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

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Abstract

Reactive RF-magnetron sputtering is used to grow Cr_{0.28}Zr_{0.10}O_{0.61} coatings at 500 °C.

Coatings are annealed at 750°C, 810 °C, and 870 °C. The microstructure evolution of the pseudobinary oxide compound is characterized through high resolution state of the art HRSTEM and HREDX-maps, revealing the segregation of Cr and Zr on the nm scale. The as-deposited coating comprises α -(Cr,Zr)₂O₃ solid solution with a Zr-rich (Zr,Cr)O_x amorphous phase. After annealing to 750°C tetragonal ZrO₂ nucleates and grows from the amorphous phase. The ZrO₂ phase is stabilized in its tetragonal structure at these fairly low annealing temperatures, possibly due to the small grain size (below ~30 nm). Correlated with the nucleation and growth of the tetragonal-ZrO₂ phase is an increase in hardness, with a maximum hardness after annealing to 750 °C, followed by a decrease in hardness upon coarsening, bcc metallic Cr phase formation and loss of oxygen during annealing to 870 °C. The observed phase segregation opens up future design routes for pseudobinary oxides with tunable microstructural and mechanical properties.

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1. Introduction

Oxide-based materials with prime examples alumina, chromia, and zirconia form important coatings for cutting tool development, owing primarily to their typical high hot hardness and chemical inertness with respect to the work piece material [1]. Depositing these oxides with physical vapor deposition (PVD) techniques permit using a wide range of temperature-sensitive substrates (e.g., high speed steels) as well as tailoring of the residual stress level in the coating. Indeed, while CVD coatings often exhibit tensile residual stresses due to the high deposition temperature, PVD coatings may have a variable degree of compressive stresses due to controlled level of ion bombardment. Hence, PVD enables new application areas for oxides.

Pseudobinary thin film oxide alloys have drawn attention in the past years, often focusing on the Al-Cr-O system. This interest stems from the possibility to stabilize the desired corundum phase in alumina, α -Al₂O₃, by introducing other elements to the alloy such as Cr in α -(Al,Cr)₂O₃ [2],[3]. Eskolaite, α -Cr₂O₃, is isostructural with corundum and is 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 [4], [5]. Two ways of stabilizing the corundum phase are template growth or alloying with an appropriate element promoting the desired phase through formation of a solid solution. Template growth means that a crystallographic seed layer, e.g., α -Cr₂O₃, helps nucleate the α -Al₂O₃ thin film [5-7], Solid-solution stabilization of a desired phase is also obtained by alloying α -Cr₂O₃ into the α -(Al,Cr)₂O₃, which then forms at lower temperatures than it is possible to form pure α -Al₂O₃ [2], [8-13]. An alternative phase formed upon deposition of this pseudobinary compound is the vacancy-stabilized cubic structure of an oxide solid solution, e.g., f.c.c. (Al,Cr)₂O₃ [3, 14-16].

Pure ZrO_2 exists in three different crystal structures: the room temperature stable monoclinic phase and the metastable phases; tetragonal (from $\sim 1170^\circ\text{C}$) and cubic fluorite (from $\sim 2300^\circ\text{C}$) [17-19]. The tetragonal phase can be stabilized at standard temperature and pressure by alloying with different early transition metal oxides, the most common being Y_2O_3 [20, 21]. Even in pure ZrO_2 , the tetragonal phase becomes stable for grain sizes smaller than $\sim 30\text{ nm}$ due to its lower surface energy compared to the monoclinic phase [22, 23]. Alloying ZrO_2 with 6-8 wt. % of Y_2O_3 yields tetragonal yttria partially stabilized zirconia (YSZ), most commonly used for its low thermal conductivity and high toughness as a thermal barrier coating in turbines. It may also be fully stabilized into its cubic crystal structure, but the toughness increase due to Y_2O_3 alloying is then reduced which limits its use [24-27]. YSZ is also used as implant material due to its toughness and biocompatibility [28]. For its ionic conductance, the cubic fluoride form is used as electrolyte in solid-oxide fuel cells [29-33] and as material with reversible oxygen storage capacity when alloyed with CeO_2 [34, 35].

Exchanging Al in Al-Cr-O system with Zr may yield an alloy system that combines the good properties of Cr_2O_3 and ZrO_2 . Some work has been done on bulk samples trying to mix these compounds [36], nanoparticles [37, 38], or by producing a composite material of Cr_2O_3 and YSZ [39] spanning different Cr contents. It has been shown, that it is possible to obtain corundum-structured solid solution thin films for high Cr-content [40], despite the facts that Zr has one higher valence than Al and that it is significantly larger in size [41]. Spitz et al. mapped the phase formation and microstructure evolution in the Cr-Zr-O system over a wide range of Cr/Zr composition by reactive RF-magnetron sputtering, and showed that the system exhibits different phases: solid solution corundum structure at low Zr-content ($< \sim 31\text{ at}\%$), cubic-(Zr,Cr) O_2 solid solutions at $\sim 50\text{ at}\%$ Zr, and monoclinic/tetragonal solid solution (Zr,Cr) O_2 for higher Zr-content [40]. Rafaja et al. [42] investigated the influence of different annealing temperatures (i.e. 500°C to 1100°C) on the microstructure of as deposited

amorphous Cr-rich Cr-Zr-O thin films with up to 15 at.% Zr content. Single-phase solid solution α -(Cr,Zr)₂O₃ and a two-phase compound with solid solution tetragonal (Zr,Cr)O₂ were found in the crystalline annealed films. High annealing temperatures (starting at 900 °C for low Zr contents of 3 at.%) as well as an increasing Zr content promoted the formation of the tetragonal phase. The detailed (sub-nm level) structural characterization and thermal stability of as deposited α -(Cr,Zr)₂O₃ solid solutions needs still to be investigated, in order to understand the material and its phase transformations.

