Features of Tribooxidation of the High-Entropy Coating (AlCrZrTiTa)N during Dry High-Speed Cutting

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Abstract: The high-entropy PVD coating (AlCrZrTiTa)N, characterized by its high hardness (50–60 GPa), elastic modulus above 300 MPa, and high heat resistance up to 1300 °C, is used for coating cutting tools operating under extreme metalworking conditions. The nanostructured monolayer 3 µm PVD coating was deposited on cutting plates in the hybrid arc deposition PVD coater. The coating had an amorphous nanocrystalline microstructure with a grain size of about 10–50 nm. The samples of SS 304 steel were investigated during dry high-speed (600 m/min) cutting. Raman spectroscopy was used to study the formation of tribooxides on the tool surface at the running-in stage of the cutting. After 130 m of cutting, CrO2 oxide appears on the wear surface while other elements are bound with N atoms. When the cutting length is increased to up to 260 m, oxide Al2O3 · ZrO2 (mullite) and amorphous oxides Ta2O5 and CrO2 are formed. The method EELS made it possible to determine the amorphous nanocrystalline structure of triboceramics based on Cr2O3 and Al2O3 · ZrO2. The nearest atomic surrounding of Cr–Cr, O–O, and Cr–O and their subsequent comparison with the available literature data allow us to calculate the equilibrium lattice constants of the CrO2 unit cell, which are equal to (a, b) = 4.3754 Å and c = 0.5927. The triboceramic films on the base of non-equilibrium Mullite Al2O3 · ZrO2 have an amorphous structure. In the first coordination sphere, the interatomic distances of Zr–O and Al–O were 1.79 and 1.89 Å. An accelerated adaptive reaction to extreme external stimuli, at the very beginning of the running-in stage, is established. The tribological adaptability of the high-entropy ultra-fine amorphous nanocrystalline coating under extremely loaded dry high-speed cutting is based on non-equilibrium phenomena: the partial oxidation of fragments of the nitride and dynamic formation of protective tribooxides, which have a good thermal barrier and frictional properties. These factors interact synergistically and determine the life of the cutting tool.

Keywords: wear-resistant hard coatings; dry high-speed machining; high-entropy coating; Raman spectroscopy; Auger electron spectroscopy; Auger mapping

1. Introduction

A great attention to high-entropy single-phase alloys (HEA) is stipulated by expectations to achieve a profitable combination of mechanical properties [1]. Ideally, such alloys should be homogeneous and amorphous, containing more than five components with their content close to equiatomic one [2] because, in this case, the mixing entropy is the key factor for the phase and structure stabilities of this single-phase disordered alloy at high temperatures. A combination of well-soluble Al and Ti with refractory metals such...
as Nb, V, Ta, Zr, Mo, Hf, and W allows the fabrication of light high-strength thermal barrier alloys [3]. There are known about 300 compositions of HEA [4] with good thermal stability of the structure and properties [5]. Presently, the ideas about single-phase high-entropy materials (HEM) are expanded to the special group of HEMs possessing a multi-phase structure [6]. It is known that we can estimate grain boundaries in polycrystals as an additional phase significantly influences the properties of a material [7]. In this case, it is hard to say that the synergetic multi-component effect and the prevailing role of the entropy of mixing are the cornerstones in the formation of the unusual combination of physical–chemical characteristics of high-entropy films and coatings. On the other hand, multi-component carbides, nitrides, and oxides are classical representatives of high-entropy structures. According to this concept, the application of such single-phase compositions as functional coatings seems very promising; single-phase nitride coatings (TiZrHfNbTaYN) and (TiZrHfNbTa)N have a high hardness at 50–60 GPa and elastic modulus of more than 300 GPa; they are stable up to 1300 °C [8]. Such coatings could be applied as a protective thermal barrier [9,10]. Most papers related to HE nitride coatings aim at their wear resistance [11], particularly in the “ball-disk” tribological tests [12]. The superior physical–chemical properties of HE coatings made their application on cutting tools promising, especially those operating at the most severe conditions of high-speed dry cutting. Earlier, it was found that resistance to damage accumulation and tribooxidation in the initial stage of cutting were the main issues that determine the lifetime of wear-resistant coatings. Our previous research [13] demonstrated the role of protective tribooxides in adaptive multi-layer coatings on the cutting tool surface: they can inhibit damage of surface layers sharply by transforming thermal and frictional conditions on the “tool-chip” contact surface when the input energy is dissipated. The plastic deformation is localized in contact with nanovolumes of a tool and a processed metal. In this case, when the stress dissipation velocity is equal to the input velocity, the system comes into the quasi-stationary state.

