Characterization of tribological behavior and wear mechanisms of novel oxynitride PVD coatings designed for applications at high temperatures

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ABSTRACT

This paper focuses on high-temperature tribotests of nanostructured Al–Cr-based oxynitride and oxide coatings. Pin-on-disk tribological tests were performed at temperatures in between room temperature and 800 °C, and the results compared to a conventional AlTiN coating. The AlCrN and AlCrON coatings showed good to acceptable wear resistance up to 600 °C while at 800 °C, both coating types failed. The new corundum-structured (Al,Cr)2O3 oxide showed excellent wear performance up to 800 °C. Imaging and chemical analysis of the high-temperature wear tracks allowed for explaining the differences in the wear mechanisms. The ability of a coating to resist oxidation and to delay substrate oxidation, together with an excellent abrasional wear resistance, were identified as the major factors influencing wear rates under severe high-temperature conditions.

1. Introduction

Over the recent years, newly developed protective coatings for cutting tools have become highly resistant to wear if exposed to the extreme environments associated with modern machining processes. These coatings are generally deposited by various PVD methods and have often been based on Ti1–xAlxN PVD coatings [1–5]. Such titanium aluminum nitride coatings have been established as a standard for many years in a wide range of applications but they commonly fail at high temperatures mainly due to oxidative wear [6–10]. In the recent years, Ti was either completely replaced by Cr resulting in Cr1–xAlxN coatings, or Cr was added resulting in Ti1–x–yCrxAlyN films [11–13]. For these chromium-containing films, the wear resistance as well as the oxidation resistance is higher than for titanium based coatings, thus offering better wear and oxidation protection to the tool [5,10,14,15]. An alternative approach, Ti1–xAlxN/SiNy, Cr1–xAlxN/SiNy, or Ti1–x–yCrxAlyN/SiNy [16–20] silicon-containing nanocomposite coatings have also been introduced, mainly for cemented carbide shank tools up to intermediate cutting temperatures.

A new generation of different coatings has recently been developed especially for the highest temperatures occurring in practice, such as in metal cutting processes using indexable cutting inserts. These coatings use the addition of oxygen to form oxynitride coatings, that provide even better oxidation resistance than nitride coatings [21]. However, substantial improvement of cutting and wear performance could be achieved only by developing an alpha-phase aluminum–chromium oxide structure in the coating in order to prevent efficiently the oxidation at high temperature [4,21–23]. These new α-(Al,Cr)2O3 (α-oxide) based coatings are known to withstand extremely high temperatures in dry milling and turning of steels and other high-strength materials while exhibiting high wear resistance. While these new coatings feature a very promising cutting performance, their wear and friction properties at high temperature have not yet been thoroughly studied. The common pin-on-disk tribological tests on these coatings have failed, resulting in practically no wear. Since tribological properties including coefficient of friction (CoF) and wear rate are crucial in the development process of these coatings, a new testing procedure had to be established. This procedure needed to be able to determine the wear resistance of the coatings not only at room temperature but at high temperatures (~800 °C) in particular. Evaluation of the pin-on-disk results at room temperature is usually quite straightforward using profilometer measurements of the wear track cross-section for calculation of
the wear rate. However, analysis of high temperature pin-on-disk wear tracks requires more careful and complex evaluation, since many other phenomena such as oxidation can affect the test results [6,12,25–27]. Therefore additional analyses have to be performed in order to properly evaluate the wear performance of the coatings of the various coatings.

This study focuses on comparing the tribological behavior of an AlTiN-based reference, a nanostructured Al–Cr–based nitride and a series of oxynitride AlCrO$_2$, and oxide (AlCr)$_2$O$_3$ coatings deposited on cemented carbide using an industrial rotating cathodes arc PVD process [24]. The tribological properties are evaluated via room temperature and high temperature (600 °C and 800 °C) pin-on-disk tests, followed by investigation of the wear tracks by various analytical methods, in order to understand the high-temperature wear mechanisms and to demonstrate the differences in failure mechanisms of the various coatings.

