Microstructure of nanocomposite carbon-, MoS$_2$- and MoO$_3$-based solid-lubricant coatings

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Abstract. Three types of coatings (Type 1: nc-TiC/a-C where, a-C means amorphous hydrogen-free carbon; Type 2: MoS$_2$(Ti,W); and Type 3: MoO$_3$ with Ag addition) were deposited by magnetron sputtering onto oxygen hardened Ti-6Al-4V titanium alloy and model $\gamma$-TiAl alloy substrates in order to improve their tribological properties. The paper describes the coatings micro/nanostructure characterized by scanning and transmission electron microscopy as well as X-ray diffractometry. The Type 1 coatings were composed of titanium carbides nanocrystals embedded in a-C matrix. The MoS$_2$(Ti,W) coatings (Type 2) consisted mainly of MoS$_2$ nanoclusters embedded in an amorphous matrix with some Ti $\alpha$ and W nanocrystals. The as-deposited MoO$_3$-Ag coating (Type 3) consisted of nanocrystalline Ag embedded in an amorphous matrix containing Mo and O. The coating’s microstructure was changed after annealing into a mixture of different silver molybdates, such as Ag$_2$MoO$_4$, Ag$_6$Mo$_2$O$_{13}$ and Ag$_2$Mo$_2$O$_7$. It was established that the applied coatings improved tribological properties of both substrates. Type 1 coatings are suitable for use at a temperature lower than 200 ºC, Type 2 ones at a temperature lower than 350 ºC, and Type 3 at an elevated temperature 450 ºC - 550 ºC.

1. Introduction

Nanocomposite coatings are novel, very important systems composed of two or more different nanocrystalline, or nanocrystalline and amorphous, phases [1, 2]. They are often used for improvement of tribological properties of metallic materials, decrease the coefficient of friction (CoF) and increase the wear resistance, under different operating conditions such as temperature and humidity. Thus, nanocomposite coatings enable to increase reliability, improve performance with less fuel consumption and reduce or eliminate greases as well as reduce environmental pollution.

Nanocomposite carbon-based coatings enable synthesis of numerous new materials with unique properties. Coatings contain a dispersion of nanocrystalline carbides in a solid low friction matrix, like hydrogen-free amorphous carbon a-C or hydrogenated amorphous carbon a-C:H, exhibit a reasonably high hardness as well as a relatively high wear resistance and low value of CoF against metallic and ceramic materials [1-3]. The performance of coatings is strongly influenced by their micro/nanostructure [2-6]. In the case of carbon-based coatings the amorphous matrix provides a low CoF, while nanocrystalline carbides increase the wear resistance of the coated materials [2-4].
Molybdenum disulphide (MoS₂) is often used as a coating material with excellent self-lubricating properties [7, 8]. These properties result from a layered structure of the hexagonal elementary cell of this sulphide, in which the axial ratio $c/a$ (where $c$ and $a$ are the parameters of the cell) amounts about 3.9. The bonding between the particular Mo and S atoms within the S-Mo-S layers of the crystal structure is strong covalent, while that between S-Mo-S layers is considerably weaker, van der Waals one [8]. These weak bondings are responsible for the low friction and good lubricating properties of the MoS₂-phase. The MoS₂-based coatings with admixture of other transition elements (such as Ti or Cr or W or Ta) exhibit higher hardness, better wear resistance, very low friction, high load bearing capacity, greater durability and oxidation resistance as well as lower sensitivity to water vapour than pure MoS₂ ones [8, 9]. Therefore, transition elements are often used as admixture to MoS₂-based coatings.

Oxides and their combinations are very interesting materials for lubrication at elevated temperature due to their high chemical stability [10]. However, the adhesion of pure oxides to the metallic substrate is poor due to their high brittleness. Therefore, in our work the Ag admixture was incorporated to the MoO₃-based coating.

The micro/nanostructure of the low-friction coatings, i.e., their chemical- and phase composition as well as the crystallite size, is very important because it influences tribological and micro-mechanical properties of the coatings and, as a result, the tribological and micro-mechanical properties of the system coating/substrate. The aim of the present study was to characterize the nano/microstructure of three types of relatively thick low-friction coatings: Type 1 - nc-TiC/a-C, Type 2 - MoS₂(Ti,W), and Type 3 - MoO₃ with Ag addition deposited on metallic substrates by magnetron sputtering.