In the present study, (Cr,Zr)₂O₃ thin films with high Cr content (28 at % total fraction and ~74 at% Cr, metal sublattice, assuming the later fully filled) were synthesized, at 500 °C, to a thickness of about 5 μ m, in the same test setup as used for the Cr-Zr-O material system screening [40]. This work addresses issues such as thermal stability and related microstructural changes of novel solid solution oxides intended as hard, protective coatings for engineering applications. The as-deposited coatings exhibit a mixed corundum and amorphous structure. The films were then vacuum-annealed to three different temperatures, 750, 810, and 870 °C, in order to investigate the phase stability and/or microstructural changes of this pseudobinary oxide system. Characterization of the hardness, phase composition, and microstructure were performed using a combination of Vickers microhardness measurements, X-ray diffractometry, and analytical scanning transmission electron microscopy on the atomic-to-nm scale.

2. Experimental details

The deposition of the Cr-Zr-O coatings was performed in a Leybold Z 550 magnetron sputtering deposition equipment with a possibility to run the magnetrons both in direct current (DC)-mode and radio frequency (RF)-mode. The Cr adhesive layer was deposited in DC-mode in a separate process, while all CrZr and CrZrO depositions were done in the RF-mode

with a segmented Cr/Zr-target. The sputtering target had a diameter of 75 mm. The depositions were power controlled. The base pressure of the chamber was 6×10^{-4} Pa. The deposition setup can be seen in Figure 1 (a). In the present article only samples from position 1 (off-normal), with higher Cr than Zr content, are being considered in distinction to ref [40]. The substrates were placed on a stationary substrate holder connected on top of a heating device. The orthogonal substrate-to-cathode distance was 40 mm. The deposition setup is further described elsewhere ADDIN EN.CITE [43] [40].

The substrate used for deposition was a TiAl alloy, commercial name TNB-V2, with composition 47 at.% Ti, 45 at.% Al, and 8 at.% Nb. This alloy was used for this heat treatment experiment since it is known to resist high temperatures. Before deposition the substrates were mirror polished and cleaned ultrasonically in acetone for 15 min. The samples dimensions were half disks with 15 mm diameter being 1 mm thick.

The substrates were introduced in the magnetron sputtering system equipped with a pure Cr target and plasma etched *in situ* in RF-mode at 0.4 Pa Argon for 10 min, resulting in a -200V DC substrate self-bias. A ~250 nm Cr layer (2.5 min) was then deposited using 0.4 Pa Argon (99.9999%), and 200 W DC power for the magnetron. No heating was applied at this stage and the sample's temperature was below 200 °C. The substrates were grounded during the Cr thin film deposition. These prepared substrates were stored in a protective box in order to prevent oxidation of the metallic Cr layer while changing from the pure Cr to the segmented Cr/Zr target (99.95 % and 99.5 % purity respectively) The pre-coated samples were reinserted to the deposition chamber, heated to 500 °C, and etched again, using the same parameters as listed above (RF-mode at 0.4 Pa Argon for 10 min). This was followed by deposition of an additional metallic layer. This deposition was done at 500 °C with 500 W RF power at the target for 1 min at a pressure of 0.4 Pa Ar, resulting in a ~250 nm thick Cr/Zr metallic layer

with the composition corresponding to its position under the segmented Cr/Zr target. The double metallic binding layer was used in order to obtain good adhesion of the oxide coating.

The reactive gas (an 80/20 Ar/O₂ mixture) was then let into the chamber instead of pure Ar, starting the oxide layer deposition up to a thickness of approximately ~5 µm (with a total pressure of 0.4 Pa). The oxide depositions were done with 500 W RF magnetron sputtering setup at a temperature of 500 °C. The same Cr/Zr ratio is then to be expected in the oxide layer as in the metal alloy layer. For all depositions, the samples were grounded. The deposition was repeated two times with three substrates next to each other in position 1, in order to obtain enough samples for the annealing study.

After the deposition, three as deposited samples were annealed in vacuum in separate runs. The base pressure of the oven (thermicon P, Heraeus) after evacuation was: 8×10^{-4} Pa. The samples were placed in a sample holder made of alumina and heated (heating rate 20 °C/min) to three different annealing temperatures, 750°C, 810°C, and 870 °C (limited by the oven), for 5 h at the respective hold temperature. Once the annealing process was finished, the oven was switched off and the samples were left inside the oven (and in vacuum) to cool down to room temperature.

The basic chemical composition of the films was determined by electron probe microanalysis (EPMA, Camebax Microbeam). The crystal structure was evaluated by means of X-ray diffraction (XRD, Seifert-Meteor, Cu_{Kα}) in Bragg-Brentano geometry.

The selected area electron diffraction (SAED) pattern as well as the overview TEM and STEM micrographs presented in Figure 3 to 9 were acquired with an FEI Tecnai G2 TF20 UT transmission electron microscope (TEM) equipped with a field emission gun operated at a voltage of 200 kV. For SAED, a large aperture was used in order to achieve a good average of the coatings property. The distance measurements were calibrated to Si (111) being 3.1355 Å.

