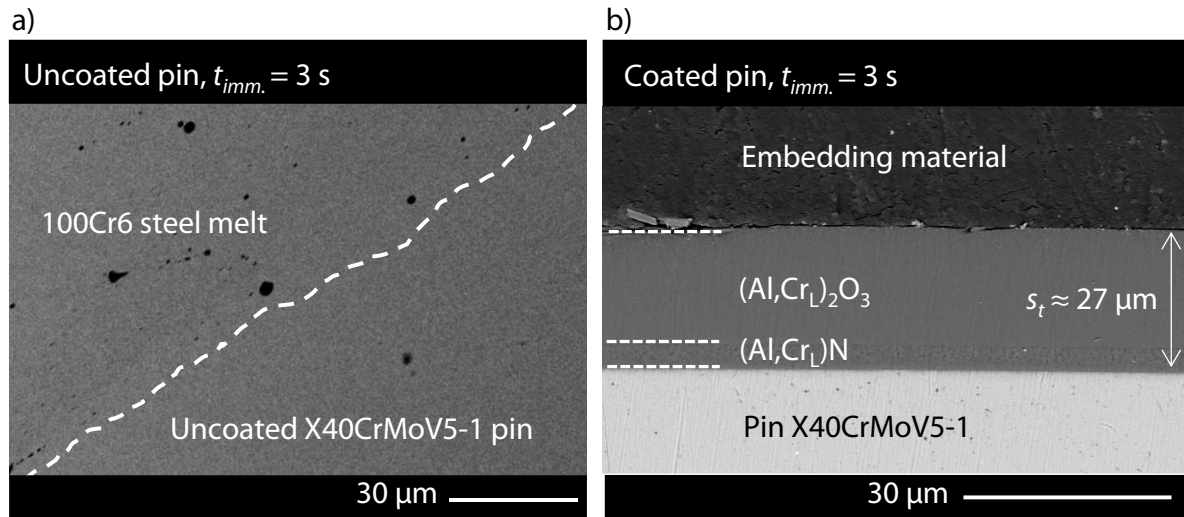


Figure 6.3: SEM cross-sectional images of a) uncoated and b) coated pin after immersion test in 100Cr6 melt steel for $t_{imm.} = 3 \text{ s}$

To further investigate the contact surface of the melt with the coating, an approach was taken to embed the coated pin together with the melt as depicted in Figure 6.4 a) and then prepare cross-sections. Thereby, the pin was embedded shortly after the immersion test, subsequently cut as shown in Figure 6.4 b). The cross-sections were investigated using SEM and marked with dashed yellow lines in Figure 6.4 b). The SEM cross-sectional images of the (Al,Cr_L)N/(Al,Cr_L)₂O₃ coated pin after the immersion test in 100Cr6 melt for $t_{imm.} = 10 \text{ s}$ are also shown in Figure 6.4 d-e). The embedding material has run between the pin and the melt, indicating a gap, as illustrated in Figure 6.4 c). This could result from the low adhesion tendency of steel melt to the coated pin. A dense coating morphology can be seen in the cross-sectional SEM images, whereby partially local defects are detectable at the surface of functional coating. No further coating defects such as cracks or pores can be observed within the functional layer and interlayer. The bond between the functional layer and interlayer shows no deficiencies. However, the cross-section visualizes the formation of small gaps between the interlayer and substrate, as shown in Figure 6.4 d).

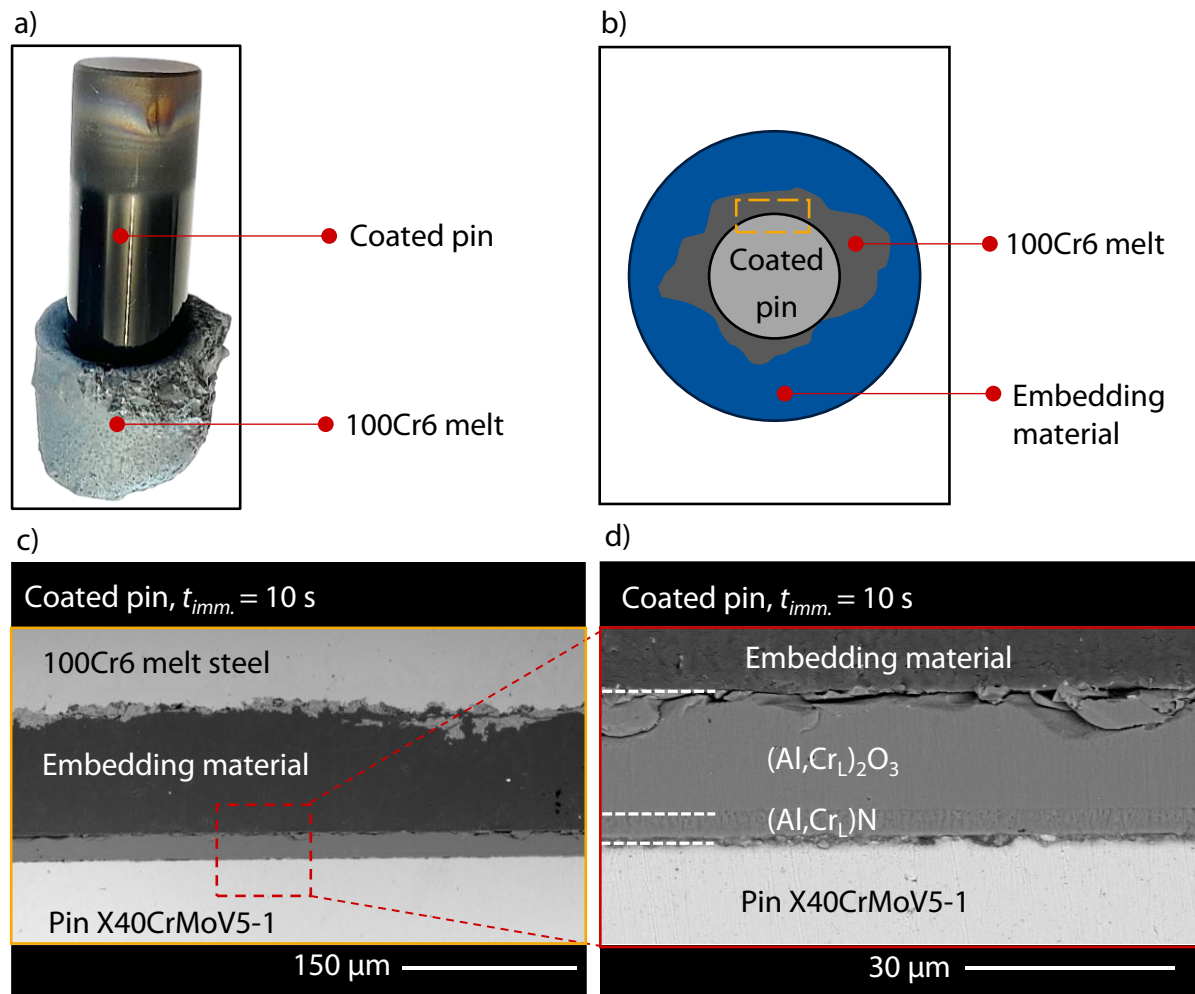


Figure 6.4: a) Coated pin after $t_{imm.} = 3$ s of the immersion, b) after embedding, c) SEM cross-sectional micrograph, and d) detailed SEM micrograph

Furthermore, EDX mappings were carried out to investigate the interaction between the molten steel and the coated pin in more detail. Figure 6.5 a) shows the elemental distribution of the coated pins after immersion in molten steel for various durations. After $t_{imm.} = 3$ s, the functional oxide layer stays intact and acts as a thick barrier. This layer shows no interaction with the steel melt, as demonstrated by the absence of Fe detected in the functional coating. The distribution of Al and Cr across the layers is uniform, indicating stable coating morphology during the early stages of immersion. Oxygen is mostly concentrated in the top layer, while nitrogen is restricted to the interlayer, ensuring the initial bilayer coating's architecture. Moreover, EDX mapping does not detect iron near the coating surface. This confirms that there is no adhesion of the molten steel to the coating. Significant changes are visible after $t_{imm.} = 10$ s, as evidenced by Figure 6.5 b).

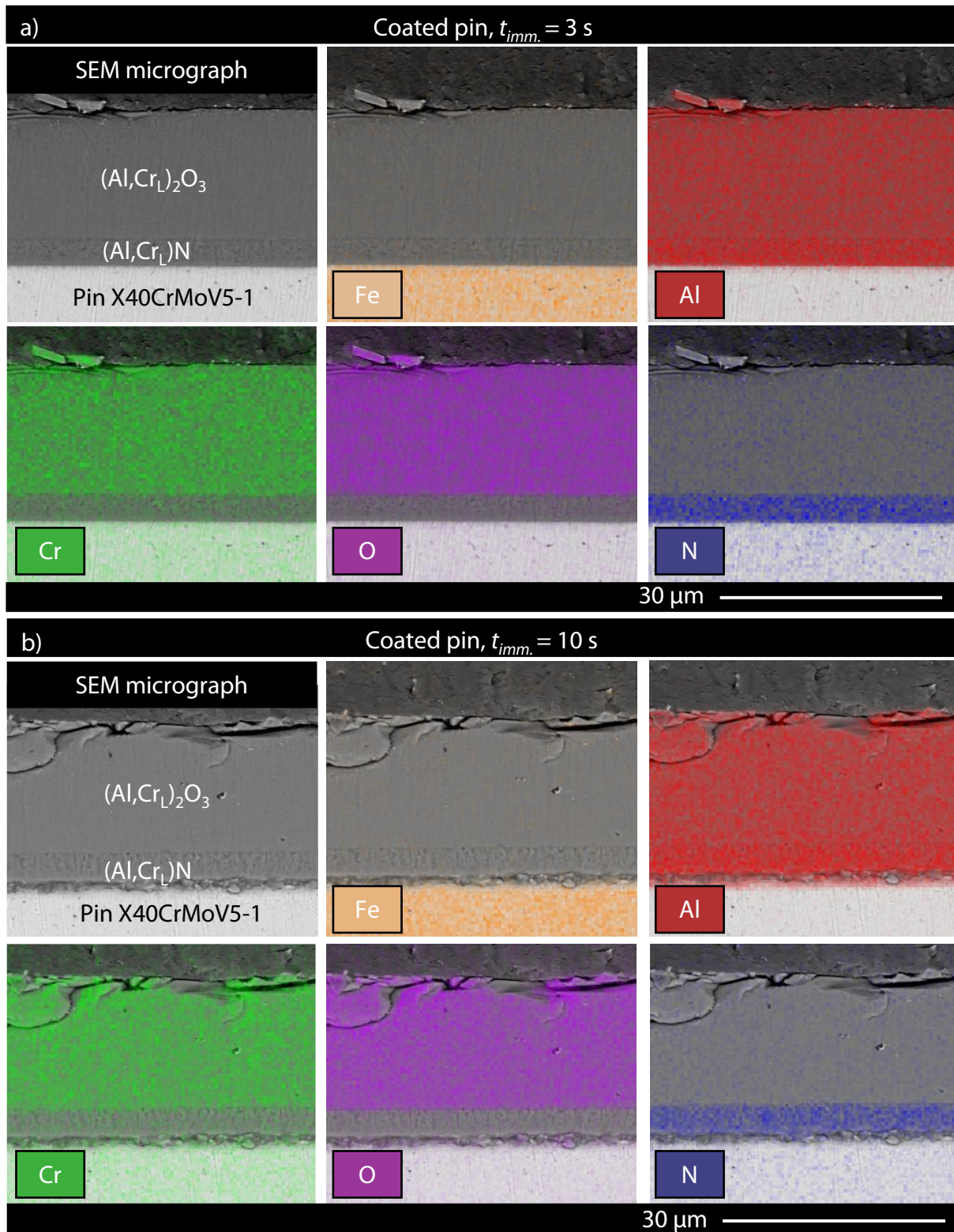


Figure 6.5: EDX mappings of coated pins after immersion tests in 100Cr6 melt

The functional layer exhibits delamination and visible cracks at the coating/melt interface. If these coating defects had occurred during the immersion tests, they would have acted as a weak point for the diffusion and interaction of the molten steel with the coating. However, the Fe mapping shows no Fe in the defects or cracks. Since the diffusion of molten steel into the coating cannot be detected by Fe signals in EDX mapping, it can be inferred that these defects occurred during the grinding preparations.

6.3 Intermediate conclusions of immersion tests in 100Cr6 melt

The developed $(\text{Al}, \text{Cr}_L)\text{N}/(\text{Al}, \text{Cr}_L)_2\text{O}_3$ coating demonstrates excellent thermal and chemical stability under short-term exposure to molten 100Cr6 steel. The coating effectively prevents wetting and adhesion of the steel melt, preserving its structural integrity and acting as a barrier against melt diffusion to the substrate. These findings provide a crucial step toward enabling advanced primary shaping processes of high melting alloys such as HPDC or SSM forming of steel that demand materials with extreme resistance to melt-induced degradation. However, long-term stability and performance under cyclic thermal and mechanical loading are required to validate durability under real processing conditions.

Additionally, utilizing a one-fold rotation mode during coating deposition only marginally decreased the deposition rate to $ds/dt \approx 27 \mu\text{m}/\text{h}$, compared to $ds/dt \approx 29 \mu\text{m}$ with rotation. This indicates that rotational coating deposition can achieve uniform tool coating without notably affecting process efficiency in HS-PVD.

7 High temperature $T_s > 700$ °C PVD process of Al_2O_3 system

The objective of this part is to verify the second hypothesis and to answer the research questions presented in chapter 3. Since the industrial synthesis of crystalline Al_2O_3 using CVD technology is conventionally carried out at $T > 800$ °C, the potential of HS-PVD was used to deposit coatings at such high temperatures. A maximum heater temperature of $T_H = (940 \pm 10)$ °C can be adjusted in HS-PVD coating unit used. The desired heater temperature T_H is set and the heater control system continuously adjusts the heater power to control the heater temperature. It is essential to note that the heater temperature does not correspond to the substrate temperature T_s . The substrate temperature is below the heater temperature and is critical for phase formation. The substrate temperature is measured with a thermocouple at a distance of $d_{\text{Thermo.}} \approx 8$ mm from the substrate. The influence of the HT-PVD processes with a substrate temperature of $T_s \approx 780$ °C and $T_s \approx 850$ °C on the properties of the Al_2O_3 coatings was investigated. Thereby, properties of Al_2O_3 coatings synthesized on WC-Co substrates via HS-PVD at $T_s \approx 780$ °C under different oxygen gas flows were studied under both as-deposited and high temperature conditions. For this purpose, the HT-XRD analysis was conducted in vacuum and at atmospheric conditions to analyze the phase stability and oxidation behavior, respectively. Moreover, High temperature nanoindentation (HT-NI) was performed to analyze the indentation hardness and modulus directly at these elevated temperatures. To analyze whether HS-PVD coatings with compressive residual stress can be deposited on WC-Co substrates at $T_s \approx 850$ °C, three coating variants were deposited under varying bias voltages and oxygen gas flows.

7.1 Effect of O_2 gas flow on properties of coatings deposited at $T_s \approx 780$ °C

The Al_2O_3 coatings were deposited in dc mode without rotation on cemented carbide indexable inserts SNUN 120412 THM of grade HB10, $x_{\text{Co}} = 6$ wt.-%, Kennametal Widia Produktions GmbH & Co. KG, Essen, Germany. Only two coating processes with different oxygen gas flow Q_{O_2} were carried out to minimize the test matrix, Table 7.1. The effect of a high substrate temperature as well as oxygen gas flow on the coating properties was the focus of initial investigations. As a reference, a coating process with the same parameters as process ID4450 was conducted at a lower substrate temperature $T_s \approx 550$ °C, Table 7.1. The fundamental coating properties deposited at $T_s \approx 780$ °C and $T_s \approx 550$ °C were investigated and discussed.

Table 7.1: Process parameters of Al_2O_3 coatings deposited at $T_s \approx 780$ °C in dc mode

Process ID	4355	4450	4451
Cathode power P_C in kW	6	6	6
Cathode current I_C in V	16	16	16
Bias voltage U_B in V	-125	-125	-125
Bias current I_B in A	3	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000	8,000
O_2 gas flow Q_{O_2} in sccm	80	80	120
Pressure p in Pa	33.4	33.4	33.6
Heater temperature T_H in °C	640 ± 10	830 ± 10	830 ± 10
Substrate temperature T_s in °C	550 ± 15	780 ± 10	780 ± 10
Rotation speed ω_{Table} in rpm	-	-	-
Coating time $t_{coat.}$ in min	60	60	60

Coating morphology and thickness

Al_2O_3 coatings were deposited at a substrate temperature of $T_s \approx 780$ °C with different oxygen gas flows of $Q_{\text{O}_2} = 80$ sccm and $Q_{\text{O}_2} = 120$ sccm. For a better comparison, the Al_2O_3 coating deposited at a lower substrate temperature $T_s \approx 550$ °C with $Q_{\text{O}_2} = 80$ sccm is also shown in Figure 7.1 a). The SEM cross-sectional micrographs of Al_2O_3 coatings deposited at a higher temperature of $T_s \approx 780$ °C are illustrated in Figure 7.1 b-c). The comparison of the cross-sectional micrographs illustrates a decreasing coating thickness with increased process temperature. It is assumed that the thickness decreases due to increased crystallinity resulting from elevated process temperature. In this case, plasma species such as atoms, ions, and clusters would gain higher energy levels. Therefore, it is more probable that a crystalline lattice forms during condensation due to ions with higher energy levels. Moreover, the results confirm that morphology strongly depends on T_s , indicated by significant differences in the column size. At $T_s \approx 550$ °C, coating morphology is coarse columnar with larger and discontinuous columns, as illustrated in Figure 7.1 a). In contrast, the columnar morphology becomes finer and more continuous at higher T_s , as shown in Figure 7.1 b). A dense and homogeneous non-columnar morphology is formed with an increased oxygen flow, as described in Figure 7.1 c). An amorphous or nanocrystalline microstructure could be the reason for this morphology. To verify this, additional investigations such as nanoindentation and XRD were carried out, and the results are presented in the following sections.

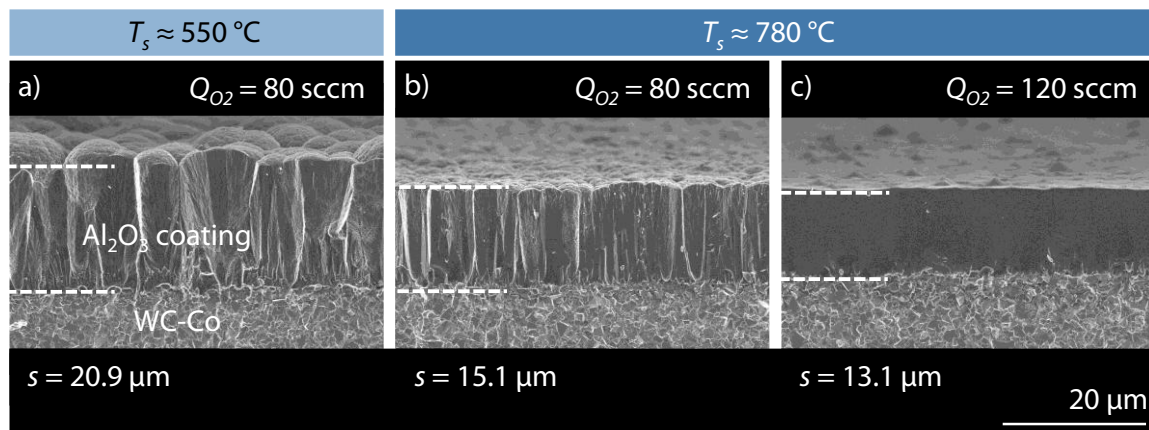


Figure 7.1: Fractured cross-sectional SEM micrographs of Al_2O_3 coatings deposited at a) $T_s \approx 550\text{ }^{\circ}\text{C}$ and at b-c) $T_s \approx 780\text{ }^{\circ}\text{C}$ [BKH22]

Phase composition

The phase composition of Al_2O_3 coatings deposited at $T_s \approx 780\text{ }^{\circ}\text{C}$ with different oxygen gas flows of $Q_{O_2} = 80\text{ sccm}$ and $Q_{O_2} = 120\text{ sccm}$ is analyzed via XRD. Results are shown in Figure 7.2.

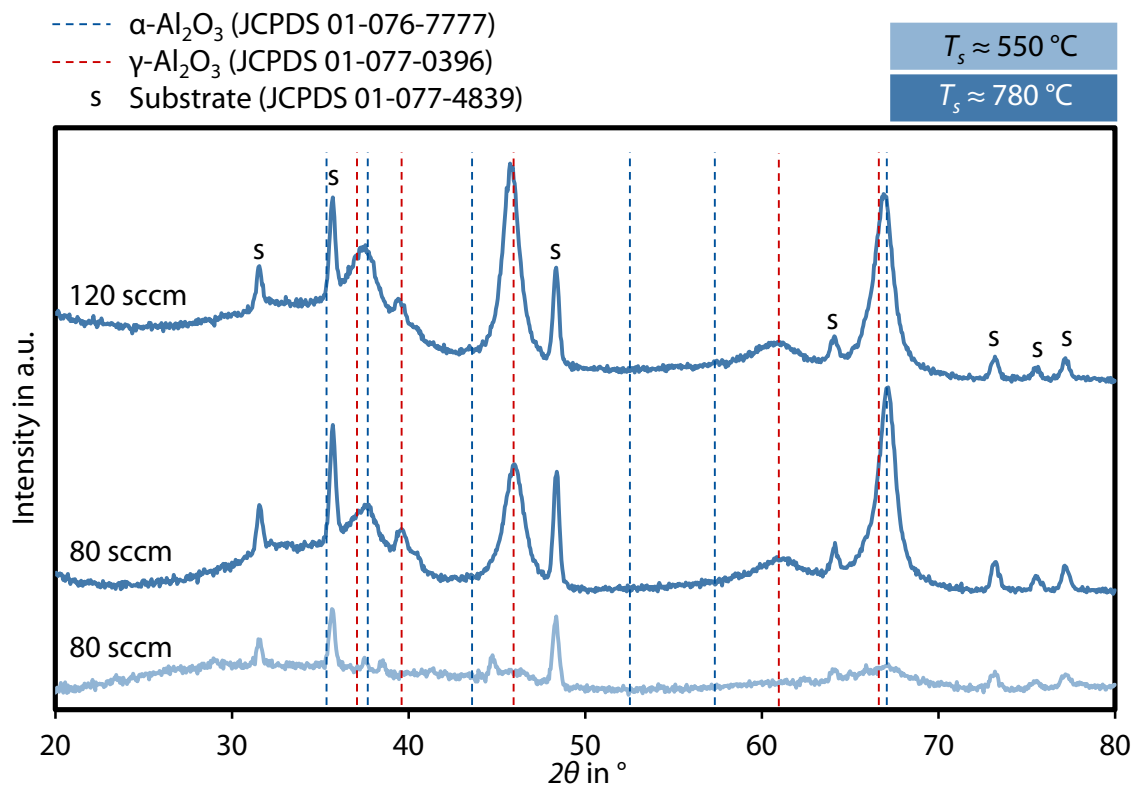


Figure 7.2: Effect of substrate temperature and oxygen gas flow on phase composition of Al_2O_3 coatings [BKH22]

The coatings deposited at higher temperature demonstrate peaks with higher intensity, which are different from the coating deposited at $T_s \approx 550$ °C. This reveals that the content of crystalline oxide phase increases with rising process temperature. Compared to $T_s \approx 550$ °C, more pronounced oxide peaks in terms of intensity are observable. The peaks can be assigned to the γ -phase. Moreover, peak intensity rises when the oxygen flow is increased to $Q_{O_2} = 120$ sccm. Considering the finer crystalline morphology of the coating in Figure 7.1 c) compared to Figure 7.1 b), higher crystallinity could be responsible for the morphology change. These observations make it clear, that the coating deposited at $Q_{O_2} = 120$ sccm is not completely amorphous and probably has a fine crystalline microstructure.

