Physical vapor deposition and thermal stability of hard oxide coatings

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Cover images

Front side from the left

- The magnetron sputtering system used in Paper I to deposit Al-V-O-coatings
- Si-rich droplet in as-deposited Al-Cr-Si-O coatings adapted from Figure 4b in Paper II. Si-rich marked yellow. STEM micrograph and EDX map merged and rotated 90° CCW from paper II for better fit on the front cover.
- Crystalline Cr (red) and Zr (green) segregation observed in a Cr-Zr-O coating after vacuum annealing at 810 °C. Adapted from Figure 10b in paper IV. STEM micrograph (top) and EDX map (bottom).

Background image on front and backside

Light optical microscope image of Al-V-O-coating after annealing in air at 700 °C, adapted to background image with filter and blue color. V₂O₅ crystals grown on the γ -Al₂O₃ coating. Magnification of part of Figure 4 in Paper I (sample with 18 at.% metal fraction V, sample F). Interesting for its beauty rather than industrial application.

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The state-of-the-art tools for machining metals are primarily based on a metal-ceramic composite (WC-Co) coated with different combinations of carbide, nitride, and oxide coatings. Combinations of these coating materials are optimized to withstand specific wear conditions. Oxide coatings, mainly α - Al_2O_3 , are especially desired because of their high hot-hardness, chemical inertness with respect to the workpiece, and their low friction. The search for possible alloy elements, which may facilitate the deposition of such oxides by means of physical vapor deposition (PVD) techniques, has been the goal of this thesis. The sought alloy should form thermodynamically stable or metastable compounds, compatible with the temperature of use in metal cutting application. This thesis deals with process development and coating characterization of such new oxide alloy thin films, focusing on the Al-V-O, Al-Cr-Si-O, and Cr-Zr-O systems.

Alloying aluminum oxide with iso-valent vanadium is a candidate for forming the desired alloys. Therefore, coatings of $(\text{Al}_{1-x}\text{V}_x)_2\text{O}_3$, with x ranging from 0 to 1, were deposited with reactive sputter deposition. X-ray diffraction showed three different crystal structures depending on V-metal fraction in the coating: α - V_2O_3 rhombohedral structure for 100 at.% V, a defect spinel structure for the intermediate region, (63 - 42 at.% V), and a gamma-alumina-like solid solution at lower V-content, (18 and 7 at.%), were observed, the later was shifted to larger d-spacing compared to the pure γ - Al_2O_3 sample obtained if deposited with only Al-target. Annealing the Al-rich coatings in air resulted in formation of V_2O_5 crystals on the surface of the coating after annealing to 500 °C for 42 at.% V and 700 °C for 18 at.% V metal fraction respectively. The highest thermal stability was shown for pure γ - Al_2O_3 -coating which transformed to α - Al_2O_3 after annealing to 1100° C. Highest hardness was observed for the Al-rich oxides, ~24 GPa. The hardness then decreases with increasing V-content, larger than 7 at.% V metal fraction. Doping the Al_2O_3 coating with 7 at.% V resulted in a significant surface smoothening compared to the binary oxide. The measured hardness after annealing in air decreased in conjunction with the onset of further oxidation of the coatings. This work increases the understanding of this complicated material system with respect to possible phases formed with pulsed DC magnetron sputtering deposition as well as their response to annealing in air.

The inherent difficulties of depositing insulating oxide films with PVD, requiring a closed electrical circuit, makes the investigation of process stability an important part of this research. In this context, I investigated the influence of adding small amount of Si in Al-Cr cathode on the coating properties in a pulsed DC industrial cathodic arc system and the plasma characteristics, process parameters, and coating properties in a lab DC cathodic arc system. Si was chosen here due to a previous study showing improved erosion behavior of Al-Cr-Si over pure Al-Cr cathode without Si incorporation in the coating. The effect of Si in the Al-Cr cathode in the industrial cathodic arc system showed slight improvements on the cathode erosion but Si was found in all coatings where Si was added in the cathode. The Si addition promoted the formation of the B1-like metastable cubic oxide phase and the incorporation led to reduced or equal hardness values compared to the corresponding Si-free processes. The DC-arc plasma study on the same material system showed only small improvements in the cathode erosion and process stability (lower pressure and cathode voltage) when introducing 5 at.% Si in the $\text{Al}_{70}\text{Cr}_{30}$ -cathode. The presence of volatile SiO species could be confirmed through plasma analysis, but the loss of Si through these species was negligible, since the coating composition matched the cathode composition also under these

conditions. The positive effect of added Si on the process stability at the cathode surface, should be weighed against Si incorporation in the coating. This incorporation seems to lead to a reduction in mechanical properties in the as-deposited coatings and promote the formation of a B1-like cubic metastable oxide structure for the $(\text{Al,Cr})_2\text{O}_3$ oxide. This formation may or may not be beneficial for the final application since literature indicates a slight stabilization of the metastable phase upon Si-incorporation, contrary to the effect of Cr, which stabilizes the α -phase.

The thermal stability of alloys for metal cutting application is crucial for their use. Previous studies on another alloy system, Cr-Zr-O, had shown solid solution, for Cr-rich compositions in that material system, in the sought corundum structure. The thermal stability of $\alpha\text{-Cr}_{0.28}\text{Zr}_{0.10}\text{O}_{0.61}$ coating deposited by reactive radio frequency (RF)-magnetron sputtering at 500 °C was therefore investigated here after annealing in vacuum up to 870 °C. The annealed samples showed transformation of $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ and amorphous ZrO_x -rich areas into tetragonal ZrO_2 and bcc-Cr. The instability of the $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ is surprising and possibly related to the annealing being done under vacuum, facilitating the loss of oxygen. Further *in situ* synchrotron XRD annealing studies on the $\alpha\text{-Cr}_{0.28}\text{Zr}_{0.10}\text{O}_{0.61}$ coating in air and in vacuum showed increased stability for the air annealed sample up to at least 975 °C, accompanied with a slight increase in ex-situ measured nanohardness. The onset temperature for formation of tetragonal ZrO_2 was similar to that for isothermally vacuum annealing. The synchrotron-vacuum annealed coating again decomposed into bcc-Cr and t- ZrO_2 , with an addition of monoclinic- ZrO_2 due to grain growth. The stabilization of the room temperature metastable tetragonal ZrO_2 phase, due to surface energy effects present with small grains sizes, may prove to be useful for metal cutting applications. The observed phase segregation of $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ and formation of tetragonal ZrO_2 with corresponding increase in hardness for this pseudobinary oxide system also opens up design routes for pseudobinary oxides with tunable microstructural and mechanical properties.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Den här avhandlingen handlar om utvecklingen av beläggningar av nya och mera slitstarka materialkombinationer på skärande verktyg. Skärande bearbetning, t.ex. svarvning, fräsning och borrar, av olika former av metall och kompositmaterial, är en av grundförutsättningarna för vårt moderna samhälle. Under de senaste dryga hundra åren har en omfattande utveckling pågått av verktygsmaterialen. Det har fått som effekt att hastigheten och volymerna som kan bearbetas på en given tid har mångdubblats. I takt med att nya, mer höghållfasta och slitstarka, material fortsätter att utvecklas krävs det slitstarkare verktyg för fortsatt ekonomisk försvarbar skärande bearbetning av dessa material.

Under skärmaterialens utvecklingsresa togs ett viktigt steg under 1930-talet när en metalkeramkomposit, bestående av volframkarbid och kobolt (WC-Co), började användas som verktygskropp istället för höglegerade stål. De högre bearbetningstemperaturerna (upp mot 1000 °C), som uppkom som ett resultat av det slitstarkare verktygsmaterialets möjliggörande av högre skärhastigheter, gav nya förslitningsmönster. I kontakten mellan metallspånen och verktyget löstes verktyget upp i det området pga. kemisk förslitning, samtidigt som omkringliggande området oxiderade i kontakt med luft.

Under 1960-talet började verktygen beläggas med tunna keramiska skikt, 2-20 miljondelsmeter (μm) tjocka. Ett hårstrå är ca 60 μm tjockt som jämförelse. De keramiska skikten, i början TiC, TiN TiCN, var slitstarkare, hårdare och mer kemiskt motståndskraftiga än WC-Co men gjorde ändå inte att verktyget blev för sprött på grund av att de bara belades på ytan. Beläggningstekniken som först användes var CVD (chemical vapor deposition eller ungefär kemisk ångdeponering) som krävde beläggningstemperaturer omkring 1000 °C. Efter ytterligare utveckling lyckades man med start under 1970/80-talet belägga verktyg med aluminiumoxid, Al_2O_3 , vilket är ett av de mest kemiskt stabila materialen i dessa miljöer. De höga beläggningstemperaturen i CVD skapade dock problem med inblandning av verktygsmaterialets Co in i skiktet samt termiska sprickor i skikten när de kylades ner från beläggningstemperaturen. Detta ledde till begränsningar i verktygslivslängden och användningsområdena för Al_2O_3 -beläggningarna. Dessa problem, med flera, ledde fram till användningen av en annan beläggningsteknik, fysikalisk förångningsteknik (PVD), som fungerade vid betydligt lägre beläggningstemperaturer ~500 °C och gav större frihetsgrader i vilka material som kunde beläggas.

Den lägre beläggningstemperaturen leder dock i fallet med Al_2O_3 till att atomerna inte hinner flytta sig (diffundera) på ett sådant sätt som ger den tätaste kristallstrukturen, Korund (α), vilket också är det termodynamiska jämviktsfasen för ämnet. Istället bildas andra halv(meta)stabila faser, d.v.s. andra ordningar av atomerna, t.ex. gamma(γ)-fasen. Dessa metastabila faser omvandlas vid högre temperaturer, när tillräckligt mycket energi finns för långväga diffusion, till Korund, med volymminskning och sprickbildning som följd. Att hitta andra metaller att blanda med Al_2O_3 och därigenom göra α -strukturen möjlig att belägga vid de lägre beläggningstemperaturen (**artikel I, II och III**) eller att göra så att metastabila faser blir tillräckligt stabila för användningstemperaturen i skärande bearbetning (**artikel I, IV och V**) var det övergripande målet med avhandlingen.

Fysikalisk förångning kan göras på flera olika sätt och i den här avhandlingen har två olika huvudgrupper används: sputtring (**artikel I, IV och V**) och katodisk arcförångning (**artikel II och III**). Vid sputtring accelereras en inert gas, oftast argon, joniserad till Ar^+ joner av en starkt negativ spänning

på en elektriskt ledande yta bestående av det material som utgör beläggningssubstratet. Ar^+ joner får på detta sätt tillräckligt hög energi för att slå loss atomer från ytan vilka blir det material som beläggs och tillsätts syre så kan oxider beläggas. Problemet med PVD är att tekniken i de flesta fall kräver en sluten elektrisk krets för att fungera vilket snabbt blir ett problem när ett isolerande material, som Al_2O_3 m.fl., bildar ett tunt skikt på de flesta ytorna i beläggningskammaren. Det krävs noggranna val av beläggningsparametrar och speciella tekniska lösningar för hur uppladdningen av ytor i kammaren ska hållas på en hanterbar nivå, t.ex. genom pulsning av strömmen med byte av polaritet på miljondelsekunds-nivå.