HRSTEM and HREDX-measurements, presented in *Figure 10*, were carried out in the Linköping monochromated double-spherical-aberration-corrected FEI Titan³ 60–300 operated at 300 kV, equipped with the SuperX EDX system. The TEM samples were chosen from the center of the half diskz, see *Figure 1*. The longest sample length was taken to be parallel ($\parallel$) to the row of samples of increasing Zr-content. Some samples, perpendicular ($\perp$) to that direction were also studied, showing a different microstructure. The definitions of the perpendicular and parallel directions are shown *Figure 1 (b)*.

The hardness was measured with a Vickers microhardness tester, Ernst Leitz Wetzlar GmbH, Wetzlar, Germany with 50 g load. The reported results are an average of 15 indents per variant.

3. Results

Table 1 presents the chemical composition, Vickers microhardness, and crystallographic structure (summarized from *Fig. 2*) of the coatings.

The EMPA composition measurement shows, as expected, a high Cr/Zr ratio of ~ 2.6 - 2.9 , both for the as-deposited and annealed coatings. The oxygen content is between 58 and 61 at% for the as-deposited coatings and the two coatings annealed at 750 and 810 °C. The accuracy of the measurement is 1-2 at % for O, Cr and Zr which leads to the conclusion that the variation of the Cr/Zr ratio (all samples) as well as the Cr+Zr/O ratio (as deposited, 750 °C and 810 °C) is within the error bars of the measurements and can be regarded as being of similar composition. This composition is close to stoichiometric Me_2O_3 (Me = metal, Cr+Zr), which was aimed for. For the coating annealed at 870 °C, significantly lower oxygen content is observed. If not stated specifically

the compounds are denoted with their nominal names not considering possible deviations from stoichiometry.

The Vickers microhardness measurements, presented in column 5 in Table 1, show an increase of the coating hardness from 950 HV_{0.05} in the as deposited sample to 1650 HV_{0.05} in the sample annealed to 750 °C. After annealing to higher temperature the hardness decreases to 980 HV_{0.05} at 810 °C to finally reach a lower hardness than in the as-deposited sample, 500 HV_{0.05}, in the sample annealed to 870 °C.

X-ray-diffractograms of the four coatings (as deposited, annealed to 750, 810, and 870 °C) are shown in Figure 2. The substrate peaks (S) were identified with the help of a separate scan made of the substrate alone. The binding layer (B) comprises the stack of metallic Cr and Cr/Zr alloy layer deposited prior to the oxide. The alloy is Cr rich with approximately the same Cr/Zr ratio as the oxide. Hence, the contribution from this specific layer is similar to the peak from Cr binding layer. The XRD results are further corroborated by TEM, presented after the XRD-results.

The as-deposited coating exhibits peaks matching the hexagonal α -Cr₂O₃ structure (PDF-38-1479). Their position is however shifted to lower diffraction angles compared to those given by the PDF-card (0.6-1.5%). This indicates a solid solution with larger Zr atoms substituted for Cr in α -Cr₂O₃. The lower intensities and larger FWHM of these peaks further indicate a very fine-scale, nanocrystalline structure of the Cr-Zr-O coatings. The sharp diffraction peaks at ~44° and ~98° can be attributed to bcc-Cr (PDF-6-694) and originate from the binding layer. The broad peak at ~43° is attributed to the Cr/Zr binding layer with a slightly increased lattice parameter compared to the pure bcc-Cr layer.

For the coating annealed at 750 °C, an additional peak appears at a diffraction angle of 30°, consistent with the tetragonal (t)-ZrO₂ (101) (PDF-42-1164), slightly shifted to higher 2 θ -

angles. A broad, low intensity, peak can also be distinguished around $\sim 50^\circ$, that can be related to the t-ZrO₂ structure. At the same time, the broad peak at $\sim 43^\circ$ disappears presumably because of phase separation in the Cr-Zr binding layer [44]. The peaks attributed to the α -Cr₂O₃ become sharper, indicating grain growth and increased crystal quality upon heating. The α -Cr₂O₃ peaks are at lower diffraction angles (0.7-1.5%) compared to the PDF-card however slightly increased compared to the as deposited except for the (01 $\bar{1}$ 2) diffraction. These data suggest the formation-onset of t-ZrO₂-like phase in the α -(Cr,Zr)₂O₃ matrix, resulting in a two-phase oxide composite coating upon annealing to 750 °C in vacuum.

The diffraction peaks related to the t-ZrO₂ phase, at 30° and 50° diffraction angle, become clearer after annealing to 810 °C. The broad peak attributed to t-ZrO₂ at a diffraction angle $\sim 50^\circ$, consists of two overlapping diffractions peaks originating from, (112) and (200), having similar plane spacing.- Yet, the two-phase oxide composite microstructure remains at 810°C.

For the maximum annealing temperature of 870 °C in this study, the α -Cr₂O₃ structure is no longer visible after annealing up to 870 °C. Instead, the t-ZrO₂ structure has developed with a sharp and intense peak for the primary peak 101, according to the PDF-file. A double peak is now also visible at 50° in addition to several other t-ZrO₂ peaks. The t-ZrO₂ peaks are all situated at higher diffraction angles than expected from the PDF which indicates substitution of Zr by a smaller atom (i.e. Cr) in the ZrO₂ lattice. The sharp peaks appearing at 64.6° and 81.7° match the 200 and 211 diffraction peaks of bcc-Cr, respectively, see further TEM-results below.

The last column in Table 1 is a list of the crystal structures indexed on the basis of the XRD results. As presented above, the main phase in the coatings is hexagonal α -Cr₂O₃ up to 810 °C, consistent with the average chemical composition of these three samples. For the samples annealed at 750 °C, a new peak appears that is attributed to the tetragonal t-ZrO₂ phase. At

750 °C and 810 °C, the diffractograms indicate a coexistence of the hexagonal and tetragonal phase in the samples. At 870 °C, t-ZrO₂ is the only clearly distinguishable phase in XRD. The bcc-Cr diffraction peaks, however visible for all samples due to the binding layers, are significantly larger for the sample annealed at 870 °C.