Nanoindentation results

Indentation hardness H_{IT} and indentation modulus E_{IT} of the Al_2O_3 coatings deposited at these two different substrate temperatures are illustrated in the form of box plots in Figure 7.3. A significant change in both indentation hardness and indentation modulus is observed with increasing substrate temperature.

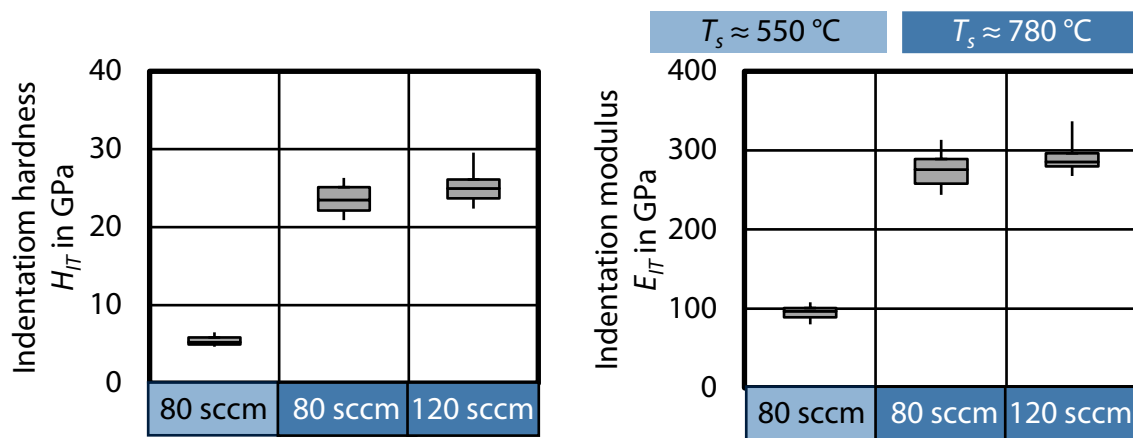


Figure 7.3: H_{IT} and E_{IT} of Al_2O_3 coatings deposited under different conditions [BKH22]

The indentation hardness increases markedly, reaching $H_{IT} = (23.7 \pm 1.5)$ GPa for the Al_2O_3 coating deposited with $Q_{O_2} = 80$ sccm. The rise in hardness is attributed to a higher content of crystalline oxide phases, which generally exhibit significantly higher hardness compared to amorphous alumina coatings. A slight increase in hardness to $H_{IT} = (25.7 \pm 2.5)$ GPa is visible for the Al_2O_3 coating deposited with $Q_{O_2} = 120$ sccm. This can be attributed to the change of columnar morphology to nanocrystalline-like morphology, as observed in Figure 7.3.

7.1.1 Phase stability by in situ HT-XRD in vacuum and atmosphere

In addition to the coating properties discussed in subchapter 7.1, the thermal stability of Al_2O_3 coatings is important concerning the high temperatures generated on tools during the cutting process. Thus, the thermal stability of the crystalline Al_2O_3 coating deposited at $T_s \approx 780$ °C was investigated. The phase transformations of metastable phases of alumina mainly occur in the temperature range of 600 °C $< T < 1200$ °C, as observed for magnetron-sputtered Al_2O_3 coatings in [ESS+09]. HT-XRD measurements were therefore performed between $T = 700$ °C to $T = 1,200$ °C in vacuum and atmosphere. HT-XRD were carried out in a Buehler 2.4 HDK high temperature chamber, Edmund Bühler GmbH, Hechingen, Germany. The inside of the high temperature chamber is shown in Figure 7.4.

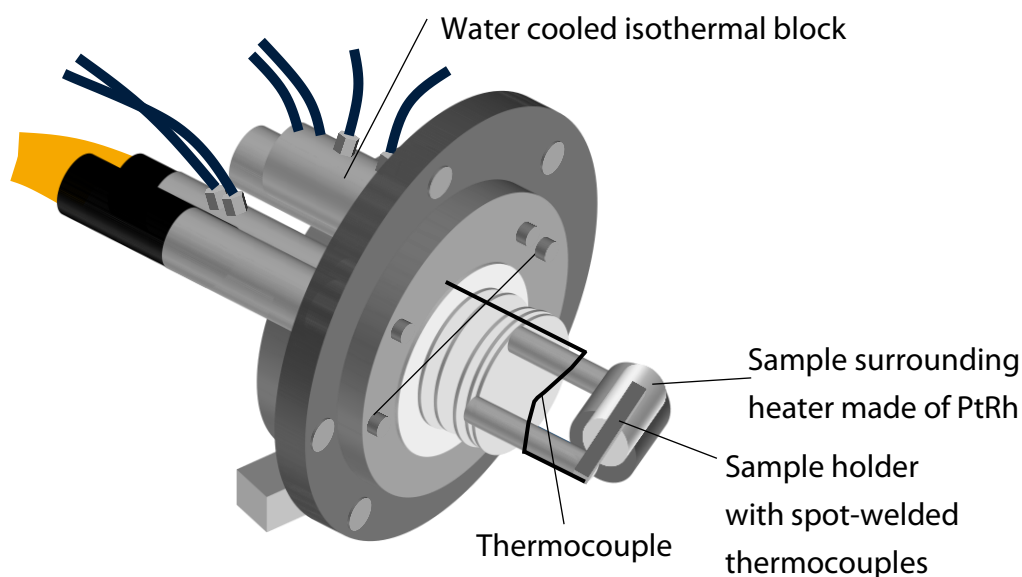


Figure 7.4: Inside of High temperature chamber of XRD equipment

Hereby the HT-XRD measurements were conducted at $T = 700$ °C, $T = 800$ °C, $T = 900$ °C, $T = 1,050$ °C and $T = 1,200$ °C using a grazing incidence (GI) X-ray diffractometer XRD 3003, GE Energy Germany GmbH, Ratingen, Germany. The temperature was measured with a spot-welded thermocouple on the sample holder inside the sample surrounding heater. The measurements were performed using Cu-K α radiation, wavelength $\lambda = 0.1540598$ nm, $U = 40$ kV and $I = 40$ mA with a diffraction angle in the range of $20^\circ \leq 2\theta \leq 80^\circ$ and an incoming angle of $\omega = 3^\circ$. Step width and step time were chosen as $s = 0.1^\circ$ and $t = 10$ s, respectively.

The measurement time at each temperature was about $t = 1.5$ h. This means that the coatings have been annealed under vacuum and atmosphere at elevated temperatures above $T = 700$ °C for a total time of about $t = 7.5$ h, as illustrated in Figure 7.5. Furthermore, besides the phase stability, the annealing conditions in HT-XRD in an atmosphere gave the first insight into the oxidation behavior of coated samples. After the measurements at $T = 1,200$ °C, the morphology of the coatings was investigated in a cross-section using SEM. Moreover, the indentation hardness and indentation modulus were analyzed by NI after annealing during the HT-XRD tests.

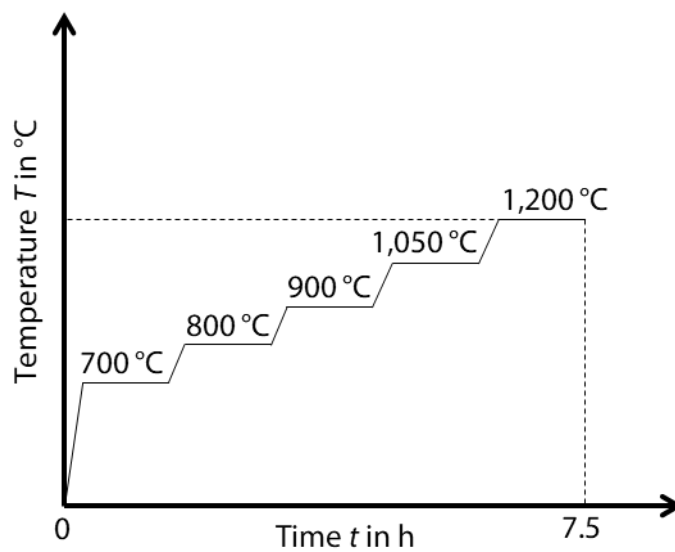


Figure 7.5: Temperature-time progressing diagram during HT XRD

In situ HT-XRD in vacuum

The XRD diffractograms of the Al_2O_3 coating deposited with $Q_{\text{O}_2} = 80$ sccm at $T_s \approx 780$ °C in an as-deposited state are also demonstrated in Figure 7.6. By increasing the temperature, the coating peaks shift slightly to the lower angles. The coefficient of thermal expansion (CTE) of the alumina coating, $\alpha_{\text{Al}_2\text{O}_3} = (8.1\text{-}8.9 \times 10^{-6}) \text{ K}^{-1}$ [WSC62], is higher than WC-Co substrate, $\alpha_{\text{WC-Co}} = (5.7\text{-}6.9 \times 10^{-6}) \text{ K}^{-1}$, corresponding to $x_{\text{Co}} = (6\text{-}15) \text{ wt.}\%$ [SVD+20]. As the temperature increases, the coating tends to expand more than the substrate, which induces compressive stresses in the coating. This stress change during HT-XRD can lead to peak shifts. The results indicate that the coating peaks remain unchanged within the limits of experimental uncertainty, and no new peaks are observed as the temperature increases. This suggests that no additional phases are formed in the coatings, demonstrating their high phase stability up to $T = 1,200$ °C.

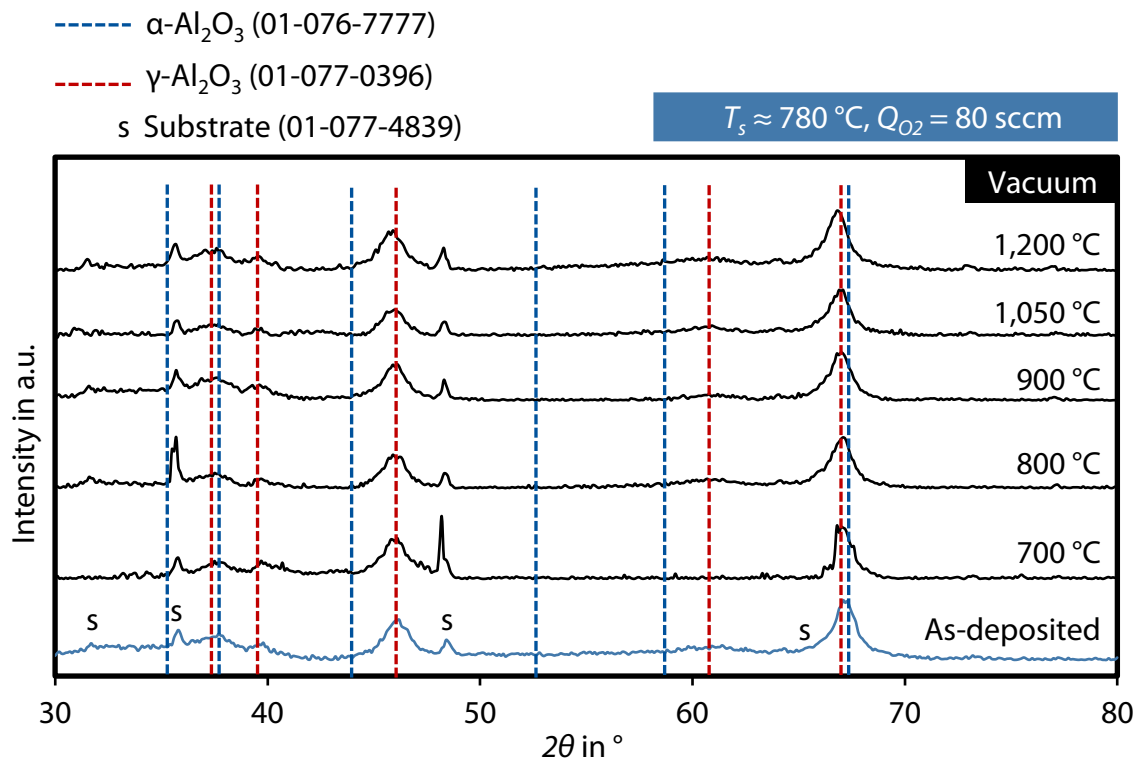


Figure 7.6: HT-XRD results in vacuum for Al_2O_3 coating deposited at $T_s \approx 780$ °C with $Q_{O_2} = 80$ sccm [BKM+24a]

The phase stability of the Al_2O_3 coating deposited at $T_s \approx 780$ °C with $Q_{O_2} = 120$ sccm was also investigated using in situ HT-XRD in vacuum. The results are shown Figure 7.7. The in situ HT-XRD spectra of the coatings up to $T = 1,200$ °C show almost no differences compared to the as-deposited state. The HT-XRD measurements do not reveal any additional peaks within the experimental uncertainty. It is worth noting that using brighter X-ray sources, such as synchrotrons, could potentially yield higher signal-to-noise ratios, allowing for the detection of weaker phase fractions. It might not be discernible with conventional lab XRD. Hence, this statement is made within the confines of the experimental uncertainty inherent in the measurement setup.

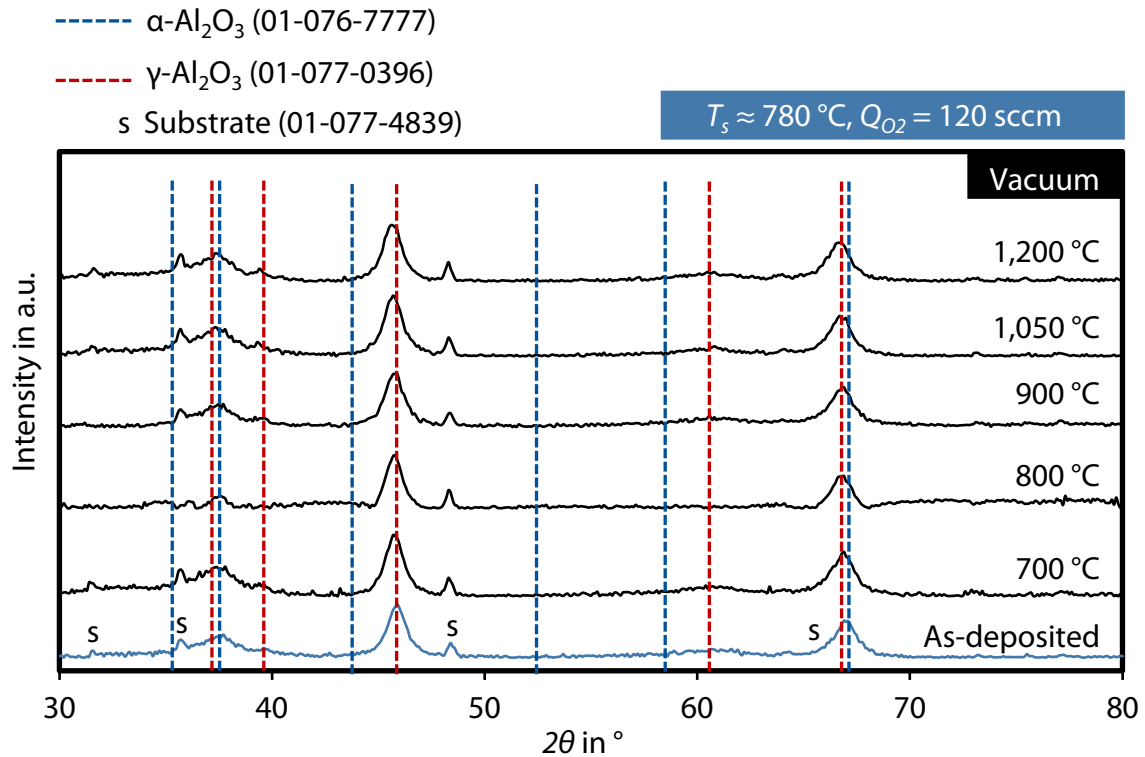


Figure 7.7: HT-XRD results in vacuum for Al_2O_3 coating deposited at $T_s \approx 780$ °C by $Q_{O_2} = 120$ sccm [BKM+24a]

In situ HT-XRD under atmosphere

Although both Al_2O_3 coatings show similar behavior during HT-XRD analysis in vacuum, only the coating deposited with $Q_{O_2} = 120$ sccm, exhibiting a denser, fine-grained like morphology, is selected for further investigation. The coating deposited with $Q_{O_2} = 80$ sccm, indicates a columnar structure, which is generally associated with lower oxidation resistance due to easier oxygen diffusion along column boundaries. Based on this assumption, and to reduce the experimental matrix, the columnar coating was excluded from detailed analysis. Instead, focus was placed on the denser coating, which is expected to offer improved oxidation protection. The in situ HT-XRD measurements were carried out over the same temperature range as tests in vacuum, as shown in Figure 7.8. Despite a combination of atmospheric environment and high temperatures during HT-XRD tests, the phase analysis reveals almost comparable findings. Based on the unchanged spectra up to $T = 1,200$ °C, no new phases are formed in the atmosphere. Moreover, oxidation of the substrate can be excluded, as no typical cobalt oxides are formed and no corresponding peaks are detected in the XRD patterns. However, signs of cobalt oxidation are observed in areas that were not coated, likely due to shadowing by the sample holder during the coating process, Figure 11.4. To minimize any influence of oxidation

of the substrate material, the SEM and nanoindentation analyses were carried out in the center of the sample, as far away from the edge of the sample as possible.

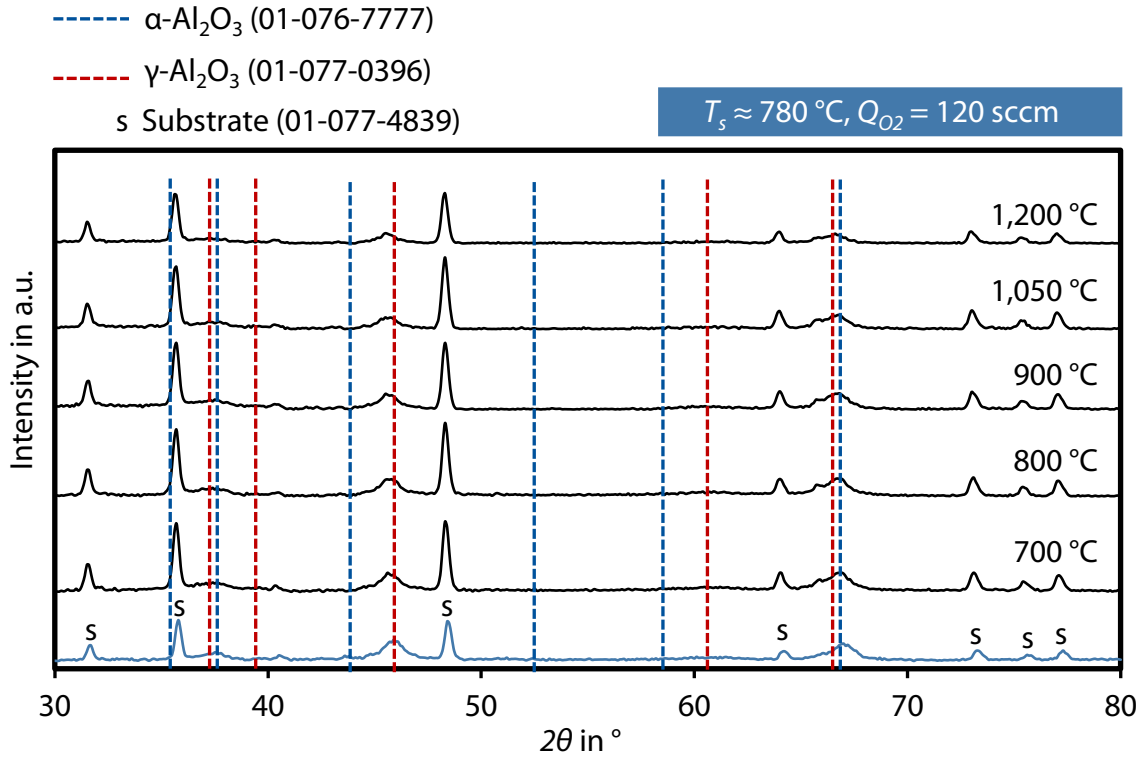


Figure 7.8: HT-XRD results in atmosphere for Al_2O_3 coating deposited at $T_s \approx 780$ °C by $Q_{O_2} = 120$ sccm [BKM+24a]

As reported by Eklund et al. in [ESS+09], the formation of $\alpha\text{-Al}_2\text{O}_3$ is strongly influenced by the fraction of amorphous phase present in the alumina coating. In coatings with amorphous phase or a low fraction of $\gamma\text{-Al}_2\text{O}_3$, the α -phase typically forms at lower temperatures $1,000$ °C $< T < 1,100$ °C. In contrast, transformation from predominantly $\gamma\text{-Al}_2\text{O}_3$ occurs at higher temperatures of $T = 1,100$ °C. It is therefore assumed that the Al_2O_3 coating deposited via HS-PVD at $T_s \approx 780$ °C consists nearly pure $\gamma\text{-Al}_2\text{O}_3$, delaying the α -phase transformation to temperatures above $T = 1,200$ °C. Another possibility is that a small amount of α -phase has formed, but its quantity remains below the detection limit of the XRD equipment.