I **artikel I** belades olika sammansättningar av aluminium-vanadinoxider, Al-V-O, och resulterande kristallstrukturer undersöktes med röntgendiffraktion (XRD). Röntgendiffraktion använder elastiska kollisioner mellan mycket kortvågigt ljus och atomerna för att se, i ett diffraktionsmönster, vilken kristallstruktur (ordning) som atomerna befinner sig i. Hårdhet utvärderades att en mycket vass diamantpyramid trycktes ner $\sim 0,1 \mu\text{m}$ i skiktet med hjälp av en gradvis ökande last samtidigt som intrycksdjupet mättes. Till skillnad från skikt rika på V värmebehandlades de Al-rika skikten till max 1100°C för att se hur de reagerade. Högre V-innehåll ledde till vanadinrika oxider på ytan vid gradvis lägre värmebehandlingstemperaturer, med minskad hårdhet som följd. Små mängder V ledde till en γ -kristallstruktur med förbättrad ytjämnhet på de nybelagda skikten, med nära bibehållen hårdhet efter värmebehandling vid 800°C .

För katodisk arc-förångning läggs en hög ström på en metallyta (katod) av det aktuella beläggningssubstratet, vilket leder till mikroskopiska blixtrar (arc/ljusbågar) på ytan. Blixterna genererar små explosioner där metallen förångas och joniseras och därmed skapas ett metallplasma, en joniserad gas. Tillsätts syre till beläggningskammaren bildas oxider av de ämnen som katoden innehåller. Val av sammansättningen på katoden kan förbättra avverkningen av katoden och leda till mindre problem med den elektriska uppladdningen vilket **artikel II** och **III** handlar om. Där undersöktes effekten av att tillsätta 5-10 atom % Si till olika sammansättningar av Al-Cr i katoden, vilket fick till följd att blixterna fördelade sig på ett bättre sätt på katodytan. Tidigare studier indikerade att Si inte togs upp i det belagda skiktet utan kanske avgick som SiO gas. Jag kunde dock visa i två olika beläggningssystem att den Si som fanns i katoden också till stor del hittades i skikten. En studie av sammansättningen av plasmat kunde bekräfta existensen av SiO i gasfas men Si-avgången via utpumpning av gasen från beläggningskammaren var liten i den studerade uppställningen. Tillsats av Si till $(\text{Al,Cr})_2\text{O}_3$ katoden ledde till en annan metastabil kristallstruktur än α , vilket resulterade i en bibehållen eller lägre hårdhet på skikten. Transmissionselektronmikroskopi (TEM) användes också för att få bilder på mycket tunna tvärsnitt ($\sim 0,05 \mu\text{m}$) av skikten där både atomernas lagring och större defekter i skikten, så som metalliska droppar, kunde urskiljas. Sammansättningen bestämdes med ett flertal olika tekniker som har olika styrkor och svagheter gällande detektionsnivå av olika ämnen (tungt respektive lätt). Metodernas analysdjup i skikten är också olika.

Värmebehandlingar, både i vacuum (**artikel IV** och **V**) och i luft (**artikel V**) utfördes på en krom-rik legering av $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ för undersöka fasens stabilitet vid höga temperaturer. Delar av värmebehandlingsstudien med samtidig analys av kristallstrukturen i provet med XRD utfördes med hjälp av en storskalig infrastruktur, kallad en synkrotron, innefattande en mycket ljusstark röntgenkälla (DESY i Hamburg, Tyskland), se **artikel V**. Vilken atmosfär provet värmebehandlas i hade inverkan på slutprodukten, där luft var fördelaktigt för att bibehålla den belagda kristallstrukturen och hårdheten.

PREFACE

This thesis contains my PhD work in Materials Science, in particular Thin Film Physics, starting in March 2013 (with breaks for 12 months parental leave in total). This work is a collaboration between the Linköping University and AB Sandvik Coromant, made possible through a Swedish Research Council (VR) industrial PhD student grant (Grant no: 621-212-4368). Furthermore, I have collaborated with the Institute for Applied Materials (IAM) at Karlsruhe Institute of Technology (KIT), Germany. Experimental work has also been done at DESY synchrotron source in Hamburg, Germany. This work is a continuation of my Licentiate thesis *Thin Film and Plasma Characterization of PVD oxides* (Licentiate thesis No. 1769, Linköping Studies in Science and Technology (2017)) and large portions of text have been adapted from that work into this work. During the course of the research, I was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University supported by the Swedish Government Strategic Research Area on Advanced Functional Materials.

LIST OF INCLUDED PAPERS

Paper I

Phase composition and transformations in magnetron sputtered (Al,V)₂O₃ coatings

L. Landälv, C.-F. Carlström, J. Lu, D. Primetzhofer, M. J. Jõesaar, M. Ahlgren, E. Göthelid, B. Alling, L. Hultman, P. Eklund

Submitted for publication

Author's contribution

I planned and coordinated the work, performed a large part of the depositions and most of the characterization. I did most of the analysis and wrote the paper.

Paper II

Influence of Si doping on properties of arc deposited (Al, Cr)₂O₃ coatings

L. Landälv, E. Göthelid, J. Jensen, G. Greczynski, J. Lu, M. Ahlgren, L. Hultman, B. Alling, P. Eklund

Manuscript in final preparation

Author's contribution

I planned and coordinated the work and was involved in the depositions, TEM, XPS and ERDA characterization. I performed the XRD, EDX, hardness measurements, did most of the analysis and wrote the paper.

Paper III

Effect of Si on DC arc plasma generation from Al-Cr and Al-Cr-Si cathodes used in oxygen

I. Zhirkov, L. Landälv, E. Göthelid, M. Ahlgren, P. Eklund, J. Rosen

Journal of Applied Physics 121, 083303 (2017)

Author's contribution

I initiated the research idea, was involved in the planning of the work and the analysis, commented on successive drafts, and largely wrote the introduction and conclusion of the paper.

Paper IV

Structural evolution in Reactive RF Magnetron Sputtered (Cr,Zr)₂O₃ During Annealing

L. Landälv, J. Lu, S. Spitz, H. Leiste, S. Ulrich, M. P. Johansson-Jõesaar, M. Ahlgren, E. Göthelid, B. Alling, L. Hultman, M. Stüber, P. Eklund

Acta Materialia 131 (2017) 543-552

Author's contribution

I planned and coordinated the work, was involved in the TEM characterization, performed most of the analysis, and wrote the paper.

Paper V

Phase evolution of RF magnetron sputtered Cr-rich (Cr,Zr)₂O₃ coatings studied by in situ synchrotron X-ray diffraction during annealing in air or vacuum

L. Landälv, L. Rogström, J. Lu, D. Ostach, F. Eriksson, M. Junaid, N. Ghafoor, E. Ekström, C.-L. Hsiao, H. Leiste, M. Ahlgren, E. Göthelid, B. Alling, L. Hultman, M. Stüber, N. Schell, J. Birch, P. Eklund

Submitted for publication

Author's contribution

I planned and coordinated the work, was involved in the TEM characterization and the extraction of the synchrotron data. I performed the hardness measurements, SEM, EDX and most of the analysis, and wrote the paper.

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Per Eklund and Emmanuelle Göthelid for being my main supervisors from the university and industry, respectively. Thanks Per for introducing me to the world of vacuum science and stressing the importance of not using sloppy wording: e.g. it is called X-ray diffractogram not X-ray spectrum! Emmanuelle thanks for your passion for the research topic and good feedback on my work and thanks both of you for your encouraging words when I needed them the most. Altogether it has helped me throughout this PhD.

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My colleagues and friends at Sandvik Coromant for helping out when needed and for showing interest when I'm around in the building. **Carl-Fredrik Carlström** for the help during the final intense deposition period in Jessie.

My lovely wife **Maria** for kind words, patience and fun times, all together making this a good time. My children **Agnes** and **Oskar**, for all the fun we do together. **Our parents** for all the support, facilitating raising children at the same time as doing a PhD.

Jesus, my Lord and Savior, for helping me to put this work into the big perspective of life, and for giving me the fundamental interest in, and the curiosity for discovering the richness of His creation, and for helping me along this race, the PhD, to finally reach its finish line.

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1 Introduction and research question

Being able to manufacture products from raw materials has been crucial to people throughout history. Depending on the type of material that should be shaped, tools and the materials they are made from have been adapted in order to reach the best possible performance with respect to manufacturing time and quality of the final product. From the start of the industrial revolution, with increased production rate demands and use of steel and other metal alloys, the machining of these materials became increasingly important. Machining operation, such as turning and milling, required tools which were more wear resistant than the workpiece material being shaped. Early turning and milling tools were made from same material as that to be machined, resulting in very poor tool life. Changing into tool steels, and later on high speed steel (*ca* 1900), gave a significant improvement in the metal removal rate. In the 1920's-30's, ceramic metal composite materials, such as hard metal cemented carbides (WC-grains in Co-metal matrix) were invented and started to be implemented into the metal cutting industry, resulting in a substantial enhancement in tool performance. This invention constituted a material with higher hot hardness than the workpiece material combined with sufficient toughness, resulting in a dramatic increase of the tool life, widening the span of possible cutting data (cutting speed, feed and depth of cut) used for machining. However, the complexity of integrating and using the new tool material in the manufacturing industry, due to the demand for more stable turning/milling machines, and the need of better grinding equipment (cutting edge regrinding), resulted in that the introduction of hard metal was slow until World War II and the following years [1].

The drawbacks of uncoated cemented carbide are their poor oxidation resistance and their reaction with the steel chip. This problem increased with the use of higher cutting speeds (resulting in higher tool temperature). In the late 60's, along with the introduction of indexable "throw-away inserts", coating of the tool with ceramic carbides TiC and later TiN and TiCN by chemical vapor deposition (CVD) was introduced. These coatings increased the surface hardness and chemical resistance without embrittling the entire tool, since the coatings were just some micrometers thick. After intense research, deposition of the first crystalline Al_2O_3 on the tool was achieved and introduced to the market 1975, followed by thicker oxide coatings in the 80's [1, 2]. This material has very low solubility in steel [3]. Combining the abrasive wear resistance of TiCN, with the high temperature chemical inertness of Al_2O_3 , boosted the tool life and productivity. The main drawback of the CVD-coatings originated from the high deposition temperatures needed ($\sim 1000^\circ\text{C}$ [4]), since these deposition techniques operate near thermodynamic equilibrium and requires high temperature to initiate chemical reactions. The high deposition temperature and the thermal expansion mismatch between the coatings and the substrate result in possible substrate-material-diffusion into the coating and a network of cooling cracks in the coating after cooling from the deposition temperature [4, 5]. In parallel

with the coating development, the hard metal development continued and resulted in a diversified offer which suited different application and coating-substrate combinations. State of the art in hard metal offer is covered in a recent review by García et al. [6].

The introduction of physical vapor deposition (PVD) techniques, permitting deposition at lower temperatures and far from thermodynamic equilibrium, made new metastable coating compounds such as TiAlN (*ca* 1985) possible [7-9]. The lower deposition temperature enables the use of temperature-sensitive substrate such as high speed steel. The thermodynamically stable α -Al₂O₃ oxide coatings, which boosted the CVD-coated products, however, proved to be difficult to obtain with these techniques. The reasons were twofold: insulating materials, such as oxides, are in opposition to the need for a closed electrical circuit in PVD deposition, and the lower deposition temperatures results in metastable phases rather than the thermodynamically stable phase.

Based on these conditions, this project explores phase control in PVD oxide coatings. Specifically, I seek to achieve oxide coatings which have a desired crystal structure and are thermally and chemically stable with respect to the workpiece material at the temperature of use during metal cutting. The general approach is to either stabilize a metastable oxide compound at the temperature of use or to obtain, during the deposition, a thermodynamically stable compound which will remain stable at the temperature of use. The stabilization of the metastable phases or promotion of the thermodynamically stable phases during growth is realized through alloying. This is investigated in the Al-V-O, Al-Cr-(Si)-O, and Cr-Zr-O systems.