In order to further understand the microstructural evolution observed, TEM studies were done. Figure 3 a and b present TEM micrographs and SAED patterns (from FEI Tecnai, if not stated otherwise) of two TEM samples cut from the same coating (in this case after annealing to 750 °C) but in different directions and shows the difference in coating microstructure depending on the TEM-sample cut orientation. The definition of the two cut directions parallel ($\parallel$) and perpendicular ($\perp$) in the coated half disks is shown in Figure 1 (b). TEM micrograph of the sample cut in the parallel direction, Figure 3 (a), shows elongated domains with different diffraction contrast. The sample cut in the perpendicular direction Figure 3 (b), shows less clear features often rounder in shape. The corresponding SAED patterns show the same diffraction rings with slightly rotated intensity maxima. These differences are observed for all four coatings, independently of the annealing temperature (results not shown), with a slight difference for the sample annealed at 870°C, where the grains are more equiaxed with only remnant columnar structures in the $\parallel$ view.

Since the elongated features are more visible in the samples cut along the $\parallel$ direction than the $\perp$ direction, the presented micrographs comes from the $\parallel$ direction if not otherwise stated.

Figure 4 shows a STEM micrograph of the as-deposited coating with an SAED pattern inset. The micrograph shows the above-noted elongated domains with different diffraction contrast, slightly inclined with respect to the sample normal. The SAED pattern confirms the findings from XRD that the as-deposited sample has a α -Cr₂O₃ crystal structure with a slightly increased lattice parameter. The deviation from the pure α -Cr₂O₃ PDF-card lattice spacing is

in the range of 1.6-2.6% for all planes, except for the $(10\bar{1}4)$. This plane exhibits a deviation of 3.1% from the PDF-card value. The broad peak visible at $\sim 43^\circ$ in the XRD plot, Figure 2, is not visible in the SAED pattern, again indicating that its origin is from the substrate or binding layers.

Figure 5 shows a TEM micrograph and an SAED pattern of the coating annealed at 750 °C. This coating exhibits similar but more visible, thicker, elongated inclined domains compared to the as-deposited coating. The SAED pattern is consistent with α -Cr₂O₃ with the addition of a single 101 diffraction peak matching tetragonal ZrO₂. This result is in accordance with the XRD diffractogram for the same temperature.

In Figure 6, a TEM micrograph and an SAED pattern of the coating annealed at 810 °C are shown. The same microstructure with elongated inclined domains is visible, similar to the microstructure of coatings annealed at lower temperature. In addition, repeating 500-nm-thick regions, running parallel to the substrate, are observed. HRTEM and STEM analyses (not reported here) show that these regions are areas with high density of small (~ 10 nm) round voids in the coating. These layers were present in the as-deposited state as well, but without discernable voids. The SAED pattern shows a tetragonal ZrO₂ phase after annealing to this temperature, in coexistence with α -Cr₂O₃. The relative intensity increase of the third diffraction ring from the center observed when comparing the SAED patterns obtained after annealing to 750 °C and 810 °C is due to the superposition of the diffraction rings from the hexagonal $(10\bar{1}4)$ with the tetragonal (002) . Many of the rings are broad due to the many diffraction ring overlaps between the two dominant phases. For the hexagonal phase, the deviation of the lattice plane distances from the PDF values has decreased even further compared to the lower annealing temperatures, ranging now from -0.1% to 0.7%, (except for the diffraction rings from the partly visible $(11\bar{2}6)$ and overlapping $(11\bar{2}9)$ having 1.7 and 1.2% deviation from the PDF-card value, respectively). The deviation of the lattice plane

distances obtained from PDF values is larger for the tetragonal phase than for the hexagonal phase, ranging from -2.5% for the (101) to 2.2% for the (102). The diffraction rings are generally continuous due to the nanocrystalline nature and random crystal orientation of the material.

The change in diameter of the α -Cr₂O₃ diffraction rings in the SAED patterns correlates to the amount of Zr dissolved in the α -Cr₂O₃ phase. The lattice spacing of the α -(Cr,Zr)₂O₃ calculated from SAED are largest in the as-deposited coating (highest amount of Zr) and smallest for the coating annealed at 810 °C degree, corresponding to a decrease of the plane distance by 1.5 to 2.7 % depending on the selected plane. The sample annealed at 870 °C shows too weak diffractions for the α -Cr₂O₃ to be part of the comparison. However, the opposite trend (Cr leaving t-ZrO₂ leading to reduced diffraction angle) cannot be seen for the ZrO₂ phase when comparing the peak positions from samples annealed at 750, 810, and 870 °C.

A TEM micrograph and SAED pattern for the coating annealed at the highest temperature, 870 °C, are shown in Figure 7. The microstructure is significantly changed compared to that of the coatings annealed at lower annealing temperature. Nearly equiaxed grains are observed, with only small indications of the inclined microstructure seen for lower-temperature-annealed samples. The SAED pattern shows that the tetragonal ZrO₂ dominates in combination with a new phase (see discussion concerning Figure 9 below). The SAED pattern contains more spots in some of the rings in contrast to the continuous rings observed for the coatings annealed at the lower temperatures.

Figure 8 shows an STEM micrograph (a) and an EDX map (b) of the same annealed to 870 °C. These analyses have been done on a sample cut in the $\perp$ -direction. The microstructure is

separated in larger Cr-rich (red) grains embedded in a Zr-rich (turquoise) matrix composed by many smaller crystallites.