2. Experimental details

2.1. Coating deposition and analysis

Four types of coatings were used in this study: AlTiN and AlCrN nitride coatings, an AlCrON oxynitride coating and a α-(AlCr)$_2$O$_3$ oxide layer. All coatings were deposited using a 311 (PLATIT AG, Switzerland) industrial arc PVD system equipped with three lateral (LARC) and one central (CERC) rotating arc cathodes. The processes were carried out either in a pure nitrogen atmosphere (for the nitrides) or a N$_2$/O$_2$ mixture (N$_2$/O$_2$ flow ratio ≥ 9:1 for the oxynitrides and ≥ 4:1 for the oxide coating) at 4 Pa pressure using a medium-frequency unipolar pulse voltage from −30 V to −100 V. During the deposition, the single side polished WC–Co substrates (Ø50 × d = 10 mm, EMT 100, Extramat AG, Switzerland) were heated to 550 °C. The layer architecture of the coatings was (from the substrate to the top): TiN adhesion layer, AlTiN, AlCrN/Si$_3$N$_4$ nanocomposite layer and a functional top layer which was varied. The top layer was selected as either AlCrN, AlCrO$_2$/Si$_3$N$_4$ or α-(AlCr)$_2$O$_3$ (see Table 1). The AlTiN reference sample contained only the TiN and AlTiN layers without any additional top layer. The overall coating thickness was ~4 μm for all samples.

The chemical composition of the films was quantitatively analyzed by calibrated wavelength dispersive (WDX) Electron Probe Micro Analysis. Annealing and oxidation tests were conducted at 900 °C in a gas-tight horizontal tube furnace under N$_2$/H$_2$ and dry air flows, respectively, using a heating ramp of 5 °C/min, a holding time of 120 min (annealing test) or 60 min (oxidation test), and natural oven cooling. XRD phase analysis was performed using Cu Kα radiation and Θ = 1° grazing incidence on equivalent samples containing only the functional top layer.

Room temperature nanoindentation testing of the coatings was performed using a Nanoindentation Tester (NHT, CSM Instruments SA, Switzerland). This instrument was calibrated using a standard procedure on fused silica reference sample (E$_p$ 73 ± 2 GPa) immediately prior to testing. A minimum of 20 indentations were performed at maximum loads of 30 mN, 50 mN and 70 mN at loading rates of 60 mN/min, 100 mN/min and 140 mN/min, respectively, and a holding time at peak load of 1 s. The values of hardness and Young’s modulus were extracted from the load–displacement curves using the Oliver and Pharr method [28] assuming a Poisson’s ratio of ν = 0.3 for the coatings. Since no load dependence was found, the values for hardness and Young’s modulus in Table 1 were averaged from all indentation results.

2.2. Tribological experiments

Three series of wear tests were performed on a High-Temperature Pin-on-Disk Tribometer (CSM Instruments SA, Switzerland) at temperatures of 24 °C (room temperature, RT), 600 °C and 800 °C. The conditions of the pin-on-disk tests varied according to test temperature and partially also according to sample type (longer tests for more wear resistant coatings) in order to generate measurable wear. All samples were mechanically polished after deposition using Master-Prep 0.05 μm alumina suspension (Bühler, Switzerland) in order to minimize roughness to a comparable level. The same media was used to recondition the surface in between the high-temperature tribotests. As static friction partner, 0.06 mm polycrystalline Al$_2$O$_3$ balls were used. Due to its high abrasive and oxidation resistance, this material is frequently used in high temperature tribology [52,30]. Preliminary tests were performed also with a 0.06 mm Si$_3$N$_4$ ball but the ball did not withstand high temperatures as also found by other groups [31,32]. The main pin-on-disk testing conditions are summarized in Table 2.

