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# Tribofilm formation and tribological properties of TiC and nanocomposite TiAlC coatings

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## ABSTRACT

In a recent work a concept for self lubricating low friction TiC and nanocomposite TiAlC coatings was developed. Here we further investigate the mechanical and tribological properties of these coatings. Under identical deposition conditions, the addition of Al initiates the formation of a nanocomposite consisting of (Ti,Al)C grains in an amorphous carbon matrix. The coefficient of friction is lowered from ~0.2 to below 0.1 in a pin-on-disc test against steel with unaffected coating wear rate. The lower friction is attributed to a more extensive formation of amorphous carbon and graphitisation on both the counter surface and in the coating wear track. The addition of Al also reduces coating hardness, Young's modulus and the residual stress, which can be explained by the weak carbide-forming ability of Al and the formation of a nanocomposite microstructure.

## 1. Introduction

The design and development of low-friction coatings are of continuously increased importance in materials science. So-called self-adaptive coatings, which change their surface composition and structure as a response to changes in the tribological contact situation or the surrounding environment, have caught a lot of attention lately. Examples of such coatings are the WC/DLC/$WS_2$ and the $MoS_2$/graphite/$Sb_2O_3$ [1–3]. The first design concept utilises a matrix of amorphous DLC with low friction properties in ambient environment. In this atmosphere the low friction is obtained by graphitisation of the DLC phase, while the $WS_2$ phase is responsible for the low friction properties in vacuum or dry atmosphere. The latter design concept utilises a hard TiCN coating with a laser textured surface for creating lubricant reservoirs filled with $MoS_2$/graphite/$Sb_2O_3$ powder. The $MoS_2$ and graphite provide low friction in dry and ambient environments, respectively, in a similar way as described for the first design concept. The above-mentioned coatings have in common the low friction attributed to easily sheared basal planes at the surface being either $MoS_2$, $WS_2$ or graphite depending on the environment. In ambient environment the low friction properties are attributed to the carbon $sp^3$ to $sp^2$ structural phase transformation, i.e. formation of easily sheared graphitic carbon made possible by the presence of humidity as explained by Savage's early experiments [4]. In other words, coatings designed to form surface layers of graphite in a tribological contact are good candidates for low friction materials. One such group of coatings is the nanocomposites of a nanocrystalline metal carbide (nc-MeC) in an amorphous carbon matrix. For example, sputtered nc-TiC/a-C coatings are known to exhibit good tribological properties and fairly low friction coefficients of 0.1–0.2 see, e.g., refs. [5–7]. Furthermore, Nilsson et al. have also demonstrated that carbon coatings alloyed with Ta, W and Zr can exhibit very low friction coefficients [8]. In all these coatings it is most likely that surface graphitisation is an important part in the low friction behaviour.

Recently, we introduced a new design concept for low friction coatings [9]. The concept is based on the idea to synthesise a nanocomposite nc-TiC/a-C coating with a solid solution of a weak carbide-forming metal such as Al. By co-sputtering at low temperatures, Al can be dissolved into the TiC matrix above the limit of solid solubility. This creates a situation where it is more favourable for the carbon in the carbide to form graphite than to stay in the carbide. This increases the driving force for graphite formation, which has been both theoretically predicted by DFT-calculations and experimentally verified by X-ray photoelectron spectroscopy (XPS) [9]. Thus, we should expect a situation where such coatings spontaneously form additional graphite, which favours a reduced friction, when exposed to high temperatures or as a response to external pressure. Preliminary tribological evaluation verified this design concept and the initial idea [9]. In that work the nc-(TiAl)C/a-C coating was shown to have a low friction coefficient below 0.1 in ball on disc test against steel. The low friction was attributed to the

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formation of a tribolayer containing graphitic carbon. In contrast, a TiC coating, without any aluminium, showed a higher friction coefficient of ~0.2–0.3. Hence a carbide coating modified to have a matrix phase of a-C does not automatically guarantee a low friction. Moreover, simply adding a-C to a carbide coating degrades the mechanical properties, while adding Al largely retains the mechanical properties and generates graphitic carbon locally at the surface and only when exposed to tribological stress [9].

Although we have demonstrated that alloying a metal carbide with a weak carbide forming element can reduce the friction, the influence of such an alloying on mechanical properties and wear properties have not yet been studied in detail. Also the formation of the tribolayer in the wear tracks and its properties remain to be studied. The aim of this work is to evaluate these aspects as Al is added to nc-TiC/a-C coatings. Due to the extent of the coating analyses, the counter surfaces are intentionally left out of this part of the work. Counter surface tribofilms are present and thorough analyses of these are to be published separately [10].