The Al-V-O system was chosen since the elementally pure binary oxide form sesquioxide M₂O₃ oxides in the corundum structure and since the pseudobinary system was not studied by direct PVD-synthesis over a wide compositional range. The possible solid solutions are tested with respect to their mechanical and thermal stability.

The Cr-Al-(Si)-O system was selected because of the need of investigating the reported cathode erosion improvement, during cathodic arc deposition, by adding Si in the cathode without subsequent Si incorporation in the coating [10]. The inherent difficulties with depositing insulating oxide films with PVD also make possible ways of improving the process stability a crucial part of this research, rendering plasma characterization important. Through plasma studies combined with coating characterization the effect on the three different material fluxes (ions, neutrals and droplets) present during cathodic arc deposition may be investigated and linked to the film growth.

The Cr-Zr-O system was chosen because it is a combination of two engineering oxides having good mechanical and/or thermal properties and showing solid solution in the corundum structure. The annealing studies of Cr-rich α -(Cr,Zr)₂O₃ coatings is aligned with the project goal of investigating the temperature stability of potentially interesting metal cutting coating compounds.

2 Background

2.1 Metal cutting

Metal cutting means removal of material, through chip formation, from a workpiece material in order to shape it into its desired form. This can be done through several different types of machining operations, which can be categorized in three main groups: turning, milling, and drilling. In Figure 1 (a), a turning operation is shown. The cylindrical workpiece material rotates around its center axis and the tool performs a facing operation towards the rotational center of the workpiece, marked with arrows. Figure 1 (b) shows a schematic figure of a plane perpendicular to the main cutting edge of the tool. The black arrows show the direction of movement of the different components. The geometry of the tool in combination with the cutting data and the intrinsic properties of the workpiece material (e.g., degree of work hardening) decide the shape of the chip and the cutting forces which in turn decide the generated maximum temperature during machining. The maximum temperature is obtained $\sim 300\text{ }\mu\text{m}$ onto the rake face, see Figure 1 (b), depending on geometry, workpiece material, cutting data and coating material [11, 12]. Most of the heat is generated where the chip starts to form in the primary shear zone [13] and is then mostly transported away with the chip, hence flowing over the rake face and thus heating that area more than the flank face [11]. The heat load is significantly lower on the flank face than on the rake face due to less plastic deformation in the workpiece material in this contact area with the tool.

Flank wear is initiated just below the cutting edge due to the sliding contact between the newly cut workpiece and the tool. Nitride and carbide coatings are generally more resistant to flank wear than crater wear.

It is in the rake face region that $\alpha\text{-Al}_2\text{O}_3$ oxide coatings historically has proven to be the most efficient coatings for reducing crater wear originating from high temperature chemical and abrasive wear loads. $\alpha\text{-Al}_2\text{O}_3$ also works as a thermal barrier layer that sometimes permit the use of a tougher but thermally softer substrate. Reduced smearing of the workpiece material due to the low chemical interactions with it, and a low friction, is another positive effect of $\alpha\text{-Al}_2\text{O}_3$ [14].

Figure 1. (a) Dry turning, a facing operation, in stainless steel © L. Landälv (b) Schematic image of a cross section perpendicular to the cutting edge of a cutting tool during cutting. Arrows mark the direction of the moment of each part. The scale bar on the tool is to give a rough estimate of the scale of the tool compared to the coating thickness.

Milling is a machining operation where the cutter body rotates at high speed around its own axis. The rotating cutter body or the workpiece is then moved in contact with the other. Machining then typically starts with some degree of radial cutter engagement which is characteristic for a milling operation compared to a turning operation. In the later continues cutting tool engagement is common. In milling on the other hand maximum cutting tool engagement is half of the machining time, often much less, resulting in high mechanical and thermal load cycling. The typical milling wear, such as thermal cracks and chipping, originates from the thermal and mechanical cycling. In strongly intermittent turning, the wear often becomes similar to that normally observed for milling.

PVD coatings are predominantly used on milling inserts or turning inserts with high intermittent load, and/or finishing operations, leading to small depth of cut and low heat loads. The PVD coatings thus covers an application area where CVD-coated inserts often run into problem due to tensile stresses in the coating originating from their high temperature deposition. The high temperature deposition also leads to cooling cracks in CVD coatings that originates from thermal expansion mismatch between substrate and coating [4, 12]. The need of very sharp cutting edges, matching small feed values, also promotes PVD coatings in milling and intermittent turning application because the PVD coatings generally are thinner coatings than CVD coatings. The possibility to tailor the residual stress levels in PVD coatings to a suitable compressive state, with different degrees of ion bombardment, is also beneficial for improving the resistance to cracks and brittle fractures. The comparable low deposition temperature with PVD helps suppressing cooling cracks during cooling after deposition. Altogether, these PVD coating specific application areas would benefit a lot from an expansion of the existing coating solutions with more PVD oxide coatings. This expansion would combine the inherently good properties from both PVD deposition techniques and oxide coating materials. Possible such oxide coating materials are explained in the next chapter.

2.2 Material systems

2.2.1 Al₂O₃ polymorphs

In this chapter a background is given on the most extensively used oxide material for metal cutting, Al₂O₃. Being the starting point for this thesis and the aim of much research, an overview is presented on the most important crystal structures of the sesquioxide Al₂O₃, and some of the previous work done on Al₂O₃ coatings in the context of metal cutting.

Aluminum oxide, Al₂O₃, exhibits many different metastable crystal structures and one thermodynamically-stable structure, the corundum phase, denoted α . The corundum structure is the most commonly sought phase of Al₂O₃ within the area of tool material (coating or bulk) for metal cutting. The structure is an $R\bar{3}c$, rhombohedral structure with Al in six-fold coordinated AlO₆ face-sharing octahedrons. Figure 2 (a) shows the rhombohedral unit cell of the α -Al₂O₃ structure with the Al³⁺ coordinated in the oxygen octahedrons. Upon heating a single-crystal sample, the lattice expands more along the c -axis than the a -axis due to the repulsive Al-Al forces. Thermal expansion data for the structure is given in ref. [15] and ref. [4]. Another way of describing the same structure is with closed packed arrays of O²⁻ ions stacked in an ABABAB order along the c -axis. Between each layer 2/3 of the octahedral holes are filled with Al³⁺. The α -Al₂O₃ structure deviates from a perfectly closed packed structure in the way that the Al-Al distances are isotropic instead of being longer along the c -axis compared to the ones parallel to the basal plane. These small shifts are, however, normally omitted [16]. Figure 2 (b) shows the ordered metal vacancies on the metallic Al-sublattice which translates one octahedral hole for each new metal sub-lattice layer, marked with the horizontal line, which increases one octahedral unit per layer.

Deposition of α -Al₂O₃ with reactive pulsed magnetron sputtering on steel substrate was reported when increasing the substrate temperature over 700 °C [17, 18]. A detrimental effect of adding bias (-50 V) on the nucleation of α -Al₂O₃ over γ -phase was reported by the same group [19]. This is somewhat contradictory to later work claiming that higher energy ion bombardment, single ionized Al⁺ ions, is positive for the formation of α -Al₂O₃ [20, 21], by filtered cathodic arc deposition (FCA) up to 200 V bias [22]. A molecular dynamics calculations on the α -Al₂O₃ system showed that energies in the range of ~35 eV/atom is needed in order for the α -phase to nucleate. It was also shown that it is important that a large fraction of these energetic species is ionic in order to create this phase. When there are many neutrals with low energy it is not possible to form this wanted structure at 500 °C [23]. This may explain why using HIPIMS, forming a large fraction ionized metal species, can produce α -Al₂O₃ with a wide range of bias voltage [24, 25]. The discrepancy in the effect of biasing is possibly due to the different ions species that are accelerated by the bias. In the pulsed magnetron sputtering case, Ar⁺ is accelerated but in the latter case it is metal ions or metal ions and Ar⁺ that are accelerated with the applied bias, resulting in completely different ion bombardment of the substrate. There are several factors that have hindered further industrialization of the process: high deposition

temperatures, deposition of an electrically insulating coating in a process demanding electrical conduction, difficulties with scaling power supplies (HIPIMS), and to create stable plasma conditions for threefold rotating substrates in a large scale deposition equipment. Thus, there are still no commercial cutting tools with PVD α - Al_2O_3 , even after more than 20 years since the first claim of such a coating.

Figure 2. (a) Rhombohedral unit cell of the α - Al_2O_3 phase oriented along the $[110]$ -projection with c -axis vertical, showing the ABAB-stacking of oxygen atoms (big red spheres). Additional O atoms has been added in order to complete all octahedral coordinated Al (small grey spheres) polygons (b) show the ordered metal vacancies on the metallic Al-sublattice which translates one octahedral hole for each new metal sub-lattice layer (shown with a growing black horizontal line)). Crystal structures made with VESTA.

The different metastable phases and their transformation routes have been reviewed by Levin and Brandon [26]. The metastable structures are divided into two main groups having a closed packed oxygen anion sublattice, either in face centered cubic ABCABC (γ cubic, η cubic, θ monoclinic, δ either tetragonal or orthorhombic) or hexagonal close packed ordering ABAB (κ orthorhombic, χ hexagonal). The different phases originate from the distinct ordering of the cations on the interstitial sites in between the two types of ordering of the oxygen sublattice. The same authors also discovered some additional monoclinic phases θ' , θ'' , and λ with face center cubic anion ordering [27]. The phase transformations between the metastable phases are not reversible upon cooling and are therefore referred to as transition phases [28]. The metastable phases primarily used in metal cutting are kappa (κ) for CVD-deposited coatings [2] and gamma (γ) for PVD-deposited coatings [29-31].

Early CVD α - Al_2O_3 coatings has since the last ~ 10 years been shown to a large extent consist of transformed κ (during deposition) instead of as grown α - Al_2O_3 . This phase transformation during growth results in a completely different defect filled microstructure than the now state-of-the-art directly deposited α - Al_2O_3 . The high defect concentration in the α - Al_2O_3 resulting from transformed κ -coatings are due to the 8% volume contraction during the $\kappa \rightarrow \alpha$ transformation [32]. This fairly recent discovery, considering the ~ 40 year's history of CVD Al_2O_3 , shows the complexity of obtaining good quality α - Al_2O_3 .

The γ phase, space group $\text{Fd}\bar{3}\text{m}$ spinel, is the most commonly obtained crystalline phase when depositing Al_2O_3 with PVD. Figure 3 shows an illustration of this structure with the unit cell marked with the black box. It is a cubic spinel-like compound with the cations distributed in three distinct interstitial positions (octahedral, tetrahedral and quasi-octahedral), thereby distinguishing it from the other cubic spinel transition phases through its cation ordering [28]. Every second layer contains octahedral coordinated Al and every second layer contains a mix of tetrahedral and octahedral coordinated Al. The quasi-octahedral position is not shown in the image since it is predominantly a reorganization of Al in the surface layers, thus more important for very fine powders. The degree of disorder of the Al ions in their respective interstitial position may lead to different shape, broadening, of the XRD-peaks from the same crystal zone axis [28]. This behavior is observed for Al-rich coatings in **Paper I** where 111, 222, and 444, show different shapes.