Taking all these factors into account, it is very interesting to investigate the tribooxidation of the thermodynamically stable HE coating because the adaptability of this coating should be less than one in non-equilibrium multi-layer coatings featuring a high level of self-organization.

The friction control of cutting tools under surface-damaging conditions means the location of the majority of external interactions at the maximum dissipation of energy generated during friction is within a thin surface layer. The running-in stage of the tool is the most important since it determines its long-term wear resistance during cutting. As we have shown earlier, damage accumulates at this stage. This process, as well as the emerging tribooxides, contains dissipative structures that dissipate the friction energy supplied from the outside. It has been estimated that a significant part of the supplied energy is dissipated in the formation of tribooxides. In addition, dynamically emerging tribooxides radically change the thermal and frictional properties of the surface. We have shown that the nanolaminate structure of such tribooxides prevents the propagation of heat due to the fundamental physical limitations of the propagation of phonon and plasmon oscillations [14]. Many tribooxides have an extremely low coefficient of friction. Thus, conditions for self-organization are created in rationally engineered protective coatings. Adaptation and self-organization take place during friction, a wear with characteristics of surface and underlying layers significantly evolving during the running-in stage. Adaptive processes are the driving forces of evolution in the biological and social world. Non-equilibrium processes, like those present in the living world, constitute one of the main goals and objectives of a radical breakthrough in modern materials science [15]. Adaptation or self-organization of materials to external influences is a tempting goal when creating new materials.

In technology, this behavior is observed in tribosystems, where there is a dynamic regeneration of wear products as a result of tribochemical reactions on friction surfaces under the influence of the environment [16]. For instance, the high-speed dry cutting of
steel is a somewhat unique case of extreme friction conditions where an adaptive system can exhibit its full potential. Unfavorable combinations of high temperatures (1000–1200 °C) and heavy loads (3–5 GPa) develop on the friction surface of coated cutting tools. In such an open thermodynamic system, nanolaminate triboceramic films (secondary dissipative structures) dynamically appear on the friction surface. We have repeatedly demonstrated the protective role of such triboceramics in extending the service life of cutting tools with multilayer nanolaminate nitride coatings. However, this effect was observed only when the coatings had an extremely non-equilibrium chemical composition and nanostructure. Considering that alloys or nitrides of high entropy composition are currently declared promising coatings for cutting tools, a paradoxical question arises: can such thermodynamically stable materials exhibit adaptation properties? This work is devoted to the issue of the appearance of triboceramics on the surface of a high-entropy coating on a cutting tool.

The probability of implementation and the intensity of development of these processes at the initial stage of cutting are essential conditions for the appearance of stable wear. They predetermine the duration of the stage of steady wear. For these reasons, in this article, phase transformations at the initial stage of cutting have been studied in detail.

This paper aimed to study phase and structure transformations of HE PVD coating (AlCrZrTiTa)N during high-speed dry cutting stainless steel SS 304.

2. Materials and Methods

The high-entropy (AlCrZrTiTa)N coating was deposited on cemented carbide ball nose end of a Kennametal K313 mill in an R&D-type hybrid PVD coater (Kobe Steel Ltd., Kobe, Japan) using a plasma-enhanced arc source. WC-Co samples were heated up to about 500 °C and cleaned by Ar ion etching. Deposition parameters of the studied coatings were as follows: pure N₂ gas was fed to the chamber at pressure 4 Pa; current of arc sources –150 A; bias voltage –100 V; substrate rotation during deposition –5 rpm. The 3.0 micron thick coating had an amorphous nanocrystalline microstructure with a size of nanocrystals in the order of 10–50 nm with a cubic NaCl type non-ordered crystal structure.