SEM cross sectional analysis was performed on the Al_2O_3 coatings following annealing tests during HT-XRD to have a deeper comprehension about their morphology change. All coatings were subjected to the same temperature-time profile, in which the temperature gradually increased in steps up to a maximum of $T = 1,200$ °C as shown in Figure 7.5. At each step, the

temperature was held constant for approximately $t = 1.5$ h, resulting in a total annealing time of roughly $t = 7.5$ h. The fractured cross-sectional images are shown in Figure 7.9. The columnar morphology of Al_2O_3 coating deposited with $Q_{O_2} = 80$ sccm, as shown in Figure 7.9 a), remains stable after HT-XRD in vacuum, as shown in Figure 7.9 b). The Al_2O_3 coating deposited with $Q_{O_2} = 120$ sccm exhibits a dense, fine crystalline structure, as illustrated in Figure 7.9 c), even after HT-XRD tests in both vacuum Figure 7.9 d) and in atmosphere Figure 7.9 e). Furthermore, strong bond adhesion between the substrate and coating is evident. The coating's cross-sectional images show that there are no obvious cracks in the coating. This can be explained by the high phase stability of the coatings up to $T = 1,200$ °C. In a previous study, Al_2O_3 coatings deposited by MS were investigated regarding oxidation behavior [BBM+13]. The $\gamma\text{-Al}_2\text{O}_3$ starts to transform into the $\alpha\text{-Al}_2\text{O}_3$ at $T = 1,100$ °C. Complete transformation to α -phase occurs after one hour of annealing at $T = 1,150$ °C [BBM+13].

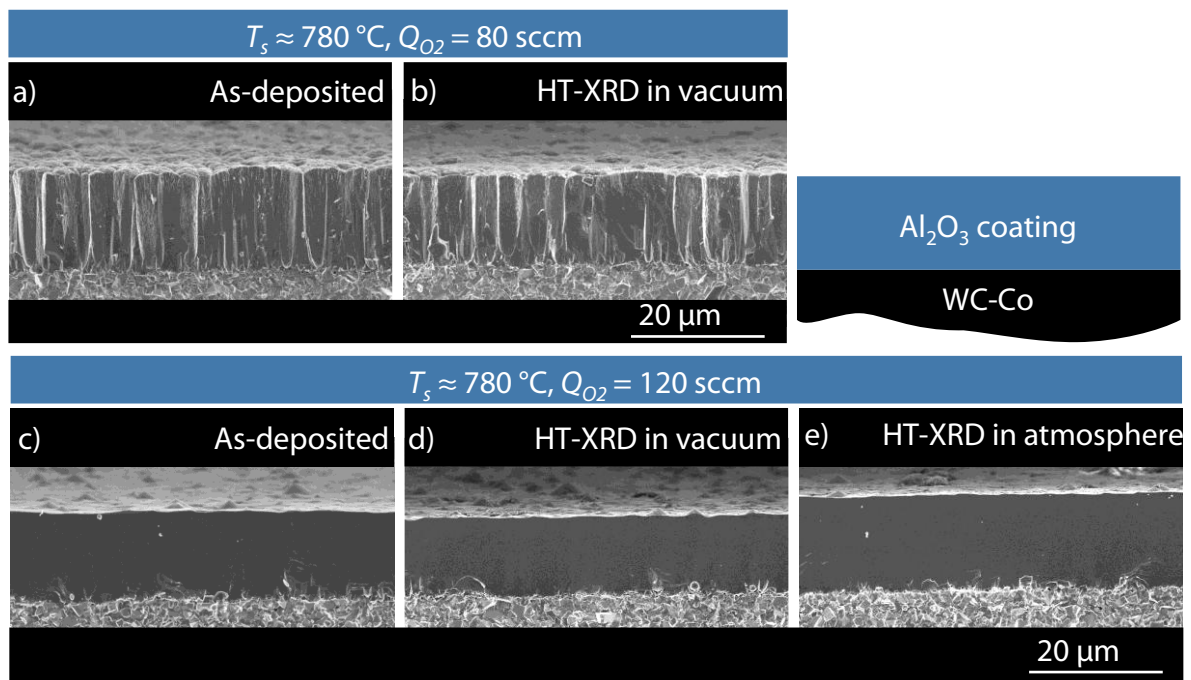


Figure 7.9: Morphology of the Al_2O_3 coatings deposited by $Q_{O_2} = 80$ sccm, a) as-deposited, b) after HT-XRD in vacuum, and Al_2O_3 coatings deposited by $Q_{O_2} = 120$ sccm, c) as-deposited, d) after HT-XRD in vacuum and e) in atmosphere [BKM+24a]

After the HT-XRD investigations, the indentation hardness H_{IT} , indentation modulus E_{IT} and elastic work percentage η_{el} were determined to analyze the effect of high temperature on these properties. The measured values are listed in Table 7.2. For a better comparison the values in

an as-deposited state are also given. Following HT-XRD tests, the indentation hardness H_{IT} remained unchanged beyond the standard deviation for both coatings deposited by different oxygen gas flows. The indentation modulus E_{IT} of coating deposited with $Q_{O_2} = 80$ sccm rose only slightly.

Table 7.2: Effect of annealing during HT-XRD on indentation values

Coating	Coating 80 sccm		Coating 120 sccm		
	As-deposited	HT-XRD, vacuum	As-deposited	HT-XRD, vacuum	HT-XRD, atmosphere
H_{IT} in GPa	23.7 ± 1.5	25.3 ± 1.6	25.7 ± 2.5	27.6 ± 1.2	26.9 ± 1.5
E_{IT} in GPa	275.1 ± 18.2	297.5 ± 13.2	305.7 ± 11.3	319.8 ± 11.1	312.9 ± 13.0
η_{el} in %	60	59	62	62	62

7.1.2 High temperature nanoindentation (HT-NI)

Temperature-dependent properties such as indentation hardness H_{IT} and indentation modulus E_{IT} of PVD coatings are mostly determined using nanoindentation at room temperature after annealing. However, this established state-of-the-art method does not correspond directly to the in situ nanoindentation properties at high temperature conditions. The coating characterization of already annealed samples can only provide insight into the high temperature behavior regarding morphology and oxidation stability. For this reason, in situ HT-NI was conducted for Al_2O_3 coatings deposited by HS-PVD in this study. Using a Berkovich indenter, measurements were carried out on polished samples with TriboIndenter TI 950, Bruker Corporation, Billerica, Massachusetts, USA. An xSol high temperature stage is available for the HT-NI tests, as shown in Figure 7.10.

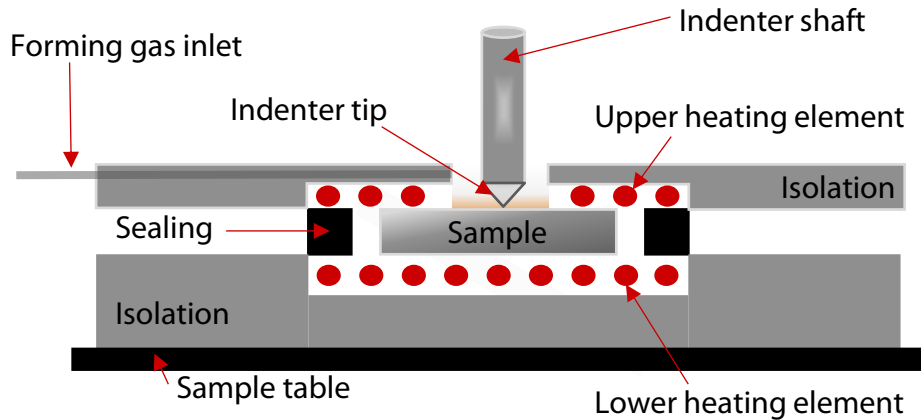


Figure 7.10: Illustration of nanoindentation with xSol high temperature stage

The effect of temperature on the coatings is analyzed at temperatures $T_{NI} = (20 \pm 2)$ °C, $T_{HT-NI} = (650 \pm 2)$ °C and $T_{HT-NI, Max} = (750 \pm 2)$ °C using an integrated heating module under a protective forming gas atmosphere with a composition of 95% N_2 + 5% H_2 . At least 15 measurements were performed at each temperature to minimize measurement uncertainty due to indenter wear, temperature, vibration, and roughness. An indentation force of $F_{NI} = 10$ mN was applied. The indentation depth was kept below 10 % of the coating's thickness.

Using nanoindentation measurements after the annealing tests given in Table 7.2, the behavior after cooling to room temperature was investigated. However, these properties can be studied directly in the heated state using HT-NI. Figure 7.11 depicts the results of HT-NI studies at room temperature and elevated temperatures on coatings deposited by different O_2 gas flows.

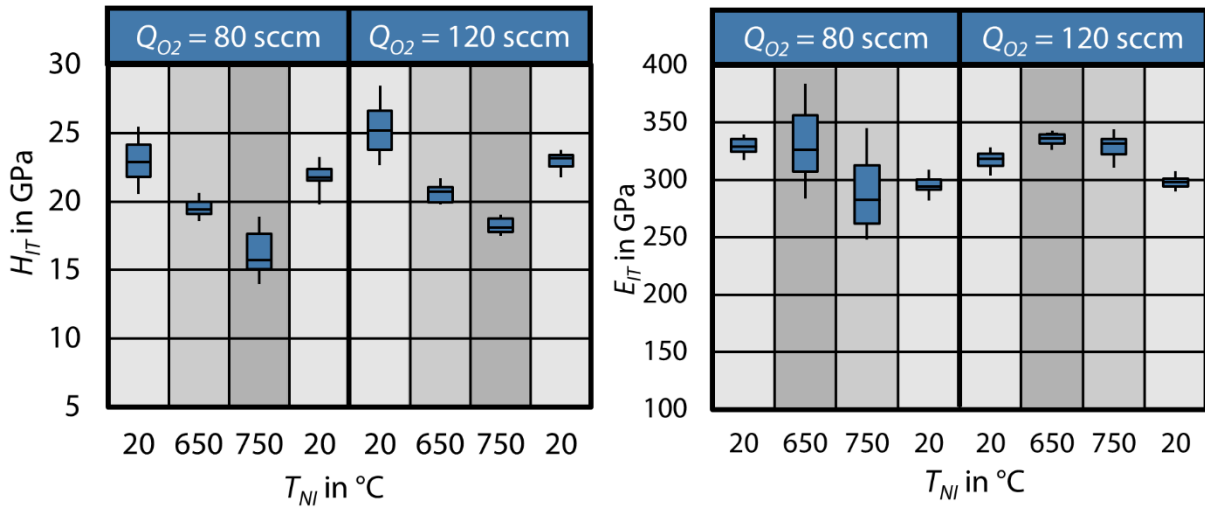


Figure 7.11: HT-NI results of Al_2O_3 coatings deposited at $T_s \approx 780$ °C [BKM+24a]

Figure 7.11 indicates that indentation hardness H_{IT} for both coatings drops dramatically between $T_{NI} = 20$ °C and $T_{NI} = 650$ °C, reaching a minimum of $H_{IT} = 16.2$ GPa at $T_{NI, max} = 750$ °C. The grain boundary sliding could be the probable reason behind the observed phenomenon. The indentation hardness rises after cooling back to $T_{NI} = 20$ °C, although it does not reach the value of as-deposited state. The reduced indentation hardness can be attributed to the grain-boundary activated phenomenon when the temperature increases. Coatings undergo thermally activated processes, such as grain boundary sliding and diffusion, at elevated temperatures. Grain boundary sliding refers to the relative displacement of neighboring crystal grains along their boundaries under mechanical or thermal stress. At higher temperatures, the grain interface can slide more easily, allowing the indenter to penetrate with less resistance. This can also be observed in the decreased elastic work percentage η_{el} . Moreover, the elastic work percentage η_{el} was reduced from $\eta_{el} = 55$ % to $\eta_{el} = 39$ % by increasing the temperature from $T_{NI} = 650$ °C to $T_{NI} = 750$ °C, indicating the lower resistance against plastic deformation at elevated temperatures. The same behavior was observed for the indentation hardness of AlCrN coatings in [FBE+06]. The indentation hardness of AlCrN coating was 25 % lower at $T_{NI} = 500$ °C than at room temperature, whereas when cooled back to room temperature the hardness was comparable to before heating.

Considering the results in Figure 7.11, after cooling back to room temperature, hardness increases again but does not fully recover to the initial value. Upon cooling, the thermally activated movement of grain boundaries stops, which leads to an increase in hardness again.

Moreover, as the temperature decreases during in situ HT-NI tests, thermal expansion comes into play, as discussed in subchapter 7.1.1. Reducing the temperature induces tensile stress in the coating, due to the thermal expansion mismatch between the coating and the substrate. This may explain the drop in hardness compared to the as-deposited state.

The indentation modulus E_{IT} of the Al_2O_3 coatings deposited with $Q_{O_2} = 80$ sccm decreases to $E_{IT} = 287.5$ GPa with increasing temperature up to $T_{NI, max} = 750$ °C, Figure 7.11. However, the E_{IT} stays in the range of the standard deviation for coatings deposited by $Q_{O_2} = 120$ sccm. This observation remains unexplained.

Until writing this work, there has been no research conducted on the HT-NI analysis of Al_2O_3 coatings deposited by PVD measurements. Therefore, the results of Al_2O_3 coatings synthesized by CVD in [RAH+15] were considered in the discussion. Hereby, HT-NI was conducted on Al_2O_3 coatings at room temperature up to $T_{NI} = 600$ °C and $T_{NI} = 700$ °C, respectively. The pronounced decrease in the hardness and reduced elastic modulus of these coatings was observed.

7.1.3 Intermediate conclusion of high temperature properties of pure Al_2O_3

HT-XRD investigations show that the crystalline Al_2O_3 coatings deposited at $T_s \approx 780$ °C, regardless of the oxygen gas flow, remain stable up to $T = 1200$ °C. After annealing during HT-XRD tests up to $T = 1,200$ °C, the coating morphology shows no thermally induced defects like cracks or delamination, which can be attributed to the high phase stability of Al_2O_3 coatings deposited by HS-PVD. The reason for such promising thermal stability of these coatings can be the high crystallinity results from the high substrate temperature of $T_s \approx 780$ °C in combination with a high process stability of HS-PVD technology. Reduced target poisoning enables high ion energies of coating species, which is advantageous for depositing a high content of crystalline stable phases. Moreover, the indentation hardness and modulus after HT-XRD are comparable with the as-deposited state. However, HT-NI results show that the indentation hardness reduces at elevated temperatures. Overall, the coatings provide promising results in terms of high temperature properties. Additionally, results indicate that in situ HT-NI measurements are necessary to gain a better insight into the hot hardness of coatings, since HT-NI results show deviations compared to nanoindentation tests at room temperature.

7.2 Effect of process parameters on properties of coatings deposited at $T_s \approx 850$ °C

In subchapter 7.1, it was shown that a high crystallinity was achieved as the substrate temperature rose to $T_s \approx 780$ °C. Therefore, the potential of HS-PVD was utilized to synthesize the coatings at higher temperatures. With a maximum heater temperature of $T_{H,max} = 940$ °C, the substrate temperature of $T_s \approx 850$ °C was achieved. The coating processes were carried out in a dc-modus with different bias voltages and oxygen gas flows.

Table 7.3: Parameters of coating process at $T_s \approx 850$ °C

Process ID	5035	5034	5039
Cathode power P_C in kW	6	6	6
Cathode current I_C in A	16	16	16
Bias voltage U_B in V	-75	-125	-125
Bias current I_B in A	3	3	3
Ar gas flow Q_{Ar} in sccm	8,000	8,000	8,000
O ₂ gas flow Q_{O_2} in sccm	80	80	120
Pressure p in Pa	33.4	33.4	33.6
Heater temperature T_H in °C	940 ± 10	940 ± 10	940 ± 10
Substrate temperature T_s in °C	850 ± 10	850 ± 10	850 ± 10
Rotation speed ω_{Table} in rpm	-	-	-
Coating time $t_{coat.}$ in min	60	60	60

7.2.1 Properties of coatings deposited at $T_s \approx 850$ °C

The SEM images in Figure 7.12 demonstrate that the morphology and topography of Al_2O_3 coatings are dependent on the corresponding process parameters such as bias voltage, oxygen gas flow rate, and substrate temperature. Coating time $t_{coat.}$ was comparable for all variations. Coating thickness generally decreases with higher oxygen gas flow and lower temperature. Under a bias voltage of $U_B = -125$ V, lower substrate temperature promotes coatings with densely packed cauliflower-like topography, whereas at $T_s \approx 850$ °C columns are smaller but with a higher porosity. Deposition rate decreases with increasing temperature. The denser coating morphology at $T_s \approx 780$ °C than $T_s \approx 850$ °C could be due to the lower film growth rate.

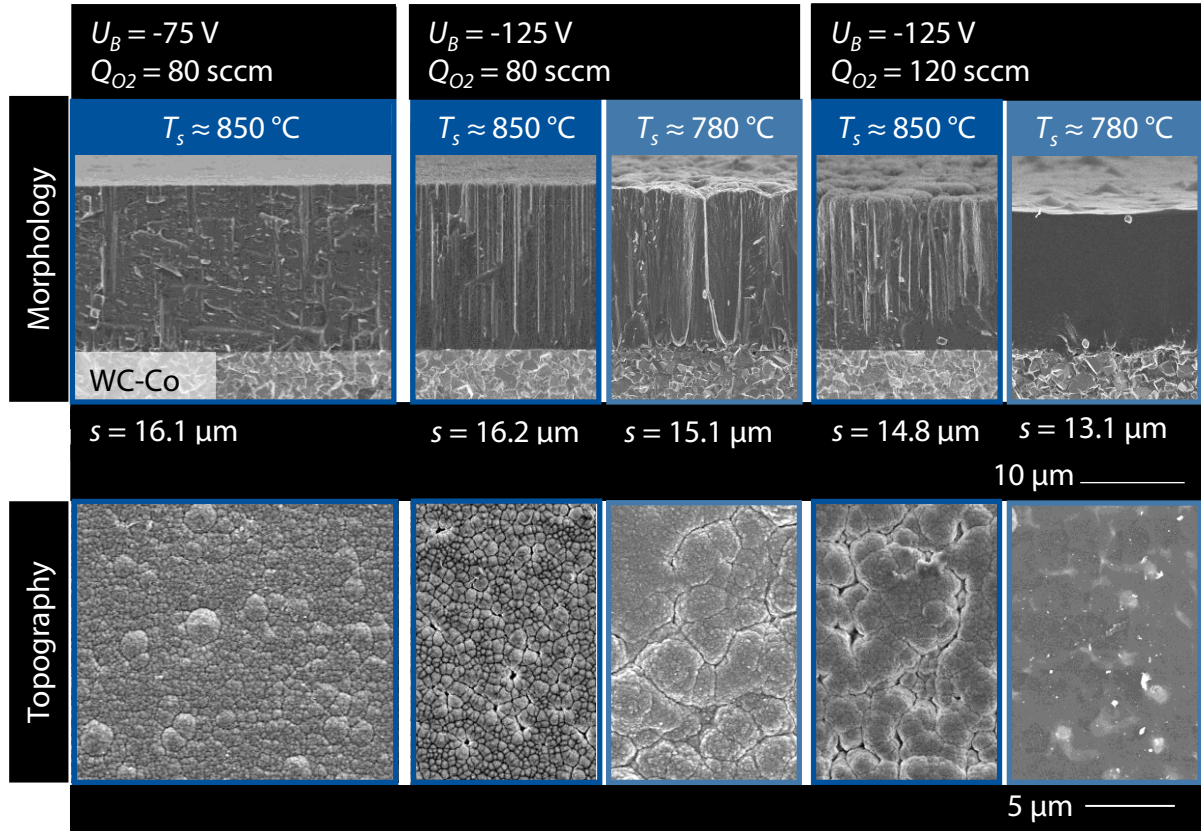


Figure 7.12: Morphology and topography of Al_2O_3 coatings deposited under different conditions

Under a constant oxygen gas flow of $Q_{O_2} = 80$ sccm and at $T_s \approx 850$ °C, the morphology changes from a fine columnar microstructure to a dense nanocrystalline-like morphology as the bias voltage decreases from $U_B = -125$ V to $U_B = -75$ V. The columnar morphology remained unchanged under a $U_B = -125$ V, as the oxygen gas flow increased to $Q_{O_2} = 120$ sccm. However, the column size increases slightly during coating growth from the interface to the coating surface. This could be explained by an increase of scattering between plasma species, and consequent lowering of ion energies and reduced adatom mobility in line with higher deposition pressure. Moreover, a slight decrease in coating thickness is visible.

The XRD micrograph of coatings deposited at $T_s \approx 850$ °C is illustrated in Figure 7.13 a). All three coatings show the same peaks. Thereby, the coating deposited at lower bias voltage $U_B = -75$ V indicates peaks with less intensity than the other coatings.