The cross-sectional profile of the wear track on the samples was measured by means of a Form TalySurf surface profilometer (Taylor Hobson, Great Britain) in six areas equally distributed around the wear track. The wear rate w of the coating was calculated as

\[ w = \frac{V}{d \times P} \]

where V is the volume of the removed material from the sample determined by surface profilometry, d is total distance and P is normal load. The pile-up and hollow scar areas were calculated automatically using a standard procedure in the MountainsMap software (Digital Surf, Besancon, France) where the pile-up and hole is defined as area

Table 2

<table>
<thead>
<tr>
<th>Pin-on-disk parameters used in tribological testing.</th>
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</thead>
<tbody>
<tr>
<td>Test temperature</td>
</tr>
<tr>
<td>24 °C</td>
</tr>
<tr>
<td>Normal load [N]</td>
</tr>
<tr>
<td>Distance [m]</td>
</tr>
<tr>
<td>Revolutions</td>
</tr>
<tr>
<td>Linear speed [m/s]</td>
</tr>
<tr>
<td>Test duration</td>
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</tbody>
</table>

* Parameters for the α-(AlCr)$_2$O$_3$ coating: distance 3000 m, 40,000 rotations, duration ~255 min.

Table 1

Chemical composition, structure and mechanical properties of the tested coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>O content [at% of (O+N)]</th>
<th>Al content [at% of metals]</th>
<th>XRD phases as deposited</th>
<th>RT hardness [GPa]</th>
<th>ΔH [GPa] and XRD phases after 2 h/900 °C in N$_2$/H$_2$</th>
<th>RT indentation modulus [GPa]</th>
<th>Application temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlTiN</td>
<td>≤ 0.5</td>
<td>56.6</td>
<td>fcc</td>
<td>33.9 ± 0.8</td>
<td>-3.1; fcc</td>
<td>550 ± 15</td>
<td>Up to 600</td>
</tr>
<tr>
<td>AlCrN</td>
<td>≤ 0.5</td>
<td>50.3</td>
<td>fcc</td>
<td>33.5 ± 1.2</td>
<td>-3.5; fcc</td>
<td>610 ± 16</td>
<td>Up to 700</td>
</tr>
<tr>
<td>AlCrON</td>
<td>73</td>
<td>50.7</td>
<td>fcc</td>
<td>34.6 ± 1.0</td>
<td>-0.4; fcc</td>
<td>467 ± 11</td>
<td>600–800</td>
</tr>
<tr>
<td>(AlCr)$_2$O$_3$</td>
<td>≥ 99.8</td>
<td>54.0</td>
<td>α-(AlCr)$_2$O$_3$</td>
<td>26.2 ± 0.9</td>
<td>0.2; α</td>
<td>446 ± 16</td>
<td>600–1000</td>
</tr>
</tbody>
</table>

* Spinodal decomposition into fcc-TiN + fcc-AlN.
above/below a mean line of the surface profile. The mean line is calculated from the surface profile not containing the wear track information. The wear rate of the alumina ball was calculated after each test using the volume of the worn cap and the same formula (1) was used for calculation of wear rate of the ball.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) analysis were carried out at 20 keV in a ZEISS EVO scanning electron microscope (ZEISS, Germany). The focused ion beam (FIB) cuts and the corresponding SEM images were realized on a Lya3 system (Tescan, Czech Republic).

After the full set of analysis had been completed, the coating surface was re-polished and the next test was done with different temperature and radius on the sample. Care was taken to begin with the ambient temperature measurement in order to avoid the necessity to polish away thick oxide layer that can form at high temperature. The residual coating thickness was greater than the wear track depth in all cases.