Cutting tests were conducted during dry high-speed (600 m/min) cutting of SS 304 stainless steel with hardness of 129 HB. In this work, 8 cutting inserts were studied, for which the width of the wear hole was determined at various cutting times from 130 to 1200 m.

Phase composition of worn surfaces was studied by Raman Spectroscopy using optical microscope software EnSpectr v.2.6.0.3623. When recording Raman spectra, the device automatically determines the wavelength of laser radiation and the line half-width in the current climatic conditions and adjusts the intensity and energy scales of the recorded spectra.

Scanning Auger Mapping (SAM) was carried out on the electron spectrometer ESCALAB MK2 (VG Scientific, East Grinstead, UK) equipped with electron gun LEG200 (VG Scientific, East Grinstead, UK), recording emission of Auger electrons O KLL (505.4 eV), N KLL (380.6 eV), Ti LMM (419.4 eV), Cr LMM (526.0 eV), Al LMM (62.2 eV), Zr LMM (181.2 eV), and Ta MNN (1680.0 eV).

Calibration of an Auger electron spectrometer using ISO 17973:2016 [17] International Standard is performed using copper, gold, and silver as reference standard samples in order to measure the kinetic energies of selected Auger electron peaks. These reference materials are chosen as they provide one Auger electron peak in the high energy range, one in the middle range, and one at low energies. Standard spectrometer control operations made it possible to align the instrument. The samples were cleaned using Ar ions in the preparation chamber of the spectrometer at a pressure of 10⁻⁶ Pa, an accelerating voltage of 8 kV, and a current of 20 mA. The parameters of spectra acquisition were selected to provide high-energy resolution of the spectrum full width at half maximum (FWHM) at about 20 meV for high-resolution electron energy loss spectroscopy (HREELS) investi-
Auger electron microscopy (AEM) and electron microscopy were applied for imaging the distributions of the elements on the HEC coatings in wear area at a primary electron energy $E_0 = 1450$ eV. The resolution of the images was $256 \times 256$ pixels at 10,000 magnification. The topographic contrast was suppressed by image acquisition software.

The atomic structure of the tribofilms was investigated using Electron Energy Losses Fine structure (EELFS) analysis [18]. The fine structure of electron loss spectra in the 250 eV range near back-scattered peak ($E_0 = 1500$ eV) has been analyzed. The diameter of spot for investigated micro area was approximately 100 microns. The fine structure of the electron energy loss spectra contains information about the type of atoms, their nearest surrounding, and interatomic distances in the thinnest surface layers. The combination of several mathematical methods of computer processing of spectra makes it possible to determine the lengths of interatomic bonds [19]. Research equipment is shown in Figure 1.

![Research equipment](image)

**Figure 1.** Electron spectrometer ESCALAB MK2 (a) and optic microscope Olympus BX43 with EnSpectr R532 system (green laser, $\lambda = 532$ nm) (b).

### 3. Results and Discussion

The running-in stage of the wear, shown in Figure 2 for common nitride and the HE coating, is the actual stage of wear when self-organization starts and develops, resulting in a wear rate stabilization with transformation to the next stage of steady-state wear. Adhesive wear build-up of machining metal occurs on the cutting edge as a result of localized severe plastic deformation and high temperature. At the initial stage, the HE coating has undeniable advantages over AlTiN when coatings are exposed to the most noticeable external influences. At this stage, the accumulation of damages occurs in the coating, determining its subsequent behavior during operation. The emergence of protective secondary structures can reduce surface damage.
Figure 2. Running-in stage of the wear of AlTiN and HE coatings.

Such built-up evolves during the running-in phase of cutting stainless steel.

The optical image of a cutting insert is presented in Figure 3a. The oval marks the wear area. SEM images of the worn surfaces are presented in Figure 3b,c. There is a built-up material on the cutting edge, which indicates a strong adhesive feature of the stainless steel.