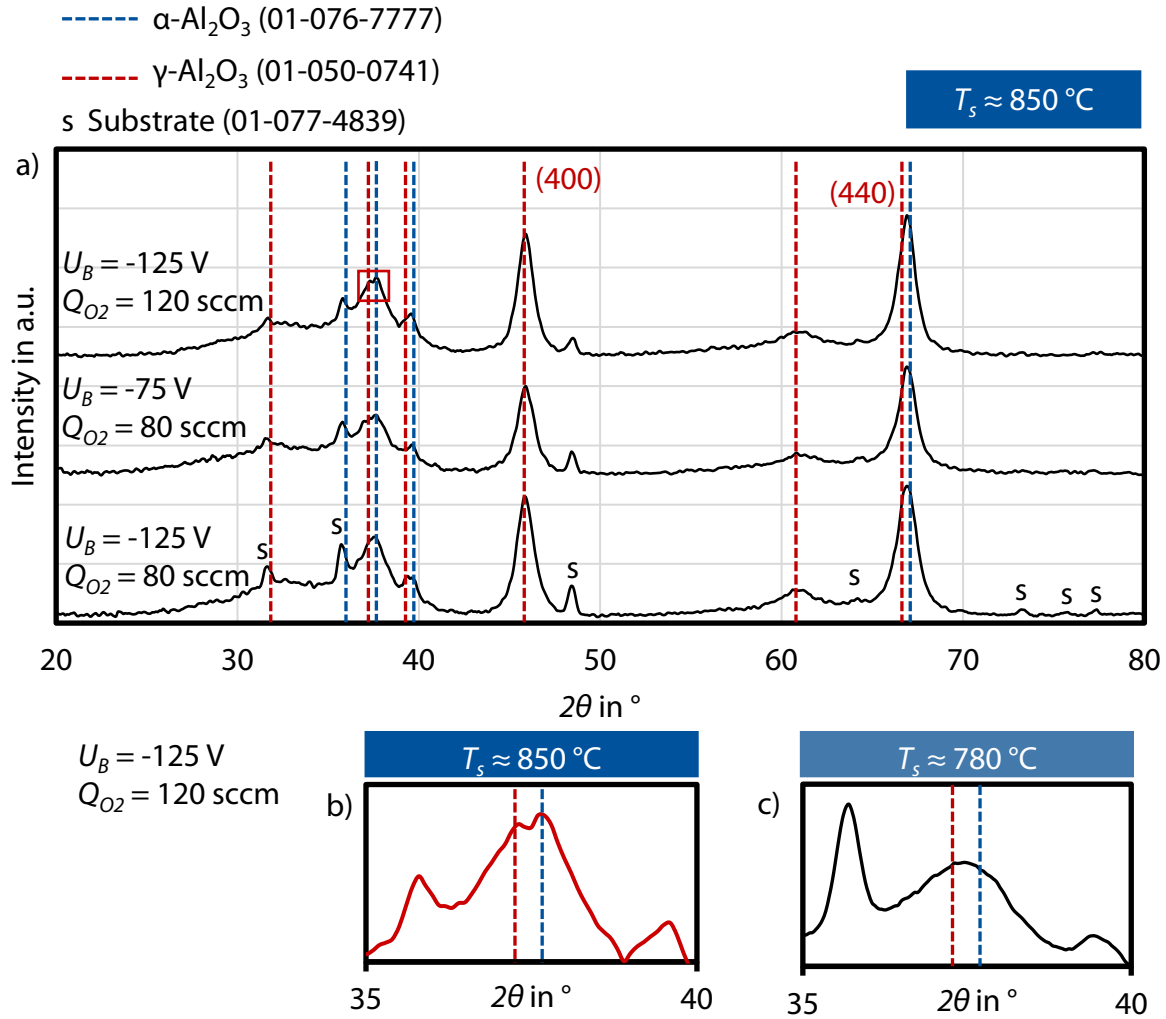


Figure 7.13: XRD results of Al_2O_3 coatings deposited at a) $T_s \approx 850$ °C, comparison of detailed XRD patterns deposited at b) $T_s \approx 850$ °C and c) $T_s \approx 780$ °C with $U_B = -125$ V and $Q_{O_2} = 120$ sccm

High-resolution XRD patterns of Al_2O_3 coatings deposited at different substrate temperatures with $U_B = -125$ V and $Q_{O_2} = 120$ sccm are shown in Figure 7.13 b) and c). These patterns highlight a notable difference between the coatings deposited at different substrate temperatures. Specifically, in the sample deposited at $T_s \approx 850$ °C, the diffraction peak around $2\theta \approx 37^\circ$ exhibits a clear splitting, Figure 7.13 b). This feature is not visible in Al_2O_3 coatings deposited at the lower substrate temperature of $T_s \approx 780$ °C, Figure 7.13 c). The observed peak splitting may indicate the formation of a second phase, potentially the $\alpha\text{-Al}_2\text{O}_3$, alongside the $\gamma\text{-Al}_2\text{O}_3$. To verify this hypothesis and gain a deeper insight into the microstructure of coatings, scanning transmission electron microscopy (STEM) analysis was carried out by a Tecnai G² F20 S-TWIN of FEI, Hillsboro, USA. STEM was conducted at GFE RWTH Aachen on a thin lamella

prepared by focused ion beam (FIB). Figure 7.14 a-c) depicts cross-sectional TEM bright-field (BF) micrograph as well as corresponding dark-field (DF) micrographs. The SAED pattern is shown in Figure 7.14 d)

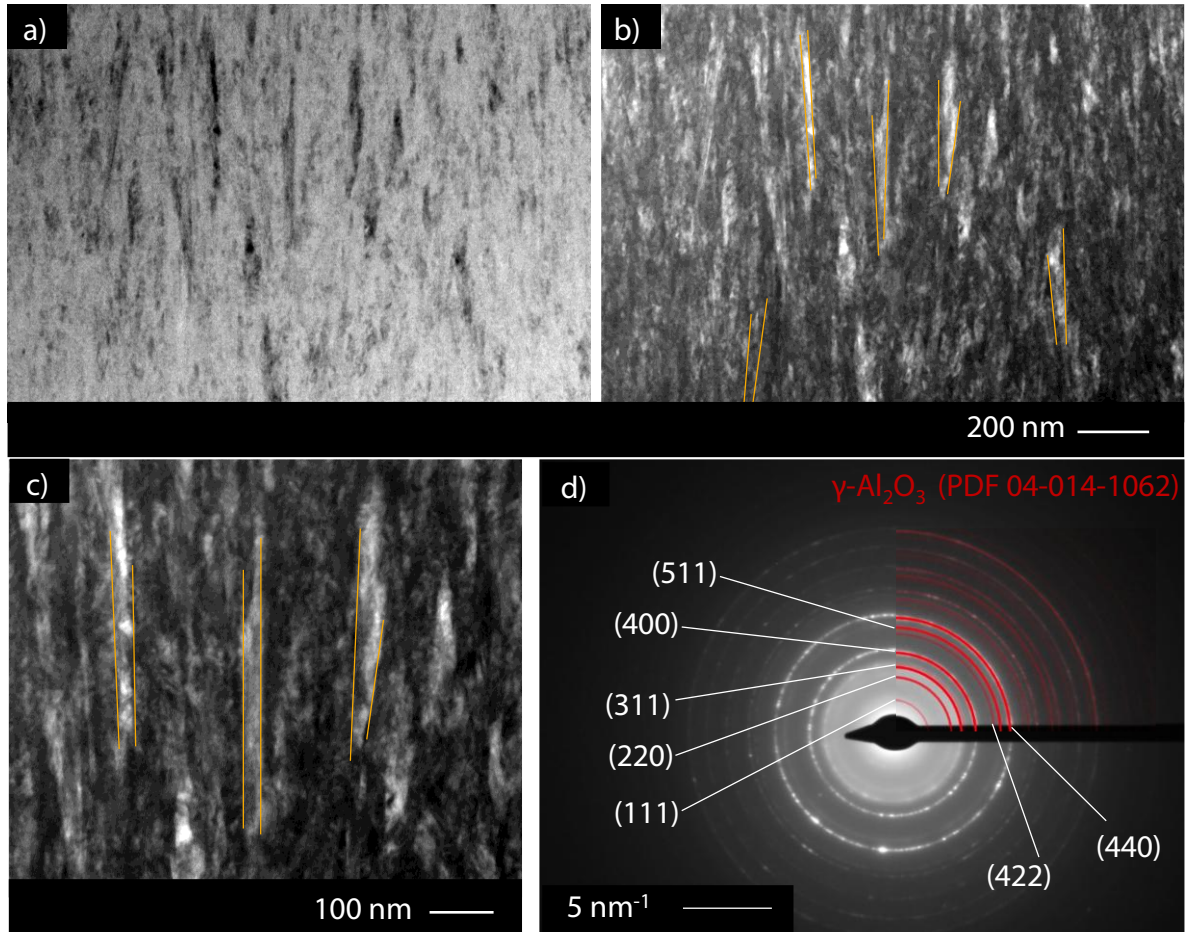


Figure 7.14: Cross-sectional STEM micrographs in a) BF, b-c) DF, and d) SAED pattern

The simulated ring diagrams, marked in red, are generated using RIng Pattern Simulation (RIPAS) program [Wei23]. In agreement with the SEM results in Figure 7.12, STEM micrographs reveal very fine columnar growth of the microstructure of coating with column's height up to $h \approx 300$ nm, Figure 7.14 a-c). According to the SAED pattern shown in Figure 7.14 d), the crystallites are preferentially oriented along (400) and (440) directions that agrees with the XRD results. Continuous diffraction rings in SAED pattern are visible rather than discrete spots. This type of pattern arises from many small, randomly oriented nanocrystals, indicating nanocrystalline coating microstructure. The rings are relatively broad,

suggesting that the grain size is likely in the range of a few nanometers to tens of nanometers. SAED pattern corresponds likely to pure $\gamma\text{-Al}_2\text{O}_3$.

There is no significant difference between the indentation values measured for the three different coatings deposited at $T_s \approx 850$ °C, as observed in Table 7.4. Therefore, the effect of the process parameters in the analyzed range on these values is negligible.

Table 7.4: Nanoindentation values of Al_2O_3 coatings deposited at $T_s \approx 850$ °C

Al_2O_3 coatings	H_{IT} in GPa	E_{IT} in GPa	η_{el} in %
$U_B = -125$ V	27.1 ± 1.4	297.2 ± 11.4	62
$U_B = -75$ V	25.5 ± 0.8	287.1 ± 5.9	60
$Q_{O_2} = 120$ sccm	27.2 ± 0.8	297.5 ± 6.1	62

7.2.2 Residual stress of coatings deposited at $T_s \approx 850$ °C

Thin coatings deposited by PVD typically exhibit intrinsic compressive residual stresses due to the energetic bombardment during deposition. However, at elevated deposition temperatures, as commonly observed in CVD, thermally induced tensile stresses can develop due to the difference in thermal expansion coefficients between the Al_2O_3 coating and the WC-Co substrate. In this study, Al_2O_3 coatings were deposited via HS-PVD at a high substrate temperature of $T_s \approx 850$ °C. Due to this elevated temperature, it is essential to investigate whether the characteristic compressive stresses of PVD coatings are still present or whether thermal tensile stresses dominate, as is typically the case in CVD coatings. Residual stresses in the Al_2O_3 coating deposited at $T_s \approx 850$ °C were determined through a conventional X-ray diffractometer using the $\sin^2\psi$ method, as described in subchapter 5.4.1. The maximum X-ray penetration depth was calculated $\tau_{max, 400} \approx 10$ μm .

The residual stress of coatings can be found in Table 7.5. The stresses along two perpendicular directions, $\phi = 0^\circ$ and $\phi = 90^\circ$, show only slight deviations. The highest compressive stress is measured for the coating deposited with $U_B = -125$ V and $Q_{O_2} = 80$ sccm. Reducing the bias voltage leads to the development of tensile stress, suggesting the existence of a bias voltage below which ion bombardment is no longer sufficient to induce compressive stress. This implies that there may be a specific bias level at which the coating could be deposited in a stress-free state.

Compressive residual stress decreases as the oxygen gas flow increases to $Q_{O_2} = 120$ sccm. This reduction can result from the coarse columnar morphology observed in Figure 7.12. Moreover, gaps between the columns are visible in topography image, which may reduce residual stresses.

Table 7.5: Residual stress in Al_2O_3 coatings deposited at $T_s \approx 850$ °C analyzed using XRD

Al_2O_3 coatings	$U_B = -125$ V	$U_B = -75$ V	$U_B = -125$ V
	$Q_{O_2} = 80$ sccm	$Q_{O_2} = 80$ sccm	$Q_{O_2} = 120$ sccm
σ in MPa, $\Phi = 0^\circ$	-1341	127	-703
σ in MPa, $\Phi = 90^\circ$	-1349	172	-719

However, the reduction in residual stress due to increased oxygen flow is less significant than the reduction caused by decreasing the bias voltage. Energetic plasma particles, bombarding the surface of the growing coating, influence the film-formation process and the properties of the deposited coating. The impact of bias voltage on energy of plasma particles, bombarding the substrate, seems to be more dominant than the gas pressure.

Despite the different compressive residual stress levels observed in these coatings, all three coatings exhibit no significant differences in H_{IT} and E_{IT} , as shown in Table 7.4. XRD primarily detects type 1 residual stresses, which are measured and averaged over a representative volume of the material. In contrast, nanoindentation probes the material at the micro- to nanoscale, where type 2 and type 3 residual stresses play a more significant role.

7.2.3 Intermediate conclusion to the coatings deposited at $T_s \approx 850$ °C

In contrast to coatings deposited at $T_s \approx 780$ °C, increasing oxygen flow results in coarser columnar growth at $T_s \approx 850$ °C. The topography of coatings deposited at $T_s \approx 850$ °C shows porosity, resulting from higher film growth rate compared to ones deposited at $T_s \approx 780$ °C. However, XRD analysis of Al_2O_3 synthesized at $T_s \approx 850$ °C shows distinct α -phase peaks rather than ones deposited at $T_s \approx 780$ °C. Moreover, TEM analysis indicates nanocrystalline Al_2O_3 coating. Based on SAED pattern, the investigated region is likely composed of pure γ - Al_2O_3 . The discrepancy between TEM and XRD results can be attributed to the vastly different sampling volumes of the two techniques. XRD probes a large area and can detect minor, localized phase formation, while TEM examines an area of hundreds of nanometers thin slices. Thus, it is possible that this specific region does not contain the same phase composition

detected in the XRD. If the FIB lamella is prepared from a region where no α -phase exists, it is plausible that the TEM would not reveal any indication of a secondary phase. Therefore, to confirm SAED results statistically, multiple FIB lamellae would be needed, but this is rarely done due to time and cost constraints. The high deposition temperature of $T_s \approx 850$ °C introduces competing mechanisms: PVD-induced compressive stress versus thermally induced tensile stress. Such high temperatures did not fully suppress PVD-type compressive stresses, implying that enough ion bombardment retains dominance over thermal expansion effects. Moreover, the results confirm the hypothesis that adjusting the ion bombardment through changing the bias voltage allows for the manipulation of stresses and can enable coatings with compressive stresses in PVD processes. However, thermal effects may play a secondary role. Furthermore, no correlation is observed between the residual stress in coatings and indentation hardness and modulus. The depth-resolved residual stress measurements in the future studies may give more insights to explain this observation. The coatings deposited at $T_s \approx 850$ °C could have more potential than ones deposited at $T_s \approx 780$ °C as wear protection for cutting tools, due to pure crystallinity, signs of α -phase existence as well as compressive residual stresses. To investigate this hypothesis, the machining performance of these coatings deposited at $T_s \approx 850$ °C using HS-PVD was examined under turning operations. Between the three variants, coating deposited with $U_B = -125$ V and $Q_{O_2} = 80$ sccm possess the highest residual stress state. In the following, this variation is therefore selected for cutting tests. The morphology of the coating on the surface near the region of this variant is however not dense and shows gaps. This is not the case in the areas of coating/substrate interface, Figure 7.15. There, morphology is dense and fine-grained like, promotes oxidation resistance.

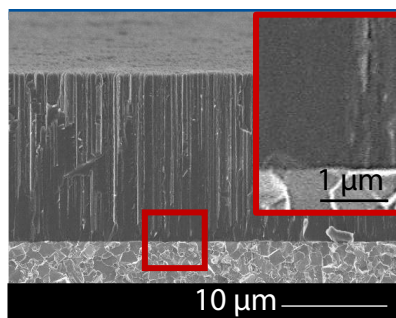


Figure 7.15: SEM cross-section of Al_2O_3 coating deposited at $T_s \approx 850$ °C with $U_B = -125$ V and $Q_{O_2} = 80$ sccm in detailed at coating/substrate interface

8 Performance in dry turning operation

This chapter deals with the cutting performance of Al_2O_3 coatings synthesized by HS-PVD at $T_s \approx 850^\circ\text{C}$. $\text{TiAlN}/\text{Al}_2\text{O}_3$ and Al_2O_3 coatings are compared to TiAlN coating in dry fine turning of C45+N steel. The TiAlN coating, as a widely used PVD tool coating, is a reference. TiAlN coatings are produced using an industrial mfMS coating unit.

8.1 Process parameters and procedure for cutting tests

The Al_2O_3 coating was deposited using the process parameters in Table 8.1. The coating time was adjusted to achieve a coating thickness in the range of $2\text{ }\mu\text{m} < s < 3\text{ }\mu\text{m}$. Additionally, since the tools required coating in a rotating mode, the process was conducted in one-fold rotation. To investigate coating and compound properties, WC-Co indexable inserts SNUN 120412 THM12, Kennametal Widia Produktions GmbH & Co. KG, Essen, Germany with $x_{\text{Co}} = 6\text{ wt. \%}$ were used. For cutting tests, WC-Co cutting tools CNMA 120404, CTS12D, CERATIZIT, Luxemburg, with $x_{\text{Co}} = 6\text{ wt. \%}$ were coated. The $\text{TiAlN}/\text{Al}_2\text{O}_3$ coating system was produced in combination of two coatings units. The HS-PVD process parameters for deposition of Al_2O_3 toplayer in $\text{TiAlN}/\text{Al}_2\text{O}_3$ are given in Table 8.1 and parameters of TiAlN interlayer deposited by mfMS coating unit are listed in Table 8.2.

Table 8.1: Process parameters of Al_2O_3 coatings deposited for cutting tests

Process ID	5344		5364	
	Plasma etching	Al_2O_3	Plasma etching	Al_2O_3 toplayer in $\text{TiAlN}/\text{Al}_2\text{O}_3$
Cathode power P_C in kW	-	6	-	6
Cathode current I_C in A	-	16	-	16
Bias voltage U_B in V	-450	-125	-450	-125
Bias current I_B in A	3	3	3	3
Ar gas flow Q_{Ar} in sccm	9,000	8,000	9,000	8,000
O_2 gas flow Q_{O_2} in sccm	-	80	-	80
Pressure p in Pa	37.4	33.2	37.4	33.2
Heater temperature T_H in $^\circ\text{C}$	940 ± 10	940 ± 10	940 ± 10	940 ± 10
Substrate temperature T_s in $^\circ\text{C}$	850 ± 10	850 ± 10	850 ± 10	850 ± 10
Rotation speed ω_{Table} in rpm	7.5	7.5	7.5	7.5
Step time t_s in min	35	12	5	8

The TiAlN coated samples were charged in the HS-PVD coating unit. After heating up to a substrate temperature of $T_s \approx 850$ °C, argon plasma etching with a bias voltage of $U_B = 450$ V and argon flow rate of $Q_{Ar} = 9,000$ sccm was conducted for $t_s = 5$ min to activate and remove of oxide reactive layer on the surface of the TiAlN coatings. Afterwards, Al_2O_3 toplayer was deposited by HS-PVD with parameters given in Table 8.1. The TiAlN interlayer in TiAlN/ Al_2O_3 as well as TiAlN reference coatings were deposited using an industrial coating machine of type CC800/9 SinOx XL, CemeCon AG, Würselen, Germany, as shown in Figure 8.1 a). The coatings were deposited using two cathodes with the same target configuration on cathode 1 and cathode 3 in a dual bipolar pulsed arrangement with pulse on time of $t_{on} = 20$ μ s and pulse off time of $t_{off} = 7$ μ s. Moreover, the coating unit has two radiant heaters with a maximum power of $P_H = 16$ kW. In order to monitor the substrate temperatures during the coating process, temperature measurements were carried out using InsiTemp, which is described in [BBK18c]. Before coating deposition, samples were plasma cleaned using a mf -power supply. Additionally, the pre-ionization of gases via a hollow cathode, known as booster etching, were conducted to enhance cleaning efficiency by optimizing the etching process. The plugged TiAl48 targets were installed on cathode one and cathode three, as shown in Figure 8.1 a).

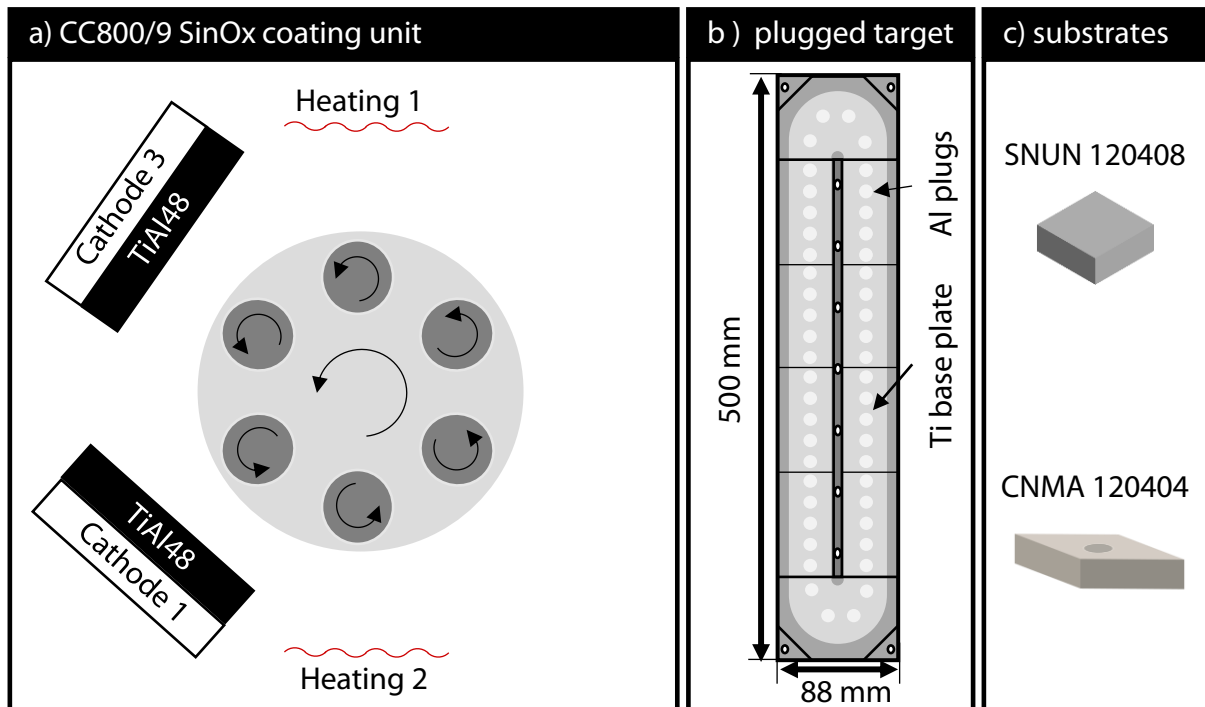


Figure 8.1: a) Illustration of CC800/9 SinOx, b) TiAl48 plugged target and c) substrates

The plugged TiAl48 targets consist of Ti base plate with 48 Al plugs, as illustrated in Figure 8.1 b). The target has a total dimension of $A_{Target} = 500 \text{ mm} \times 88 \text{ mm}$. Each plug has a diameter of $d_{Plug} = 15 \text{ mm}$. The substrate samples were subjected to a three-fold rotation during deposition, whereby the substrate table was rotated at a speed of $\omega_{Table} = 2 \text{ rpm}$. The substrates are shown in Figure 8.1 c). The TiAlN reference coating was deposited with process parameters in Table 8.2. The Al_2O_3 and TiAlN/ Al_2O_3 coating variants were first analyzed regarding coating properties and compound adhesion strength.