Figure 3. The γ - Al_2O_3 structure along $[\bar{1}10]$ zone axis (slightly off axis to show the depth perspective) with (021) normal pointing upward. Red big spheres are O and small silver spheres are Al. ABC stacking is marked and O for octahedral coordinated Al and T for tetrahedral coordinated Al. Black box is the unit cell but the cell is repeated 5 times in all directions to make the image. Crystal structure made with VESTA.

In order to obtain γ - Al_2O_3 without amorphous phase, by means of reactively pulsed DC sputtering, a substrate temperature of at least 500°C (using floating bias voltage) [33]. Similar deposition temperatures for reactive pulsed DC processes has been reported by several authors [17, 18, 34, 35]. With RF-sputtering it has been obtained at $450^\circ\text{C} - 500^\circ\text{C}$ [36, 37]. Adding

an RF-coil for further ionization of the material flux together with bias made deposition of γ -phase possible down to ~ 300 °C [38]. The transformation from γ to α upon annealing in air, under non-isothermal annealing, took place ~ 1200 °C [33] For isothermal annealing in air, the transformation from γ to α could be observed already after annealing at 1100 °C [35, 39]. The latter temperature being in line with the transformation temperature observed in **Paper I**.

The effect on phase formation and relative phase stability by adding Si to the Al_2O_3 was recently investigated by Nahif et al. [39-41]. Adding 2 at.% Si when depositing Al_2O_3 with filtered cathodic arc may increase the transformation temperature from γ to α by ~ 200 °C, from ~ 1100 °C to ~ 1300 °C [39]. Reactively pulsed DC sputtered amorphous Al_2O_3 coatings with up to 2.7 at.% Si showed an increased transformation temperature from amorphous to γ with ~ 110 °C and from γ to α with more than 120 °C compared to pure Al_2O_3 . The increased transformation temperatures were attributed to the increased Si-O bond strength compared to Al-O [42]. The increased stabilization of the γ -phase may improve the performance and broaden the application area of the coating further than has been reported so far for pure γ - Al_2O_3 phase [29, 31, 43]. The thermal load of a reported metal cutting test was not enough to cause transformation of the γ -phase [31].

The work to deposit corundum-structured coatings or stabilized metastable phases has continued to focus more onto alloying with different elements in order to try to obtain stable phases at the temperature of use. This was the motivation for the sputter deposition of $(\text{Al,V})_2\text{O}_3$ coatings in **Paper I**, as well as cathodic arc deposition of coatings and a plasma study of a pseudoternary oxide $(\text{Al,Cr,Si})_2\text{O}_3$, **Paper II** and **Paper III**, respectively.

2.2.2 α - Cr_2O_3

Eskolaite, α - Cr_2O_3 , is isostructural with corundum, see Figure 2 (a), and is - in contrast to the Al_2O_3 system - the only crystalline form of Cr_2O_3 . It has a slightly larger unit cell (a and b 4.959 Å, $c = 13.594$ Å) than α - Al_2O_3 (a and b 4.759 Å, $c = 12.993$ Å), due to the larger atom size of Cr. The oxide form from metallic Cr upon high temperature air exposure and stabilize many metal alloys from further oxidation [44, 45]. α - Cr_2O_3 being the only crystal structure at this oxygen stoichiometry for Cr makes it easier to obtain this structure with PVD-techniques than the α - Al_2O_3 . α - Cr_2O_3 has been deposited at temperatures of ~ 480 °C [46] with cathodic arc technique, and with different kind of sputtering techniques from ~ 60 °C [47] and ~ 300 °C (higher crystallinity) [48, 49]. This makes it suitable for stabilizing other compounds in the corundum structure. Stabilization can be done either by template growth (e.g., another material, such as Al_2O_3 , is grown on α - Cr_2O_3 and adopts that crystal structure) [50-52] or by alloying. When alloying other materials with Cr_2O_3 it promotes a solid solution in the corundum structure [37, 53-57]. The $(\text{Al,Cr})_2\text{O}_3$ phase evolution will be further treated in section 2.3.

α -Cr₂O₃ is also one of the hardest naturally occurring oxide, with a hardness near 30 GPa. This hardness level is also seen for sputter-deposited phase-pure, dense stoichiometric α -Cr₂O₃ [52, 58]. α -Cr₂O₃ has not been used in its pure form as metal cutting tool material, but is extensively used for its good corrosion protection in, e.g., high-alloyed steels.

On the other hand, Cr₂O₃ has been heavily used for alloying with Al and in this work also with Al and Si, see **Paper II**, and **Paper III**. The stabilizing effect of α -Cr₂O₃ has also been investigated in the Cr-rich part of the (Cr,Zr)₂O₃ system in two annealing studies, isothermal vacuum annealing, **Paper IV**, and *in situ* synchrotron X-ray diffraction during annealing in vacuum and in air, **Paper V**.

It is worth noticing that, contrary to Al, Cr can adopt three other valances states, 2⁺, 4⁺, and 6⁺, which opens up for other types of oxides CrO, CrO₂, and CrO₃. The latter is a highly toxic and carcinogenic compound due to the high oxidizing effect of Cr⁶⁺. The possible reaction of Cr₂O₃ to volatile CrO₃ in an oxidizing environment [44, 59] may be a reason that it has not been used in metal cutting in its pure form.

2.2.3 ZrO₂ polymorphs

Pure ZrO₂ exists in three different crystal structures: the standard temperature and pressure (STP) stable monoclinic phase P2₁/c, and the metastable phases; tetragonal P4₂/nm c (from ~1170 °C) and cubic fluorite Fm $\bar{3}$ m (from ~2300 °C), both at ambient pressures [60-63]. The crystallographic structure of the tetragonal phase is illustrated in Figure 4. See **Paper IV**, and **Paper V** for the characterization of that phase in a pseudobinary oxide compound together with Cr.

The unit cell of pure tetragonal ZrO₂ is constituted by two Zr atoms in 8-fold coordination with O-atoms. Upon addition of doping elements with other ionic size and valance than Zr the unit cell is distorted. The distortion is larger for dopants with smaller ionic radius, like Cr³⁺ and Fe³⁺, than for oversized dopants, like Y³⁺ and Gd³⁺. Introducing a dopant with another valance, like Cr³⁺ (**Paper IV** and **Paper V**) creates oxygen vacancies that tend to be arranged between two Cr³⁺ dopants (in 6-fold oxygen coordination) with a common oxygen vacancy. This distortion promotes the tetragonal phase over the monoclinic phase, however, to a lesser extent than an oversized dopant, like Y³⁺ [64]. The alloy content marking the boundary between monoclinic, tetragonal and cubic phase for some common, mostly rare earth, alloy element are described in ref [65].

Figure 4. Crystallographic structure of the tetragonal ZrO_2 phase along the $[110]$ -projection (slightly off axis to show the depth perspective) with c -axis vertical showing the ABAB-stacking of oxygen layers (small red spheres) and Zr-layers (big purple spheres). The unit cell is marked with a black box. The image consist of 5 unit cells in each direction. Crystal structures made with VESTA.

The tetragonal phase is the most commonly used phase and can be stabilized at STP by alloying with different early transition metal oxides, the most common being Y_2O_3 [66, 67]. This phase is often used as a thermal barrier coating in high-temperature applications, coated on, e.g, turbine components [68]. The cubic fluoride phase is used as electrolyte in solid-oxide fuel cells due to its high ionic conductivity [69, 70].

The mechanical properties of ZrO_2 varies significantly with crystal structure, and indirectly with alloying element needed for phase stabilization of the tetragonal phase or cubic phase. The monoclinic ZrO_2 has a nanoindentation hardness of ~ 10 GPa [71, 72] and the tetragonal ZrO_2 in the range of 13-14 GPa [73] or ~ 17 -18 GPa in other works [71, 72].

2.2.4 Vanadium oxides

Vanadium can adopt several oxidation states, V^{2+} , $3+$, $4+$, $5+$, which results in many possible oxides with varying properties. From low to high oxidation state, the most common phases are: V_2O_3 , which historically, primarily been investigated for its magnetic properties [74-76], V_3O_5 a Magnéli series oxide [77], showing interesting magnetic properties with the highest metal to insulator switching temperature of all vanadium oxides [78, 79], VO_2 , as primarily investigated for its thermochromic property, i.e., for architectural glass [80-82], and V_2O_5 , which shows catalytic properties and good ionic conduction [83] as well as low friction due to low melting temperature ~ 700 °C [84]. The O-V phase diagram summarizes these phases [85]. Calculated mechanical properties are surveyed by Reeswinkely et al. [86].

The focus in this thesis, **Paper I**, has been on the V_2O_3 oxide since it has the same crystal structure, rhombohedral $R\bar{3}c$, as the $\alpha\text{-Al}_2\text{O}_3$, see figure 2. Heating V_2O_3 powder in air at ~ 550 °C result in oxidation to V_2O_5 [87]. $\alpha\text{-V}_2\text{O}_3$ has been shown to have higher compressibility than

other sesquioxides, like α -Al₂O₃ and α -Fe₂O₃ [88]. Hence it needs to be alloyed with other elements in order to enhance mechanical properties. V₂O₃ electrical properties also change dramatically, upon incorporation of just 1-2 At.% of Al, from being an poor conductor to an insulator at room temperature [89].

V₂O₅ crystalizes in the orthorhombic structure, Pmmn space group, with lattice parameters $a=11.510$ Å, $b=3.563$ Å, and $c=4.369$ Å, with a layer-like structure. This is the most stable vanadium oxide under oxygen rich environment, with the highest oxidation state [83], but however a fairly low melting temperature of ~ 680 °C [90]. It has for the combination of layered crystal structure and low melting temperature been evaluated as low friction agent in wear reducing application [91, 92]. In this thesis, V₂O₅ was obtained after annealing (Al,V)₂O₃ coatings in air, **Paper I**.

2.3 Pseudobinary and -ternary oxides

Pseudobinary and pseudoternary oxide refers to two and three metals being mixed respectively with oxygen in contrast to a binary oxide being one metal and oxygen, e.g., Al₂O₃.

Predicting what kind of crystal structure that will be obtained upon alloying is difficult for oxides, due to the varying degree of ionic-covalent nature of the bonds. Several possible coordination and oxidation states of the transition metals, as well as a wide range of different plausible crystal structures also in the binary oxide system adds to the difficulties. Parameters to consider when entering the area of phase tailoring of ABO₃ materials through alloying has been reviewed by Giaquinta and Loye [93]. The possibility to model the stability of new phases directly from first principles has become increasingly possible over the last decade due to the rapid growth in computational power. The development of the theoretical and numerical framework for electronic structure calculations based on density functional theory has also matured [94]. The studies of materials formed under non-equilibrium conditions such as PVD can, if care is taken, also benefit strongly from first-principles calculations as exemplified by the reviews of Abrikosov et al. [95], and Music et al. [96]. The pseudobinary and pseudoternary oxide coatings studied in this thesis, namely Al-V-O (**Paper I**), Al-Cr-Si-O (**Paper II and Paper III**), and Cr-Zr-O (**Paper IV, and Paper V**) systems, were however not selected based on prior calculations but on earlier experimental work [97, 98], [10, 99], and [56] for the three material systems.