Figure 3. Optical image of cutting insert type DNMM-OR Sandvic Coromant (a), SEM images of the HE (AlCrZrTiTa)N coating after 130 m (b) and 260 m (c) cutting. The regions marked by the ovals correspond to the area of Raman spectroscopy and SAM studies.

The structure of the coating is partially worn. The length of the crater wear is 240 µm and 400 µm for 130 m and 260 m cutting, respectively.

The adhesion wear and the destruction of a build-up are critical points at the running-in stage. Usually, a pile-up zone is a nucleation point of multiscale destruction of cutting tools; the formation of a big enough build-up could lead to its break, together with part of the cutter body, as well as to its premature failure. In our case, the build-up covered less than 28 and 36% of the wear hole correspondingly for these two cutting stages. In other words, the build-up separation area for HEC is no more than 36% of the total contact area at this stage of wear. Tribooxides on the surface, in the wear zone, reduce the likelihood of adhesive wear of the coating at the steady cutting stage.

Raman spectra from areas marked by white ovals in Figure 3b,c are presented in Figure 4. Computer data processing of the vibrational spectra made it possible to identify the specific types of interatomic bonds forming during tribooxidation. Spectra interpretation was carried out by comparing known experimental and calculated data presented in [18,20–27]. At 130 m of cutting on the coating surface in the initial stage, the Cr-N interatomic bonds are oxidized. There is a Cr-O component with an energy of 383.1 cm⁻¹ at 130
The presence of a single Cr-O vibration peak, among other peaks characteristic of metal–nitride interatomic bonds, indicates that chromium oxides appear on the surface in the wear flank at this stage of cutting. The other components of the HEC nitride do not form oxide structures. This is also a very early stage for chromium triboxide formation.

![Figure 4. Raman spectra of crater wear after cutting length 130 m (a) and 260 m (b).](image)

One can see in Figure 4b that, after further cutting to 260 m, chromium, tantalum, and complex zirconium–aluminium triboceramics (Al2O3 × ZrO2, Mullite) appear. This oxide protects the surface of the HE coating from the accumulation of damage. It should be noted that Raman spectroscopy is intensively used in mineralogy and organic chemistry. It is rarely used in the study of friction and wear. However, the method of phase-structural analysis in conventional optical microscopy is very tempting. This is due to the extreme complexity of interpreting such vibrational spectra.

Fourier transforms (analogous to the radial distribution function [18]) are shown in Figure 5a,b. These Fourier images were obtained for two different locations in the wear hole after a cut length of 130 (running-in) and 260 m (wear after running-in), respectively. Each peak corresponds to the radius of the corresponding coordination sphere, which makes it possible to establish the distance between the nearest neighboring atoms of the environment. The interpretation of the Fourier transforms was based on standard crystallographic data of interatomic distances in a unit cell. Figure 5 shows the interatomic distances of 1–3 coordination spheres for the Cr2O3 [28] and Al2O3 × 2ZrO2 phases with the mullite structure [29]. The seven peaks in the Fourier transforms in Figure 5a correspond to the inter-atomic distances of Cr2O3, which crystallize in a tetragonal rutile-type structure with space group P42/mnm. The lattice parameters of the phase and their subsequent comparison with the available literature data allow us to calculate the equilibrium lattice constants of the Cr2O3 unit cell, which are equal to a = b = 4.3754 Å and c = 0.5927. Distinct and easily distinguished peaks are observed on the Fourier transforms up to distances in the order of 7 Å. This means near- and long-range orders in the atomic surroundings are observed in these thin oxide films. The Fourier transform in Figure 5b was calculated for the other area at the worn surface after a length of cut of 260 m. In this case, four peaks at 1.0–4.0 Å inter-atomic intervals were found. The first peak less than 1.0 Å is non-structural. The complex chemical composition of the tribofilms provides a large set of paired inter-atomic distances. The interatomic bonds with high concentration make the biggest input in the radial distribution function. The first structural intense peak is formed by Zr-O, Al-O, and O-O bonds in the mullite triboceramic film (Figure 5b). The triboceramic films on the base of non-equilibrium mullite Al2O3 · ZrO2 have an amorphous structure. In the first coordination sphere, the interatomic distances Zr-O and Al-O were 1.79 and 1.89 Å. The measured lengths of the nearest inter-atomic Al-O, O-O Zr-O, and Zr-Zr distances are
fully consistent with the standards for $\text{Al}_2\text{O}_3 \times 2\text{ZrO}_2$ amorphous structure. This region is outlined with an oval in the Fourier transform. This effect is due to a high concentration of defects in the tribofilms and their amorphization.

