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Advanced characterization methods for wear resistant hard coatings: A review on recent progress

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ABSTRACT

Due to economical demands to further increase the efficiency of production processes, it is essential to exploit the full potential of wear resistant hard coatings. This is, however, possible only if the coating microstructure and properties are well characterized. Thus, in the present work, recently suggested advanced characterization techniques for coatings are reviewed. The application of atom probe tomography, electron backscatter diffraction and synchrotron X-ray nanodiffraction enables previously unrevealed insights in their chemical composition, microstructure and crystallographic structure. For the determination of mechanical and tribological properties at elevated temperatures, high-temperature nanoindentation and high-temperature ball-on-disk tests in combination with *in-situ* measurement techniques are discussed. Utilization of micromechanical tests for coatings provides information about their fracture toughness and rupture strength. High-temperature X-ray diffraction and biaxial stress temperature measurements for the determination of the coefficient of thermal expansion are compared. The thermal conductivity as well as the specific heat capacity of coatings can be studied using the 3-ω technique, time domain thermoreflectance and differential scanning calorimetry. The introduced portfolio of characterization techniques enables the determination of a complementary microstructural, mechanical and thermo-physical fingerprint of wear resistant hard coatings, which allows to understand the complex structure–property relations in these materials and subsequently to further improve their performance.

Contents

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1. Introduction

Hard and wear resistant coatings are commonly deposited on tools which are used for severe cutting, forming and casting applications, where the conditions typically result in high temperatures, mechanical loads and pronounced wear [1–4]. Fig. 1a and b show scanning electron microscopy (SEM) images of a worn κ-Al_2O_3 coating, deposited by chemical vapor deposition (CVD), on a cemented carbide cutting insert at the end of its life time [5]. There, different effects which can be related to the severe operating conditions as well as to the high deposition temperatures can be observed. Distinct abrasive and diffusion wear is visible in Fig. 1a in the region where the highest temperatures during operation are present [6]. A focused ion beam (FIB) cross-section from the marked area at the edge of the wear crater was prepared for further investigations and is shown in more detail in Fig. 1b. Within the FIB cross-section, a thermal crack is visible which can be attributed to significant differences between the coefficient of thermal expansion (CTE) of coating and substrate material. The mismatch of the CTEs results in high tensile residual stresses for the common CVD hard coatings on cemented carbide substrates, which have typically a significantly lower CTE than the coatings. Consequently, cracks during cooling after deposition are formed [7–9]. These degradation effects occurring during coating deposition and application highlight the importance to gain not only knowledge on the microstructure of the used coatings to be able to tailor their design for the particular application, but also on a wide range of properties, including mechanical properties at elevated temperatures and thermo-physical properties. In the last decade, huge progress in advanced characterization techniques and methods available for coating characterization and testing has been achieved, which will be summarized within this review. Table 1 gives an overview of the methods reviewed within this work including advantages, requirements and limitations compared to conventional characterization techniques.