3. Results

The main chemical, physical and structural properties of the tested coatings are summarized in Table 1. All tested coatings share an aluminum content of slightly above 50 at% of the metals. The two nitride and the oxynitride coatings all have a single-phase fcc cubic structure and a room temperature hardness well above 30 GPa, which decreases about 10% after annealing at 900 °C in inert atmosphere except for the oxynitride, which nearly retains its hardness. The cubic phase of these three nitrogen-containing coatings is maintained during the annealing test, and no hexagonal phase formation is observed. The test conditions represent an upper estimate for the temperature in the wear track during testing at the highest macroscopic temperature, 800 °C, given that a friction induced heating is expected to contribute less than 100 K at this already high temperature. In comparison with the nitride and oxynitride coatings, the (Al,Cr)₂O₃ oxide starts off with a lower room temperature hardness, which is however even slightly increased by the annealing. As expected, no phase transformation is observed here, too.

Another difference between the tested coatings is their oxidative behavior. As evident from Fig. 1, the oxide scale thickness of the AlTiN sample is rather high after annealing in air at 900 °C, while it is drastically thinner for the AlCrN counterpart. Both of the oxygen-containing AlCr-based coatings show hardly detectable impact of the one-hour treatment on the coating. Based on these results, one would thus expect both the AlCrOₓN₁₋ₓ and the (Al, Cr)₂O₃ coatings to be valid candidates for high-temperature applications, from an oxidative point of view.

3.1. Coefficient of friction

The evolution of coefficient of friction (CoF) during the pin-on-disk tribological tests at room temperature, 600 °C and 800 °C is summarized in Fig. 2. The coefficient of friction of the AlTiN, AlCrN and AlCrON coatings was stable at room temperature while at 600 °C and 800 °C, the CoF varied strongly during the measurement, indicating important wear damage. Optical images and SEM observation of the wear track including EDX elemental mapping revealed areas with severe wear of the AlTiN coating after the 600 °C and 800 °C tests. The α-(Al,Cr)₂O₃ oxide coating, on the other hand, presented very stable CoF at all temperatures. Furthermore, the average value of the CoF of this oxide coating decreased...
from \(\sim 0.5\) at room temperature to \(\sim 0.3\) at 800 °C indicating excellent stability of this coating even at very high temperatures.

3.2. Wear rate

The wear rate of the coatings was calculated from the wear track profiles according to Eq. (1) for each of the tested coatings at room temperature, 600 °C and 800 °C. Although the volume of the material removed during the tests was an adequate measure of wear rate at room temperature, at high temperatures also the so-called ‘build-up’ had to be taken into account. Build-up [33] was considered as the growth or re-deposition of material around or in the wear track. The build-up rate was calculated analogically to the wear rate according to Eq. (1). The wear rates and build-up rates for all tested coatings are summarized in Fig. 3.

Room temperature: Comparison of the wear rates at room temperature revealed the highest wear for the AlTiN coatings. Wear rates of the AlCrN, AlCrON and \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) coatings were almost non-measurable. This is in agreement with very low wear rates for AlCrN and AlCrON coatings reported in the literature [5,12].

600 °C: At 600 °C the AlTiN-based coating showed the highest wear out of all tested coatings, although the wear rate was remarkably lower than for the test of the same coating, performed at room temperature. The wear rate of both the AlCrON and the AlCrN coating increased in comparison to room temperature. However, the most significant change observed was the apparition of build-up on these three coatings. The build-up was not present at room temperature and can therefore be considered as a temperature-activated process. The build-up rate on the AlCrN coating was significantly higher than that on the AlCrON coating. In contrast, the wear rate of the \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) oxide coating was very low and no build-up on this coating was observed.

800 °C: Wear of nitride and oxynitride (AlTiN, AlCrN, AlCrON) coatings was characterized by high wear rates with important build-up rates. Interestingly, the wear rate of the AlTiN coating at 800 °C apparently decreased with respect to the wear rate of the same coating at 600 °C and at room temperature. This ‘anomalous’ behavior will be discussed in more detail later. The results of the pin-on-disk tests of the \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) oxide coating at 800 °C revealed very low wear rate with only minor build-up.