The ternary Al-V-O material system has mainly been studied along the pseudobinary Al₂O₃-V₂O₅ phase diagram, where the triclinic AlVO₄ phase is present as the only intermediate compound [90]. AlVO₄ melts incongruently at ~ 745 °C according to ref. [90], although a wider range of melting temperatures are stated in earlier studies. AlVO₄ has been found at the interface between vanadium oxide based catalyst with Al₂O₃ as supporting oxide, and was shown to be unstable for prolonged reduction conditions [100]. The cubic spinel AlVO₃ is the only reported

compound in the Al_2O_3 - V_2O_3 pseudobinary phase diagram [97]. This phase is possibly not easy to obtain considering the instability reported for AlVO_4 in the redox study. In addition to these studies, liquid phase (V_2O_5) sintering of Al_2O_3 has been shown to decrease the α -phase formation temperature slightly in conjunction with enhanced grain growth [101, 102]. These works are based on synthesis being wet chemistry, calcination process or sintering and very few studies are done with PVD. One such study covers the $\text{Al}_{0.5}\text{V}_{0.5}\text{O}_x\text{N}_{1-x}$ with x up to 80 at.% oxygen, where increasing oxygen content lead to metal vacancies in order to maintain charge neutrality in the obtained cubic sodium chloride structure [103]. This exemplifies the lack of direct synthesis of Al-V-O by PVD-techniques covering a wider range of Al-V compositions. Therefore, filling this gap was pursued in **Paper I**, with the aim to see what phases that was possible to obtain along the Al_2O_3 - V_2O_3 pseudobinary phase line as well as their thermal stability.

The pseudobinary phase diagram of Al_2O_3 - Cr_2O_3 shows full solid solution in the α -structure over the entire compositional range at high temperatures, and a miscibility gap, shifted towards the Al_2O_3 -rich side, at lower temperatures [104, 105]. When depositing the material system by pulsed cathodic arc ($\text{Al}=0.70$ - 0.25 at.% metal fraction), at temperatures ~ 550 °C, a corundum solid solution structure was obtained [53]. Similar alloying of the AlCrO phase has been done with sputtering [37, 54]. Additional studies on the material system, using RF-sputtering [106] and pulsed cathodic arc [99, 107] led to the discovery of a new cubic oxide phase. The phase was identified to be a defect-stabilized B1-like cubic phase with 33% vacancies on the metal sublattice [108]. Most of the research has been focused on cathodic arc deposition and there several studies show that the B1-structure become the dominant phase for coatings deposited with Al-content larger than ~ 70 at. %. Theoretical calculations show that the corundum structure is the thermodynamically stable phase over the entire compositional range, but that the B1-like phase has a lower formation energy than the γ -phase up to 85 at.% of Al. Defects associated with PVD growth, like point defects, promotes the cubic oxides [109]. Introducing start layers with 75 at.% Cr content have been shown to promote corundum structure growth for as high as 85 at.% Al-containing coatings [110] as well as tailoring of the bias level [111]. A transition from the cubic B1-like structure to the thermodynamically stable corundum structure has been observed during growth [57, 110, 112]. Annealing of the B1-like phase makes it transform to the corundum structure at ~ 1000 °C; if annealed in vacuum this transformation is preceded by a γ , θ -structure starting to form at ~ 800 °C. In air the formation onset for the θ -structure is increased to ~ 950 °C, the full corundum formation is increased to slightly below 1100 °C [57]. Annealing of Cr-rich B1-like coatings in air yields transformation already at ~ 900 °C to the corundum phase [113]. Another way to increase the corundum structure formation has been shown to be by Fe alloying, creating Fe-rich droplets which serves as nucleation spots for the corundum structure [114-117].

Cathodic arc deposition of Al-Cr-O coatings, as described above, results in severe uneven cathode erosion, making its production on an industrial scale inefficient and costly owing to

poor use of the cathode material. This is due to the extensive oxide island formation on the cathode surface, also referred to as cathode poisoning [118, 119]. The oxide island growth is promoted the most for the Al-composition of 50-80 at.% [120], above 85 at.% it can be evaded by the cathode Al-melt solidifying below the formation temperature needed for corundum growth [118]. However, this is the most interesting range, from a production perspective, since the corundum structure can be stabilized by the Cr, while having a high Al-content. Adding 5 at.% Si to the 70 at.% containing Al-Cr cathode was reported to improve the cathode erosion and to reduce the oxide island formation. Surprisingly, the Si was not reported to have been incorporated in the coating. This was tentatively explained through formation of volatile SiO and changed melt composition of the cathode surface [10]. Reactive magnetron sputtering of $\text{Al}_{0.52}\text{Cr}_{0.4}\text{Si}_{0.08}$ in almost pure O_2 atmosphere resulted, however, in the B1-like cubic structure with similar Si-content in the coating as in the cathode [121]. Another recent study on cathodic arc evaporated AlCrSiO film also reports Si in the deposited coating [122]. The reported improvement of cathode erosion upon Si addition and the apparent discrepancy in Si uptake tendency for the oxide between different studies motivated the research in **Paper II** and **Paper III**, covering both coating characterization and plasma analysis for this material system, respectively. In **Paper II**, the same type of industrial equipment was used as in the paper claiming the benefit of Si for the first time and coatings with different Al/Cr ratio and Si-content was synthesized. In **Paper III**, a plasma study was performed on two cathode compositions, $\text{Al}_{0.7}\text{Cr}_{0.3}$ compared with $\text{Al}_{0.7}\text{Cr}_{0.25}\text{Si}_{0.05}$. The aim of the studies was to clarify the effect of Si on the coating composition including the presumable loss of Si through volatile SiO.

From a metal cutting tool material perspective, combining Cr_2O_3 with ZrO_2 is interesting due to the low solubility of ZrO_2 in iron [3] and ZrO_2 low thermal conductivity [68]. The hardness and crystallographic stability could potentially be introduced by the naturally hard and stable $\alpha\text{-Cr}_2\text{O}_3$ [58]. The Cr-Zr-O was first deposited over the whole compositional range with reactive RF-magnetron sputtering by Spitz et al. [56]. They showed solid solution in the corundum structure at the Cr rich end of this pseudo binary system. This was possible despite the facts that Zr has one higher valence than Cr and is significantly larger in size [123]. The high temperature binary phase diagram state higher solubility of ZrO_2 in Cr_2O_3 than the other way around [124]. The thermal stability of Cr-rich $(\text{Cr,Zr})_2\text{O}_3$ coatings was investigated through isothermal vacuum annealing and post-annealing characterization, see **Paper IV**. The observed dissociation of the $\alpha\text{-Cr}_2\text{O}_3$ phase to bcc-Cr in **Paper IV**, lead to a continuation of the annealing study on the same coating material. The effect of annealing in vacuum and in air atmosphere was investigated during *in-situ* X-ray diffraction at a synchrotron radiation source followed by post-annealing characterization in **Paper V**.

3.1 Deposition techniques

Applying of a coating has been part of mankind's history for thousands of years, where the goal has been to improve the appearance or usefulness of an item [125]. Nowadays, applying a coating of some thickness, ranging from atomic monolayer to several hundreds of μm is part of the advanced surface engineering field, an increasingly important field of research and engineering over the last couple of decades [126]. There is a vast number of different ways of producing a coating onto a bulk material of some kind. Among these can be mentioned: thermal spraying (e.g., thermal barrier coatings for turbine blades, $\sim 500\ \mu\text{m}$ thick [68]), electro plating $\sim 10\ \mu\text{m}$ (e.g., platinum bond coating [68]), Chemical vapor deposition [126], Physical vapor deposition [126], and many more. The common feature of PVD techniques is the vaporization of a solid through physical ejection of atoms or molecules into a low pressure vapor or plasma. The vapor or plasma consist of neutral or ionic species that condensates onto a substrate. Adding a reactive gas, e.g., N_2 or O_2 , allows the formation of nitride or oxide compounds, respectively. PVD techniques encompass a vast array of different ways of vaporizing the source material: thermal evaporation, electron beam evaporation, different kinds of sputtering, filtered and unfiltered cathodic arc deposition, and pulsed laser deposition, each one having its advantages and drawbacks [126]. In this thesis, two types of PVD techniques have been used, magnetron sputtering and cathodic arc deposition, which are described below.

3.1.1 Need for vacuum systems

PVD techniques require controlled atmosphere and pressure. Therefore, vacuum systems are used with varying degree of ultimate pressures. The vacuum system used in this work are either high vacuum (HV) system ($\sim 7 \cdot 10^{-4}$ Pa ultimate pressure), which only need Viton o-rings as sealing materials, or ultra-high vacuum (UHV) system ($\sim 7 \cdot 10^{-6}$ Pa ultimate pressure) that needs copper gaskets.

The level of ultimate pressure needed (also called base pressure) is determined by the demands of cleanness from gas impurities in the final deposition product. The most difficult impurities to reduce in a vacuum system is water vapor (easy condensing and available abundant in air) and hydrogen (permeating most materials, and difficult to pump) [127]. To reduce the water vapor content and obtain UHV condition in reasonable time, the vacuum system walls need to be baked, i.e., heated to $\sim 150\ ^\circ\text{C}$ for several hours in order for the vapor to desorb. The cleanness demands are generally much higher for electrical and optical coating application compared to industrial wear resistant coating applications. For the wear resistant coating industry, a plasma etch prior to coating deposition cleans the surfaces that should be

deposited. That in combination with high deposition rates (compared to impurity deposition rates) makes it possible to use HV systems with a base pressure of $\sim 6 \cdot 10^{-4}$ Pa, as shown in the appended paper (**Paper II**).

When lowering the pressure to these levels the motion of the gas particles changes from being collective/fluid to become individual and ballistic. This change in behavior is characterized by the gas particle mean free path, the distance between gas-gas collisions. At UHV pressure this is typically of the order of a meter, or at deposition pressure (~ 0.4 Pa) 5-10 cm, similar to or slightly smaller than the typical deposition distance ~ 10 -20 cm. The degree of gas-gas collisions is a very important feature in PVD-techniques since it is one of the parameters influencing the energy of the species arriving at the substrate.

3.1.2 Unbalanced reactive magnetron sputtering

The process of sputtering consists of bombarding a material, named target, with accelerated inert gas ions, most commonly Ar^+ . The inert gas ions are generated in what is called a plasma, a quasi-neutral electron gas. Plasma is commonly referred to as the fourth state of matter and is an ionized gas which is electrically neutral when averaged over the entire plasma. In order for the sputter process to work the gas ions need to be accelerated by a negative potential at the target to a high enough kinetic energy in order to eject (sputter) new atoms from the target upon impact. This causes a collision cascade within the atomic surface layers of the target material upon impact.

If a constant negative voltage is applied (typically of the order of a few 100 V) to the target, the technique is called direct current (DC)-sputtering. This gives the highest deposition rates compared to different sputtering techniques since the sputtering process is on 100% of the time. This technique works well for depositing conducting materials. If the material is insulating to some degree, a pulsing of the voltage, with some degree of reversed polarity is needed in order to discharge the extra charge built up on the deposited isolated areas. The need for discharging the charge built up is important both at the target and at the substrate. In this work, pulsed DC power supplies (50 KHz at the target and 100 kHz at the substrate), were used for **Paper I** and a RF (Radio Frequency: reserved 13.56 MHz) power supply was used to deposit the coatings annealed in **Paper IV** and **Paper V**. The pulsed DC supply generated a pulse set so that 90% of the time having negative voltage and 10 % of the time the voltage was reverted to a small positive value (10 % of the negative bias value). The RF-power supplies use a sinusoidal voltage pulse ($\sim 50\%$ on time compared to DC-sputtering) with the RF frequency to clear the target surface from charge built up. RF pulsing was originally used for sputtering of completely insulating ceramic targets [128], but can also be used for sputter from metallic target in reactive gas, such as O_2/Ar mixture. It then helps discharge the insulating layer formed on the target, which is the case in this work, **Paper IV** and **Paper V**. The challenges and possibilities with reactive sputtering is detailed in a recent tutorial by Strijckmans [129].

