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**Tribologie otěruvzdorných povlaků za vysokých teplot**

**High Temperature Tribology of Protective Coatings**

## Summary

High temperature tribology of protective coatings prepared by physical vapour deposition is an emerging field of material science. Friction and wear analysis at high temperature requires multidisciplinary approach combining different theoretical and experimental techniques.

This habilitation lecture introduces nitrogen-based protective coatings and their key structural and mechanical properties. The complexity of high temperature tribology is briefly discussed. It is demonstrated that the coating wear at high temperature cannot be easily predicted by oxidation and thermal stability analyses.

## Souhrn

Vysokoteplotní tribologie otěruvzdorných povlaků připravovaných metodami PVD je nová oblast materiálového inženýrství. Třecí a otěrová analýza za vysokých teplot vyžaduje multidisciplinární přístup kombinující různé teoretické a experimentální metody.

Habilitační přednáška definuje tenké otěruvzdorné povlaky na bázi dusíku včetně popisu jejich struktury a mechanických vlastností. Stručně je diskutována i komplexnost vysokoteplotní tribologie. Na jednom příkladu se demonstruje nutnost vysokoteplotní analýzy otěru povlaků, který nelze predikovat na základě znalosti odolnosti vůči oxidaci a stabilitě struktury za zvýšené teploty.

Klíčová slova: vysokoteplotní tribologie; povlak; oxidace;  
tření; otěr

Keywords: high-temperature tribology; coating; oxidation;  
friction; wear

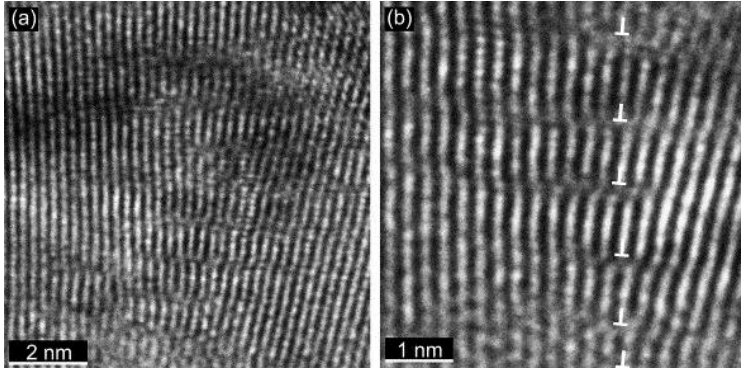
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## **1. Modern protective coatings for high temperature applications**

Deposition of hard thin films with a few microns in thickness is a common technology to improve the performance of tools, dies, and molds for many different applications. Starting with thermally activated chemical vapor deposition (CVD), different methods have been developed including plasma-assisted physical vapor deposition (PVD), plasma-assisted chemical vapor deposition (PACVD) and laser-assisted methods like pulsed laser deposition (PLD). The importance of wear-resistant hard coatings is given by the following facts. About 90% of all indexable inserts for metal cutting, based on cemented carbide substrates, are coated for wear protection by CVD or PVD techniques, with PVD being used in about 25% of the cases. The important issue for the future is not which deposition technology is used, but instead which properties can be achieved at which production cost.

The main advantage of thin films is hardness well above that of the respective bulk materials due to deposition using high ion energies, making use of strain hardening by high defect densities where the defects responsible for the residual stresses also act as obstacles for dislocation movement (Fig. 1). In fact, an apparent linear relationship between residual stress and hardness has been reported for several single-phase coatings deposited by different PVD methods. The strengthening effect of TiN and CrN coatings with decreasing grain size (or column diameter) follows the Hall–Petch relationship (HPR). For reactively and non-reactively sputtered TiN films, which follow the HPR, the highest hardness values could be obtained for those layers showing the smallest grain size. However, for other single phased coatings, such as CrN, the hardness reaches maximum for certain grain size (about 12 nm) and then decreases again for smaller grains [1].



*Fig. 1 (a) Dislocations and strained areas and a low-angle grain boundary. (b) Detail of the low-angle grain boundary. TiN film [1].*

If the neighboring grains in a material are of different lattice structures (hence different phases) they probably have different slip systems, so it becomes more difficult for dislocations to run through the respective grains. Such coatings belong to the group of phase-modulated hard layers. For example, a  $\text{CrN}_{0.6}$  coating, which consists of CrN phase (fcc, number of possible slip systems: 12) and  $\text{Cr}_2\text{N}$  phase (hcp, number of possible slip systems: 3) shows an extremely high hardness of 39 GPa (2).