Figure 9 (a) shows TEM-micrographs of two Cr-rich grains oriented along two different zone-axis $[111]$ and $[001]$ (left and right respectively). A local EDX point measurement was made on each grain, resulting in the EDX spectrum, Figure 9 (b) for the respective grain. At the same focus, a local diffraction pattern of the grain was obtained through convergent beam diffraction (see Figure 9 (c)). HRTEM micrographs are shown in Figure 9 (d) for each grain. The grains are $\sim 30\text{-}80$ nm in diameter. The EDX measurements for both grains show a complete depletion of Zr within the grains. The lattice spacings for the two orientations were measured for the (110) set of planes, yielding 2.04 Å in both grains after calibrating against Si (111) . This makes us conclude that the Cr-rich domains are metallic bcc-Cr, with $a=2.89$ Å. The measured lattice parameter is in good agreement with the relaxed unit cell parameter, 2.8839 Å, from powder diffraction reported in the bcc-Cr (PDF-6-694). In the 870 °C coating, these Cr-rich grains are ubiquitous. However, a few bcc-Cr grains were also observed in the sample annealed at 810 °C. Their grain size is fairly large compared to the ZrO_2 matrix, which explains the larger dots in the otherwise continuous rings in the SAED of the coating annealed at 870 °C (Figure 7). This is most clearly seen for the overlapping diffractions of t- ZrO_2 102 and bcc Cr 110 in the SAED in Figure 7.

Diffusion of material from the metallic binding layers or the substrate into the oxide part of the coating was not observed with TEM EDX-maps (not shown) for the studied annealing temperatures. However, a reaction between the substrate and the metallic binding layer is observed at 870 °C. At this temperature, Ti from the top part of the substrate diffuses into the former Cr/Zr-binding layer. Cr in this layer diffuses both toward the oxide forming a sharp and thin layer at the interface and into the initial Cr binding layer. The Zr does not migrate from the original position in the Cr/Zr binding layer.

Figure 10 shows HRSTEM micrographs and EDX-maps of the as deposited sample (a) and the 810 °C annealed sample (b). From the top, the figures show a HRSTEM micrograph, an EDX map, and an EDX line scan, acquired from the left to right in the micrograph. The elongated domains, with different diffraction contrast as seen in Figure 3-Figure 6, are here visible at the atomic level. The as-deposited sample Figure 10 (a) exhibits crystalline and amorphous domains in the HRSTEM micrograph. The crystalline areas are darker, showing that they contain lighter elements than the amorphous areas. Comparing with the EDX-map, it can be seen that the crystalline regions are the ones with high Cr-content, while the Zr-rich regions coincides with the amorphous domains. The line scan shows the alternating content of Cr and Zr. The depletion of the two elements in the respective domains is not complete. Hence, some degree of solid solution in both types of domains is expected since there is a significant signal originating from Cr in Zr-rich domains and vice versa. The lateral widths of the domains are approximately equal for both Cr- and Zr-rich ones with a distance of ~3-4 nm. The Zr-rich amorphous domain is most likely a (Zr,Cr)O_x amorphous phase since the O-signal does not change significantly between the Cr- and Zr-rich domains (O-EDX not shown). The appearance of the coating annealed at 810 °C Figure 10 (b), has changed significantly compared to the as deposited sample. The HRSTEM micrograph shows crystalline phases for the entire studied area. The bright elongated domains, indicating heavy element Zr, are thinner than the darker ones (lighter element Cr). The EDX-map confirms the presence of thin (~2-3 nm) Zr-rich domains, alternated with thicker (~5nm) Cr-rich domains. The XRD and SAED presented in Figure 2 and Figure 6 respectively indicate that the Zr rich domains are made of t-ZrO₂ with dissolved Cr, while the Cr rich domains consists in α-(Cr,Zr)₂O₃. The line scan for 810 °C shows larger concentration variations of Cr and Zr between the alternating domains compared to the as-deposited sample line scan.

4. Discussion

This study includes thorough characterization of a Cr-rich Cr-Zr-O coating in the as-deposited state and after annealing at three different temperatures, 750, 810, and 870 °C. The effect of annealing on solid solution formation and phase segregation through structure, and chemical composition characterization will be discussed.

In the as-deposited coating, with an average composition of $\text{Cr}_{0.28}\text{Zr}_{0.10}\text{O}_{0.61}$, $\alpha\text{-Cr}_2\text{O}_3$ is the only crystalline phase. The diffraction angles are slightly decreased compared to pure $\alpha\text{-Cr}_2\text{O}_3$ indicating a solid solution by substitution of the Cr^{3+} ion by the larger, Zr^{4+} ion [41, 45].

There is a segregation of Cr- and Zr-rich alternated elongated domains (~3-4 nm thick) present in the as-deposited state. The EDX map and line scan show some degree of mutual solubility of the Cr and Zr in the respective oxide-phases. The pseudobinary $\text{Cr}_2\text{O}_3\text{-ZrO}_2$ phase diagram shows that the Cr_2O_3 has a higher tendency to dissolve ZrO_2 than ZrO_2 to dissolve Cr_2O_3 [46], at equilibrium conditions. It is therefore expected that solid solution could form due to the low temperature growth, here made possible by the inherent kinetic limitations of PVD.