The sputtering process is today almost always enhanced by a set of permanent magnets behind the target material. The sputtering process is then called a magnetron sputtering process. The permanent magnets cause a magnetic field $\mathbf{B}$ close to perpendicular to the accelerating electric field $\mathbf{E}$ in front of the target. This field traps a larger fraction of the electrons resulting from the sputter process. These electrons will remain in front of the target surface bouncing alternating back and forth between the two poles of the magnets at the same time as they drift along the $\mathbf{E} \times \mathbf{B}$ path. The locally increased electron density in front of the target will increase the degree of ionization of the Ar gas and hence increase the plasma density. This leads to a higher sputtering rate even though a lower pressure of Ar can be used in the deposition chamber [130].

If the magnetic strength of the center magnet is equivalent to the sum of the magnets at the periphery of the target, the magnetron is called balanced. In order to enhance the plasma density further away from the target (closer to the substrate) as well as increasing the deposition rate, an unbalanced magnetron is often used. This means that the center magnet has a lower strength than the surrounding magnets, opening up the magnetic confinement in front of the target, lowering the degree of ionization of the gas, but extending it further out in the deposition chamber [130]. Using an unbalanced magnetron increases the gas ion and electron bombardment of the substrate and may lead to structural defects in sensitive coatings (e.g., aimed for electronic applications) [131]. This is not the case for metal machining coating and therefore unbalanced magnetrons have been used in the present work (**Paper I, Paper IV, and Paper V**).

The substrate, which is the object to be coated with the vaporized sputtered species, could either be at grounded, floating or biased potential. This will greatly influence the properties of the resulting coating, since the arriving ion bombardment will transfer different amount of energy to the ad-atom on the growing coating surface, depending on the magnitude of the applied voltage on the substrate. The change in energy on the incoming species will affect the surface mobility and hence the crystal structure as well as the microstructure and density of the coating to be grown. Grounded substrate will lead to a small bias corresponding to the potential difference between ground and the slightly positive plasma potential ~ 5 V. Floating potential means that the substrate is electrically separated from the ground and will adapt to the plasma potential, resulting in a slightly negative self-biasing of the substrate due to the electron bombardment, ~ -5 V. Having a biased substrate means that the substrate is connected to an external voltage source where it is possible to set a sought substrate potential in order to obtain a specific energy level of ion bombardment. Having set a negative bias voltage will result in an electrical current proportional to the impinging Ar^+ ion current. A typical voltage profile for sputtering can be seen in Figure 5, showing the cathode fall (target), the plasma potential V_p , the anode (being the grounded chamber wall in many lab systems) and the floating V_f or biased substrate (middle).

Figure 5. Schematic illustration of the voltage variation over cathode-plasma-anode setup in magnetron sputtering with large anode (chamber wall). V_p plasma potential, V_f floating potential for an inserted metal piece, e.g., substrate, V_g ground potential. Rework from [126].

A drawback of both DC, pulsed DC, and RF magnetron sputtering is that the target material is not ionized to any significant extent. The only significantly ionized species are the Ar^+ , which will not be incorporated into the coating, unless the bias is high. In that case some Ar^+ could become implanted and trapped in the growing film. The residual Ar in the coating is an unwanted defect and limits the use of high bias in order to achieve, i.e. densification of the film. Over the last ~15 years increasingly more work has been put into realizing depositing techniques permitting sputtering with a large fraction of metal ions, commonly grouped under the name High Power Impulse Magnetron Sputtering (HIPIMS) techniques [130, 132, 133]. These techniques permit among other things to deposit denser films without incorporating Ar at otherwise similar conditions as for DC-sputtering, by means of careful synching of the bias voltage to the metal ions part of the pulse [134, 135].

Another way of reaching high degree of ionization of the target material is the cathodic arc deposition technique, commonly used in industry since many years, and described in the next chapter.

3.1.3 Cathodic arc deposition

Cathodic arc deposition take place in a different I-V regime compared to sputtering. Cathodic arc deposition is characterized by a small cathode fall voltage, generally referred to as burning voltage, of approximately 20 V [136] and a large currents 10 to hundreds of A. This is contrary to sputtering, having large voltage drop (hundreds of V) and small currents (mA/cm² range). The different I-V areas for the two techniques can be seen in Figure 6, sputtering between point G and H and cathodic arc deposition typically around point J.

Figure 6. The universal voltage-current characteristics of the DC electric discharge tube, used with permission from [137]

The difference in I-V regime is due to a completely different plasma regime in cathodic arc deposition compared to sputter deposition. The cathodic arc deposition proceeds through consecutive microexplosions on the cathode surface. One way of starting the process is by setting a current in the power supply followed by that a pneumatically driven trigger rod touches the cathode surface, initiating the first arc through a voltage breakdown. When the initial arc has formed new emission centers are continually formed, in a highly dynamic way, in the positions where the conditions are the most optimal on the cathode surface, as described below. An individual arc spot event is on the time scale of tens of nanoseconds. There are several models for describing the detailed arc event, giving different weight to different stages of the arc event. The general notion is that each arc spot, arc explosion, or emission center, can be divided into four stages: 1) the pre-explosion stage, 2) the explosive emission stage, 3) the immediate post-explosion stage and 4) the final cooldown stage. In the first stage the conditions for creating an arc need to be met: physical protrusions generating high local electrical field due to rapid change in electric potential. This high electric field create high degree of electron

emission and generates local heat and a more intense plasma. The work function of the cathode material also influences the ease with which an arc is ignited. Adding an insulating surface oxide compound changes the work function and electron emission, hence the arc spot initiation. When all the conditions are met in a specific spot electron emission with thermal runaway brings the spot into stage two. Stage two is characterized of explosive electron emission. This lead to a micro explosion of the heated cathode volume, transforming the solid material directly to plasma with high degree of cathode material ions, leaving a crater on its surface. In the third stage, the post-explosion stage, the molten cathode material in the crater emit electrons and evaporates cathode material neutrals that are ionized in close proximity to the cathode surface. In the fourth stage the intense emission is over, and the area is cooling down, some metal vapor may still be emitted depending on material vapor pressure. The next arc has already ignited possibly on the prostrations from the previous arc, and in this way the process continues. The arc events have been showed to have fractal character: same appearance on a wide range of length scales. This gives a measure of the stochastic nature of the arc process. The violent arc events explains the high degree of observed ionization (almost 100 % of the material flux) in an arc process, as well as it gives an explanation to the cathode material droplets that one observes in the coating [136].

As mentioned above, the arc formation is affected by the formation of insulating compound on the cathode surface. The arc spot formed during insulating surface conditions may dissociate into several arcs that will run in parallel, sharing the total current drawn through the cathode. This is called type 1 arc. Increasing the arc current to burn away the insulating compound may revert the arc mode to metallic, type 2 mode, for a given oxygen or nitrogen flow [136, 138]. A too high increase in DC-arc current may lead to melting of the cathode material outside of the arc spot, especially for low melting temperature materials, like Al. Hence, this approach may not be possible to use as the only way for facilitating industrial application of reactive cathodic arc deposition of insulating compounds. Another way of obtaining the controlled erosion of the cathode in reactive atmosphere, without the risk of melting the cathode due to too high current, is pulsed-DC arc. With this technique the average power is held within the limits of what the cathode material can sustain without melting. On the same time the high current pulses clear the cathode from insulating compounds [53]. In this work both pulsed DC arc and DC arc have been used. For the compositional study of cathodic arced $(\text{AlCrSi})_2\text{O}_3$ coatings, **Paper II**, an industrial equipment (Innova from Oerlikon Balzers) was used. This system was equipped with both pulsed arc and pulsed bias functionality. The improvement of using pulsed cathodic arc in combination with pulsed bias for the AlCrO material system, in the same type of deposition equipment as used for **Paper II** is described in the following references [53, 139]. The use of pulsed arc is reported to increase the ion flux at the substrate, mainly through the increase of O_2 gas ionization, counteracting slightly the reduction in ion current at the substrate, otherwise observed for reactive cathodic arc deposition in O_2 [139]. In **Paper III**, a lab-scale DC cathodic arc system was used for studying the cathodic arc plasma generation from $\text{Al}_{0.7}\text{Cr}_{0.3}$ and

$\text{Al}_{0.7}\text{Cr}_{0.25}\text{Si}_{0.05}$ cathodes, in both vacuum and O_2 environment. DC arc was used in order to study the most fundamental phenomena of these material systems.

In order to reduce the problem of metallic droplets, but benefit of the ionized metallic flux, different kinds of filters, magnetic and mechanic, have been used to reduce the particle flux, yet while transmitting the ionized metallic flux to the substrate. The drawback with this technique is the reduced deposition rate in combination with the extra equipment needed for the filters, which has limited the industrial use of such techniques to coatings for optical, microelectronics, and optoelectronic applications, being highly sensitive for metallic droplet defects. This technique is well described in a review article on how to deposit metal oxides with this approach [140].

3.2 Plasma analysis

The plasma analysis, **Paper III**, was performed with a mass-energy-analyzer (MEA, Hiden Analytics model EQO). This analyzer combines an electrostatic energy analyzer and a quadrupole mass spectrometer permitting acquisition of charge-state-resolved ion energy distribution (IED) functions. The first step in the plasma analysis is to perform mass-scans at fixed ion energy. This helps to determine which mass-to-charge ratio that should be chosen for each element, and respective charge state [141]. Isotope distribution of the elements, most important for Cr, has been corrected for as described in ref. [141]. Finally, the energy scans at fixed mass-to-charge ratio was performed.

These distributions are important tools to understand the plasma composition since the asymmetric nature of the ion energy distribution, having a high-energy tail, makes the plasma characterization underdetermined if just considering the most likely values, the peak values [142]. The main outcome from a plasma analysis as performed in **Paper III** are: 1) To “see” what kind of species, ions and neutrals, that are present in the deposition flux. 2) To determine the energy distribution of the ion species, especially if a high energy tail is present. The latter will be highly influenced by an applied bias.

When performing the plasma characteristics the mass-energy analyzer was mounted at the position where normally the substrate holder is situated. Previous studies showed that the heat generated from the arc source itself could be enough to damage the analyzer. Therefore, no external heating was used. Substrates for depositing coatings were mounted, one at time, on the orifice plate of the analyzer in order to have the same position as for the analyzed plasma. Since no additional heating was used, the coatings were thus expected to be amorphous (and were not characterized with XRD).

It is difficult to compare plasma studies in detail between different systems if the plasma potential is not known. This is due to the complexity and adapting nature of the plasma potential which among other things can depend on the anode potential. Without a correct value for the

plasma potential it is not possible to account for the acceleration of the ions in the sheath in front of the analyzer [143]. In the present study, **Paper III**, the chamber wall was the anode which was grounded. The plasma analyzer was also kept at grounded potential. No independent plasma potential measurement was done. However, the plasma potential was calculated from the difference in anode sheath acceleration, observed for the different ionic charge states, according to method described in ref. [144]. This calculation determined the plasma potential to be in the range of 3-5 V. For the high pressure (30 and 40 sccm) at low arc current (60 A) situation in **Paper III**, not showing several charge states, these calculations of the plasma potential were not possible. These values were therefore not corrected in the same way as for the lower flows. The focus for this study was, however, the general trends of ion energy distribution, and to find out what kind of species that was present in the plasma.