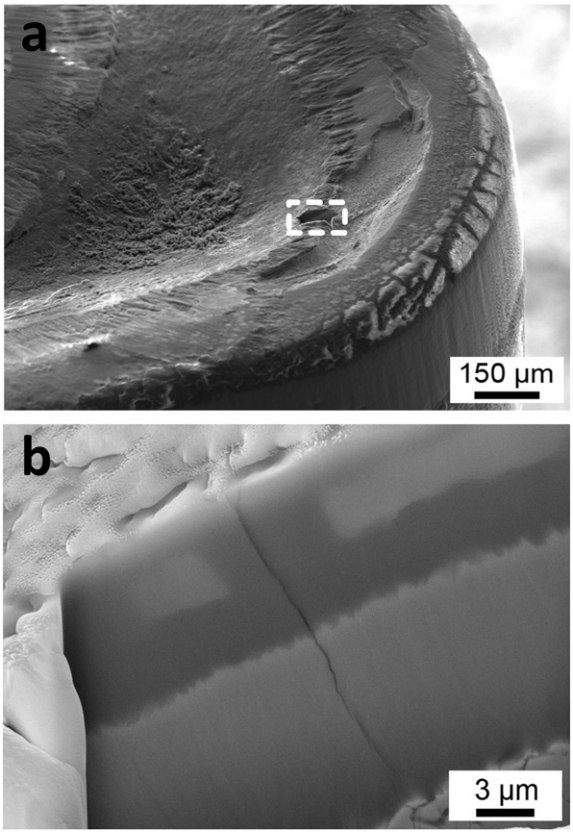

Fig. 1. (a) SEM micrograph of a worn CVD κ-Al_2O_3 coating exhibiting pronounced crater wear after cutting a 42CrMo4 quenched and tempered steel. A FIB cross-section was prepared in the marked area. (b) Detail of the FIB cross-section, exhibiting a thermal crack developed during cooling due to the different CTEs of coating and substrate [5].

2. Chemical composition and microstructure

2.1. Chemical composition on the atomic scale

Common analytical methods applied as a characterization tool in the development of hard coatings such as energy- or wavelength-dispersive X-ray spectroscopy provide a limited local resolution; the analyzed volume is typically in the range of 1 μm^3 or slightly less. On the other hand, glow discharge optical emission spectroscopy, Auger electron and X-ray photoelectron spectroscopy as well as secondary electron mass spectroscopy offer the possibility of depth-resolved measurements, but again with only limited lateral resolution. These limitations have recently been overcome with the implementation of atom probe tomography (APT), which offers the possibility of chemical analysis on the atomic scale. In the early 1950's Müller *et al.* [10] developed the field ion microscope (FIM), which enables the field ionization of noble gas atoms like He or Ne at a very sharp metal tip. The gas ions are subsequently accelerated towards a fluorescence screen where they are used for imaging and thus, represent the crystallographic arrangement of the atoms within the metal tip. The atom probe, introduced in the late 1970's represents a further improvement of the FIM, where the imaging ions originate directly from the sample tip [11]. With integration of time-of-flight mass spectrometry and position resolved channeling plate detectors, it is nowadays possible to determine the species and position of atoms or clusters within the sample on the atomic scale. The collected data allows to reconstruct the three-dimensional arrangement of the atoms within the sample; this method is referred to as three-dimensional atom probe tomography [12–16].

In order to evaporate ions from electrically conducting specimens by means of field evaporation, a high positive DC base-voltage of about 10 kV is applied to a sharp tip which is held at cryogenic temperatures, to prevent diffusion, under ultra-high vacuum (base pressure $< 10^{-8}$ Pa). The typical tip radius of less than 100 nm results in a high electric field of approximately 10–40 V/nm at the apex [13,14]. Voltage pulses which are 10–20% higher than the base-voltage with a frequency in the kHz range are applied to the tip, resulting in evaporation of the sample material [12]. In modern APT devices, instead of positively pulsing the sample tip, field evaporation is achieved by applying negative pulses on local counter electrodes situated next to the specimen, which is referred to as local electrode atom probe [17]. A further development is the laser-pulsed APT [18], which induces sample evaporation by utilization of short (< 1 ns) intense laser pulses and the subsequent temperature increase. Using laser assisted evaporation makes APT also suitable for investigations on electrically non-conducting samples [18,19]. Modern systems are operated with evaporation/analysis rates in the range of 10^8 ions/h, which corresponds to a volume of about 8×10^6 nm^3 (i.e. about 4.8×10^8 atoms) or a sample size of $100 \times 100 \times 1000$ nm^3 investigated within 1 h [15]. The atomic resolution of APT and the restriction to very small sample volumes make it interesting for coatings and thin films, which recently can be prepared with a small volume and site-specific by precise high-performance FIB workstations [20–22]. An example for FIB assisted preparation of an atom probe specimen cut out of a thin film sample is shown in Fig. 2a to c. After choosing an area of interest, two opposite wedges are cut into the sample in order to prepare a lamella (Fig. 2a), which is subsequently attached to a micromanipulator and cut free at both sides and the bottom. The lamella is then transferred (Fig. 2b) and attached to a pre-assembled sample holder (e.g. a Si tip) and detached from the micromanipulator. The final preparation step is annular FIB milling and polishing of the sample to sharpen the tip until the desired tip radius is reached (Fig. 2c).

Recently, topics related to the thermal stability of TiAlN based coatings [21,23–26], as well as fluctuations and distributions of the