3.3. Wear track morphology and wear mechanisms

The typical morphology of the wear tracks on the nitride and oxynitride samples was characterized by two features: material removal and build-up. The hollowing out was created due to erosive material removal during the wear tests while build-up was mainly due to re-deposition of the wear debris originating from the displaced material from both the wear track and the alumina ball. Both the hollowing out and the build-up morphological features were observed on all nitride and oxynitride samples to a various extent, depending on the type of the coating and temperature. At room temperature, the hollowing out was present only on the AlTiN and the AlCrON coating. At this temperature, build-up was observed on neither of the tested coatings. Fig. 4 shows the typical wear track morphology on AlTiN and \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) after room temperature pin-on-disk tests. The wear track on the oxide coating is almost invisible.

The wear of the coatings at room temperature was governed mainly by an abrasive mechanism with potential contributions of micro-scale cohesive fracture, as observed also in Ref. [33]. The main wear mechanisms at high temperature (see Table 3 and Figs. 7 and 8) were oxidative attack accompanied by gradual material removal [4,30]. On coatings with lower wear resistance also formation of build-up was observed at high temperatures (600 °C and 800 °C). The optical and SEM observation of the wear track obtained at 600 °C and 800 °C on the \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) oxide coating revealed only very shallow and uniform wear track. The build-up on this coating was non-measurable at 600 °C and only small build-up was observed after the 800 °C pin-on-disk tests. Figs. 4–5 show a comparison of the wear track on the AlTiN and \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) coating after the room temperature and 800 °C tests. Note the large build-up on the AlTiN coating after the 800 °C tests and very low damage on the \(\alpha-(\text{Al},\text{Cr})_2\text{O}_3\) coating. Especially at 800 °C, point wise local oxidation of the coated cemented carbide surface could be observed, in the form of cobalt-tungsten oxide features growing out of pinhole defects. However, this did not noticeably affect the overall wear behavior except for the AlTiN coating, where the main part of the wear track was found to consist of oxidized substrate material after the pin-on-disk test at 800 °C (Fig. 6).
3.4. Wear of the alumina ball

The results of the wear of the alumina ball are summarized in Table 4. The wear of the ball reflected the wear resistance of the tested coatings: the ball wear rate was highest against the AlTiN coating and lowest against the α-(Al,Cr)₂O₃ coating. Even at 800 °C, the wear of the ball against the α-(Al,Cr)₂O₃ coating was hardly measurable. In general, the ball wear rate was increasing with increasing temperature.

4. Discussion

4.1. Nitride and oxynitride coatings

The AlTiN, AlCrN and AlCrON showed increasing variation of the CoF with increasing temperature of the pin-on-disk tests. This behavior is strongly related to the progressing degree of damage during the wear tests: The nitride and oxynitride coatings exhibited more extensive damage (higher wear rate) at 600 °C and 800 °C compared to the test at room temperature. As observed also by other researchers, increase of the surface roughness due to oxidation of the coating can lead to increase of variation of the CoF [7,12,26,30].

The wear rate of the nitride and oxynitride coatings was expected to increase even despite the possible formation of an oxide passivation layer [15,27,34,35]. However, an opposite trend, i.e. apparent decrease of wear rate (better wear resistance), was observed mainly on the AlTiN coating at high temperature. This is illustrated in Fig. 6 which shows typical profiles of the wear tracks on the AlTiN sample after test at room temperature, 600 °C and 800 °C.

Table 3
Wear resistance and the main wear mechanisms of the nitride, oxynitride and oxide coatings at 24 °C, 600 °C and 800 °C.

<table>
<thead>
<tr>
<th>Coating</th>
<th>24 °C</th>
<th>600 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlTiN</td>
<td>Fair</td>
<td>Good</td>
<td>Bad</td>
</tr>
<tr>
<td>AlCrN</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>AlCrON</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>α-(Al,Cr)₂O₃</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images (secondary electron contrast) of the wear tracks after room temperature experiments on the AlTiN (a) and α-(Al,Cr)₂O₃ sample (b). The insets show typical surface profiles across the wear track.