If grain boundary sliding or the propagation of dislocations can be avoided or suppressed by an appropriate design of nanocrystalline materials with strong grain boundaries, the strengthening of materials can be adjusted by extremely small grains as critical grain size decreases. Such materials can reach hardness values higher than 40 GPa [3,4]. This can especially be obtained by materials, which are composed of at least two different phases in the nanoscale regime, either obtained by composition or phase modulation.

An alternating layer-by-layer arrangement of two phases is obtained in a multilayer or, when the periodicity is in the nanometer range (i.e. one-dimensional nanostructure), in the

superlattice form. The superlattice approach provides a challenging method for the synthesis of materials with superhardness. Such lamellar materials, either designed by an alternating growth of individual layers in an artificial superlattice (e.g., TiN/VN [5]), or inherently nanolaminated phases (e.g., the so-called  $M_{n+1}AX_n$  ( $n = 1-3$ ) phases [6], where M is a transition metal, A represents a group A element such as Al or Si, and X is C and/or N) are promising materials as they combine high hardness and toughness.

Nitrogen-based protective coatings are together with  $Al_2O_3$ -based films the only candidates for harsh conditions combining high temperature and contact pressure thanks to their mechanical properties, thermal stability and oxidation resistance.

## **2. Thermal stability and oxidation**

Increase of ambient temperature has a complex effect on the coating microstructure, chemical composition and mechanical properties. Coating oxidation strongly depends on type of bonding, microstructure and properties of oxides formed on the film surface. Chromium and aluminium oxides are known to form a thin diffusion barrier inhibiting further oxidation of the coating. On the other hand, titanium or tungsten oxides do not protect the surface. Fig. 2 shows dramatic oxidation of various tungsten nitride coatings; at 600 °C the nitride film is completely oxidized.

Thermal stability is very important parameter for majority of high temperature applications. CrN stoichiometric coatings undergo phase transformation to  $Cr_2N$  and Cr (Fig. 3). Unlike oxidation, this transformation takes place in entire volume in the coating. Deliberated nitrogen diffuses to the surface. In some cases it can form nitrogen-rich layer below oxidized surface, which acts as diffusion barrier [7].



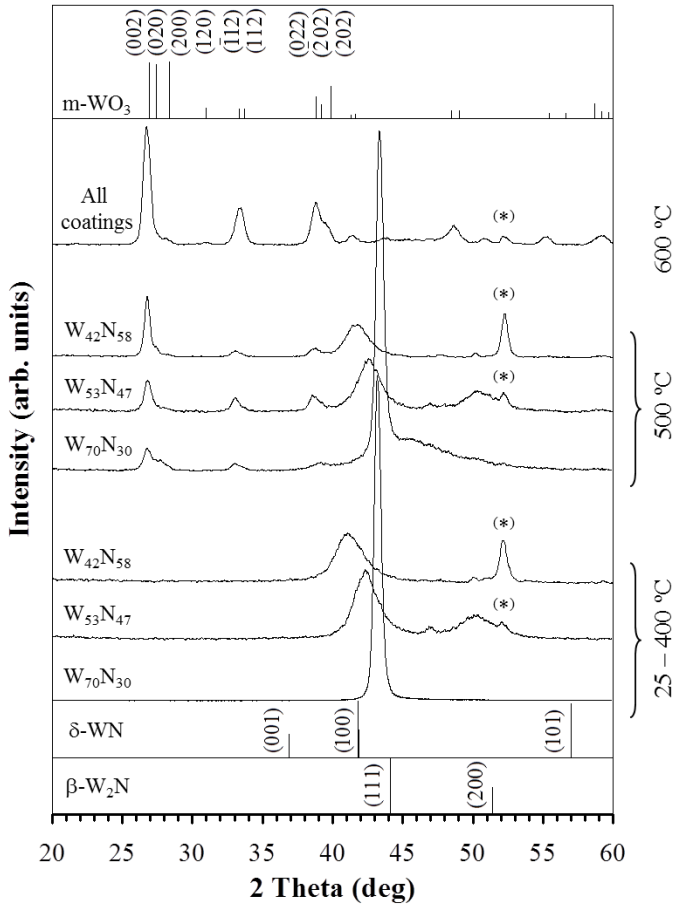


Fig. 2 XRD diffractogram of W-N films at different temperatures [8].

