# Tribological Characterization and Wear Mechanisms of Novel Oxynitride PVD Coatings Designed for Applications at High Temperatures

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## Introduction

In recent years, newly developed protective coatings for cutting tools have become more and more wear and abrasion resistant to the extreme environments associated with modern machining processes. On these new coatings the common pin on disk tribological tests have failed, resulting in practically no wear or strongly heterogeneous wear. For efficient tribological testing and determination of wear resistance of the new hard coatings it is therefore crucial to establish a valid set of room temperature and high-temperature wear test conditions. After a large number of preliminary tests performed on a state-of-the-art high-temperature pin on disc tester we identified optimized conditions for characterization of these new types of hard coatings. The investigated coatings comprised AlTiN-based reference, nanostructured Al-Cr-based nitride, oxynitride and oxide coatings deposited using an industrial rotating cathodes arc PVD process on cemented carbide. The nitrogen in the coating was progressively substituted by oxygen up to 100 at.% to create oxide structure in order to avoid oxidation of the coatings at high temperatures. These new oxide coatings are known to withstand extremely high temperatures in dry milling and turning of high-strength materials while exhibiting high wear resistance. However, characterization of their wear resistance by the common tribological tests had proven to be very difficult and new testing procedures had to be established.

## Materials and experimental details

Four types of coatings were used in this study: AlTiN-based and AlCrN nitride coatings, AlCrON oxynitride coating and $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating. All coatings were deposited using $\pi$ Technology: LARC® Lateral- and CERC® Central Rotating Arc Cathodes (Platit AG, Switzerland) in $N_2/O_2$ atmosphere (oxynitride and oxide coatings) at 4 Pa pressure and bias voltage from -30 V to -100 V using medium frequency. During the deposition the substrates from WC-Co (Extramet, Switzerland) in form of cylinders with 50 mm diameter and 10 mm thickness were heated to 550°C. The stack of layers was (from the substrate toward the top surface): TiN adhesion layer, AlTiN, nACo nanocomposite layer and top layer. The top (functional) layer, crucial for the wear properties, was AlCrN, $AlCrO_xN_{1-x}$ or $\alpha$-$(Al,Cr,X)_2O_3$ (see Table 1). The AlTiN reference sample contained only the TiN and AlTiN layers without any additional top layer. The thickness of the whole coatings was ~4 $\mu$m.

*Table 1 – Oxygen content and temperature for which the coating was designed.*

| Coating denomination | Oxygen content | Designed for temperature |
|---|---|---|
| AlTiN | 0 at. % | up to 600°C |
| AlCrN | 0 at. % | 600°C |
| AlCrON | 70 at. % | 600°C-800°C |
| $\alpha$-$(Al,Cr,X)_2O_3$ | 99.8 at. % | 800°C-1000°C |

The wear tests were performed by pin on disk method on THT 800 instrument (CSM Instruments, Switzerland) at temperatures of 24°C, 600°C and 800°C. The normal load was 7 N (10N respectively for 24°C), the counterbody was alumina ball with 6 mm diameter and the linear velocity was 20 cm/s. The pin on disk tests were performed with 32'000 laps and the total duration of the tests varied between 120 minutes and 240 minutes depending on the radius of the wear track. Scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDX) and focused ion beam (FIB) cuts was done on Lyra3 scanning electron microscope (Tescan, Czech Republic).

## Results

The results of the tribological tests at room temperature, 600°C and 800°C are summarized in Fig. 1. The AlTiN based reference coating performed well only at room temperature but its coefficient of friction varied strongly at 600°C and 800°C indicating severe wear. Optical images and SEM observation of the AlTiN wear track at 600°C and 800°C revealed areas with catastrophic failure. The AlCrN and AlCrON coatings showed better stability of the coefficient of friction and better wear resistance up to 600°C but they failed during tribological tests at 800°C. The $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating, on the other hand, presented practically no signs of wear even at 800°C. Furthermore, the coefficient of friction of this new oxide coating decreased to ~0.3 at 800°C (compared to ~0.6 at 600°C) indicating excellent wear resistance and negligible degradation of this coating at high temperatures (see Fig. 1, 800°C, blue line).