The used DC-arc setup had no permanent magnet behind the cathode. There are studies indicating that the addition of the magnet, primarily steering the arc and creating a more even cathode erosion, also can lead to increased ion energies, according to the findings by Anders and Oks [143]. The lack of a magnet in the present study may contribute to lower ion energies compared to what was generated, but not measured in the original study of the effect of Si in an Al-Cr cathode, using pulsed steered arc [10]. However, the effect of adding a pulsed bias, also used in the previous study, is the parameter having the highest effect on increasing the ion energies, affecting the final film properties, hence translating the non-biased IED to higher energies.

3.3 SEM and compositional analysis with EDX/WDX

Scanning electron microscope (SEM) is a versatile characterization tool with little need for sample preparation except for cleaning prior to analysis. The sample is put in a high vacuum chamber. The accelerated e-beam is scanned over the sample surface and interact with the surface of the sample. The interaction volume depends on the electron energy (~1-20 kV) and the analyzed material. The resulting scattered electrons may be analyzed with several different detectors. Each detector gives different contrast. The most common detectors are: Secondary electron (SE) detector giving a topographical view of the sample, In-lens detector (high magnification SE-detector) with less topographical information, and Backscattered electron detector giving an elemental mass contrast (bright intensity = heavy element). Chemical composition of the studied material is also possible to extract by measure of the characteristic X-rays, generated by de-excitation of electrons between distinct energy levels in each element, called Energy-dispersive X-ray spectroscopy (EDX) [145].

In order to image electrically insulating samples without excessive charging and without the need to coat the samples with a thin (~nm) conducting metallic film, image settings need to be optimized. A balance needs to be found between needed magnification and image quality and the level of induced distortion from sample charging, since lower magnifications and/or high

scan rates both reduce the charging and the sought resolution and quality, respectively. Lowering the acceleration voltage of the electron also helps mitigating the charging problem but may result in lost EDX-signal for high Z-elements as well as lost backscatter contrast. Using conducting copper adhesive in a way so that it also covers part of the top of the sample and then performing the analysis in proximity to the Cu help to reduce the surface charge.

Chemical analysis with EDX is quick and easy to perform and the quality and capability of the measurements have increased significantly over the last decade with the introduction of new sensor techniques. The qualitative measurement of the used detector in **Paper II**, **Paper III**, and **Paper V**, is valid down to Be and the quantitative measurement is reliable for heavier elements, above Ne. Significant X-ray fluorescence giving rise to signal in the material next to the right in the period table makes it difficult to quantify N due to the C-window of the analyzer. This fluorescence may also affect the O-signal to a lesser extent. There is also an overlap between the O K α (0.525 keV) peak and the Cr L α (0.573 keV) and the V L α (0.511 keV) peak that make it difficult to quantify O when having Cr or V in the sample. Especially V has such close overlap (0.014 keV) that it was not possible to extract reliable compositions for **Paper I**. Using the non-overlapping K α peak from the metal is the way forward, but rely on a proper deconvolution of the corresponding L α signal from the O K α peak. EDX was used for the chemical characterization in **Paper III**, as well as one of the analysis techniques in **Paper II** and **Paper V**. Due to the mentioned uncertainty for oxygen, only the heavier elements were quantified in **Paper III**. The full chemical EDX analysis results were used in **Paper III** and **Paper V** and corroborated with additional measurements techniques.

Another chemical analysis technique based on the same electron transitions in the material but analyzed in a different way is electron probe microanalysis (EPMA, Camebax Microbeam) or wavelength-dispersive X-ray spectroscopy (WDX), used for chemical analysis in **Paper IV**. This technique operates in wavelength mode instead of energy mode (EDX) using several different crystals, each one having a distinct wavelength band. The wavelength of the X-rays need to fulfill the brags diffraction condition for each crystal in order to pass to the analyzer. This increase the energy resolution significantly (~10 times better resolution than EDX), but also increase the acquisition time significantly. However, development of automation of the acquisition and analysis in such system, make this historically slow and difficult to use technique more accessible. Lately, combined system with EDX as a survey scan and WDX for high resolution measurements has come into use. Hence, combining the increased energy resolution of WDX with standard samples also permit to quantify the O content in the coatings with WDX [145].

3.4 X-ray diffraction (XRD)

XRD is a powerful and easy-to-access materials characterization technique permitting to determine the crystal structure of the sample through a nondestructive method without the need of prior sample preparation. The underlying principle is that when the wavelength of the incoming rays, irradiating the sample surface, have at least the same order of magnitude as the atomic spacing ($\sim 0.5 \text{ \AA} - 10 \text{ \AA}$) diffraction is possible. This work in analogy with what is observed in optics for visible light diffracted through a grating. There are several possible scattering mechanisms active when exposing the sample with X-rays. The one resulting in diffraction patterns, characteristic for the crystal structure, is elastic scattering on the electron, called Thomson scattering. In this type of scattering the wavelength of the X-rays is conserved when scattered and obey Bragg's law $2d_{hkl}\sin\theta = \lambda$. The most basic and commonly used X-ray diffraction setup is having a symmetric incoming and outgoing beam using slits for controlling the X-rays divergence (resolution). This setup is called θ - 2θ Bragg-Brentano. The symmetric angle used results in that only the planes parallel to the sample surface will fulfill the Bragg condition. For polycrystalline samples without high preferential orientation, this setup is enough to yield a good average of the samples crystal structure. Since this work deals with thin films on a bulk substrate the X-rays will penetrate into the substrate yielding reflections both from the coating and the substrate. These peaks may overlap and cause problems when interpreting the results. A way to mitigate this problem is to use grazing incidence, a non-symmetric diffraction setup, where the incoming angle is fixed at a low angle (in **Paper I** and **Paper II** equal to 1.5°) and the acquisition angle is varied in order for probing 2θ angles fulfilling Bragg's law. In order to fulfill the Bragg condition in this asymmetric setup a parallel beam mirror is used on the incidence X-ray beam side and a parallel plate collimator 0.27° on the diffracted X-ray beam side. In this setup, the X-ray penetration depth is reduced and the incoming X-rays are spread over a constant, possibly large sample area. This results in higher coating/substrate signal ratio or even keeping the diffraction only to be within the coating thickness [146].

In **Paper IV**, X-ray diffraction (XRD, Seifert-Meteor, $\text{CuK}\alpha$) in Bragg-Brentano mode was used in order to determine the crystal structure of the coatings. Some overlap between the coating and substrate was observed which was interpreted with the help of transmission electron microscopy (TEM), permitting to study the coatings crystal structure in detail without substrate interactions. This characterization technique is explained in the next chapter.

3.5 Transmission electron microscopy (TEM)

TEM is, like SEM, based on accelerating electrons in order to probe the material properties. The electrons inside TEM are accelerated to very high energies (200-300 kV acceleration voltage was used in this work) which results in short wavelengths, in the picometer range (10^{-12} m), permitting material analysis with atomic resolution [147].

High energy electrons strongly interact with materials. In order to perform TEM analysis, the sample thickness should therefore be reduced enough to achieve electron transparency. The TEM sample thickness needed for this to be achieved depends on the elements present in the sample as well as the acceleration voltage used in TEM, but typically it should be below 100 nm. The main drawback with TEM is the time consuming, difficult and destructive (to the original sample) sample preparation. The sample preparation can even create artifact in the sample if not performed carefully. Due to the small sample volume, care needs to be taken in order to obtain the sought sample area within the thin electron transparent region. If the sample is anisotropic, considerations about sample cut direction is important, as was the case for **Paper IV**. If for example a phase has been observed on the macroscopic scale with a large sample volume technique, as XRD it is not easy to discard those findings with TEM, since the sample volume analyzed with TEM is so small, e.g., identification of the Cr₃Si phase with XRD, but not found in TEM in **Paper II**. TEM is rather used for finding a more detailed description of what is already observed with the large sampling volume techniques [147].

Once high-energy electrons interact with a thin enough sample, some will be transmitted through and some will be scattered by the sample. Depending on the interaction mechanisms involved, various imaging and spectroscopy techniques can be applied in order to characterize the material on atomic level. The transmission electron microscope can be operated in two main modes: Transmission (TEM) or scanning transmission (STEM) mode. In ordinary TEM mode, a parallel electron beam is illuminating the sample, and apertures are controlling from which part of the sample that should give rise to mass/thickness, diffraction or phase contrast image reconstructions. In STEM mode, the electron beam is focused to a probe converged to a sub-nm spot which is scanned over the sample surface, enabling high resolution imaging and local chemical information through detecting emitted X-rays (EDX-spectroscopy) [147].

The basic principle for EDX analysis in TEM is the same as for EDX in SEM, described under chapter 3.3. The main difference is that the high energy electrons on a small sample volume make it risky to perform long time mapping scans. The sample may be damaged, or phase transformation may even be initiated due to the energy transmitted from the bombarding electrons to the studied area. Therefore, high-resolution mapping is only possible with new large area detector EDX, positioned close to the sample (like the SuperX EDX system used on FEI Titan³ in **Paper II** and in **Paper IV**). These new EDX-detectors significantly reduce the acquisition time (from hours to minutes). Less time also means less sample drift while measuring, hence better image quality. A positive aspect of using EDX with TEM, as opposed to in SEM, is the insignificant absorption in the sample of the emitted X-rays due to the small sample volume. This leads to better spatial resolution. On the other hand, the small sample volume results in less signal which may lead to low signal-to-noise ratio, especially when making quick scans in order to protect the sample from irradiation damage.

With samples consisting of nanocrystalline material, it is difficult to obtain atomic resolution since there are often several grains present, stacked on top of each other even though the sample

is prepared to optimal TEM-sample thickness (<50 nm thick). If not studying atomically flat 2D materials like graphene, one is always concerned with columns of atoms which need to be oriented parallel with the incoming electron beam in order to image the atomic arrangement. Not having this long-range arrangement in nanocrystalline materials makes the analysis more difficult and requires extensive searching for grains with the correct orientation. The grains need to be situated in a sample region being sufficiently thin so that a low degree of grain overlap is possible as well as having the orientation revealing characteristics zone axes of the specific material. See **Paper IV** for an example of where the adequate grains have been found, which made it possible to determine the bcc Cr-phase in the annealed coating.

The TEMs used in the present work were an FEI Tecnai G2 TF20 UT and the Linköping monochromated double-spherical-aberration-corrected FEI Titan³. The latter one is state of the art and made possible the high-resolution STEM and EDX micrographs seen in **Paper II and Paper IV** through the used probe aberration corrector. The aberration correctors compensates aberrations in the electromagnetic “lenses” resulting in better spatial resolution [147].

4 Main results and contribution to the field

The main motivation for this thesis has been to synthesize and characterize new pseudobinary and pseudoternary oxide compounds having potential beneficial properties, mechanical and thermally, in metal machining application. The main findings of the five appended papers are summarized in this chapter, under the three covered topics.

4.1 Reactive pulsed DC magnetron sputtering of Al-V-O

The objective for this topic in the thesis was to search for new thermodynamically-stable phases such as pseudobinary corundum-structured materials, or kinetically-stabilized phases, e.g., cubic spinel-like structures (γ -like phase), synthesizable with magnetron sputtering. The chosen method for synthesis was reactive pulsed DC magnetron sputtering with pulsed DC bias in a lab scale UHV system. The combination of Al and V was based on both elements forming Me_2O_3 compounds with possible solid solution in gamma- or corundum-structure. The compositional range between respective pure oxide was synthesized on Si(100) substrates and characterized with respect to phase composition in XRD, as well as the mechanical properties with nanoindentation. The hardness and phase stability after annealing in air up to 1100 °C was investigated for the high Al-containing coatings, since they showed the most promising mechanical properties in the as-deposited state.