Ternary systems, such as CrAlN, are thermally stable at temperatures exceeding 1000 °C. Addition of Si could further increase thermal stability [9]. Recently, Si-B-C-N coatings have shown excellent stability even at 1700 °C [10].

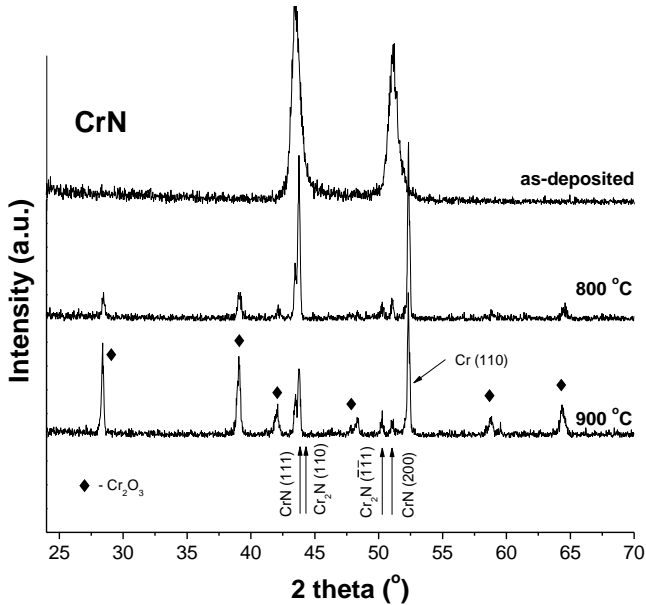
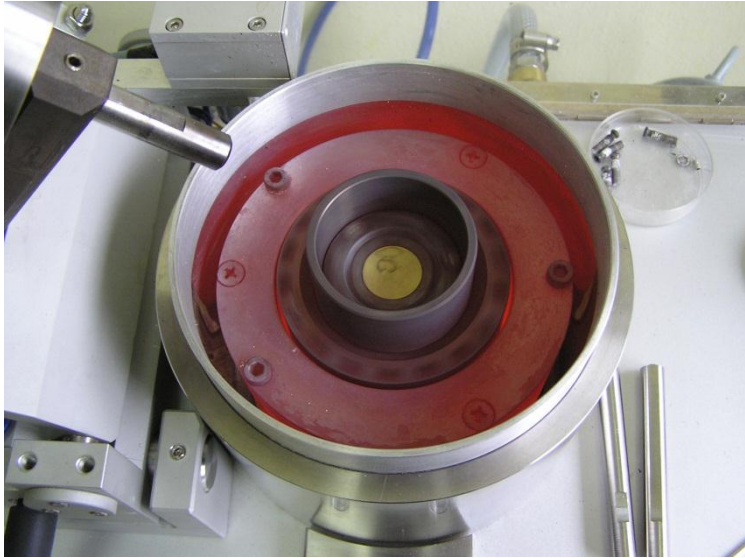


Fig. 3 Phase transformation and oxidation of annealed CrN coatings [7].

### 3. High temperature tribology

Friction and wear analysis of the wear resistant coatings at elevated temperatures is relatively recent. The methodology is still not fully standardized and the access to proper instrumentation is limited. The most used technique is a pin-on-disc, where the pin, typically ball, is pressed against rotating sample at predetermined temperature. Ceramic materials are exclusively used as a counterpart material ( $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$ ). Maximum testing temperature is limited to  $1000\text{ }^\circ\text{C}$ . Fig. 4 shows pin-on-disc based at FEE.



*Fig. 4 Wear testing of protective coating at high temperature – pin on disc.*

Friction coefficient is measured continuously during the tests; the wear rate is calculated after the test as worn volume per sliding distance per load. It is relatively easy to measure worn volume; the challenge is to understand why we measured such friction and wear rate values. Wear of materials is extremely complex problem. Traditionally four wear mechanisms were classified - abrasive or adhesive wear, fatigue, and oxidation wear. In the case of thin films, where interface and nanoscale effects play dominant role, is such classification insufficient. Surface sensitive measurements must be carried out to identify the structure, chemical bonding, composition, and morphology of worn surfaces. The results are then related to fundamental wear models and measured friction coefficient and wear rate. Finally, the tribological performance is related to coating as-deposited properties.