Table 8.2: Process parameters for the deposition of TiAlN by CC800/9 SinOx

Process ID	5443		5364
Parameters	Plasma etching	TiAlN	TiAlN interlayer in TiAlN/Al ₂ O ₃
cathode 1 power P_{C1} in kW	-		5
cathode 3 power P_{C3} in kW	-		5
Frequency f in kHz	250		37
Bias voltage U_B in A	-650		-90
Booster voltage $U_{Booster}$ in V	-		-80
Ar gas flow Q_{Ar} in sccm	Pressure controlled		120
Kr gas flow Q_{Kr} in sccm	50		80
N ₂ gas flow Q_{N2} in sccm	-	Pressure controlled	
Pressure p in Pa	0.2		0.5
Heater power P_H in kW	16		16
Substrate temperature T_s in °C	530 ± 5		545 ± 5
Rotation speed ω_{Table} in rpm	2		2
Step time t_s in min	60	245.5	160.2

8.2 Coating and adhesion strength properties

TiAlN shows a chemical composition of $x_{Al} \approx 57 \text{ at.}\%$ and $x_{Ti} \approx 43 \text{ at.}\%$ in the metallic portion analyzed by EDX. In Figure 8.2 a), the Al_2O_3 coating exhibits a finer crystalline morphology compared to TiAlN coating, Figure 8.2 b). The TiAlN/ Al_2O_3 coating reveals a slight difference in morphology, with the Al_2O_3 toplayer exhibiting a more fine-grained morphology than TiAlN interlayer, Figure 8.2 c). This can be attributed to differences in coating growth on the TiAlN

interlayer surface compared to the uncoated WC-Co substrate. Although the individual layers were deposited in different coating units, an intact bonding between the two layers can be observed.

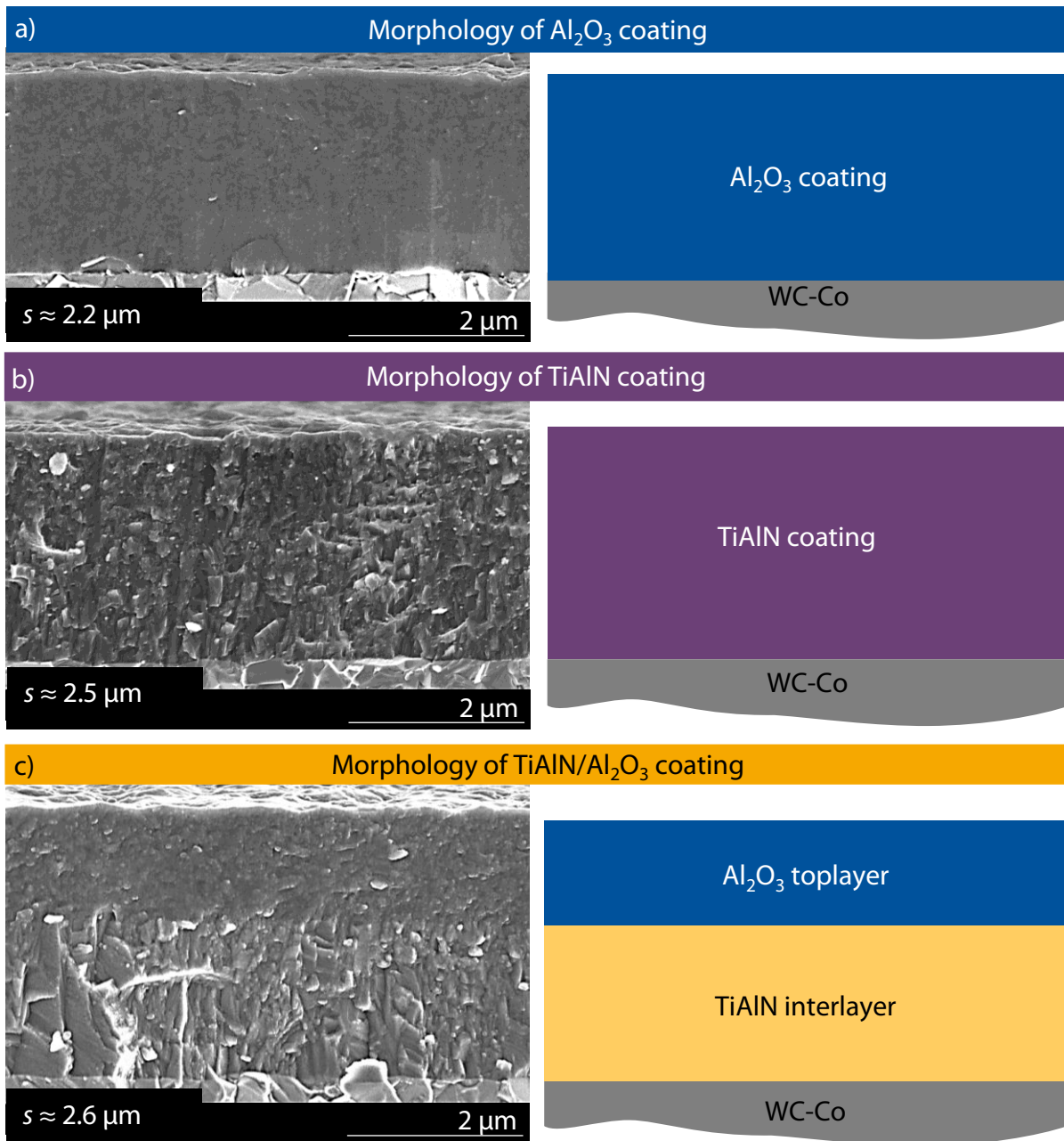


Figure 8.2: Morphology of a) Al_2O_3 and b) TiAlN and c) $\text{TiAlN}/\text{Al}_2\text{O}_3$ coating on WC-Co substrate [BMA26]

The indentation hardness and indentation modulus as well as elastic work percentage of the coatings on the WC Co substrate were analyzed on the polished surface of the coatings. The

results are shown in Table 8.3. The lower indentation hardness and modulus of TiAlN/ Al_2O_3 coating than Al_2O_3 monolayer can be attributed to the denser Al_2O_3 coating morphology observed in Figure 8.2 a). TiAlN coating has the highest elastic work percentage η_{el} , resulting in highest resistance against plastic deformation.

Table 8.3: Indentation values of Al_2O_3 , TiAlN and TiAlN/ Al_2O_3 coatings on WC-Co substrate

Coating	Al_2O_3	TiAlN	TiAlN/ Al_2O_3
Indentation hardness H_{IT} in GPa	29.8 ± 3.2	33.1 ± 2.6	23.8 ± 2.6
Indentation modulus E_{IT} in GPa	459.0 ± 23.4	381 ± 27	357 ± 28
Elastic work percentage η_{el} in %	62	70	62

The adhesion strength of the two coating variants on the cemented carbide CNMA tools was analyzed using Rockwell indentation tests, as shown Figure 8.3 a-c). The coating adhesion on the substrate is assigned to adhesion class *HF 1*, which is the best possible adhesion class for industrial applications according to DIN 4856.

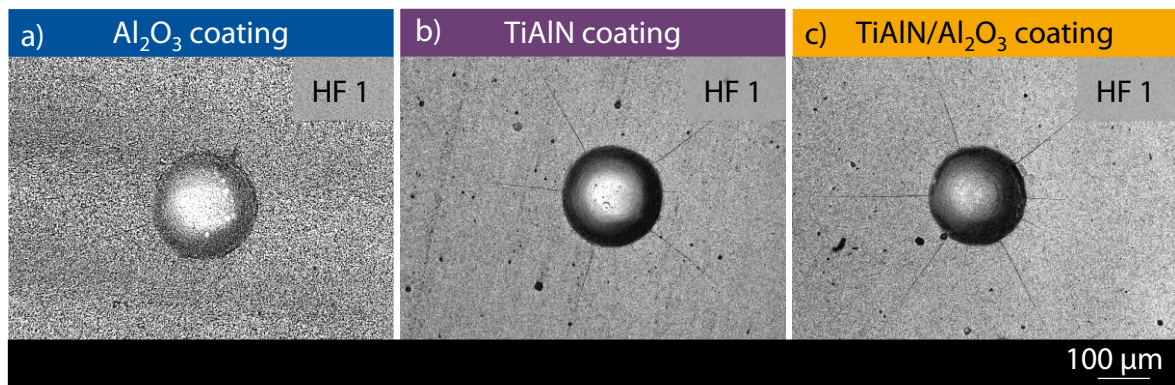


Figure 8.3: CLSM images of Rockwell imprints on a) Al_2O_3 and b) TiAlN and c) TiAlN/ Al_2O_3 coated CNMA tools [BMA26]

8.3 Cutting behavior of coated tools in turning of C45+N steel

The cutting performance of HS-PVD coated tools was investigated during the turning of C45+N steel. C45+N steel was chosen as the workpiece due to its industrial relevance, balanced mechanical properties, and suitability for benchmarking tool performance. Its widespread use in manufacturing ensures that the results are practically applicable, while its machinability

allows for controlled and reproducible testing conditions. Additionally, C45+N offers a challenging yet manageable cutting environment, making it ideal for evaluating the wear behavior of HS-PVD coated tools. Thereby, this selection can give first insights into the HS-PVD coatings' potential for future industrial applications.

Cutting experiments were carried out on a CTX520 Linear lathe from Gildemeister Drehmaschinen GmbH, Bielefeld, Germany, at the Institute of Production Engineering and Machine Tools (IFW) of Leibniz University Hannover in Germany. The workpiece considered for turning tests in this work was cylindrical shafts made from normalized C45+N, Figure 8.4 a). The rake angle was set to $\gamma = -6^\circ$. The negative rake angle was chosen to increase the wedge stability and to avoid early cutting-edge failure. The initial cutting speed was set to a lower value of $v_c = 120$ m/min to gain preliminary insights into cutting performance. Subsequently, the cutting speed was increased to $v_c = 200$ m/min. Other cutting parameters were also set within industrial application ranges, with a feed rate of $f = 0.2$ mm and the depth of cut $a_p = 1$ mm. To investigate the wear development, the tests were conducted in defined cutting intervals of $t_c = 0.16$ min, $t_c = 1$ min, $t_c = 2$ min, $t_c = 3$ min, $t_c = 5$ min, $t_c = 6$ min, $t_c = 9$ min, $t_c = 10$ min, $t_c = 12$ min, $t_c = 15$ min, and $t_c = 18$ min. The same cutting edge was tested during cutting time of $0 \text{ min} \leq t_c \leq 18 \text{ min}$. To validate the results, each test was conducted twice and each time an unused cutting edge was tested. The failure criterion was defined as a maximum flank wear land width of $VB_{max} = 100 \mu\text{m}$. The abortion criterion for the cutting tests was a cutting time of $t_c = 18$ min. The wear development of the rake and flank face as well as the flank wear land width was analyzed with a Keyence VHX-970 microscope, Keyence Corporation, Osaka, Japan. The Keyence VHX analyzer software was used to determine the maximum wear land width. A straight line was drawn along the initial cutting edge, and the distance was then measured parallel to the cutting edge along the flank face up to the most prominent detectable wear point, Figure 8.4 b).

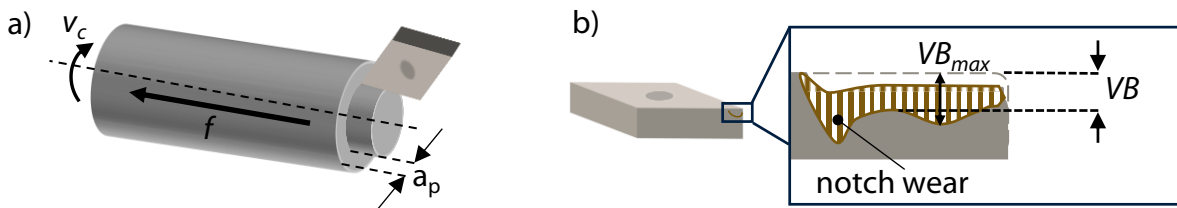


Figure 8.4: Schematic illustration of the turning process and b) VB_{max} on the flank face

To evaluate the wear behavior of the three coated tool variants, the maximum flank wear land width VB_{max} was measured. Results are shown in Figure 8.5.

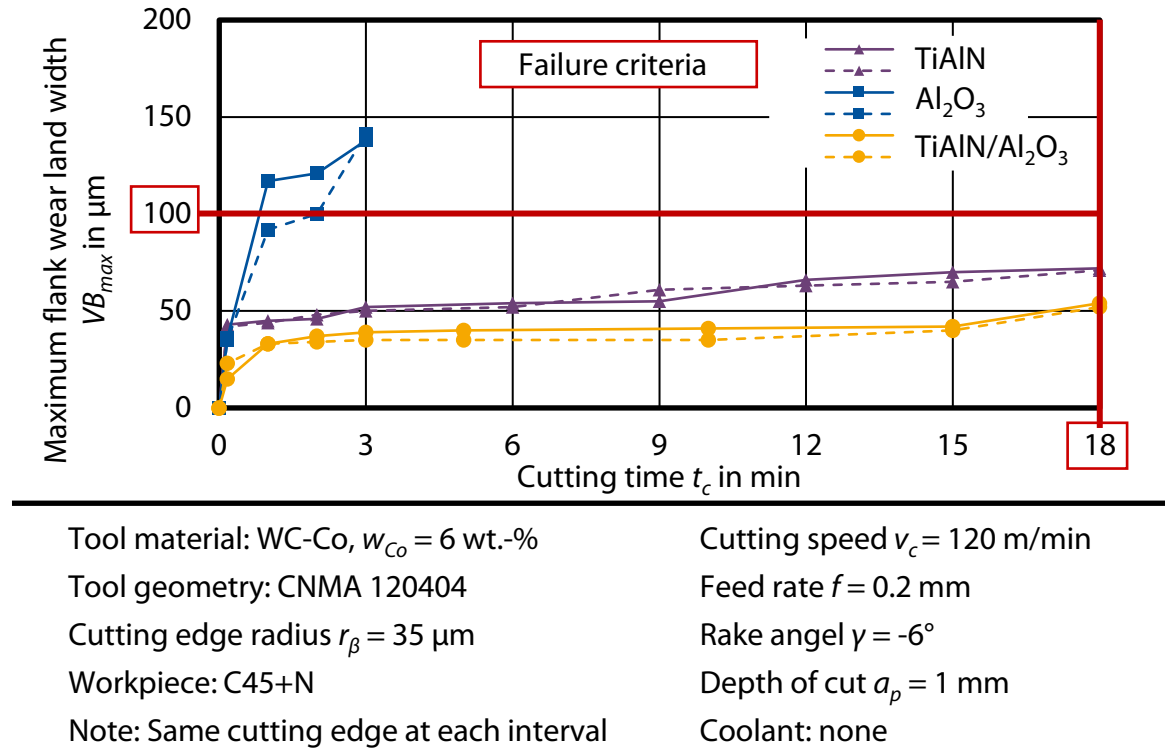
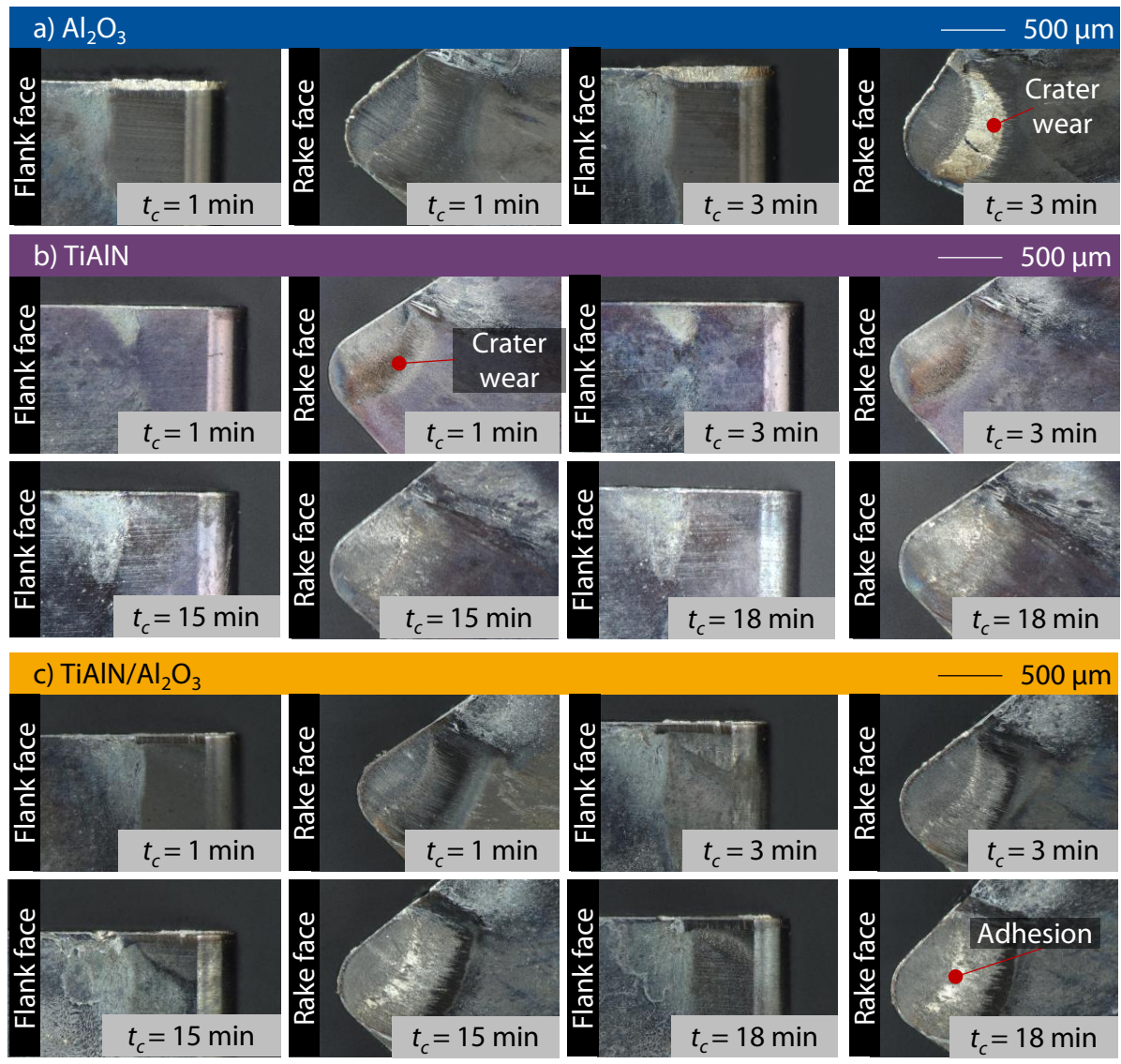


Figure 8.5: Maximum flank wear land width of VB_{max} of coated cutting tools as a function of the cutting time t_c for $v_c = 120$ m/min [BMA26]

The Al_2O_3 coated tools exhibit a rapid increase in wear land width with increasing cutting time, reaching the failure criteria before a cutting time of $t_c = 3$ min, as shown in Figure 8.5. In contrast, TiAlN and TiAlN/ Al_2O_3 coated tools achieve the tool life criterion of $t_c = 18$ min. TiAlN/ Al_2O_3 coated tools show lower flank wear land width VB_{max} compared to TiAlN variants until $t_c = 18$ min. For TiAlN/ Al_2O_3 tools, the maximum flank wear land width remains approximately by $VB_{max} \approx 40 \mu m$ up to $t_c = 15$ min. However, the flank wear land width of $VB_{max} = 50 \mu m$ is already exceeded for TiAlN coated tools after $t_c = 6$ min. Figure 8.6 exemplary shows light microscopic images at the flank and rake face of the coated tools as the cutting time increased under a cutting speed of $v_c = 120$ m/min.



Tool material: WC-Co, $w_{\text{Co}} = 6$ wt.-%

Tool geometry: CNMA 120404

Cutting edge radius $r_\beta = 35$ μm

Workpiece: C45+N

Note: Same cutting edge at each interval

Cutting speed $v_c = 120$ m/min

Feed rate $f = 0.2$ mm

Rake angle $\gamma = -6^\circ$

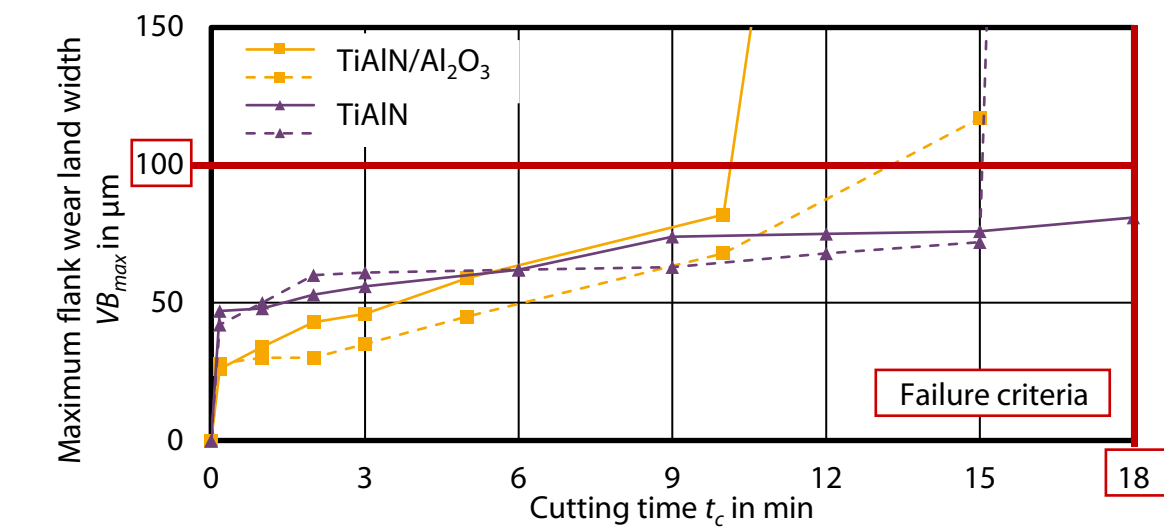
Depth of cut $a_p = 1$ mm

Coolant: none

Figure 8.6: Light microscopic images of the flank and rake face of the a) Al_2O_3 , b) TiAlN and c) $\text{TiAlN/Al}_2\text{O}_3$ coated tools under $v_c = 120$ m/min over the tool service life [BMA26]

After a cutting time of $t_c = 1$ min, significant flank face wear is already visible on Al_2O_3 coated tools. Moreover, flank face wear develops rapidly for the Al_2O_3 coated tools with increasing cutting time, compared to TiAlN and $\text{TiAlN/Al}_2\text{O}_3$ coated tools. Due to the inherent brittleness

and the absence of an interlayer, Al_2O_3 coating delamination is assumed to occur at the early stages of cutting on both the rake and flank faces. Subsequently, severe Fe adhesion on the uncoated rake face leads to pronounced crater wear on the Al_2O_3 coated tools. After a cutting time of $t_c = 1$ min, initial signs of crater wear become visible on the rake face of TiAlN coated tools, appearing as brown, crater-shaped discolorations. At cutting time of $t_c = 18$ min, the TiAlN/ Al_2O_3 coated tools show small workpiece material adhesion but no crater wear. The cutting tools with TiAlN/ Al_2O_3 indicate higher resistance against crater wear. The TiAlN and TiAlN/ Al_2O_3 coated tools showed a longer lifetime compared to the Al_2O_3 coated tools under $v_c = 120$ m/min. Therefore, the TiAlN/ Al_2O_3 and TiAlN coated tools were tested under an increased cutting speed of $v_c = 200$ m/min, while maintaining a constant feed rate and depth of cut. The tests under $v_c = 200$ m/min were conducted over almost comparable cutting intervals as in the previous turning experiments under $v_c = 120$ m/min. Figure 8.7 presents the VB_{max} after each cutting interval.