## 2. Experimental

### 2.1. Synthesis of the coatings

The coatings denoted TiC and TiAlC were synthesised in a Balzers BAI640R PVD coating system utilising simultaneous magnetron sputtering of elemental C and Ti of 99.995% and 99.995% purity, respectively. When depositing the TiAlC coating the Ti-target was partially covered with Al-foil of 99.0% purity, a method earlier described in ref. [11]. The TiC and TiAlC coatings were deposited on powder metallurgical high speed steel substrates with a Rockwell C hardness of about 66–69 HRC. The substrates were manually polished to an initial surface roughness of Ra ~5 nm. The substrates were ultrasonically degreased for 5 min each in an alkali solution (UPON) heated to ~60 °C and thereafter cleaned in ethanol. Any remaining surface contaminants were removed by substrate pre-heating to the process temperature of ~250 °C followed by an Ar-etch in the deposition chamber. For increased coating adhesion e-beam evaporation of a ~100 nm thick Ti-interlayer initiated the deposition process followed by the simultaneous sputtering of the elemental C- and Ti-targets. To ensure a homogeneous composition the substrates were rotated over the planar targets with the surface to be coated facing downwards. The base pressure was $2.0 \times 10^{-5}$ mbar and during the deposition process the Ar-pressure was $3.0 \times 10^{-3}$ mbar. A substrate bias of −100 V was applied and an arc-current of 170 A was utilised for substrate heating and for enhanced ionisation of the Ar-gas. The final thickness of the TiC and TiAlC coating was ~850 nm and ~1350 nm, respectively.

### 2.2. Analysis and characterisation of the coatings

The phase compositions of the coatings were analysed using a Philips X'Pert X-ray diffractometer (XRD) with a Cu Kα X-ray source at a grazing incidence (GI) of 0.5° in the interval $30° < 2\theta < 90°$. The GI setup used a Goebbels mirror on the primary side and a 0.27° parallel plate collimator on the secondary side. The elemental compositions were analysed using depth profiling X-ray photoelectron spectroscopy measurements in a PHI ESCA Quantum 2000 utilising a monochromatic Al Kα X-ray source in combination with Ar-ion sputter-etching. A $Ti_3AlC_2$ standard sample provided by Kanthal, Sweden, was used to calculate the sensitivity factors for the quantitative analysis. The hybridisation of the carbon in the wear track tribolayer were analysed with Raman spectroscopy utilising a Renishaw Micro-Raman system equipped with a green laser of wavelength 514.5 nm and a notch filter for suppression of the incident laser light. The coating microstructure was depicted in fractured cross-sections using a LEO 1550 field emission gun scanning electron microscope (FEG-SEM) and by FEI Tecnai F30 ST high resolution transmission electron microscopy (HR-TEM) as well as scanning TEM (STEM) with EDX analysis. The TEM-samples were all prepared using a FEI Strata DB235 focused ion beam (FIB). The FIB enables TEM sample preparation from specific areas of interest by combining an ordinary SEM for depicturing and focused ion beam for ion etching, i.e. milling out and polishing the TEM samples.

Surface roughness as well as the wear track cross-section areas were analysed by light interference microscopy utilising a Wyko NT-1100 in vertical scanning interferometry mode (VSI). The mechanical properties, i.e. hardness and elastic modulus were measured using a nanoindenter XP equipped with a Berkovich diamond tip. The indent depth was limited to 150 nm, i.e. close to 10% of the coating thickness to avoid substrate influence. The indents were analysed according to the Oliver-Pharr method [12]. The coating residual stress was determined by XRD $\sin^2\psi$-method and by measuring the deflection of a cut out sample and applying the Stoney equation [13]. The deflection technique utilised samples with dimension ~3 × 3 mm and a coating to substrate thickness ratio of about 1/100. A scratch tester, CSM Revetester equipped with a Rockwell C diamond stylus with a tip radius of 200 μm, was utilised for evaluation of coating adhesion, i.e. the critical load for coating fracture and spallation. The scratch was achieved by continuously increasing the normal load by 100 N/min and simultaneously sliding the coated sample at a velocity of 10 mm/min. Hence, the resulting scratch has a load-resolution of 10 N/mm. The scratches were studied and depicted by light optical microscopy (LOM).

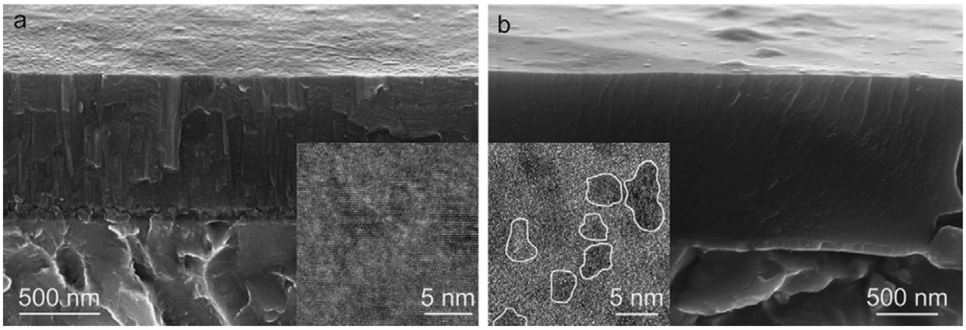

**Fig. 1.** (a) TiC coating depicted with FEG-SEM and inset of HR-TEM, shows the 850 nm thick coating with a columnar structure. (b) TiAlC coating depicted with FEG-SEM and inset of HR-TEM, shows the 1350 nm thick coating with a non-textured nanocrystalline microstructure with some crystallites highlighted. For both coatings a Ti interlayer of ~100 nm thickness was deposited by e-beam evaporation to enhance the adhesion.