Tribology at room temperature is very challenging and, particularly considering multiscale nature of wear process, still in an embryonic state. When sliding occurs at high temperature, the process is even more complicated. The materials in contact differ from those analysed at room temperature, oxidation is strongly promoted, and several new processes could take place (diffusion, melting, etc). It is not surprising that almost all models and simulations of coating tribological properties fail at elevated temperatures.

Finally, there is one more important drawback of high temperature tribology. The tests are complicated and time consuming; thus, the statistical approach is strongly limited – we cannot repeat measurement to get significant statistical data.

Unfortunately, the relationship between coatings fundamental properties and tribological performance is often simplified and misleading. It has been long time believed that the hardness is the most important parameter controlling the wear of protective films. Interestingly, we know it is not true for decades, and still as-high-as-possible hardness values are demanded by industry for applications, where softer but tougher films would perform better. The same applies for hardness to elastic modulus ratio. Again, it is only mere indication, not ultimate parameter. Moreover, there is no instrumental technique available to measure mechanical properties at temperatures higher than 750 °C (in fact, such nanoindentation device was introduced only in 2011).

High temperature tribological properties are often “guessed” from static oxidation tests, thermal stability and room temperature sliding properties.

In next chapter we will demonstrate importance of in situ high temperature analysis of protective coatings. We will present one example, where an estimation of high temperature wear based on oxidation resistance, thermal stability and microstructure fails.

#### 4. Case study – high temperature properties of CrAlN, CrAlSiN, AlCrSiN and TiAlCrN coatings

CrAlN, CrAlSiN, AlCrSiN and TiAlCrN coatings were prepared by cathodic arc deposition from composite targets in nitrogen/argon atmosphere [11,12,13,14]. The chemical composition measured by electron probe microanalysis is shown in Table 1.

*Table 1 Chemical composition and thickness*

Chemical comp. (at.%)	CrAlN	CrAlSiN	AlCrSiN	TiAlCrN
Cr	25.0	29.9	17.4	15.8
Al	31.0	25.6	32.7	30.2
Si/Ti	0.1	3.8	3.3	7.0
N	40.0	39.1	44.3	45.5
O	3.8	1.7	2.3	1.5
Thickness ( $\mu\text{m}$ )	2.17	2.28	2.13	2.2

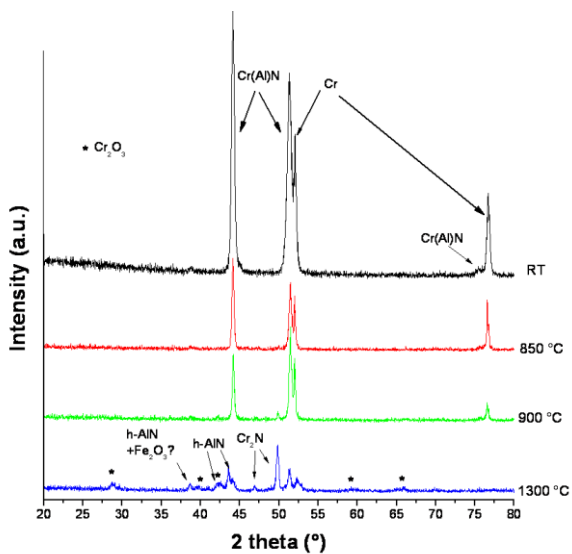
CrAlN exhibited several intense peaks belonging to the (111), (200) and (220) of a fcc phase related to Cr(Al)N. All peaks were localized between chromium nitride (ICDD card 76-2494) and aluminium nitride (ICDD card 25-1495) suggesting a possible complete solution of chromium and aluminium in the NaCl type lattice. The CrAlSiN coating, i.e. the coating with similar Cr/Al ratio as CrAlN, showed almost identical spectra but with different preferential orientation, (111) and (220), compared with the dominant (200) orientation of CrAlN coating. In both cases, a weak peak representing pure Cr was observed originated probably either from droplets or from the thin adhesive interlayer. Considering the peaks position, the residual stresses should be negligible. TiAlCrN showed

similar structure with fcc Cr(Al)N phase; TiN was not detected, possibly due to low Ti content.

