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Properties of nanocomposite film combining hard TiN matrix with embedded fullerene-like WS_2 nanoclusters

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ABSTRACT

We have developed hard self-lubricant coatings combining a hard matrix (TiN) and a self-lubricant phase in the form of inorganic-like WS_2 fullerene. The nanoparticles were injected from the preparation chamber directly to the sample surface during reactive sputtering from a Ti target in Ar/N_2 atmosphere. The injection of the particles led to the local oxidation of the matrix due to the flow of residual oxygen from the preparation chamber; therefore, the final composite was TiN/Ti–O–WS_2. The observation of the composite film by scanning and transmission electron microscopies showed the incorporation of the WS_2 nanoparticles; however, their bonding with the matrix was weak. The analysis of the wear tracks did not show any presence of WS_2 in the contact.

1. Introduction

The production of nanocomposite tribological coatings consisting of a hard matrix containing self lubricant Inorganic Fullerene-Like Nanoparticles (IFLN) [1], for instance IF-WS_2 nanoclusters, could allow the independent control of tribological properties usually known as antagonists: low friction and high wear resistance. This is a radical innovation in the lubrication and wear protection concepts, rather than an incremental advance in either reducing wear or improving friction behaviour.

TiN is widely used as hard coating due to its high hardness (greater than 20 GPa), good wear resistance, suitable chemical stability and good thermal and electrical conductivities [2–4]. However, TiN shows relatively high friction coefficient [5]. IF-WS_2 clusters (close caged onion like) can be produced in large scale by chemical reactions consisting of the sulfidation in a reducing atmosphere at high temperatures of solid and vapour phase precursors based on W [6]. Such nanoparticles exhibit unique electronic, mechanical (anti shock materials up to 30 GPa), and tribological (low friction coefficient ~0.06) properties [7–10].

Among several nanocomposite processing techniques existing [11–13], nanocomposite deposition system (NCDS) has been recently developed in our laboratory by combining a nanocluster gun and a dc magnetron reactive sputtering equipment, used for injecting preformed IF-WS_2 nanoclusters and depositing the TiN matrix, respectively [14]. By controlling the incorporation of the IF-WS_2 nanoclusters in the TiN matrix, the tribological performance can be tailored since the IF-WS_2 nanoclusters will determine the frictional behaviour due to their superior solid lubrication ability [15,16] by either easily roll or slide when a shear force is applied. Thus, in the TiN–WS_2 nanocomposite coating the matrix composed by TiN will confer a high wear resistance whilst the incorporated IF-WS_2 nanoclusters assure low friction properties.

The references in the literature on the use of pre-formed clusters for the production of nanocomposite coatings are very limited. Preliminary studies on the crystal structure, surface morphology and chemical composition of TiN–WS_2 nanocomposite coating were presented recently by the present authors [17]. Piazzoni et al. [18] also deposited TiN–MoS_2 nanocomposite coatings by connecting a cluster source, consisting of a pulsed supersonic beam of MoS_2 clusters, to an industrial cathodic arc reactive evaporation chamber. Finally, Chen et al. [19] used the electroless deposition technique and produced Ni–P–(IF-WS_2) composite coatings exhibiting better tribological performance than Ni–P–(2H-WS_2) and Ni–P graphite coatings deposited by the same technique.

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In this paper, the structure, microstructure, chemical composition, mechanical and tribological properties of TiN–(IF-WS_2) nanocomposite coatings produced by an NCDS system are presented and discussed. The final aim is to demonstrate the potentiality of these coatings to control and reduce the friction and wear in rolling and sliding contacts for applications in the areas of aerospace, automotive, energy and manufacturing engineering sectors.

2. Experimental techniques

The prototype NCDS system involving a dc magnetron sputtering equipment and the nanocluster gun was described in detail in previous papers [14,17]. The dc magnetron sputtering chamber has a pair of titanium targets (200mm × 100mm), placed directly opposite to each other, and a substrates holder positioned parallel to the symmetrical centre line of the two targets. The deposition chamber is pumped down to pressure lower than 10^{-4} Pa prior deposition. The clusters gun consists mainly of two parts: (a) the cylindrical chamber and (b) the electromagnetic injector. A normal fuel injector (purchased from Bosch) was connected to the extreme side of the tube connecting the nanoclusters gun with the deposition chamber. The injector is normally closed and it opens to inject the pressurised gas when an electrical signal is applied to its solenoid coil. The injector has a disc-type outlet with four holes with diameter of about 150 mm (in total, 600 mm for the four holes). The frequency, the duration of the cycle and the repetition time can be varied through a dc pulse square wave generator. The IF-WS2 nanospheres were synthesised employing WO_3 as precursors by a solid gas reaction [6,7]. Prior to injections, the IF-WS_2 nanospheres are kept inside the clusters chamber under different pressure (200 mbar–2 bar) of argon gas. Three case fans are used inside the clusters chamber in order to facilitate the dispersion of the IFLMs inside the clusters gun and to direct the flow close to the inlet of the injector.

A Ti interlayer (approximately 100 nm thickness) was deposited between the nanocomposite and the substrate in order to improve its adhesion. The working pressure (Ar + N2) was kept at approximately 0.3 Pa; the substrate was not heated.