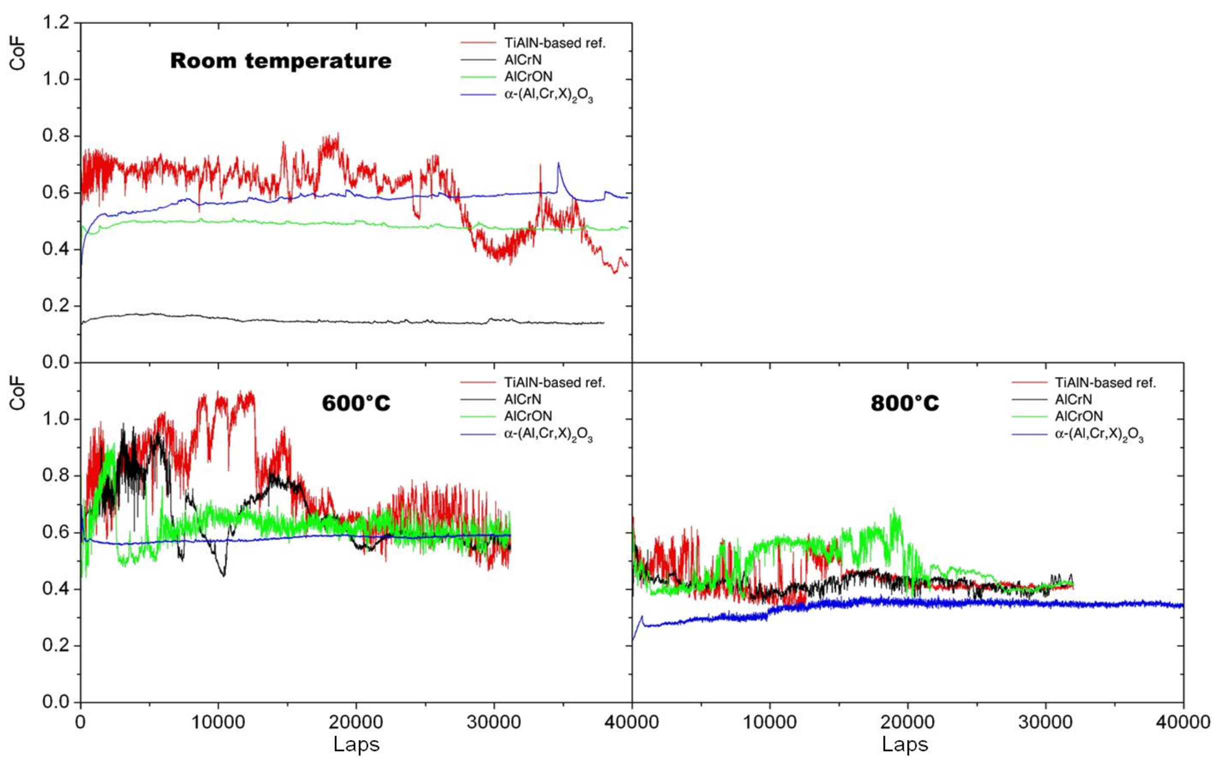


*Figure 1 – Comparison of coefficient of friction of all tested samples at 24°C, 600°C and 800°C. Note excellent stability and low value of coefficient of friction of the $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating (blue line).*

The evaluation of the wear rate at room temperature via profile of the wear track revealed low wear for the AlTiN coating and almost non-measurable wear for all other coatings. At 600°C the AlTiN-based coating showed moderate wear. The wear rates for AlCrN and AlCrON were higher at 600°C and even higher at 800°C compared to room temperature.

The $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating, on the other hand, showed minor wear with very little traces of interaction with the alumina counterpart at 600°C and 800°C – see Fig. 2. As noted above, also the coefficient of friction at 800°C on this coating was very stable. Surprisingly enough, the wear track profiles in some areas on the AlTiN and AlCrN coatings at 800°C did not show a typical 'worn-out' profile but rather a large material build-up. Figure 2 shows the relatively 'low' wear rate of the AlTiN coating at 800°C whereas the build-up rate was the highest on this coating. Nevertheless, both wear rate and build-up rate were significantly higher than that of the oxide coating.

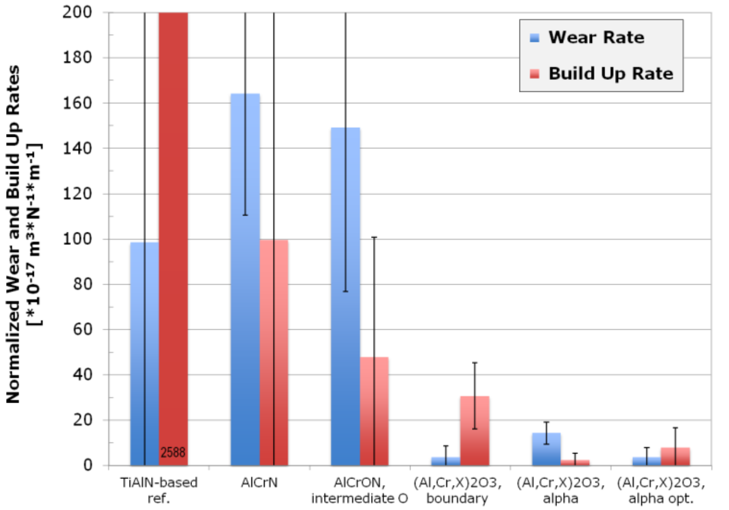


*Figure 2 – Wear and build up rates of all tested coatings. Apart from the $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating (alpha opt.) also two other variations of oxide coating are included.*