2. Materials and methods

The Type 1 and Type 2 coatings were deposited on two-phase ($\alpha + \beta$) titanium alloy Ti-6Al-4V, while Type 3 coating was deposited on model $\gamma$-TiAl alloy. In addition, prior to the coatings deposition, the surface of the specimens made of Ti-6Al-4V alloy was hardened with interstitial oxygen atoms as a result of the diffusion process at 900 °C in the Ar+O₂ atmosphere in the presence of the glow discharge plasma. A detailed description of the microstructure of the oxygen hardened Ti-6Al-4V alloy was given in Ref. [11].

In order to increase the adhesion of the coating to the substrate at first a thin intermediate layer was deposited onto the substrate materials by magnetron sputtering. This intermediate layer was composed of Ti and C atoms in case of Type 1 coatings, of metallic Ti$_\alpha$-phase in case of Type 2 ones and of Ag in case of Type 3 one. In the next step, the proper nanocomposite coating was deposited by magnetron sputtering as well. The MoO₃-Ag coated alloy was additionally annealed at 450 °C during 3 hours. A detailed description of the coatings deposition procedure was given in Refs. [11-15].

The investigations of the coatings nano/microstructure were carried out by scanning and transmission electron microscopy (SEM, TEM), as well as by X-ray diffractometry (XRD) and grazing incidence X-ray diffractometry (GIXRD). The SEM investigation was performed by NEON® 40EsB of Zeiss. TEM and HRTEM investigation was carried out by JEOL JEM-2010 ARP (200 kV), ARM 1250 (1250 kV), and Titan Cubed G2 60-300 (300 kV) FEI microscopes on cross-section lamellas. The lamellas were prepared by focussed ion beam (FIB) NEON CrossBeam 40EsB of Zeiss followed by a short ion-beam thinning using precision ion polishing system (PIPS) of Gatan. The XRD and GIXRD patterns were recorded using Siemens D500 Kristalloflex diffractometer with use of Cu Kα radiation on plane-view specimens.

Phase identification was performed by means of selected area electron diffraction (SAED) and fast Fourier transformation (FFT) as well as XRD and GIXRD techniques. The SAED and FFT patterns were interpreted with the help of a Java electron microscopy software (JEMS) [16]. The phase identification was supplemented by chemical microanalyses with use of energy-dispersive X-ray spectroscopy (STEM-EDS). The STEM images of a size of 512x512 pixels were acquired utilizing approx. 3 nm probe. Image analyses were performed using ‘digital micrograph’ software of Gatan.
The particles’ size and spatial distribution were determined based on several different HRTEM micrographs supported by ‘AnalySIS 3.1’ and ‘digital micrograph’ software.

3. Results and discussion

3.1. nc-TiC/a-C coating

SEM and TEM investigation revealed that the coating was dense and had an uniform thickness of 3.3 ± 0.2 µm (figure 1). Due to a high volume fraction of the amorphous carbon, the electron diffraction patterns taken from the coating were diffused and difficult for unequivocal interpretation. However, the rings corresponding to \{200\} and \{220\} TiC (face-centred cubic; fcc) crystallographic planes might be distinguished and are visible on diffraction pattern intensity profile (figure 1, diffraction pattern no A, right up corner).

![Figure 1. Microstructure of the nc-TiC/a-C coating on oxygen hardened Ti-6Al-4V alloy as well as SAED pattern taken from the area marked as A in the figure. An intensity profile along a line marked on the SAED pattern A is given as well. B) Magnified details of the intermediate layer; TEM-FIB lamella.](image)

Identification of the carbides occurring in the coatings was performed by means of the XRD (GIXRD) as well as of the HRTEM techniques. Based on the XRD and GIXRD pattern analyses, nanocrystallities of two phases, TiC (fcc) and TiC\textsubscript{0.62} (fcc), were identified in the coating. The size and spatial distribution of the carbide nanocrystallites within the coating were estimated using HRTEM. It was found that the coating is composed of the nanocrystallites (equivalent circle diameter, ECD = 5 ± 4 nm) embedded in an amorphous carbon matrix (figure 2). The calculated diffraction patterns were obtained by performing FFT. Based on the FFT images, the particles present in the coating were identified as the nanocrystallites of the TiC (fcc) phase. As an example, a FFT image taken from the coating area containing several TiC particles, marked as a square is shown in figure 2. The titanium carbide nanocrystals were separated by an amorphous carbon matrix. The nanocrystallities were uniformly distributed within the coating.