To confirm the formation of the nanocomposite material and its tribological properties, the following characterization techniques were used: field emission scanning electron microscopy (SEM; JEOL JSM 6700F, operating voltage 15 kV) for the superficial and cross section morphological analysis, X-ray diffraction (XRD, Philips diffractometer with Co-Kα radiation in Bragg–Brentano configuration) for the structure and energy dispersive X-ray spectrometry (EDS) for the chemical composition, transmission electron microscopy (TEM; Philips CM-20 microscope using a 200 kV accelerating voltage) for the analysis of the as-deposited coating. Focused ion beam (FIB) was used to cut a slice through the sample surface, which was then observed and analyzed by high resolution SEM (Zeiss NVision 40 CrossBeam, 30 kV Ga ion source). The chemical bonding was studied by Raman spectrometer (Xplora, Horiba Yvon); the analyses were performed before and after pin-on-disc tests. The nanohardness was evaluated from nanoindentation tests (MicroMaterials) with an applied load of about 5 mN. The tribological tests were carried out using a ball-on-disc tribometer at room temperature (CSM Instruments). This device allowed measurements of the friction coefficient continuously during the sliding test. The counterpart used in this measurement was a 100Cr6 steel ball with 6 mm diameter. The tests were carried out with a load of 5 N and a sliding speed of 5 cm s^{-1} in air with humidity of 35%.

3. Results and discussion

3.1. Fundamental coating characterization

The coatings exhibited different colours and surface roughness. The film at the centre of the substrate, where the flow of injected particles was the highest, showed a grey colour and visible surface roughness, while the rest of the coating shows mirror-like appearance with gold colour typical of stoichiometric TiN film. X-Ray diffraction (Fig. 1) revealed the formation of a mixture of TiN (PCPDF card 38-1420) and Ti–O phases (Ti_2O_3, PCPDF 71-1057 and possible existence of rutile and anatase phases in agreement to PCPDF cards 87-0920, and 84-1286, respectively). Besides these reflections, a relatively strong peak was observed at ~16.5º (in 2θ) corresponding to the (002) plane of the hexagonal WS_2 phase demonstrating the incorporation of the IF-WS_2 nanoclusters in TiN/Ti–O matrix. The SEM images permit to observe the presence of very small particles with sizes ranging from 50 up to 150 nm (Fig. 2) undoubtedly identified by EDS analysis as the IF-WS_2 nanoclusters (Fig. 2 inset). The surface coverage by IF-WS_2 nanoclusters was estimated to be about 5% which was considered as sufficient to enhance the tribological properties of the coatings. In fact, with similar amounts, Piazonni et al. [16] showed significant improvement of the tribological behaviour of TiN–(IF-MoS_2) nanocomposite coating.

A closer analysis of the EDS spectrum allows detecting a very intense peak of O, particularly compared to that corresponding to the N position even when the overlapping with the L-line of Ti is considered. It suggests that the matrix in the zone containing the WS_2 clusters has high O contents justifying the detection of the Ti–O phases by XRD, as well as the dark colour observed in the central zone compared to the typical stoichiometric TiN gold colour in the borders of the sample. Indeed, EDS analysis performed in the gold zones shows only a small O peak. Thus, it can be concluded that the nanocomposite part of the matrix is predominantly Ti–O with TiN as a minor phase.

The difference in the phases in the centre compared with the border of the sample is a consequence of the deposition process leading to locally different deposition conditions in referred zones. In fact, the pressure of working gas is established inside the chamber by the flux of Ar coming from the clusters gun. This is the only Ar admission, which, in addition to the N flux injected through the bottom of the chamber, determines the final deposition pressure. The Ar + clusters flux is injected through a thin tube oriented perpendicular to the substrate; the nozzle–substrate distance is 20 mm. Even if very pure Ar is used for filling in and mixing the WS_2 clusters in the gun chamber (after evacuating it down to 10^{-2} Pa), there is always residual O_2 contamination in the atmosphere. The partial pressure of injected O_2 is relatively small considering either the nitrogen flow or the chamber volume and, under normal condition, it would not significantly influence the final chemical composition of the TiN matrix. However, as the injection flux hits the sample surface directly, oxygen atoms immediately react with the sputtered Ti atoms. It should be pointed out that the deposition rate is kept very low

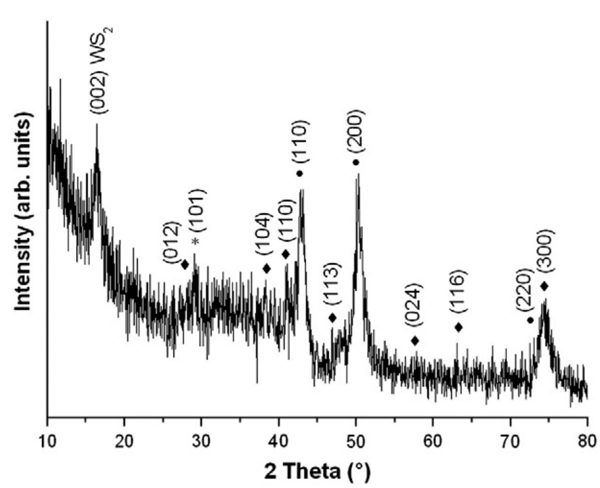

Fig. 1. XRD pattern of nanocomposite coating. Symbols correspond to TiN (●), Ti_2O_3 (◆) and anatase (*). The peak at ~16° 2θ belongs to WS_2.