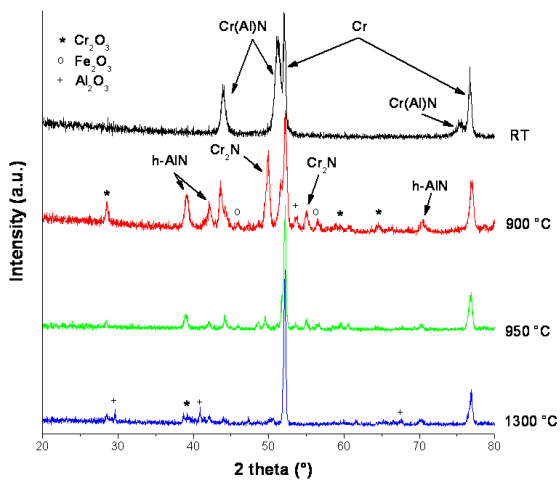
As expected, AlCrSiN exhibited a significantly different XRD spectrum showing a mixture of Cr(Al)N cubic phase together with the hexagonal AlN phase (ICCD 79-2497). The peaks are shifted towards higher  $2\theta$  indicating tensile stress. Thus, the limit of Al solubility in CrN matrix was reached and wurzite AlN was formed. Again, Cr peak was observed, but only as a minor component.

XRD analysis carried out in-situ at high temperatures showed significant difference between CrAlN and CrAlSiN films. CrAlN coating was thermally stable up to 900 °C, where the first vestiges of Cr<sub>2</sub>N phase were observed as a result of CrN thermal decomposition (Fig. 5a). On the other hand, the CrAlSiN was much less stable; the Cr(Al)N phase transformation to wurtzite-type AlN and hexagonal Cr<sub>2</sub>N was clearly visible (Fig 5b). Coatings with high aluminium content showed the best thermal stability with no transformation observed at 900 °C.

Hardness measured by depth sensing nanoindentation was in the range 33-38 GPa. All films showed excellent adhesion evaluated by scratchtest with critical load exceeding 80 N. Based on presented results, it might be speculated that the wear resistance at lower temperatures (up to 700 °C) should be similar. Coatings annealed for 1 hour at 1300 °C were investigated by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). AlCrSiN coating exhibited only limited oxidation on the surface, whereas more than half of TiAlCrN coating was oxidized. Iron from the substrate diffused toward coating surface accumulating below oxide layer and thus indirectly demonstrating its diffusion barrier function. A very thin oxide film was observed at 900 °C in case of TiAlCrN and CrAlSiN coatings.

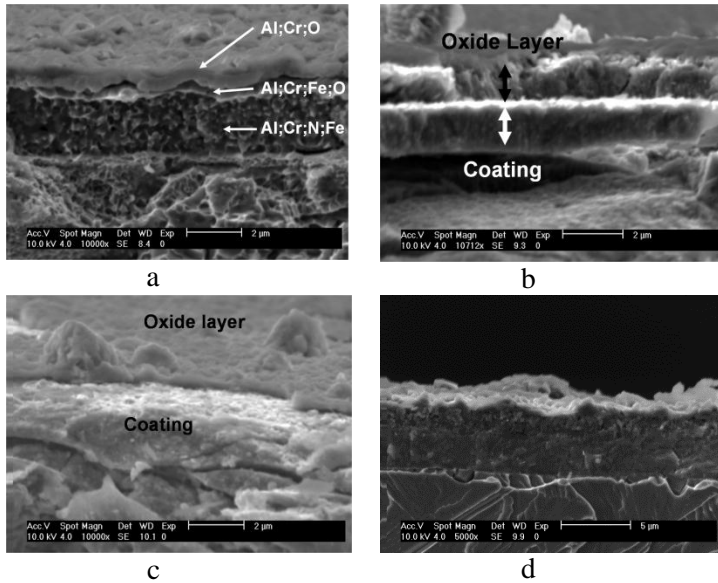


a)



b)

Fig. 5 XRD spectra of CrAlN (a) and CrAlSiN (b) films.