Fig. 5. SEM image (secondary electron contrast) of the wear tracks after 800 °C temperature experiments on the AlTiN (a) and α-(Al,Cr)₂O₃ sample (b). The insets show typical surface profiles of the wear track.

Table 4
Wear of the alumina ball.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Ball wear rate [m²/N/m × 10⁻¹⁷]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 °C</td>
</tr>
<tr>
<td>AlTiN</td>
<td>54.2</td>
</tr>
<tr>
<td>AlCrN</td>
<td>3.6</td>
</tr>
<tr>
<td>AlCrON</td>
<td>0.1</td>
</tr>
<tr>
<td>α-(Al,Cr)₂O₃</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Fig. 6. SEM images, EDX maps and wear profile on the AlTiN coating at room temperature, 600 °C and 800 °C. Note the increasing build-up in the track associated with temperature increase.
800 °C. The material removal within the wear track gradually decreased with increasing temperature, accompanied by increasing build-up. Since the wear rate calculation was based on the profile of the wear track, the apparent wear rate was also decreasing with increasing temperature. To understand this ‘anomalous’ behavior, EDX analysis of the 800 °C wear track in the AlTiN coating was performed. The results of the EDX analysis (Figs. 6 and 7) revealed high content of oxygen not only in the wear track but also in the initially oxygen-free coating. As furthermore evident from Fig. 6, in the wear track center no wear track but also in the initially oxygen-free coating. As the AlTiN coating was performed. The results of the EDX analysis not only wear rate but also build-up rate has to be taken increased build-up rate. Thus, for proper evaluation of tribological temperatures; growth of the oxides above the surface lead to re-deposition of oxidized, worn particles from the substrate originating from local oxidized spots. Damaged and rough surface of the AlTiN coating, as well as the presence of wear particles, also resulted in higher wear of the alumina ball counterpart (see Table 4) at higher temperatures.

4.2. Analysis of the wear track using focused ion beam tomography combined with SEM

To further understand the high temperature oxidation and to explain the decrease of the wear rate, a focused ion beam (FIB) cut was prepared in the AlTiN wear track after the 800 °C test. The EDX analysis in the FIB cut (Fig. 7) showed a high content of oxygen in the center of the wear track (region with the most severe damage) and under the coating (peripheral part of the wear track) as well as at the coating surface. Furthermore, presence of tungsten and cobalt (WC–Co substrate) was also detected in the central region of the wear track (Figs. 6 and 7) and none of the coating elements Ti, Al and N could be detected anymore in this location. These results indicate that the coating was completely removed in the wear track resulting in a catastrophic failure and rapid oxidation of the exposed WC–Co substrate to such extent that it filled completely the hollow area created during the wear tests. Filling the removed material space with oxidized WC–Co substrate was reflected in a low apparent wear rate at high temperatures; growth of the oxides above the surface lead to increased build-up rate. Thus, for proper evaluation of tribological results not only wear rate but also build-up rate has to be taken into account and further analyses have to be conducted in order to understand properly the wear processes.

Similar FIB cuts with subsequent cross-sectional EDX analysis were performed on the AlCrN and AlCrON coatings after the 800 °C tests. As shown in Fig. 8 for the case of AlCrON, the top layer is eventually worn through and as soon as the Ti-based sublayers are exposed, oxidation becomes dominant and especially in the AlTiN base layer, a distinct, granular oxide layer is formed as evident from the cross-sectional FIB cut of position 1. There is oxygen present at the coating surface too, but the already high oxygen content in the oxynitride coating covers any tribooxidation phenomena. Oxidized WC–Co substrate was found in some regions on the wear track, however with less extent than on the AlTiN coating. Oxidation of the substrate in the wear track was less pronounced for the AlCrON coating than for the AlCrN coating due to a better high-temperature oxidation resistance of the oxynitride coating. The presence of oxygen in the AlCrON coating lead to improvement of the wear resistance of this coating, which resulted in lower wear and build-up rates compared to AlCrN coating (see Fig. 3). Interestingly, it seems from the FIB cut into the AlCrO1.5N0.5 wear track that that the oxidation proceeds much more mildly in the AlCr-based top layer than it does in the TiAl-based underlying coatings, especially the AlTiN. However, the partial incorporation of oxygen into the nitride coating was clearly not sufficient to create coating material capable to withstand tribological tests at 800 °C without severe damage, as evident from the fact that even the AlCrO1.5N0.5 top layer is worn through in the center of the wear track (Fig. 8).