Tool material: WC-Co, $w_{Co} = 6$ wt.-%

Tool geometry: CNMA 120404

Cutting edge radius $r_\beta = 35 \mu\text{m}$

Workpiece: C45+N

Note: Same cutting edge at each interval

Cutting speed $v_c = 200$ m/min

Feed rate $f = 0.2$ mm

Rake angle $\gamma = -6^\circ$

Depth of cut $a_p = 1$ mm

Coolant: none

Figure 8.7: Maximum flank wear land width of VB_{max} of TiAlN/ Al_2O_3 and TiAlN coated tools as a function of the cutting time t_c for $v_c = 200$ m/min [BMA26]

The TiAlN coated tools exhibit a relatively stable and moderate wear progression throughout the cutting time. Both tests show a similar trend, with VB_{max} values increasing gradually from approximately $VB_{max} \approx 50 \mu\text{m}$ at $t_c = 3 \text{ min}$ to around $VB_{max} \approx 75 \mu\text{m}$ at $t_c = 18 \text{ min}$. However, the second test showed a sudden breakage of cutting edge by $t_c = 15 \text{ min}$, indicating a potential case of localized tool failure or coating delamination. However, the beginning of crater wear is observed at earlier stages compared to TiAlN/ Al_2O_3 coated tools. The reason is the more adhesion tendency of Fe on the rake face of TiAlN coated tools than TiAlN/ Al_2O_3 coated tools with Al_2O_3 toplayer. The TiAlN/ Al_2O_3 coated tools demonstrate slightly lower or comparable wear levels to TiAlN, particularly within the first $t_c = 5 \text{ min}$. However, beyond this point, differences become pronounced. A breakage of the cutting edge occurred in one test after $t_c = 10 \text{ min}$, indicating rapid tool failure. In the other test, wear progresses more steadily but crossed the failure criterion $VB_{max} = 100 \mu\text{m}$ by $t_c = 15 \text{ min}$. The results suggest that while TiAlN/ Al_2O_3 coatings can offer competitive wear resistance in early stages, they may be susceptible to sudden degradation mechanisms, such as coating delamination or thermal cracking, particularly under extended cutting speed.

Considering the flank and rake face light microscopic images in Figure 8.8, abrasion is the dominant driver of the wear on the tool flank face and crater wear on the tool rake face is the dominant wear type. Thereby, compared to the TiAlN-coated inserts, the TiAlN/ Al_2O_3 variant is more prone to flank wear. This can be explained by the lower indentation hardness of TiAlN/ Al_2O_3 compared TiAlN coatings. Furthermore, the observed increase in flank wear for TiAlN/ Al_2O_3 tools can be linked to the brittleness of the Al_2O_3 layer, which may be more susceptible to micro-chipping or crack propagation under mechanical loading at the flank face. Compared to TiAlN/ Al_2O_3 variants, the TiAlN coated tools show earlier crater wear on the rake face. With increasing cutting time, the area of crater wear increases, but still does not reach the cutting edge of the tool in both variants. The higher resistance to crater wear of TiAlN/ Al_2O_3 coated tools can be attributed to the distinct thermal and chemical properties of the Al_2O_3 top layer. The chemical inertness of Al_2O_3 offers lower adhesion tendency with Fe workpiece materials, further preventing material at the rake face. It can be concluded that the TiAlN/ Al_2O_3 coated tools possess lower resistance against abrasion.

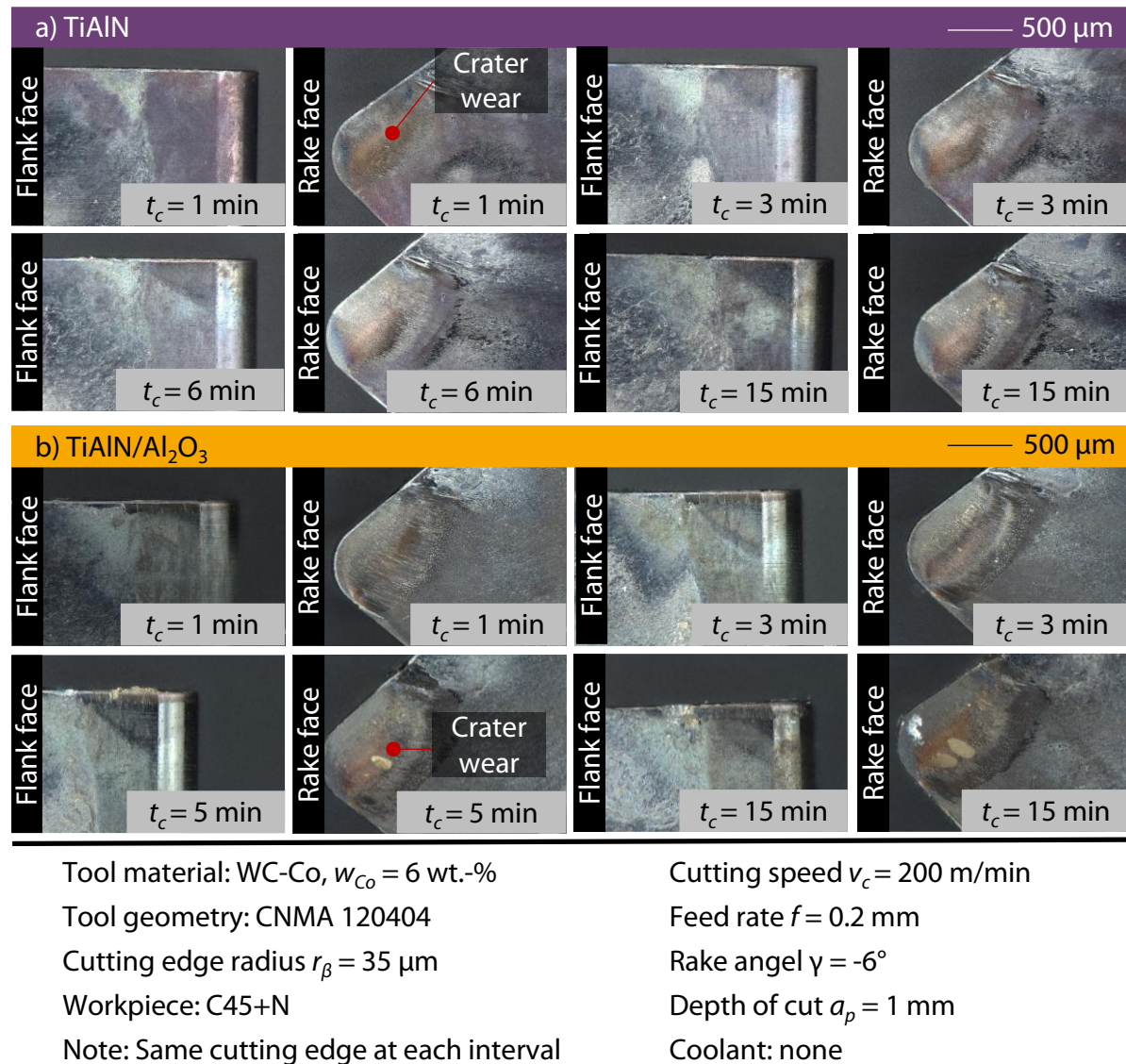


Figure 8.8: Wear on flank and rake face of TiAlN and TiAlN/Al₂O₃ coated tools over tool service life under $v_c = 200 \text{ m/min}$ [BMA26]

To deeper investigate wear phenomena of TiAlN/Al₂O₃ coated tools by HS-PVD, EDX mappings of the tool rake face were performed at the end of their service life. The SEM images under cutting speeds of $v_c = 120 \text{ m/min}$ and $v_c = 200 \text{ m/min}$ are presented Figure 8.9 a) and b), respectively. EDX mappings were conducted in the frame marked corresponding to the areas considered as adhesion and crater wear. The Ti and Al as coating elements are represented using a purple and blue color, the W in the tool material or substrate by yellow and Fe-containing adhesions from the workpiece material by green.

As illustrated in Figure 8.9 a) iron smearing due to adhesion can be observed on the rake face, which becomes more pronounced with increasing distance from the cutting edge. However, the EDX mappings show almost no signal for element W, indicating that the substrate is not exposed, as shown in Figure 8.9 a). It can be assumed that no coating delamination occurred. In Figure 8.9 a), the Al signal is still relatively strong, which indicates that the Al_2O_3 toplayer of the coating is largely intact. This suggests that abrasion of the coating is still in its early stage. As time progresses, abrasive wear leads to exposure of the underlying TiAlN interlayer, which is more prone to adhesion with workpiece material.

Moreover, the EDX mapping was conducted in the marked region in Figure 8.9 b). In contrast, areas with W signals can be detected on the rake face as the cutting speed increased to $v_c = 200$ m/min, Figure 8.9 b).

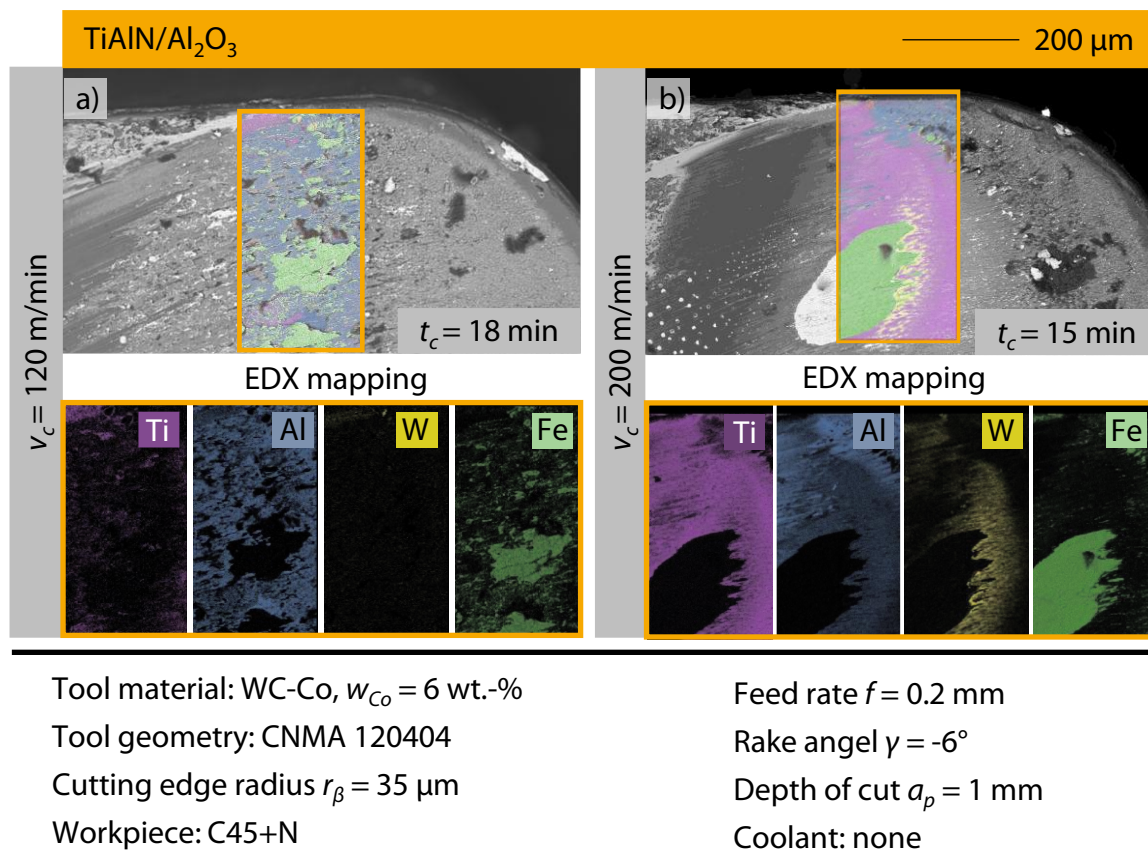


Figure 8.9: SEM images and EDX mappings on rake face of TiAlN/ Al_2O_3 coated tools under a cutting speed of $v_c = 120$ m/min a) and b) $v_c = 200$ m/min [BMA26]

In these areas, Al and Ti are also detected, however with a reduced signal. It can be assumed that the coating is worn but still no delamination occurred. Moreover, the Ti signal is stronger than the Al signal, indicating that the Al_2O_3 layer has been removed due to more intense abrasion, and the TiAlN layer is now exposed. The strong Fe signal in this region confirms significant adhesion of the workpiece material onto the tool surface. This combination of advanced abrasion and increased adhesion is typical when the harder TiAlN layer is exposed, as it has a higher tendency to bond with iron.

Figure 8.10 displays SEM image and EDS mapping on the flank face of the TiAlN/ Al_2O_3 coated tool after the tool service life is reached under a cutting speed of $v_c = 200$ m/min. This cutting speed is selected for this analysis because it represents the most severe cutting condition, where the coating undergoes accelerated wear and adhesion phenomena become more pronounced. The primarily abrasive wear on the flank face discussed from the light microscopic images in Figure 8.8 can be confirmed with EDS mappings. Thereby, no coating delamination can be detected. W signals are also detected, however with overlap of Al and Ti coating signals. Due to this, it can be assumed that the tool damage on flank face started initially with abrasive wear of the coating resulting in development of a flank wear land zone. Again, iron adhesion is visible and is concentrated at the cutting edge.

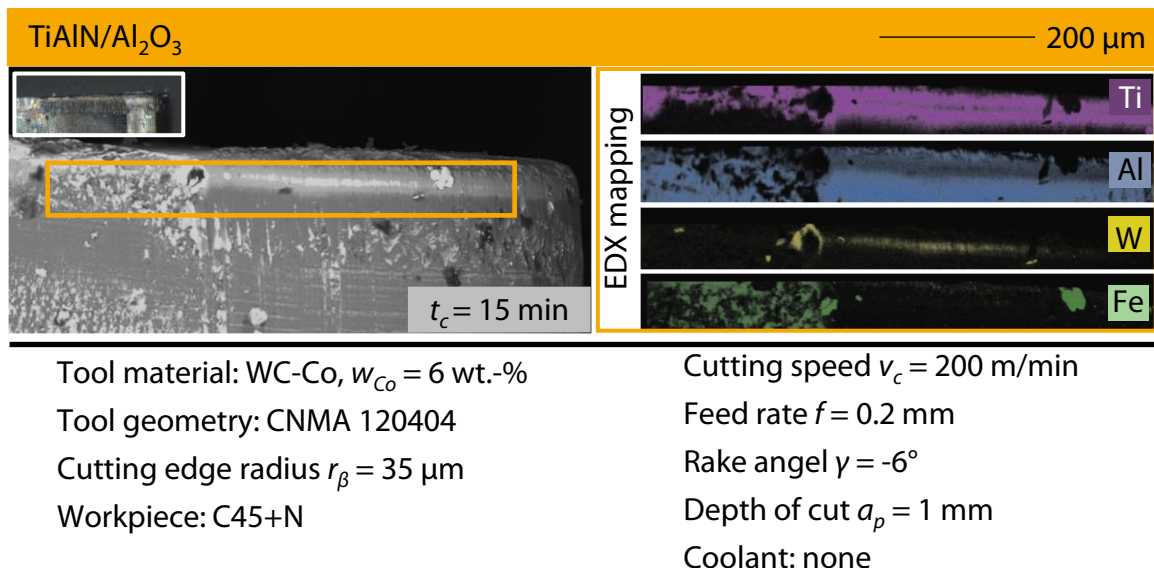


Figure 8.10: SEM image and EDX mappings on flank face of TiAlN/ Al_2O_3 coated tool under a cutting speed of $v_c = 200$ m/min [BMA26]

8.4 Intermediate conclusion of performance in turning operation

The morphology analysis indicates that both TiAlN/Al₂O₃ and Al₂O₃ coating variants exhibited a fine-grained crystalline morphology of Al₂O₃. Despite being deposited in separate coating units, the layers in TiAlN/Al₂O₃ coatings maintain an intact bonding. Adhesion tests classify coatings as *HF* 1, meeting industrial application standards. Wear analysis under a cutting speed of $v_c = 120$ m/min reveals that Al₂O₃ coated tools undergo rapid wear progression, failing before $t_c = 3$ min. In contrast, the TiAlN/Al₂O₃ coated tools achieve a significantly longer tool life of $t_c = 18$ min. The TiAlN/Al₂O₃ coating offers higher resistance against crater wear compared to TiAlN coating, delaying wear progression under $v_c = 120$ m/min. All tools exhibit accelerated wear at an increased cutting speed of $v_c = 200$ m/min. EDX analysis suggests that wear primarily originates from abrasion, with no evidence of coating delamination. Crater wear on the rake face is more pronounced at higher speeds, but the substrate remains largely protected.

The TiAlN/Al₂O₃ variant shows a higher tendency to flank wear while showing a higher resistance to crater wear compared to TiAlN coated inserts. Flank wear occurs due to abrasion. Thus, it can be concluded that the TiAlN/Al₂O₃ coated tools possess lower resistance against abrasion. Thereby, the TiAlN shows higher abrasion resistance. This can be explained by the lower indentation hardness of TiAlN/Al₂O₃ compared to TiAlN coatings. Furthermore, the observed increase in flank wear for TiAlN/Al₂O₃ tools can be linked to the brittleness of the Al₂O₃ layer, which may be more susceptible to micro-chipping or crack propagation under mechanical loading at the flank face. The higher resistance to crater wear of TiAlN/Al₂O₃ coated tools can be attributed to the distinct thermal and chemical properties of the Al₂O₃ top layer. The chemical inertness of Al₂O₃ offers lower adhesion tendency with workpiece material, further preventing material transfer and higher adhesion resistance.

9 Summary and future perspectives

This dissertation investigated the synthesis, high temperature stability, and performance of Al_2O_3 -based coatings produced by HS-PVD for two distinct applications: protection of temperature sensitive tool materials such as hot work steel X40CrMoV5-1 and enhancement of wear resistance of cemented carbide tools in turning operations. The research focused on validation of two hypotheses based on synthesis of alumina-based coatings at low $T_s < 700^\circ\text{C}$ and high substrate temperatures $T_s > 700^\circ\text{C}$.

Validation of Hypothesis 1:

The XRD results confirm the synthesis of $(\text{Al,Cr})_2\text{O}_3$ coatings at $T_s \approx 550^\circ\text{C}$ with varying Cr contents which maintained a dense, crystalline structure. Moreover, a h-AlCrN interlayer combined with coating thickness and architecture adjustments significantly enhances adhesion strength of thick γ - $(\text{Al,Cr})_2\text{O}_3$ coatings to the X40CrMoV5-1. Reducing the Cr content from $x_{\text{Cr}} = 28$ at.-% to $x_{\text{Cr}} = 12$ at.-% in combination with a h-AlCrN interlayer enhance compound adhesion strength under high temperatures in vacuum. While Cr-rich coatings with $x_{\text{Cr}} = 28$ at.-% are already delaminated at $T_{\text{vac}} = 1,000^\circ\text{C}$, Al-rich coated samples, despite completely phase transformation, are still intact up to $T_{\text{vac}} = 1,200^\circ\text{C}$. Moreover, h-AlCrN interlayer is a more promising barrier layer against Fe diffusion from substrate to coating compared to metallic AlCr. Furthermore, immersion tests of AlCrN/ $(\text{Al,Cr})_2\text{O}_3$ coated X40CrMoV5-1 steel in molten 100Cr6 steel exhibit high resistance against diffusion and adhesion of molten steel, supporting its promising suitability insights for primary forming applications.

Validation of Hypothesis 2

Crystalline γ - Al_2O_3 coatings deposited by HS-PVD under a stable process at $T_s \approx 780^\circ\text{C}$ and $T_s \approx 850^\circ\text{C}$ demonstrated promising results. HT-XRD analysis confirms that coatings remain phase-stable up to $T = 1,200^\circ\text{C}$ in both vacuum and atmospheric conditions, exhibiting no morphological changes and delamination. Comparable indentation hardness and modulus are determined after annealing for more than 7 hours during HT-XRD. Adjusting bias voltage and gas pressure successfully introduced compressive stress, even at $T_s \approx 850^\circ\text{C}$. Turning tests on C45+N steel confirmed Al_2O_3 coated tools could achieve extended tool life, particularly when combined with a TiAlN interlayer. Al_2O_3 coated tools exhibited rapid wear, failing within a cutting time of $t_c = 3$ min at a cutting speed of $v_c = 120$ m/min. In contrast, TiAlN/ Al_2O_3 coated

tools demonstrated higher wear resistance, achieving a tool life of $t_c = 18$ min. Even at an increased cutting speed of $v_c = 200$ m/min, these tools maintain a gradual wear progression without delamination. EDX analysis reveals that wear primarily resulted from abrasive mechanisms, while crater wear is more pronounced at higher speeds but does not compromise the coating's adhesion to the substrate. Compared to significant studies dealing with cutting performance of PVD coated tools using conventional PVD methods, no studies were available in this context at the time of writing for HS-PVD coated tools. This dissertation contributes the first knowledge about tools coated by HS-PVD technology and their performance in real cutting applications. Thereby, the introduction of optimized interlayers, precise process control, and strategic compositional modifications prove essential in enhancing adhesion, wear resistance, and high temperature properties. These findings provide a strong foundation for the industrial application of HS-PVD alumina coatings in manufacturing applications.