The as-deposited sample contains crystalline Cr-rich $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ with amorphous Zr-rich $(\text{Zr,Cr})\text{O}_x$ domains, Figure 10 (a), which shows the superior crystal forming quality of Cr over Zr, possibly related to Zr^{4+} larger ion size and lower diffusivity relative to Cr^{3+} [45]. Trinh et al. found Zr-Al-O coating with 10 at% Zr to be completely amorphous after deposition at 450°C [47], having similar Zr-content and deposition conditions as in this study. This shows the difficulty to obtain crystalline ZrO_2 upon alloying it to this degree with Al, whereas Cr is known for its ability to form corundum structure when alloyed at such low temperature [9, 11].

The as-deposited coatings contain the elongated inclined Zr- and Cr-rich oxide-domains, on the 3-4 nm scale, which in most part remains during annealing. There are two features that need explaining: the inclination and shape of the elongated domains and the Cr-Zr segregation. The inclination of the elongated domains is related to the off-normal deposition geometry for sample position 1, as expected for low energetic off-normal deposition [48]. The thickness of the thin (~3-4 nm) elongated domains seen from the TEM-sample cut in the $\parallel$ direction (Figure 4 and Figure 10 (a)) is most probably related to the diffusion length of the adatoms on the surface during growth. The domains are confined in both in-plane directions perpendicular to the normal of the inclined elongated domains (not shown), supposedly mirroring the round cathode shape. No effects from the sharp interface between Cr and Zr in the segmented cathode are observed in the coatings.

According to the Cr_2O_3 - ZrO_2 phase diagram below 1840 °C (pressure 1.3 atm Ar) the stable phases are a tetragonal ZrO_2 solid solution with 9 ± 2 mass % Cr_2O_3 and a Cr_2O_3 solid solution with 40 ± 7 mass % ZrO_2 [46]. The previous study by Spitz et al. [40] showed full solubility of Zr in the as deposited α - Cr_2O_3 phase up to 8.5 at % Zr without any ZrO_x amorphous phase. In the present study, the Zr content was 10-11 at%, resulting in the separation of Zr from Cr and the formation of a Zr-rich $(\text{Zr,Cr})\text{O}_x$ amorphous phase. This indicates that the system is sensitive to the Zr content and that phase separation is expected for ~10 at% Zr in the present deposition conditions. Possible routes to promote the solid solution for higher Zr at % could include better atomic mixing using a different deposition setup, with compound targets with specific Cr/Zr ratios, substrate rotation and bias. Also, changing deposition technique to high-power impulse magnetron sputtering (HIPIMS) with pulsed bias or pulsed cathodic arc deposition may also promote further alloying of Zr into a single phase solid solution with Cr.

After annealing to 750°C, the amorphous Zr-rich (Zr,Cr)O_x domains start to crystallize. The principal 101 tetragonal ZrO₂ diffraction is observed both in XRD and SAED patterns (Figure 2 and Figure 5, respectively). The formation of tetragonal rather than monoclinic, ZrO₂ is noteworthy and probably related to the small grain size, since the surface energy of the tetragonal crystal structure is lower than that of the monoclinic, the former being promoted below a grain size of ~30 nm [22, 23]. This threshold grain size is larger than the observed grain sizes for the ZrO₂ phase in these samples, thus explaining the obtained tetragonal phase.

When annealed to, 810°C, the XRD and SAED patterns (Figure 2 and Figure 6) show a two-phase material of α -Cr₂O₃ and t-ZrO₂. Alternating Cr- and Zr-rich elongated crystalline domains with a thickness of, ~5 nm and 2-3 nm, respectively, are present (HRSTEM micrograph and EDX analyses in Figure 10 (b)). The thickness difference between domains is probably related to the relative concentration of the Cr and Zr, with Cr being ~3 times more abundant, see Table 1.

The α -(Cr,Zr)₂O₃ solid solution, present in as-deposited state, persists up to 810 °C. However, the amount of Zr dissolved in α -Cr₂O₃ phase decreases with increasing annealing temperature, as judged from the decreased lattice spacings derived from SAED. Calculation based on changes in molar volume, assuming Vegard's law, when exchanging the measured content of Zr in the film into the Cr₂O₃ structure correlate with the observed peak shifts. The effect of macroscopic stress relaxation influencing this trend is minor since it is observed when measuring SAED ring distances in TEM-samples. After annealing to 870 °C, the corundum phase has vanished. The reverse trend that is, Cr leaving the t-ZrO₂ phase (thus resulting in an increase of all t-ZrO₂ related lattice spacing), is not observed upon annealing to 750-870 °C. This is possibly due to the different formation path for the t-ZrO₂ (amorphous→ crystallization + grain growth) compared to the α -(Cr,Zr)₂O₃ formed during PVD deposition.

After annealing to 870°C, the principal phases present in the coating are t-ZrO₂ and bcc-Cr (Figure 2 and Figure 7). The microstructure has changed radically to being a mixture of two equiaxed phases, see Figure 8. This new microstructure is constituted by larger (~30-80 nm) relaxed metallic bcc-Cr grains, see Figure 8 and Figure 9, surrounded by a t-ZrO₂ matrix with smaller crystallites (below ~30 nm), which explains the tetragonal structure [22] as previously discussed.

The void formation in these samples is correlated with the formation of the ZrO₂ phase and related to the molar volume reduction by recovery of point defects (vacancies condense onto voids), during the phase transformation. The small ~10-nm-large round voids appear more frequently in the ZrO₂ elongated domains than in the Cr₂O₃ phase (not shown). The thicker (~500 nm) and repeating (period ~1 μm) regions parallel to the substrate, with slightly different microstructure, (Figure 5 and Figure 6) contain a higher amount of voids than the regions with more visible inclined elongated domains. There are additional voids forming after annealing to 870 °C due to the transformation of α-(Cr,Zr)₂O₃ to bcc-Cr upon loss of oxygen.