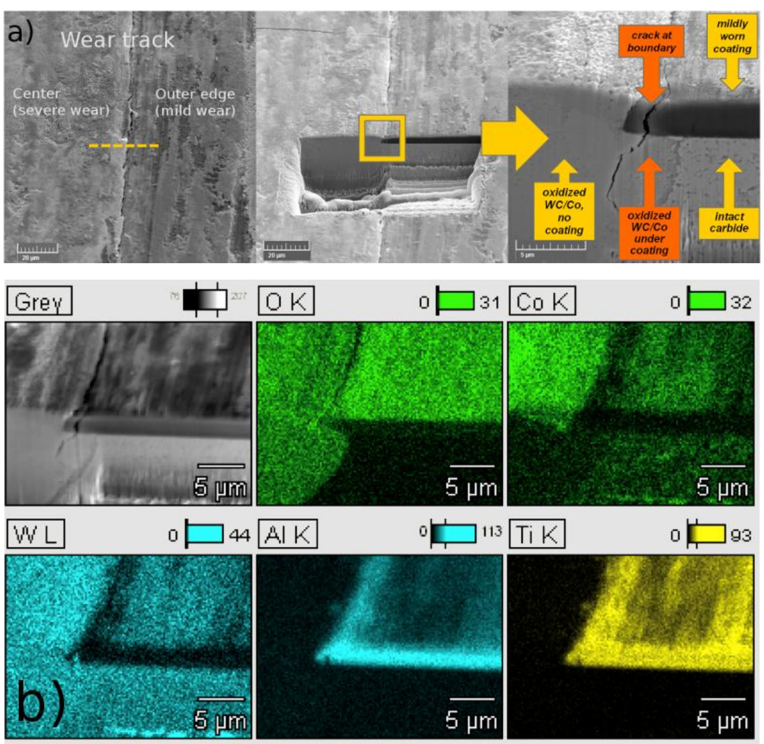


*Figure 3 – a) SEM micrograph (secondary electrons) of the wear track on the TiAlN coating after 800°C pin on disk test, showing the position of the FIB cut. b) EDX in the FIB cut showing strong oxidation of the WC-Co substrate.*

## Discussion

Although the AlTiN, AlCrN and AlCrON coatings showed good wear resistance at room temperature and at 600°C, they all failed during tribological tests at 800°C. AlTiN, AlCrN and AlCrON showed signs of severe wear including catastrophic failure in several regions. EDX analysis of the worn surface and also FIB cuts in the wear track revealed oxidation of the substrate in the regions of severe wear. The FIB cuts of the wear track on AlTiN coating tested at 800°C revealed oxidation of the substrate also beneath the coating in regions where the coating was not completely removed. This indicates insufficient resistance of the AlTiN coating to oxidation at high temperatures.

SEM analysis of the wear tracks revealed that the wear on samples with low oxygen content was governed by an abrasive mechanism with limited micro-scale cohesive fracture. EDX mapping showed that oxidation played a negative role for AlTiN and AlCrN coatings while $AlCrO_xN_{1-x}$ coating remained relatively intact at 600°C. The $\alpha$-$(Al,Cr,X)_2O_3$

oxide coating retained high wear resistance up to 800°C. The EDX and SEM images showed that the wear mechanisms especially at high temperatures are very complex and characterization of wear resistance cannot be based only on the wear track profile and simple calculation of volume of material removal. To further elucidate these wear mechanisms, FIB cuts were performed in the wear track of the AlTiN and the $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating after the 800°C pin on disk tests. Figure 3a shows this FIB cut in the AlTiN wear track and Fig. 3b shows corresponding EDX analysis in this area. The oxidation of the substrate in the wear track lead to the growth of the material in the wear track thus almost completely filling up the cavity created by the wear test. This process resulted in erroneously low wear rate and in build-up of the WC-Co oxides on the periphery of the wear track. The evaluation of wear rate especially at high temperature tribological tests requires therefore a more complex analysis than simple measurement of the profile of the wear track. In contrast, the $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating showed practically neither wear nor material build-up thus confirming excellent oxidation and wear resistance of this new type of coating.

**Conclusions**

This work presents a thorough study of tribological behavior of new types of hard coatings designed for use at high temperatures. The novel $\alpha$-$(Al,Cr,X)_2O_3$ oxide coating confirmed its excellent wear resistant properties and oxidation resistance at temperatures up to 800°C. The AlTiN, AlCrN and AlCrON coatings showed good wear resistance at room temperature, acceptable wear resistance at 600°C; at 800°C all these coatings exhibited severe wear. The superior wear resistance of the oxide coating was due to high oxygen content in this coating which hindered high temperature oxidation and subsequent catastrophic degradation of the coatings with lower oxygen content.