Future perspectives

Future research work is expected to be investigation regarding the service life under thermally induced cyclic load. In initial immersion tests, metallurgical corrosion and adhesive steel attachments to the molten steel are successfully eliminated. However, tools undergo thermal shock loading considering the primary forming applications such as die casting. Due to this, investigations into the service life under cyclic load in contact with molten steel are still lacking to assess the potential in depth, considering conditions in real primary forming applications. These aspects should be addressed in future studies.

Since the HS-PVD coating unit used in this study is a prototype, it offers significant potential for further development. Implementing advanced deposition techniques, such as modifying the substrate bias supply with a pulsed bias voltage, which is widely established in conventional PVD processes, could further enhance adhesion strength through optimized ion bombardment and stress control. Additionally, incorporating two hollow cathodes in the unit can enable multilayer coatings with varying elemental compositions. for advanced applications. Furthermore, the results demonstrated that coatings with compressive residual stresses can be synthesized even at $T_s \approx 850$ °C by adjustment of process parameters. Therefore, investigations regarding synthesise of Al_2O_3 at higher substrate temperatures $T_s > 850$ °C combined with pulsed plasma can be considered in the next steps. This approach promotes the further synthesis of α -alumina coatings, enhancing wear performance under cutting applications.

10 Literature

- [Ahr52] L. H. Ahrens, The use of ionization potentials Part 1. Ionic radii of the elements, *Geochimica et Cosmochimica Acta*, 2 (1952), 155–169, DOI: 10.1016/0016-7037(52)90004-5
- [ALH+99] D. E. Ashenford, F. Long, W. E. Hagston, B. Lunn, A. Matthews, Experimental and theoretical studies of the low temperature growth of chromia and alumina, *Surface and Coatings Technology*, 116-119 (1999), 699–704, DOI: 10.1016/S0257-8972(99)00181-4
- [ÅSF+04] M. Åstrand, T. I. Selinder, F. Fietzke, H. Klostermann, PVD Al_2O_3 coated cemented carbide cutting tools, *Surface and Coatings Technology*, 188-189 (2004), 186–192, DOI: 10.1016/j.surfcoat.2004.08.021
- [Bar95] I. Barin, *Thermochemical data of pure substances*, Weinheim, New York: VCH, 1995, ISBN: 978-3-527-61982-5
- [BBI08] K. Bobzin, N. Bagcivan, P. Immich, Deposition of Oxides as Tool Protection for Large Thixoforming Dies by Using the Pulsed MSIP-PVD Process, *Solid State Phenomena*, 141-143 (2008), 249–254, DOI: 10.4028/www.scientific.net/SSP.141-143.249
- [BBK+18a] K. Bobzin, T. Brögelmann, C. Kalscheuer, M. Welters, Thick HS-PVD $(\text{Al,Cr})_2\text{O}_3$ coatings for challenging cutting and die casting applications, *Thin Solid Films*, 663 (2018), 131–142, DOI: 10.1016/j.tsf.2018.06.061
- [BBK+18b] K. Bobzin, T. Brögelmann, N. C. Kruppe, S. Basturk, F. Klocke, K. Gerschwiler, W. Kölker, S. Bolz, J. Kohlscheen, Entwicklung von HPPMS- Al_2O_3 -Beschichtungen für die Zerspanung von schwer zerspanbaren Werkstoffen, *Materialwissenschaft und Werkstofftechnik*, 49 (2018), 1287–1300, DOI: 10.1002/mawe.201800008
- [BBK+19] K. Bobzin, T. Brögelmann, C. Kalscheuer, M. Welters, Structure, mechanical characteristics and thermal stability of high speed physical vapor deposition $(\text{Al,Cr})_2\text{O}_3$ coatings, *Thin Solid Films*, 690 (2019), 137529, DOI: 10.1016/j.tsf.2019.137529

- [BBK18c] K. Bobzin, T. Brögelmann, N. C. Kruppe, Enhanced PVD process control by online substrate temperature measurement, *Surface and Coatings Technology*, 354 (2018), 383–389, DOI: 10.1016/j.surfcoat.2018.07.096
- [BBM+11] K. Bobzin, N. Bagcivan, M. Müller, M. Ewering, Influence of the interlayer on the thermal stability of γ -Al₂O₃, In: 9th Internat. Conf. THE-"A" Coatings in Manufact. Engineering, 2011-10-05 - 2011-10-07 (2011)
- [BBM+13] K. Bobzin, N. Bagcivan, M. Müller, M. Ewering, R. H. Brugnara, Thermal stability of silicon-doped Al₂O₃ PVD coatings, *Materialwissenschaft und Werkstofftechnik*, 44 (2013), 679–683, DOI: 10.1002/mawe.201300175
- [BBM+21] K. Bobzin, T. Brögelmann, H. J. Maier, T. Heidenblut, C. Kahra, M. Carlet, Influence of residual stresses in hard tool coatings on the cutting performance, *Journal of Manufacturing Processes*, 69 (2021), 340–350, DOI: 10.1016/j.jmapro.2021.08.011
- [BBR+10] K. Bobzin, N. Bagcivan, A. Reinholdt, M. Ewering, Thermal stability of γ -Al₂O₃ coatings for challenging cutting operations, *Surface and Coatings Technology*, 205 (2010), 1444–1448, DOI: 10.1016/j.surfcoat.2010.07.040
- [BBT13] N. Bagcivan, K. Bobzin, S. Theiß, (Cr_{1-x}Al_x)N: A comparison of direct current, middle frequency pulsed and high power pulsed magnetron sputtering for injection molding components, *Thin Solid Films*, 528 (2013), 180–186, DOI: 10.1016/j.tsf.2012.08.056
- [BKH22] K. Bobzin, C. Kalscheuer, P. Hassanzadegan Aghdam, An Approach to Synthesize Thick α - and γ -Al₂O₃ Coatings by High-Speed Physical Vapor Deposition, *Advanced Engineering Materials* (2022), 2201195, DOI: 10.1002/adem.202201195
- [BKM+03] R. Brill, F. Koch, J. Mazurelle, D. Levchuk, M. Balden, Y. Yamada-Takamura, H. Maier, H. Bolt, Crystal structure characterisation of filtered arc deposited alumina coatings: temperature and bias voltage, *Surface and Coatings Technology*, 174-175 (2003), 606–610, DOI: 10.1016/S0257-8972(03)00539-5
- [BKM+23] K. Bobzin, C. Kalscheuer, M. Möbius, P. Hassanzadegan Aghdam, Enhanced adhesion and thermal stability of thick (Al,Cr)₂O₃ coatings on hot work steel,

- Surface and Coatings Technology (2023), 130179, DOI: 10.1016/j.surfcoat.2023.130179
- [BKM+24a] K. Bobzin, C. Kalscheuer, M. P. Möbius, P. Hassanzadegan Aghdam, Thermal stability of thick α - and γ - Al_2O_3 coatings deposited by high-speed PVD, Surface and Coatings Technology, 477 (2024), 130411, DOI: 10.1016/j.surfcoat.2024.130411
- [BKM+24b] K. Bobzin, C. Kalscheuer, M. P. Möbius, P. Hassanzadegan Aghdam, Residual Stress Analysis in High-Speed Physical Vapor Deposition Coatings, Advanced Engineering Materials, 26 (2024), DOI: 10.1002/adem.202401095
- [BKM+24c] K. Bobzin, C. Kalscheuer, M. P. Möbius, P. Hassanzadegan Aghdam, Jahrbuch 2023, Einflussanalyse der Cr-Dotierung in Al_2O_3 -Beschichtungen abgeschieden mittels High-Speed PVD, Eugen G. Leuze Verlag, 2024, ISBN: 978-3-87480-385-4
- [BKM+25] K. Bobzin, C. Kalscheuer, M. P. Möbius, P. Hassanzadegan Aghdam, Deformation behavior of high Al content CrAlON coatings with varying oxygen content, Surface and Coatings Technology, 496 (2025), 131639, DOI: 10.1016/j.surfcoat.2024.131639
- [BKR+99] H. Bolt, F. Koch, J. L. Rodet, D. Karpov, S. Menzel, Al_2O_3 coatings deposited by filtered vacuum arc, characterization of high temperature properties, Surface and Coatings Technology, 116-119 (1999), 956–962, DOI: 10.1016/S0257-8972(99)00180-2
- [BKS05] T. M. Besmann, N. S. Kulkarni, K. E. Spear, Thermochemical Analysis and Modeling of the Al_2O_3 – Cr_2O_3 , Cr_2O_3 – SiO_2 , and Al_2O_3 – Cr_2O_3 – SiO_2 Systems Relevant to Refractories, Journal of the American Ceramic Society, 89 (2005), 638–644, DOI: 10.1111/j.1551-2916.2005.00719.x
- [BLM+06a] K. Bobzin, E. Lugscheider, M. Maes, C. Piñero, Relation of hardness and oxygen flow of Al_2O_3 coatings deposited by reactive bipolar pulsed magnetron sputtering, Thin Solid Films, 494 (2006), 255–262, DOI: 10.1016/j.tsf.2005.08.162

- [BLM06b] K. Bobzin, E. Lugscheider, M. Maes, Innovative PVD-Beschichtungen für das Thixoforming von Stahl, Jahrbuch 2006, Eugen G. Leuze Verlag, 2006, ISBN: 3-87480-213-2
- [BLT05] S. Baragetti, G. Lavecchia, A. Terranova, Variables affecting the fatigue resistance of PVD-coated components, *International Journal of Fatigue*, 27 (2005), 1541–1550, DOI: 10.1016/j.ijfatigue.2005.06.011
- [BMA26] K. Bobzin, M. P. Möbius, P. Aghdam Tönnißen, Cutting performance of Al_2O_3 coatings deposited by High Speed PVD, *Surface and Coatings Technology*, 520 (2026), 132997, DOI: 10.1016/j.surfcoat.2025.132997
- [Bob13] K. Bobzin, *Oberflächentechnik für den Maschinenbau*, Weinheim: Wiley-VCH, 1. Aufl., 2013, ISBN: 9783527330188
- [Bob17] K. Bobzin, High-performance coatings for cutting tools, *CIRP Journal of Manufacturing Science and Technology*, 18 (2017), 1–9, DOI: 10.1016/j.cirpj.2016.11.004
- [CN91] T. C. Chou, T. G. Nieh, Nucleation and Concurrent Anomalous Grain Growth of $\alpha\text{-Al}_2\text{O}_3$ During $\gamma - \alpha$ Phase Transformation, *Journal of the American Ceramic Society*, 74 (1991), 2270–2279, DOI: 10.1111/j.1151-2916.1991.tb08295.x
- [CTS+04] D. J. Christie, F. Tomasel, W. D. Sproul, D. C. Carter, Power supply with arc handling for high peak power magnetron sputtering, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 22 (2004), 1415–1419, DOI: 10.1116/1.1688365
- [Dav93] C. A. Davis, A simple model for the formation of compressive stress in thin films by ion bombardment, *Thin Solid Films*, 226 (1993), 30–34, DOI: 10.1016/0040-6090(93)90201-Y
- [DRK+17] V. Dalbauer, J. Ramm, S. Kolozsvári, C. M. Koller, P. H. Mayrhofer, On the phase evolution of arc evaporated Al-Cr-based intermetallics and oxides, *Thin Solid Films*, 644 (2017), 120–128, DOI: 10.1016/j.tsf.2017.10.055
- [DSL+10] D. Diechle, M. Stueber, H. Leiste, S. Ulrich, V. Schier, Combinatorial approach to the growth of $\alpha\text{-(Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution strengthened thin films by reactive

- r.f. magnetron sputtering, *Surface and Coatings Technology*, 204 (2010), 3258–3264, DOI: 10.1016/j.surfcoat.2010.03.029
- [EMW+10] V. Edlmayr, M. Moser, C. Walter, C. Mitterer, Thermal stability of sputtered Al_2O_3 coatings, *Surface and Coatings Technology*, 204 (2010), 1576–1581, DOI: 10.1016/j.surfcoat.2009.10.002
- [EPL+13] V. Edlmayr, M. Pohler, I. Letofsky-Papst, C. Mitterer, Microstructure and thermal stability of corundum-type $(\text{Al}_{0.5}\text{Cr}_{0.5})_2\text{O}_3$ solid solution coatings grown by cathodic arc evaporation, *Thin Solid Films*, 534 (2013), 373–379, DOI: 10.1016/j.tsf.2013.02.046
- [ESS+09] P. Eklund, M. Sridharan, G. Singh, J. Böttiger, Thermal Stability and Phase Transformations of γ -/Amorphous- Al_2O_3 Thin Films, *Plasma Processes and Polymers*, 6 (2009), DOI: 10.1002/ppap.200932301
- [Ewe12] M. T. Ewering, Synthese, thermische Stabilität und tribologisches Verhalten nanokristalliner γ - Al_2O_3 -Schichten (γ - Al_2O_3 -Schichten) für die Zerspanung, RWTH Aachen University, Dissertation, in: K. Bobzin (Hrsg.), Schriftenreihe Oberflächentechnik, Band 25, 2012, Aachen: Shaker Verlag, ISBN: 978-3-8440-1047-3
- [FBB+78] M. S. Flemings, F. Boylan, R. Bye, Thixocasting steel parts (DAAG-46-77-C-0033), Department of Materials Science and Engineering, Massachusetts Institute of Technology MIT, Final Technical Report Army Materials and Mechanics Research Center AMMRC, 1978
- [FBE+06] G. S. Fox-Rabinovich, B. D. Beake, J. L. Endrino, S. C. Veldhuis, R. Parkinson, L. S. Shuster, M. S. Migranov, Effect of mechanical properties measured at room and elevated temperatures on the wear resistance of cutting tools with TiAlN and AlCrN coatings, *Surface and Coatings Technology*, 200 (2006), 5738–5742, DOI: 10.1016/j.surfcoat.2005.08.132
- [FSK+10] F. Klocke, S. Cordes, K. Gerschwiler, D. Lung, K. Bobzin, N. Bagcivan, M. Ewering, Deposition of γ -Alumina PVD Coatings and Analysis of Their Performance in Machining of Austenitic Steels, in: *College International pour L'Etude Scientifique des Techniques de Production*, International Conference on

- High Performance Cutting, 24-26th October 2010, Gifu, Japan, Osaka, Japan, CIRP, 2010, ISBN: 978-4-915698-02-6
- [FVC+17] Y. Fu, J. P. Verboncoeur, A. J. Christlieb, X. Wang, Transition characteristics of low-pressure discharges in a hollow cathode, *Physics of Plasmas*, 24 (2017), DOI: 10.1063/1.4997764
- [GST+19] M. Gassner, N. Schalk, M. Tkadletz, C. Czettl, C. Mitterer, Thermal crack network on CVD TiCN/ α -Al₂O₃ coated cemented carbide cutting tools, *International Journal of Refractory Metals and Hard Materials*, 81 (2019), 1–6, DOI: 10.1016/j.ijrmhm.2019.02.006
- [Gün23] A. Günther-Schulze, Die Stromdichte des normalen Kathodenfalles, *Z. Physik (Zeitschrift für Physik)*, 19 (1923), 313–332, DOI: 10.1007/BF01327567
- [Hal73] T. E. Hale, Coated cemented carbide product, US-Patent, 3736107, 1973, USA
- [HK09] G. Hirt; R. Kopp, Thixoforming: Semi-solid Metal Processing, Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2009, ISBN: 9783527623969
- [Hol84] H. Holleck, Binäre und ternäre Carbid- und Nitridsysteme der Übergangsmetalle, Mit 29 Tabellen, Zugl.: Karlsruhe, Univ., Diss., 1981, Berlin: Borntraeger, 1984, ISBN: 3443230075
- [HS95] H. Holleck, V. Schier, Multilayer PVD coatings for wear protection, *Surface and Coatings Technology*, 76-77 (1995), 328–336, DOI: 10.1016/0257-8972(95)02555-3
- [IHT88] K. Ishii, S. Handa, H. Terauchi, Sputtering of Cu in a high pressure atmosphere, *Applied Surface Science*, 33-34 (1988), 1107–1113, DOI: 10.1016/0169-4332(88)90423-0
- [JW93] T. Jung, A. Westphal, High rate deposition of alumina films by reactive gas flow sputtering, *Surface and Coatings Technology*, 59 (1993), 171–176, DOI: 10.1016/0257-8972(93)90078-3
- [KKS02] M. Kawate, A. Kimura, T. Suzuki, Microhardness and lattice parameter of Cr_{1-x}Al_xN films, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 20 (2002), 569–571, DOI: 10.1116/1.1448510

- [KLJ+12] A. Khatibi, J. Lu, J. Jensen, P. Eklund, L. Hultman, Phase transformations in face centered cubic ($\text{Al}_{0.32}\text{Cr}_{0.68}$) $_2\text{O}_3$ thin films, *Surface and Coatings Technology*, 206 (2012), 3216–3222, DOI: 10.1016/j.surfcoat.2012.01.008
- [Klo18] F. Klocke, *Fertigungsverfahren 1, Zerspanung mit geometrisch bestimmter Schneide*, Berlin, Heidelberg: Springer Berlin Heidelberg, 9. Aufl. 2018, 2018, ISBN: 9783662542071
- [KSA+04] F. Kütke, A. Schönbohm, D. Abel, R. Kopp, An automated Thixo-Forging Plant for Steel Parts, *steel research international*, 75 (2004), 593–600, DOI: 10.1002/srin.200405816
- [KSG+12] A. Khatibi, J. Sjölen, G. Greczynski, J. Jensen, P. Eklund, L. Hultman, Structural and mechanical properties of Cr–Al–O–N thin films grown by cathodic arc deposition, *Acta Materialia*, 60 (2012), 6494–6507, DOI: 10.1016/j.actamat.2012.08.010
- [Küb91] E. Kübel, New developments in chemically vapour-deposited coatings from an industrial point of view, *Surface and Coatings Technology*, 49 (1991), 268–274, DOI: 10.1016/0257-8972(91)90067-7
- [LB98] I. Levin, D. Brandon, Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences, *Journal of the American Ceramic Society*, 81 (1998), 1995–2012, DOI: 10.1111/j.1151-2916.1998.tb02581.x
- [LHK+01] E. Lugscheider, T. Hornig, R. Kopp, J. Kallweit, T. Möller, Oxide PVD-Coatings for Use on Dies for Semi-Solid Metal (SSM-) Forming of Steel, *Advanced Engineering Materials*, 3 (2001), 998, DOI: 10.1002/1527-2648(200112)3:12<998::AID-ADEM998>3.0.CO;2-1
- [LL05] M. A. Lieberman, A. J. Lichtenberg, *Principles of plasma discharges and materials processing*, Hoboken, NJ: Wiley-Interscience, Second edition, 2005, ISBN: 9780471724247
- [MAA+17] R. M'Saoubi, O. Alm, J. M. Andersson, H. Engström, T. Larsson, M. P. Johansson-Jöesaar, M. Schwind, Microstructure and wear mechanisms of texture-controlled CVD α - Al_2O_3 coatings, *Wear*, 376-377 (2017), 1766–1778, DOI: 10.1016/j.wear.2017.01.071

-
- [Mat85] A. Matthews, Titanium Nitride PVD Coating Technology, Surface Engineering, 1 (1985), 93–104, DOI: 10.1179/sur.1985.1.2.93
- [MC25] M. Wegst, C. W. Wegst, Stahlschlüssel, = Key to Steel = La clé des aciers, Marbach am Neckar: Verlag Stahlschlüssel, 26. Auflage, 2025, ISBN: 978-3-922599-38-8
- [MP15] S. Muhl, A. Pérez, The use of hollow cathodes in deposition processes: A critical review, Thin Solid Films, 579 (2015), 174–198, DOI: 10.1016/j.tsf.2015.02.066
- [NN14] N.N., Cutting Tools, (2014), www.dedalusconsulting.com, accessed on 11.2025
- [Nog11] B. Nogowizin, Theorie und Praxis des Druckgusses, Berlin: Schiele & Schön, 2011, ISBN: 9783794907960
- [PO92] G. M. Pharr, W. C. Oliver, Measurement of Thin Film Mechanical Properties Using Nanoindentation, MRS Bulletin, 17 (1992), 28–33, DOI: 10.1557/S0883769400041634
- [RAH+15] M. Rebelo de Figueiredo, M. D. Abad, A. J. Harris, C. Czettl, C. Mitterer, P. Hosemann, Nanoindentation of chemical-vapor deposited Al_2O_3 hard coatings at elevated temperatures, Thin Solid Films, 578 (2015), 20–24, DOI: 10.1016/j.tsf.2015.01.069
- [RDH+05] A. E. Reiter, V. H. Derflinger, B. Hanselmann, T. Bachmann, B. Sartory, Investigation of the properties of $\text{Al}_{1-x}\text{Cr}_x\text{N}$ coatings prepared by cathodic arc evaporation, Surface and Coatings Technology, 200 (2005), 2114–2122, DOI: 10.1016/j.surfcoat.2005.01.043
- [Ryc84] J. Rychlewski, On Hooke's law, Journal of Applied Mathematics and Mechanics, 48 (1984), 303–314, DOI: 10.1016/0021-8928(84)90137-0
- [Saa64] H. Saalfeld, Strukturuntersuchungen im System Al_2O_3 – Cr_2O_3 , Zeitschrift für Kristallographie, 120 (1964), 342–348, DOI: 10.1524/zkri.1964.120.4-5.342
- [SBK+18] W. M. Seidl, M. Bartosik, S. Kolozsvári, H. Bolvardi, P. H. Mayrhofer, Influence of coating thickness and substrate on stresses and mechanical properties of (Ti,Al,Ta)N/(Al,Cr)N multilayers, Surface and Coatings Technology, 347 (2018), 92–98, DOI: 10.1016/j.surfcoat.2018.04.060