$(\text{Al}_{1-x}\text{V}_x)_2\text{O}_3$ coatings with x ranging from 0 to 1 were deposited and characterized in **Paper I**. The resulting crystal structures from XRD for the -120 V biased coating series were shown to be separated into three different regions depending on Al/V content: The sample without Al was synthesized in α - V_2O_3 rhombohedral structure. A defect spinel structure was obtained for the intermediate region, 63 - 42 at.% V metal fraction, with a possible two-phase structure for the 63 at.% V metal fraction sample consisting of a α - V_2O_3 and γ - Al_2O_3 . For low V-metal fraction, 18 and 7 at.%, a gamma-alumina-like solid solution was observed, shifted to larger d-spacing compared to pure γ - Al_2O_3 .

Annealing the Al-rich samples in air resulted in formation of V_2O_5 crystals on the surface of the coating after annealing to 500 °C for 42 at.% V and 700 °C for 18 at.% V metal fraction respectively. The highest thermal stability was shown for pure γ - Al_2O_3 -coating, which transformed to α - Al_2O_3 after annealing to 1100° C with associated coating cracking and flaking upon cooling.

The highest hardness was observed for the Al-rich oxide, ~24 GPa. Hardness then decreased with increasing V content larger than 7 at.% V metal fraction. The 7 at.% V in the Al_2O_3 coating resulted in a significant surface smoothening compared to the binary oxide. The measured hardness after annealing in air decreased in conjunction with the onset of further oxidation of

the coatings and no age hardening was observed. My thesis work increases the understanding of this material system with respect to phase formation and its response to annealing in air.

Another positive aspect of reactive co-sputtering from elemental target, as used in the present work, instead of reactive cathodic arc deposition from an Al-V compound cathode is that it may permit to circumvent the observed problem with oxide island formation at the cathode surface in cathodic arc deposition in this material system known from previous related work [118]. The problem with oxide islands when performing reactive cathodic arc deposition is treated in other detail for another material system in the second part of this thesis.

4.2 Cathodic arc deposition and plasma analysis of Al-Cr-Si-O

Depositing isolating hard oxide coatings with cathodic arc is challenging. The main obstacle is to achieve a stable process when dielectric film forms on all surfaces in the deposition chamber (to varying degree) including the cathode. Alloying Cr to the Al-O system has proved to promote growth of the highly sought α -(Al,Cr)₂O₃ at ~500 °C [53]. The cathodes, however, are then covered by protruding Al₂O₃ oxide, which restrict the arc movement and lead to an inefficient use of the cathode material. For the Al₇₀Cr₃₀ cathode composition, a way to mitigate the problem with oxide island formation has been proposed by means of adding small amount of Si (~5at.%) [10]. In addition to dramatic reduction in oxide island formation on the cathode surface, loss of Si was reported since Si could not be detected in the deposited films. This discrepancy in Si balance motivated further study. Therefore, the Al-Cr-(Si)-O system was investigated here in the same type of deposition system (Oerlikon Balzers, Innova) as was used in the initial study. Similar depositions conditions were used, scanning the effect of O₂ flow and Si content for two ~Al/Cr-ratios and linking these parameters to the resulting coatings properties with the help of SEM, XRD, TEM, X-ray photoelectron spectroscopy (XPS), and nanoindentation in **Paper II**. Since one possible explanation to the loss of Si was the formation of SiO volatile species, plasma analysis was also judged to be important for further understanding of what species that can be present in such plasmas, see **Paper III**.

Paper II showed the influence of adding 5 or 10 at. % of Si to the Al-Cr cathode on the (Al,Cr)₂O₃ coating properties, in an industrial cathodic arc deposition system Al/(Al+Cr) = 0.5 or Al = 70 at. %. It was shown that Si in the cathode resulted in Si detected in all coatings (including the oxide phase) independently of Al content and oxygen flow. The detected droplet phases depended on the cathode composition with enrichment of Si in the droplets, in different kinds of intermetallic phases. Si was found with XPS to be bound to both oxygen and metal phases in the coating. The Si-addition led to a shift in crystallographic phase, from corundum to B1-like defect cubic oxide phase, and the shift in crystal structure led to a decreased hardness.

The improved (in the sense more uniform) cathode erosion, with significantly less oxide island formation, especially for the cathode with 70 at.% Al, was observed in the work of

Paper II. However, the Si incorporation in the coating, with resulting changes in crystal structures, needs to be considered for final verdict of usability of this alloy element. The process window for obtaining Si-free coatings [10], may be very narrow if at all present, in the light of the work in **Paper II** and other recent published work, showing Si in the coating [122], appreciating the applied sensitive analytical analyses to detect Si.

In **Paper III**, the plasma composition was studied for DC cathodic arc deposition of $\text{Al}_{0.7}\text{Cr}_{0.3}$ and $\text{Al}_{0.7}\text{Cr}_{0.25}\text{Si}_{0.05}$ cathodes in O_2 atmosphere. This was done in order to link the plasma composition to the process parameters: oxygen flow and cathode arc current, as well as the final coating composition. The study showed possible improvements, on the measurement error level, in cathode erosion and process stability (lower pressure and cathode voltage) when introducing 5 at.% Si in the AlCr-cathode. Also, slightly less droplet formation was observed at low cathode current and intermediate O_2 flow when introducing Si. Larger effect with respect to cleaning the cathode from oxide contamination was observed when increasing cathode current with 50%. However, higher cathode current also resulted in increased droplet formation, which is not desired. Through plasma analysis in **Paper III**, the presence of volatile SiO species could be confirmed as well as the presence of Si in all three deposition fluxes (ions, neutrals, and macro particles). The latter resulted in a similar metallic composition for the coating as for the cathode. The conclusion is therefore that, the loss of Si through volatile SiO species is negligible.

From previous work, both theoretical and experimental, Si is known to destabilize the corundum phase and stabilize the γ -phase for pure Al_2O_3 [39-41], counteracting the addition of Cr, which is present for promoting the sought corundum phase formation [49, 53, 54]. These combined results lead to the conclusion that the observed positive effect of Si at the cathode side may be detrimental at the substrate side depending on the phase stability of the B1-like cubic-oxide phase. This is exemplified with a recent vacuum annealing study on a similar Si-containing Al-Cr coating. This work showed slight stabilization of the B1-like phase before transforming to a gamma/theta-like phase. This Al-Cr-Si gamma phase was stable to significant higher temperature than pure gamma- Al_2O_3 phase [122]. The question of how the effect of annealing atmosphere would have influenced the transformation route, and what happened with the coating in the transition between B1-like and gamma/theta phases (a possible crack formation step due to possible difference in density of the two phases) is still an open question that should be considered for future industrial optimization of this material system.

The important effect of annealing atmosphere has further been shown in the third part of this thesis, dealing with the phase stability of Cr-rich Cr-Zr-O coatings.

4.3 Phase stability of $\text{Cr}_{0.28}\text{Zr}_{0.10}\text{O}_{0.61}$ coatings during annealing in vacuum and air environments

In **Paper IV**, reactive RF-magnetron sputtering was used to grow Cr-rich corundum structured- $(\text{Cr,Zr})_2\text{O}_3$ at 500 °C. These coatings were subsequently isothermally annealed in vacuum at three temperatures, with a maximum of 870 °C. The investigation of the thermal stability of the synthesized oxide compounds is crucial since the temperature during machining can approach 1000 °C in combination with high mechanical loads. The performed characterization of the annealed samples show the transformation of α - $(\text{Cr,Zr})_2\text{O}_3$ and amorphous ZrO_x -rich areas into tetragonal ZrO_2 and bcc Cr. The presence of the tetragonal ZrO_2 phase at room temperature was linked to its small grain size, <30 nm, stabilizing it compared to the RT thermodynamically stable monoclinic phase, due to surface-energy effects. [148, 149].

The proved stabilization of the tetragonal phase is important since the monoclinic phase cannot be used in high temperature applications requiring mechanical stability. It would then transform into the tetragonal phase with accompanied volume contraction. The effect of annealing atmosphere on the coatings thermal stability remained unanswered and led to the work in **Paper V**. New annealing tests were therefore done, with the same as-deposited $(\text{Cr,Zr})_2\text{O}_3$ coatings as used in **Paper IV**, this time in an *in situ* XRD setup, at the synchrotron radiation facility DESY in Hamburg. The phase evolution during annealing was monitored continuously during both air and vacuum annealing, followed by post-annealing characterization with TEM, SEM, and nanoindentation hardness measurements.

In **Paper V** the annealing in vacuum shows t- ZrO_2 formation starting ~800 °C, which is followed by decomposition of the α - Cr_2O_3 structure in conjunction with bcc-Cr formation, starting at ~950 °C. The resulting coating after annealing to 1140 °C is a coarse-grained mixture of tetragonal ZrO_2 , monoclinic ZrO_2 and bcc-Cr, with intermediate voids.

The air-annealed sample shows tetragonal ZrO_2 formation starting at ~750 °C. The α - $(\text{Cr,Zr})_2\text{O}_3$ starts to transform to α - Cr_2O_3 at ~945 °C at the same time as the tetragonal ZrO_2 formation increases. The resulting coating after annealing to 975 °C is a mixture of α - Cr_2O_3 with dissolved Zr and t- ZrO_2 with dissolved Cr. The microstructure coarsened slightly, but the mechanical properties are maintained, with no detectable bcc-Cr formation.

Comparing the relative integrated peak intensities of t- ZrO_2 and α - Cr_2O_3 at 975 °C, a larger tetragonal ZrO_2 fraction is shown in the vacuum-annealed coating, compared to the air-annealed coating, already at this temperature. The results indicate that the studied pseudobinary oxide is more stable in air atmosphere than in vacuum.

4.4 Conclusions

In summary, this thesis covers the three different material systems Al-V-O, Al-Cr-Si-O, and Cr-Zr-O with the corundum phase as the common crystal structure as well as gamma and B1-like solid solutions. Mapping of the Al-V-O system along the Me_2O_3 phase showed three different phases depending on metal fraction, the Al-rich part showing the best mechanical properties and thermal stability, however being inferior to pure gamma- Al_2O_3 . Al-Cr-Si-O investigation revealed Si in the coating if Si was present in the cathode, leading to a change in crystal structure of coating to B1-like cubic oxide phase. The SiO volatile compound was detected in the plasma study, but no significant loss of Si in the coating could be detected. The results demonstrate that there is a delicate balance between process stability and coating properties. The observed phase segregation of $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ and formation of tetragonal ZrO_2 with hardness increase, showed better thermal stability in air than in vacuum, which opens up future design routes for pseudobinary oxides with tunable microstructural and mechanical properties.

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Paper I

Phase composition and transformations in magnetron sputtered (Al,V)₂O₃ coatings

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Paper II

Influence of Si doping on properties of arc deposited (Al,Cr)₂O₃ coatings

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Manuscript in final preparation

Paper III

Effect of Si on DC arc plasma generation from Al-Cr and Al-Cr-Si cathodes used in oxygen

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Paper IV

Structural evolution in reactive RF magnetron sputtered (Cr,Zr)₂O₃ during annealing

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Paper V

Phase evolution of RF magnetron sputtered Cr-rich (Cr,Zr)₂O₃ coatings studied by in situ synchrotron X-ray diffraction during annealing in air or vacuum

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Papers

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