4.3. Oxide coating

The coefficient of friction of the novel α-(Al,Cr)2O3 oxide coating was very stable at all temperatures and it even decreased from μ ≈ 0.5 at room temperature to about μ ≈ 0.3 at 800 °C. This indicates very low damage of the coating at temperatures up to 800 °C where other nitride and oxynitride coatings failed mainly due high temperature oxidation and abrasion. Although some wear was observed at 800 °C, the wear track remained very shallow and its morphology was very similar to the one obtained from the room temperature tests on the same coating (compare Figs. 3 and 4). SEM observation of the FIB cut through the wear track revealed only mild abrasive wear without any spallation or delamination of the coating, thereby confirming an excellent protection of the substrate even at 800 °C. This means that the main wear mechanism, high-temperature oxidation, was entirely eliminated for this coating. In this context, it is worth noting that the hardness of this coating, even if found to be lower at room

Fig. 7. FIB cut into the AlTiN wear track (left and middle) and EDX elemental maps (right) after the 800 °C test. Note the extensive oxidation in the center of the wear track (coating completely removed) and under the coating. Brighter areas correspond to higher content of the given element.
temperature compared to the other tested coatings (Table 1), may be favorable at elevated temperatures. The magnitude of this effect would need to be confirmed by high-temperature micromechanical testing. Furthermore, the underlying coating base layers and except for local pinhole-type defects, even the WC/Co substrate had efficiently been protected from high temperature oxidation by the oxide coating. The EDX analysis in the FIB cut in the wear track (see Fig. 9) correspondingly showed only negligible substrate oxidation. The substrate remained fully intact, without any signs of cracks or other type of damage. Unlike the AlCrO\textsubscript{2-x}N\textsubscript{x} coating, where high temperature oxidation by further replacement of N by O is still possible, the alpha oxide coating remained inert; in addition, it showed an excellent resistance to abrasive wear in the entire investigated temperature range, including the highest test temperature (800 °C).

5. Conclusions

This work presents a study of the tribological behavior of nitride, oxynitride and oxide wear-resistant coatings designed for use at high temperatures. Cubic AlTiN, AlCrN and AlCrON nitride and oxynitride coatings deposited by an industrial rotating arc cathodes PVD processes showed good wear resistance at room temperature and reasonable wear resistance at 600 °C. The replacement of titanium by chromium was found to be beneficial for the wear resistance in a temperature range up to 600 °C. However, at 800 °C all nitride and oxynitride coatings exhibited severe wear. Only the new \(\alpha-(AlCr)_2O_3\) coating, deposited by rotating cathodes arc PVD in a nitrogen/oxygen atmosphere at 550 °C, maintained an excellent wear resistance even at 800 °C. The superior wear resistance of this oxide coating was due to the nitrogen-free,
purely oxidic composition and its stable alpha-alumina structure, which hindered high temperature oxidation and subsequent severe wear. EDX and SEM analyses of FIB cuts into the wear tracks showed that even if coating adhesive failure could be ruled out, the wear mechanisms at very high temperatures are still very complex and characterization of wear resistance cannot merely be based on the wear track profile and calculation of material removed. Especially during high-temperature tribological tests, a more complex evaluation needs to be applied, using complementary analytical methods in order to understand the oxidative and diffusive wear mechanisms of coating and substrate. Using the FIB-SEM method, we could confirm the decisive role of coating oxidation especially if combined with abrasion of the formed oxide, but also of the cemented carbide substrate oxidation during wear of PVD coatings at up to 800 °C.

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