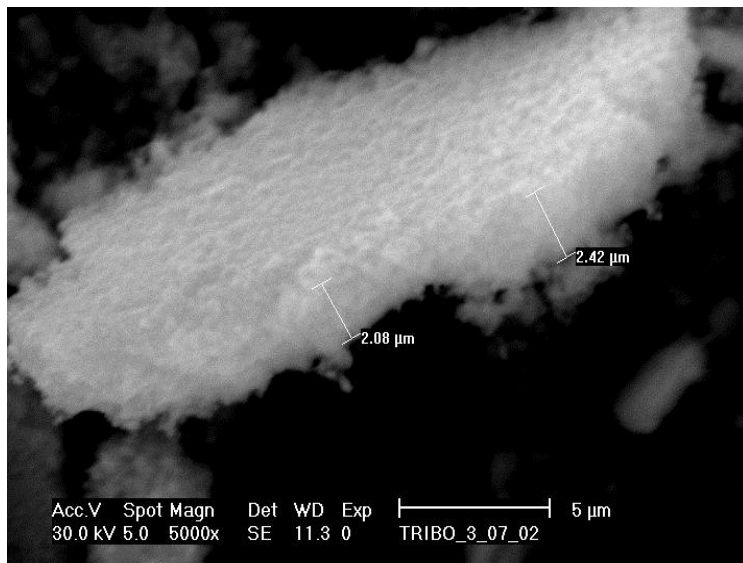


*Fig. 6 SEM images of coating cross-sections after annealing at 1300 °C; a) CrAlN, b) CrAlSiN, c) AlCrSiN, d) TiAlCrN*

Sliding tests were performed in temperature range 20-800 °C with alumina balls as counterpart. As expected, the wear of the films at room temperature was negligible. However, CrAlSiN coating was completely worn through at 400 °C. At 600 °C, all coating failed except for TiAlCrN. Such behaviour was very surprising, since all coatings should perform well at least up to 700 °C. To understand the failure mechanisms, we investigated the wear track by Raman spectroscopy, SEM/EDX, transmission electron microscopy, and 3D optical profilometry. Moreover, we collected and analysed wear debris. It was clear that the films delaminated from the WC



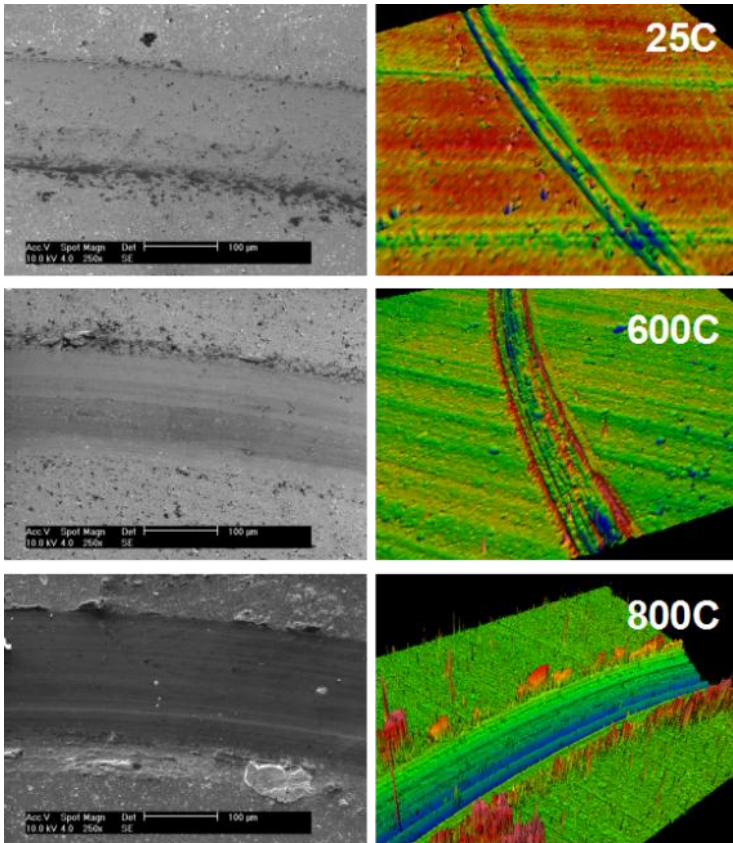
substrate, since the thickness of the wear debris particles was identical with that of coatings (Fig. 7).



*Fig. 7 Wear debris particle, CrAlN, sliding at 600 °C.*

Wear debris particles or the surface of the wear tracks were not oxidized; thus, the failure was exclusively caused by low adhesion, not oxidation. All properties of damaged coatings (i.e. measured after high temperature sliding tests), such as hardness, elastic modulus, and adhesion were similar to as-deposited ones. Thus, we concluded that the destruction of the films was caused by high-temperature adhesion failure. Such failure cannot be predicted by any standard method; it can be only observed experimentally.

The only coating surviving the sliding tests at 800 °C was TiAlCrN (Fig. 8), i.e. the film with the “worst” oxidation resistance. It further underlines the need for high tribology testing of protective thin films, since there is no effective method available to predict film wear resistance.



*Fig. 8 SEM micrographs (left) and 3D profiles (right) of the TiAlCrN coating wear tracks.*

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