In order to increase the coating adhesion to the underlying substrate a 200 ± 10 nm thick intermediate layer was deposited between the coating and the alloy (figures 1 and 3). Analyses of the electron diffraction patterns and FFT patterns (figure 3) taken from the intermediate layer revealed the occurrence of Ti \(\alpha\) (hexagonal close-packed; hcp) and TiC\textsubscript{0.62} (fcc) phases. ECD of nanocrystallites,
evaluated from dark-field TEM and HRTEM images, was estimated in the range 10 ± 1 nm to 70 ± 1 nm. The Ti α and TiC_{0.62} (fcc) nanocrystals were found in the coating/intermediate layer interface as well.

Figure 3. HRTEM micrograph of the intermediate layer between the nc-TiC/a-C coating and the oxygen hardened Ti-6Al-4V alloy and a corresponding FFT pattern calculated from the square area marked with the broken line in the micrograph and its identification; FIB lamella.

3.2. Microstructure of MoS2(Ti,W) coating
The coating thickness evaluated from SEM and TEM images equals 3.1 ± 0.2 µm (figure 4). SEM-EDS microanalysis revealed the following mean chemical composition of the coating (in at%): 27 ± 1 Mo, 56 ± 1.2 S, 15.6 ± 0.5 Ti, and 1.4 ± 0.2 W.
Analysis of the coating microstructure was performed using TEM by electron diffraction, STEM-EDS and HRTEM methods. The electron diffraction patterns and the FFT ones obtained from the coating were diffuse. Nevertheless, a strong incomplete \{002\} diffraction ring as well as two weaker ones \{100\} and \{103\} ones belong to the MoS$_2$-phase are clearly visible, as shown in figure 5 (FFT pattern calculated from figure 5a).

The HRTEM investigation revealed the occurrence of fine nanoclusters of ECD equalling 6 ± 3 nm (marked as ovals in figure 5a) embedded in an amorphous matrix (figure 5a). The HRTEM images show numerous short black lines with interplanar spacing close to \{002\} planes of MoS$_2$-phase. The planes of the nanoclusters were in general differently oriented to the surface of the coating. Nevertheless, in the area near to the coatings surface, the \{002\} planes were approx. parallel to the coating surface. Such orientation of nanoclusters with \{002\} planes parallel to the substrate surface is conductive to favourable tribological properties of these coatings.
Sporadically, inhomogeneously distributed nanocrystallities of the ECD equalling 7 ± 3 nm were observed in the coating as well. The interplanar spacings measured for particular nanocrystallities and analyses of the FFT patterns calculated from the nanocrystals revealed presence of Ti α (hcp) and W (body-centred cubic; bcc) phases. Typical FFT pattern calculated from the coating area marked as a square and indexed as Tiα and W is shown in figure 5b.

An intermediate titanium layer, 30 ± 5 nm thick, was deposited in order to increase the coating adhesion to the substrate. The layer was well adhering to the surface of the hardened titanium alloy substrate. Analysis of the SAED- and FFT-patterns confirmed that the intermediate layer was composed of Tiα (hcp) nanocrystallities. Nevertheless, an amorphous phase containing Mo and S was also found in the areas of the interlayer close to the coating.

3.3. Microstructure of MoO₃-Ag coating

The coating thickness was measured from TEM images as 1.9 ± 0.1 μm (figure 6). The as-deposited coating was dense; however, the adhesion of the coating to the underlying substrate was relatively poor.

Characterisation of the coating microstructure was performed by TEM with use of electron diffraction and EDS chemical microanalysis methods. It was found that the as deposited coating microstructure consisted of Ag (fcc) nanocrystallities (figure 6, SAED pattern marked as B) embedded in an amorphous matrix (a diffuse ring characteristic of an amorphous phase occurs in the SAED pattern). ECD of the Ag nanocrystallities was estimated from dark-field TEM images as up to 10 ± 1 nm.

A graded intermediate layer (250 ± 20 nm thick) was present between the coating and the substrate alloy (figure 7). This layer was composed mainly of Ag nanocrystallities of ECD up to 30 ± 1 nm. In addition, a diffuse ring was found in the SAED pattern taken from the intermediate layer (SAED pattern marked as 1 in figure 7). It proves that an amorphous phase occurs in the interlayer after deposition as well.
STEM-EDS line analysis and chemical element distribution maps confirmed a presence of Mo, O and Ag in the coating as well as Ag (mainly) and Mo and O (sporadically) in the intermediate layer. The XRD and GIXRD investigation revealed also a presence of crystalline Ag and amorphous phase in the coating.