- [SCC+04] W. D. Sproul, D. J. Christie, D. C. Carter, F. Tomasel, T. Linz, Pulsed Plasmas for Sputtering Applications, *Surface Engineering*, 20 (2004), 174–176, DOI: 10.1179/026708404225010711
- [Sel98] J. Sellers, Asymmetric bipolar pulsed DC: the enabling technology for reactive PVD, *Surface and Coatings Technology*, 98 (1998), 1245–1250, DOI: 10.1016/S0257-8972(97)00403-9
- [Sim13] S. H. Simon, *The Oxford solid state basics*, Oxford: Oxford University Press, First edition, 2013, ISBN: 9780199680771
- [SKF+98] S. Schiller, K. Gedicke, F. Fietzke, O. Zywitzki, M. Sjöstrand, B. Ljungberg, V. Alfredsson, T. Hilding, PVD Al₂O₃ beschichtetes Schneidwerkzeug, DE, 2004, Germany
- [Smi95] D. L. Smith, *Thin-film deposition, Principles and practice*, Boston, Mass.: McGraw-Hill, Internat. ed., 1995, ISBN: 9780070585027
- [SQG96] A. T. Santhanam, D. T. Quinto, G. P. Grab, Comparison of the steel-milling performance of carbide inserts with MTCVD and PVD TiCN coatings, *International Journal of Refractory Metals and Hard Materials*, 14 (1996), 31–40, DOI: 10.1016/0263-4368(96)83415-9
- [STS+09] L. Spieß, G. Teichert, R. Schwarzer, H. Behnken, C. Genzel, *Moderne Röntgenbeugung*, Wiesbaden: Vieweg+Teubner, 2009, ISBN: 978-3-8351-0166-1
- [SVD+20] R. Stylianou, D. Velic, W. Daves, W. Ecker, M. Tkadletz, N. Schalk, C. Czettel, C. Mitterer, Thermal crack formation in TiCN/ α -Al₂O₃ bilayer coatings grown by thermal CVD on WC-Co substrates with varied Co content, *Surface and Coatings Technology*, 392 (2020), 125687, DOI: 10.1016/j.surfcoat.2020.125687
- [WCR+00] M. Witthaut, R. Cremer, K. Reichert, D. Neuschütz, Preparation of Cr₂O₃-Al₂O₃ Solid Solutions by Reactive Magnetron Sputtering, *Microchimica Acta*, 133 (2000), 191–196, DOI: 10.1007/s006040070092
- [Wei23] T. E. Weirich, RIPAS: Eine minimalistische Desktop-Anwendung zur Simulation von Elektronenpulverdiffraktogrammen

- [Wel20] M. Welters, Potenzial der High-Speed Physical Vapour Deposition Technologie zur Abscheidung oxidischer Werkzeugbeschichtungen, RWTH Aachen University, Dissertation, in: K. Bobzin (Hrsg.), Schriftenreihe Oberflächentechnik, Band 67, 2020,, Düren: Shaker Verlag, ISBN: 978-3-8440-7903-6
- [WSC62] J. B. Wachtman, T. G. Scuderi, G. W. Cleek, Linear Thermal Expansion of Aluminum Oxide and Thorium Oxide from 100° to 1100°K, Journal of the American Ceramic Society, 45 (1962), 319–323, DOI: 10.1111/j.1151-2916.1962.tb11159.x
- [WWŠ+24] C. Wächtler, C. Wüstefeld, M. Šíma, J. Pikner, D. Rafaja, Effect of the substrate treatment on the microstructure of CVD Ti(C,N)/ α -Al₂O₃/TiN hard coatings, Surface and Coatings Technology, 477 (2024), 130296, DOI: 10.1016/j.surfcoat.2023.130296
- [YSS19] Y. Yusuf, R. Syahidah Azis, M. Syazwan Mustaffa, Spin-Coating Technique for Fabricating Nickel Zinc Nanoferrite (Ni_{0.3}Zn_{0.7}Fe₂O₄) Thin Films, in: Andres Perez-Taborda, Jaime; G. Avila Bernal, Alba, Coatings and Thin-Film Technologies, IntechOpen, 2019, DOI: 10.5772/intechopen.80461
- [ZH97] O. Zywitzki, G. Hoetzs, Correlation between structure and properties of reactively deposited Al₂O₃ coatings by pulsed magnetron sputtering, Surface and Coatings Technology, 94-95 (1997), 303–308, DOI: 10.1016/S0257-8972(97)00341-1
- [ZHF+96] O. Zywitzki, G. Hoetzs, F. Fietzke, K. Goedicke, Effect of the substrate temperature on the structure and properties of Al₂O₃ layers reactively deposited by pulsed magnetron sputtering, Surface and Coatings Technology, 82 (1996), 169–175, DOI: 10.1016/0257-8972(95)00270-7

11 Appendix

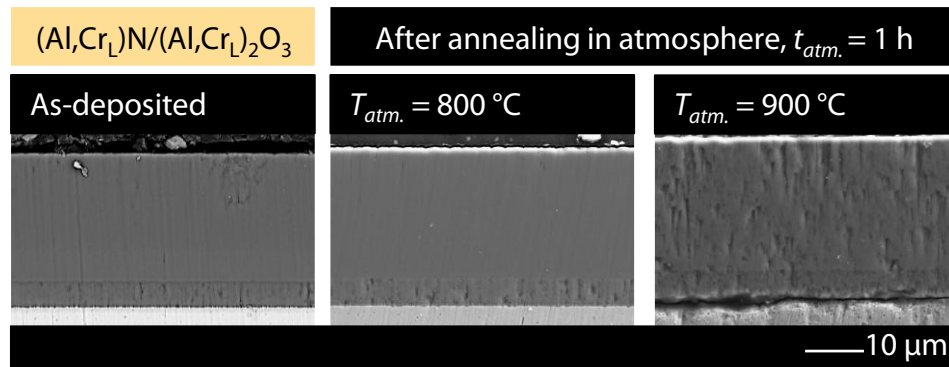


Figure 11.1: SEM-images before and after annealing in in atmosphere for $t = 1$ h

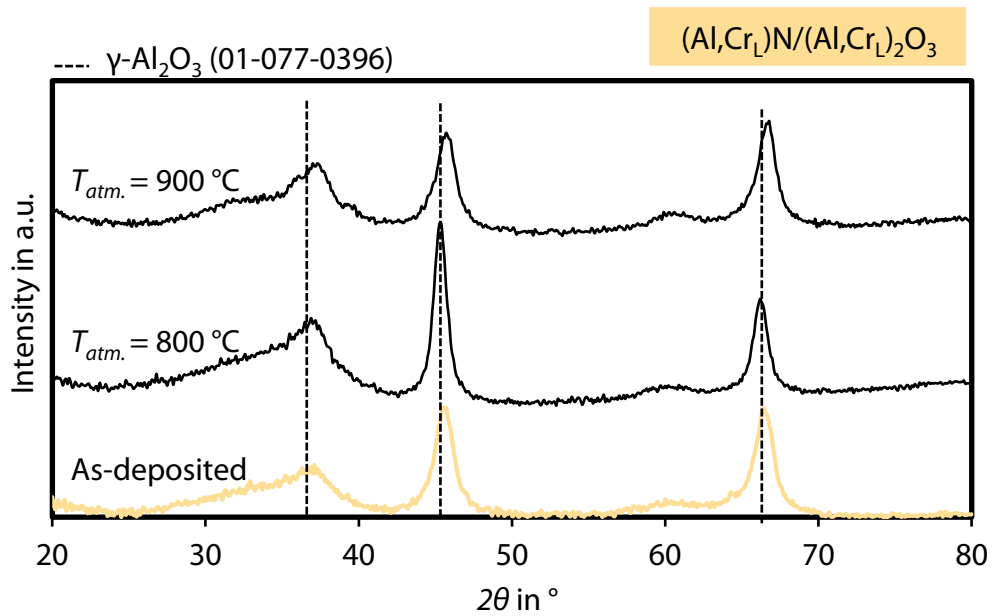


Figure 11.2: XRD results after annealing in atmosphere for $t = 1$ h

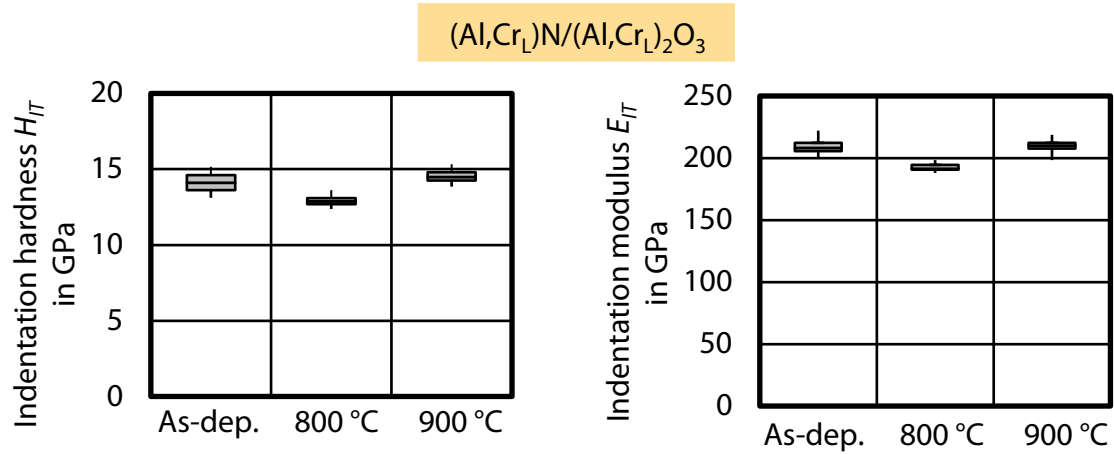


Figure 11.3: Indentation values of coatings after annealing in atmosphere for $t = 60$ min

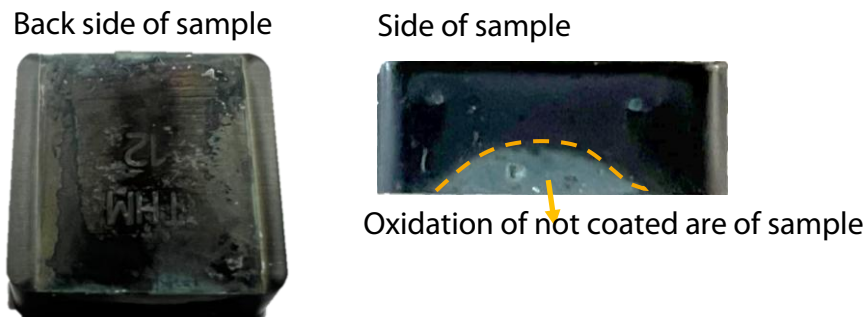


Figure 11.4: Al_2O_3 coated sample after HT-XRD in atmosphere

In der Schriftenreihe Oberflächentechnik des Instituts für Oberflächentechnik der RWTH Aachen sind bisher erschienen:

- Band 1: Seemann, Klaus: Vorhersage von Prozess- und Schichtcharakteristiken beim atmosphärischen Plasmaspritzen mittels statistischer Modelle und neuronaler Netze
- Band 2: Parco, Maria: Thermische Beschichtung von Leichtbaulegierungen aus Magnesium zum Verschleiß- und Korrosionsschutz
- Band 3: Bobzin, K. (Hrsg.): Oberflächentechnik Jahrbuch 2004/2005
- Band 4: Bobzin, K. (Hrsg.): 1. Aachener Oberflächentechnik Kolloquium 2006
- Band 5: Nickel, Reimo: Die beschichtungsprozessabhängige Materialmodellierung von EB-PVD- und APS-Wärmedämmschichten
- Band 6: Ernst, Felix: Qualitätskontrolle auf Basis optischer Prozessdiagnostik und neuronaler Netze beim Thermischen Spritzen
- Band 7: Maes, Michel: Gepulste Abscheidung von (Cr,Al)N PVD-Niedertemperaturschichtsystemen für Hochleistungsbauteile
- Band 8: Bobzin, K. (Hrsg.): 2. Aachener Oberflächentechnik Kolloquium 2007
- Band 9: Hurevich, Vitalii: Einfluss einer Verschleißschuttschicht bei Skalierung des Bohrprozesses in den Mikrobereich
- Band 10: Zwick, Jochen: Herstellung und Charakterisierung oxiddispersionsverstärkter Pulver für das Thermische Spritzen
- Band 11: Comenares de Piñero, Carmen Leonor: Entwicklung nanostrukturierter PVD-Schichtsysteme für Zerspanung und Kaltumformung durch Einsatz der Pulstechnologie
- Band 12: Bobzin, K. (Hrsg.): 3. Aachener Oberflächentechnik Kolloquium 2008
- Band 13: Bagcivan, Nazlim: Entwicklung von EB-PVD-Wärmedämmschichten auf Lanthanzirkonatbasis und gesputterten Oxidationsschutzschichten für den Einsatz auf intermetallischen Ni-Basislegierungen
- Band 14: Richardt, Katharina: Eigenschaften und Potentiale Atmosphärischer Plasmaspritzsysteme
- Band 15: Bobzin, K. (Hrsg.): 4. Aachener Oberflächentechnik Kolloquium 2009
- Band 16: Meeß, Rudolf: Entwicklung von Mikrowälzführungen
- Band 17: Bobzin, K. (Hrsg.): 5. Aachener Oberflächentechnik Kolloquium 2010
- Band 18: Immich, Heinrich Philipp: Maßgeschneiderte oxidische und nitridische PVD-Werkstoffverbunde für metallische Werkzeuge in der Stahlformgebung
- Band 19: Rojas Yoris, Yelena: Entwicklung von Lotwerkstoffen zum Vakuumlöten von Nickel- und Titanaluminiden

- Band 20: Stephan Bolz: Abscheidung nanostrukturierter Verschleißschutzschichten für Zerspanwerkzeuge mittels Kathodenzerstäubung
- Band 21: Daniel Parkot: Simulative und plasmadiagnostische Untersuchungen des Magnetron Sputterns
- Band 22: Stefania Ferrara: Entwicklung von Weichaktivloten und Transient-Liquid-Phase-Lotsystemen für Mikrolötverbindungen im Bereich der Medizin und Luft- und Raumfahrt
- Band 23: Bobzin, K. (Hrsg.): 6. Aachener Oberflächentechnik Kolloquium 2011
- Band 24: Nils Kopp: Reactive Air Brazing
- Band 25: Mara Ewering: Synthese, thermische Stabilität und tribologisches Verhalten nanokristalliner gamma-Al₂O₃-Schichten für die Zerspanung
- Band 26: Kirsten Bobzin (Hrsg.): 7. Aachener Oberflächentechnik Kolloquium 2012
- Band 27: Konstantinos-Dionysios Bouzakis, Kirsten Bobzin, Berend Denkena, Marion Merklein (Eds.): Proceedings of the 10th International Conference The "A" Coatings 2013
- Band 28: Thomas Warda: Thermisch gespritzte eisenbasierte Feinstpulverschichtsysteme für Verschleiß- und Korrosionsschutzanwendungen
- Band 29: Sebastian Theiß: Analyse gepulster Hochleistungsplasmen zur Entwicklung neuartiger PVD-Beschichtungen für die Kunststoffverarbeitung
- Band 30: Marcel Pascal Schäfer: Modellierung, Simulation und Optimierung von kerosinbetriebenen HVOF-Beschichtungssystemen
- Band 31: Sabrina Michelle Puidokas: Design of Highly Stressed Brazed Joints
- Band 32: Kirsten Bobzin (Hrsg.): 8. Aachener Oberflächentechnik Kolloquium 2013
- Band 33: Hasan Koray Yilmaz: Untersuchung der Einflussgrößen auf das Reibverhalten von Kohlenstoffschichten in geschmierten Tribosystemen
- Band 34: Raphael Weiß: Entwicklung und Untersuchung mehrlagiger PVD-Kohlenstoffschichten als Schutz vor tribologischer und korrosiver Beanspruchung
- Band 35: Ivica Petković: Modellierung und Simulation als Werkzeug zur Verbesserung des APS-Prozesses mittels Mehrlichtbogen-Plasmagenerator
- Band 36: Markus Brühl: Elektromagnetische Eigenschaften von thermisch gespritzten ferromagnetischen Schichten
- Band 37: Kirsten Bobzin (Hrsg.): 9. Aachener Oberflächentechnik Kolloquium 2014
- Band 38: Tobias Münstermann: Synthese, Charakterisierung und Qualifizierung von MSIP-Edelmetallbeschichtungen für das Präzisionsblankpressen von Glas
- Band 39: Marc-Manuel Matz: Lichtbogendrahtspritzen zur Armierung der ersten Kolbennut für moderne Verbrennungsmotoren

- Band 40: Thomas Schläfer: Entwicklung von Verfahren zur Bestimmung der Haftzugfestigkeit von thermisch gespritzten Zylinderlaufbahnen
- Band 41: Baycan Yildirim: Mehrlagige EB-PVD-Wärmedämmschichten auf Basis von Seltenerdoxid
- Band 42: Kirsten Bobzin (Hrsg.): 10. Aachener Oberflächentechnik Kolloquium 2015
- Band 43: Ricardo Henrique Brugnara: Hochtemperaturaktive HPPMS-Verschleißschutzschichten durch Bildung reibmindernder Magnéli-Phasen im System (Cr,Al,X)N
- Band 44: Mehmet Öte: Understanding Multi-Arc Plasma Spraying
- Band 45: Martin Hilaire Djoufack: Tribological Evaluation of Hydrogenated a-C:H and Hydrogen-free ta-C Diamond-like Carbon Coatings in Diesel Lubricated Model Tests
- Band 46: Leander Schramm: Development of a Robust Cylinder Bore Coating Process and Investigation of Different Feedstock Materials
- Band 47: Kirsten Bobzin (Hrsg.): 11. Aachener Oberflächentechnik Kolloquium 2016
- Band 48: Tobias Brögelmann: Reibungsreduzierung durch gradierte diamantähnliche Kohlenstoffschichten a-C:H:Zr und a-C:H:Ti in EHD-Kontakten des Automobylantriebsstrangs
- Band 49: Christiane Schulz: Thermisch gespritzte ZnMgAl-Schichten als Korrosionsschutz in chloridhaltiger Atmosphäre
- Band 50: Thomas Frederik Linke: Entwicklung eines thermisch gespritzten Oxidationsschutzsystems zur Erhöhung der Lebensdauer von γ -Titanaluminiden
- Band 51: Kirsten Bobzin (Hrsg.): 12. Aachener Oberflächentechnik Kolloquium 2017
- Band 52: Serhan Bastürk: Oxidische und sulfidische HPPMS-Beschichtungen für den Einsatz in der Zerspan- und Umformtechnik
- Band 53: Stefanie Wiesner: Einfluss der Ag-Basislote auf das Alterungsverhalten reaktiv gelöteter Verbunde aus Keramik und Metall
- Band 54: Kirsten Bobzin (Hrsg.): 13. Aachener Oberflächentechnik Kolloquium 2018
- Band 55: Mostafa Arghavani: Elastic-Plastic Deformation and Cracking Behavior of Thin Hard Chromium-Based Coatings
- Band 56: Martin Gottfried Engels: Korrelation von Plasma- und Schichteigenschaften bei der reaktiven Plasmasynthese von Hartstoffschichten
- Band 57: Xifang Liao: Metallisierung von Kunststoffbauteilen mittels In-Mold-Metal-Spraying
- Band 58: Martin Andreas Knoch: Korrosionsverhalten thermisch gespritzter ZnAl₁₅-Korrosionsschutzschichten
- Band 59: Kirsten Bobzin (Hrsg.): 14. Aachener Oberflächentechnik Kolloquium 2019

- Band 60: Nathan C. Kruppe: Entwicklung hybrider PVD-Prozesse zur Abscheidung nanostrukturierter, oxinitridischer Hartstoffschichten
- Band 61: Jan Sommer: HVOF-gespritzte FeCr25B5-Beschichtungen für den Verschleiß- und Korrosionsschutz
- Band 62: Tiancheng Liang: Schichtentwicklung zum Oxidationsschutz von Titanaluminiden mittels HS-PVD
- Band 63: Christian Kalscheuer: Entwicklung triboaktiver (Cr,Al,X)N-Beschichtungen für den Einsatz auf Maschinenelementen
- Band 64: Matthias Thiex: Wechselwirkungen zwischen gradierten diamantähnlichen Kohlenstoffschichten und additivierten Schmierstoffen
- Band 65: Tim Denis Stefan Königstein: Eisenbasierte, teilamorphe Hochleistungsbeschichtungen
- Band 66: Mona Naderi: Nitride and Oxynitride High Performance PVD Hard Coatings with Laser-processed Surfaces
- Band 67: Martin Welters: Potenzial der High-Speed Physical Vapour Deposition Technologie zur Abscheidung oxidischer Werkzeugbeschichtungen
- Band 68: Leonid Gerdt: Beschichtungen für das Druckgießen von stoffschlüssigen Hybridbauteilen aus Aluminiumguss und Stahlblech
- Band 69: Wolfgang Maximilian Wietheger: Maßgeschneiderte Gleitlagerbeschichtungen für hochbelastete Lagerstellen durch Thermisches Spritzen
- Band 70: Ilkin Alkhasli: Multiscale Modelling of Plasma Spraying
- Band 71: Kirsten Bobzin (Hrsg.): 15. Aachener Oberflächentechnik Kolloquium 2021
- Band 72: Julian Hebing: Ti-Impfen von Ni-Basisloten zur Steigerung der Präzision im Lötgut
- Band 73: Kirsten Bobzin (Hrsg.): 16. Aachener Oberflächentechnik Kolloquium 2022
- Band 74: Seyed Ruhollah Dokhanchi: Towards Digital Shadow in Plasma Spraying
- Band 75: Marco Carlet: Potentiale oxinitridischer PVD-Hartstoffschichten für Zerspanwerkzeuge
- Band 76: Kirsten Bobzin (Hrsg.): 17. Aachener Oberflächentechnik Kolloquium
- Band 77: Andreas Schacht: Thermisch gespritzte Heizschichten für das Kunststoffspritzgießen
- Band 78: Hendrik Heinemann: Plasmaspritzen mit einem kaskadierten Einzellichtbogen
- Band 79: Marvin Schulz: Metallisch dichtende Beschichtungen im Armaturenbau
- Band 80: Kirsten Bobzin (Hrsg.): 18. Aachener Oberflächentechnik Kolloquium
- Band 81: Elisa Olesch: Methodik zur Bewertung und Entwicklung plasmagespritzter Schichten zur elektrischen Isolation

Band 82: Nina Isabell Inge Stachowski: Triboaktive Beschichtungen aus CrAlVN und CrAlMoN für den Einsatz in der Drehbearbeitung von TiAl6V4

Band 83: Christoph Franz Robert Schulze: OES-Datenerfassung in reaktiven HPPMS-Prozessen und Datenanalyse mittels künstlicher neuronaler Netze

Band 84: Kirsten Bobzin (Hrsg.): 19. Aachener Oberflächentechnik Kolloquium

Band 85: Muhammad Tayyab: Deformation and Fracture Mechanics of Compounds with Nitride Hard Coatings for Tooling Applications

Band 86: Parisa Aghdam Tönnißen: Synthesis of Crystalline Tool Coatings Based on Al_2O_3 Using High Speed PVD