The formation of the metallic bcc-Cr phase in the oxide coating explains the relatively high peak intensity for Cr in the top diffractogram in Figure 2, since there is a peak overlap between the Cr-binding layer and the metallic Cr in the oxide coating. The segregation of Zr and Cr is in accordance with expectations from the phase diagram [46]. However, note that the phase diagram was constructed under 1.3 atm Ar pressure, hence not addressing the observed instability of the α-(Cr,Zr)₂O₃ phase under vacuum annealing.

The formation of elongated domains in the growth direction instead of close to spherical particles is possibly due to kinetic limitations inherent to the deposition conditions and setup. At the highest annealing temperature, 870 °C, spherically-shaped grains are present instead of

the elongated domains. The significant substitutional diffusion at 870 °C explains the tendency for coarsening of the fine elongated domains, supported by the strong driving force for separation of the Zr- and Cr-rich phases.

In order to explain why metallic Cr is formed while metallic Zr is not (see Figure 9), the relative stability of the two competing oxide phases needs to be compared. A first approximation of the relative stability of the considered phases was obtained by taking the estimated zero-Kelvin formations enthalpies from [49] based on existing experimental databases [50] for the two pure oxide phases and compare it to the values for the respective metallic phase + O₂. This shows that the α -Cr₂O₃ has a formation enthalpy of -2.384 eV/atom with respect to bcc-Cr + O₂, or -3.9735 eV/oxygen atom. ZrO₂, in contrast, has the formation energy vs hcp-Zr and O₂ of -3.823 eV/atom which corresponds to -5.735 eV/oxygen atom. Thus, there is a clear preference for oxygen to bind to Zr. If the background pressure is very low, as during these annealing experiments, the driving force for loss of oxygen is large. The transformation to t-ZrO₂ has largely taken place already at 810 °C without a measurable loss of oxygen. That indicates that the oxygen is not lost during the formation of t-ZrO₂ from Zr-rich (Zr,Cr)O_x amorphous phase but more probably due to the instability of α -(Cr,Zr)₂O₃ at high temperature and low pressure conditions. This distinguishes the present results from the α -(Al,Cr)₂O₃ system [3].

5. Conclusions

We have studied Cr-rich Cr-Zr-O coatings in the as-deposited state and after annealing in vacuum up to 870 °C. As-deposited Cr_{0.28}Zr_{0.10}O_{0.61} coatings exhibits segregation of Cr and Zr on the nm scale. The coating comprised a Cr-rich α -(Cr,Zr)₂O₃ solid solution and a Zr-rich (Zr,Cr)O_x amorphous phase. These two phases are present as anisotropic elongated domains

in the growth direction and stem from the inclined, stationary deposition setup, with a segmented Cr/Zr cathode.

After annealing at 750 °C, the Zr-rich amorphous oxide-phase starts to crystallize into tetragonal ZrO_2 phase with dissolved Cr. After annealing at 810 °C the tetragonal phase has further developed and is clearly observed together with $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ as alternating crystalline domains.

After annealing at 870 °C, a near complete transformation to t- ZrO_2 and relaxed metallic bcc-Cr is observed combined with a loss of oxygen. The ZrO_2 phase is stabilized in its tetragonal phase at these fairly low annealing temperatures due to the small grain size (below ~30 nm), which by surface energy effect make it more stable than standard temperature and pressure stable monoclinic phase.

These results show that it is possible to form $\alpha\text{-(Cr,Zr)}_2\text{O}_3$ solid solutions for up to ~10 at% Zr. However, it is less stable upon annealing in vacuum than coatings from the $\alpha\text{-(Cr,Al)}_2\text{O}_3$ system. During the oxide composite formation towards $\alpha\text{-(Cr,Zr)}_2\text{O}_3 + \text{t-(Zr,Cr)O}_2$ we see a significant increase of the microhardness. Such age hardening is notable for functional oxide solid solutions, motivates investigation of other ternary and multinary oxide systems. This leads to additional understanding of the pseudobinary oxide systems relevant for the wear-resistant-coating industry.

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Figure and table list

Table 1. Chemical composition, structural information and Vickers microhardness of as-deposited and annealed Cr-Zr-O coatings. The compositional balance consist of C, and N and traces of Ar. The standard deviations are ~0.5 at % and below for Cr, Zr and O.

Figure 1. (a) Deposition setup. The deposition setup image is a remake of the original image from ref [40]. (b) Orientation designation of the TEM-sample orientation on the substrate half disks.

Figure 2. X-ray-diffractograms of the as-deposited and annealed Cr-Zr-O coatings. Bragg-Brentano geometry with $\text{CuK}\alpha$. S= substrate, B= binding layer.

Figure 3. TEM micrographs and SAED patterns showing the difference in microstructure of the Cr-Zr-O coatings with respect to orientation of the TEM-sample cut, exemplified with the sample annealed at 750°C . Parallel ($\parallel$) (a) and perpendicular ($\perp$) (b) with respect to the segmented cathode direction from Cr-rich side to Zr-rich side. Note, not full coating thickness on image, however, similar appearance for the entire thickness.

Figure 4. STEM micrograph, $\parallel$ -cut of the as deposited coating (500°C), with inset SAED pattern, showing hexagonal $\alpha\text{-Cr}_2\text{O}_3$ structure.