The coated specimen was next annealed at 450 °C in order to produce silver molybdates, which are characteristic of a layered graphite-like structure conductive to favourable tribological properties at elevated temperature. The coating microstructure was significantly changed after annealing. XRD investigation revealed a presence of Ag$_2$MoO$_4$ (fcc), Ag$_2$Mo$_3$O$_7$ (monoclinic primitive; mp), and Ag$_6$Mo$_{10}$O$_{33}$ (mp) phases in the coating. The TEM investigation was performed for wear track after ball-on-disc tribotest conducted at 450 °C for 20000 rotations against Al$_2$O$_3$ ball (1 mm diameter under load of 1 N) on FIB lamella cut from an appropriate coating area. It was found that 820 ± 10 nm thick coating was not destroyed. Mainly Ag$_2$MoO$_4$ (fcc) grains were present in the Ag$_6$Mo$_{10}$O$_{33}$ (mp) matrix of the investigated area of the coating (figure 8). The grain size of Ag$_2$MoO$_4$ was measured as in the range from several nm to 250 ± 5 nm.
3.4. Tribological properties

Tribological properties of coated materials were described in detail in our earlier studies [11-15]. The results showed that all investigated nanocomposite coatings improved tribological properties, decreased coefficient of friction (CoF) and increased wear resistance of surface treated materials.

Very low value 0.05 ± 0.01 of the CoF of the nc-TiC/a-C coatings deposited on oxygen hardened Ti-6Al-4V alloy during dry sliding against 5 mm alumina ball at RT was measured in the ball-on-disk tests, in contrast of 0.5 ± 0.1 and 0.85 ± 0.15 values for the annealed and oxygen hardened Ti-6Al-4V alloy, respectively [13]. This low value of CoF is attributed to formation of a self-lubricating film in the sliding contact.

The MoS2(Ti,W) coating decreased the CoF from 0.85 ± 0.15 for the oxygen hardened Ti-6Al-4V alloy to 0.15 ± 0.02 (at RT) and to 0.09 ± 0.01 (at 300 °C) for the coated one and increased essentially the wear resistance of the alloy [14].

The MoO3-Ag coating decreased the CoF of the γ-TiAl alloy at elevated temperature of 450 °C and 550 °C from 0.6 ± 0.2 to about 0.2 ± 0.07. The wear resistance of the coated alloy was not satisfactory, both at RT and at elevated temperature [15].

4. Summary

Micro/nanostructure of the low-friction solid-lubricant coatings was examined in detail by various electron microscopy and X-ray diffractometry techniques. It was found that 3.3 ± 0.2 µm thick nc-TiC/a-C coating was composed of TiC nanocrystallities of a size of few nanometres embedded in an amorphous carbon matrix. A 200 ± 10 nm thick graded interlayer consisting of a mixture of Tiα (hcp) and TiC0.62 (fcc) nanocrystallities was present between the coating and the oxygen hardened alloy substrate.

The MoS2(Ti,W) coating (3.1 ± 0.2 µm thick) was dense and of a good quality. A well adhering, intermediate layer composed of Tiα nanocrystallities and some amorphous phase containing Mo and S was present between the coating and the hardened titanium alloy substrate. The MoS2(Ti,W) coating was composed of MoS2 nanoclusters embedded in an amorphous matrix. Some Ti α and W nanocrystals were also found in the coatings’ microstructure.

The MoO3-Ag coating (1.9 ± 0.1 µm thick) was dense. The as-deposited coating microstructure consisted of nanocrystalline Ag particles embedded in an amorphous matrix containing O and Mo. A gradient intermediate layer (250 ± 20 nm thick) was present between the coating and the substrate. This layer was composed mainly of Ag nanocrystallities and some amorphous phase containing O and Mo. The content of the amorphous phase increased gradually with the distance from the substrate. The coating microstructure changed after annealing. Different silver molybdates, Ag2MoO4, Ag6Mo10O33, and Ag2Mo2O7 were formed in the coating.

It was established that the applied coatings essentially improved tribological properties of the substrate materials used in the experiments. Type 1 coatings are suitable for tribological contact in the temperature range from RT to 200 °C, Type 2 coatings for temperature not exceeding 350 °C, and Type 3 ones for application at elevated temperature 450 - 550 °C.

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