![Diagram of EELFS Fourier transformant of crater wear after cutting length 130 m (a) and 260 m (b).](image)

**Figure 5.** EELFS Fourier transformant of crater wear after cutting length 130 m (a) and 260 m (b).

Quite unusual features of the spatiotemporal behavior of the tribofilms can be observed under particular tribological conditions. SAM confirms the obtained results. Figure 6 demonstrates the AEM maps of elemental distribution for Al, Zr, O, N, Ta, and Cr. First of all, the Auger imaging shows that tribofilms are forming island-like patterns that indicate their dynamic nucleation, destruction, and re-appearing. Furthermore, mullite films ($\text{Al}_2\text{O}_3 \times 2\text{ZrO}_2$) do not overlap chromium oxide films. The standard intensity of the Ta MNN Auger line (cross-section of Auger transitions) is six times less than that for other nitride components. Although we see that it is in an oxidized state, it is difficult to say whether it forms its own oxide films.
Raman spectra and EELFS show that, at the running-in stage, the structural vibrational peaks correspond to interatomic distances in the oxidizing nitride phases at 130 m wear, or CrO$_2$ and mullite-like aluminum–zirconium oxide together with CrO$_2$ at 260 m wear. Despite their strong oxidation resistance of the high-entropy phases, tribooxide films form in conditions of high temperature and localize severe plastic deformation on (AlCrZrTiTa)N coating during dry high-speed cutting. At the early stage, in equilibrium, chromium tribooxide is forming, while mullite-like (Al$_2$O$_3$ · ZrO$_2$), TaO$_2$, and CrO$_2$ are formed at the later stage. A wear-resistant coating based on a thermodynamically stable high-entropy (AlCrZrTiTa)N nitride oxidizes under extreme tribological conditions to form nanocrystalline and amorphous triboceramics.

4. Conclusions

It was found that (AlCrZrTiTa)N ion plasma coating wears out through an adhesion mechanism at the running-in stage at high-speed dry cutting. The build-up area occupies 25 and 34% of the wear hole after cutting 130 m and 260 m, respectively.

A wear-resistant coating based on a thermodynamically stable high-entropy (AlCrZrTiTa)N nitride oxidizes under extreme tribological conditions to form nanocrystalline and amorphous triboceramics.

At the initial stage of the running-in process, we observe films on non-equilibrium oxide CrO$_2$, but later, a complex of tribooxides of mullite (Al$_2$O$_3$ · ZrO$_2$), TaO$_2$, and CrO$_2$ protects the coating from the accumulation of damage and its wear.

The method EELFS made it possible to determine the amorphous nanocrystalline structure of triboceramics based on CrO$_2$ and Al$_2$O$_3$ · ZrO$_2$. The nearest atomic surrounding of Cr-Cr, O-O, and Cr-O and their subsequent comparison with the available literature data allow us to calculate the equilibrium lattice constants of the CrO$_2$ unit cell, which are equal to $a = 4.3754$ Å and $c = a/0.5927$. The triboceramic films on the base of non-equilibrium mullite Al$_2$O$_3$ · ZrO$_2$ have an amorphous structure. In the first coordination sphere, the interatomic distances of Zr-O and Al-O were 1.79 and 1.89 Å.

The emergence of such triboceramics is a consequence of non-equilibrium phase transformations in the process of tribosystem self-organization under extreme external influences (high-speed dry cutting).
For the first time, the ability to self-organize a thermodynamically stable HEC coating on a cutting tool under extreme loads during high-speed dry cutting has been established. A paradoxical phenomenon of the realization of nonequilibrium phase transformations in a thermodynamically stable high-entropy nitride is observed.

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