Figure 5. TEM micrograph of the coating annealed at 750°C , with inset SAED pattern, showing hexagonal $\alpha\text{-Cr}_2\text{O}_3$ structure with traces of tetragonal ZrO_2 structure (orange). Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 6. TEM micrograph of the coating annealed at 810°C , with inset SAED pattern, showing that the sample is a mixture of hexagonal $\alpha\text{-Cr}_2\text{O}_3$ and tetragonal ZrO_2 structure (orange) with several overlapping diffraction rings. Primary diffractions indexed. Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 7. TEM micrograph of the coating annealed at 870°C , with inset SAED pattern showing that the sample is a mixture of tetragonal ZrO_2 (orange) and bcc-Cr (green) with the main diffraction of Cr being 110. Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 8. STEM micrograph (a) of the Cr-Zr-O coating annealed at 870°C , and corresponding EDX map (b) show segregation of equiaxed Cr-rich and Zr-rich domains (red=Cr and turquoise=Zr). This analysis has been done on a sample cut in the $\perp$ - direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 9. TEM and HRTEM micrographs (a and d), local EDX (b), convergent beam diffraction patterns (c) showing the presence of bcc-Cr grains in the coating annealed at 870°C . To the left Cr-rich grain along the $[111]$ zone axis and to the right another Cr-rich grain along the $[001]$ zone axis. These analyses have been done on a sample cut in the $\perp$ -direction.

Figure 10. HRSTEM micrographs and EDX analyses on as-deposited coating (a) showing crystalline Cr-rich elongated domains alternating with Zr-rich $(\text{Zr,Cr})\text{O}_x$ amorphous domains, and the coating annealed at 810°C (b) showing crystalline Cr-rich and Zr-rich alternating elongated oxide domains with different relative width (uniform O EDX-map not shown). The top image is a HRSTEM micrograph, the second from the top show the EDX-map on the same region, and the third is a line scan perpendicular to the elongated domains. Samples in $\parallel$ -cut orientation.

Figure 1 . (a) Deposition setup. The deposition setup image is a remake of the original image from ref [40]. (b) Orientation designation of the TEM-sample orientation on the substrate half disks.

Table 1. Chemical composition, structural information and Vickers microhardness of as-deposited and annealed Cr-Zr-O coatings. The compositional balance consist of C, and N and traces of Ar. The standard deviations are ~0.5 at % and below for Cr, Zr and O.

Coating variants	Elemental composition [at %]			$\frac{Cr}{Zr}$	$\frac{(Cr + Zr)}{O}$	HV _{0.05}	Structure (XRD)
	Cr	Zr	O				
As deposited (500°C)	28	10	61	2.80	0.62	950	α -Cr ₂ O ₃
Annealed (750°C)	29	11	58	2.64	0.69	1650	α -Cr ₂ O ₃ + t-ZrO ₂
Annealed (810°C)	29	10	59	2.90	0.66	980	α -Cr ₂ O ₃ + t-ZrO ₂
Annealed (870°C)	43	16	38	2.69	1.55	500	t-ZrO ₂ + bcc-Cr

Figure 2. X-ray- diffractograms of the as-deposited and annealed Cr-Zr-O coatings, Bragg-Brentano geometry with CuK α . S= substrate, B= binding layer.

Figure 3. TEM micrographs and SAED patterns showing the difference in microstructure of the Cr-Zr-O coatings with respect to orientation of the TEM-sample cut, exemplified with the coating annealed at 750°C. Parallel ($\parallel$) sample (a) and perpendicular ($\perp$) sample (b) with respect to the segmented cathode direction from Cr-rich side to Zr-rich side. Note, not full coating thickness on image, however similar appearance for the entire thickness.

Figure 4. STEM micrograph, $\parallel$ -cut, of the as deposited coating (500°C), with inset SAED pattern, showing hexagonal α -Cr₂O₃ structure.

Figure 5. TEM micrograph of the coating annealed at 750°C, with inset SAED pattern, showing hexagonal α - Cr_2O_3 structure with traces of tetragonal ZrO_2 structure (orange). Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 6. TEM micrograph of the coating annealed at 810°C, with inset SAED pattern, showing that the sample is a mixture of hexagonal α -Cr₂O₃ and tetragonal ZrO₂ structure (orange) with several overlapping diffraction rings. Primary diffractions indexed. Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 7. TEM micrograph of the coating annealed at 870°C, with inset SAED pattern showing, that the sample is a mixture of tetragonal ZrO_2 (orange) and bcc-Cr (green) with the main diffraction of Cr being 110. Sample in $\parallel$ -cut orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 8. STEM micrograph (a) of the Cr-Zr-O coating annealed at 870°C, and corresponding EDX map (b) showing segregation of equiaxed Cr-rich and Zr-rich domains (red=Cr and turquoise=Zr). This analysis has been done on a sample cut in the $\perp$ direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 9. TEM and HRTEM micrographs (a and d), local EDX (b), convergent beam diffraction patterns (c) showing the presence of bcc-Cr grains in the coating annealed at 870°C. To the left Cr-rich grain along the $[111]$ zone axis and to the right another Cr-rich grain along the $[001]$ zone axis. These analyses have been done on a sample cut in the $\perp$ direction.

Figure 10. HRSTEM micrographs and EDX analyses on as-deposited coating (a) showing crystalline Cr-rich elongated domains alternating with Zr-rich (Zr,Cr) O_x amorphous domains, and the coating annealed at 810°C (b) showing crystalline Cr-rich and Zr-rich alternating elongated oxide domains with different relative width (uniform O EDX-map not shown). The top image is a HRSTEM micrograph, the second from the top show the EDX-map on the same region, and the third is a line scan perpendicular to the elongated domains. Samples in $\parallel$ -cut orientation.