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Comparison of arc evaporated Mo-based coatings versus Cr_1N_1 and ta–C coatings by reciprocating wear test

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ABSTRACT

Cathodic arc evaporation was utilized to synthesize Cr–N, ta–C, Al–Mo–N, Mo–N, Mo–O–N and Mo–Cu–N coatings. The coatings were characterized with respect to their stoichiometry, morphology and mechanical properties. A reciprocating wear test was used to compare the wear behavior for the unpolished coatings under dry conditions and polished coatings under lubricated (Mo-DTC) conditions. The test allows a classification of the coatings with respect to material transfer similar to scuffing or fretting and with respect to wear of the counter-part and may be utilized for a pre-selection of coatings for engine tests.

1. Introduction

Development in the automotive industry is driven by the market demand for higher fuel efficiency of vehicles and the proposed legislation to control their emission, e.g., the regulation No 715/2007 of the European Community [1]. This has an influence on the technology road maps of the automotive industry, especially for larger vehicles. New technological approaches which do not only include engine efficiency, but also the entire power train system are promoted for future vehicle generations and for concepts of CO_2 reduction. Lighter materials for moving parts in the power train, low-friction lubricants and an improved temperature cycling management in combination with higher operation temperature of the engine will contribute to better fuel economy. Concurrently, the addition of bio-products and new oil additives to the fuel challenge the materials for increased chemical and mechanical stability at higher temperatures. In addition, cost pressure in automotive industry requires reduced fabrication and machining expenses which in turn constricts the material selection.

Engineering of material surfaces by the application of coatings has become an important aspect for the design of tribological systems [2]. Thin PVD coatings consisting of metal nitrides, metal–carbon compounds and hard carbon layers have been used successfully to coat different components of the power train [3–6]. Cr_xN coatings have been found to reduce the wear of piston rings and improve the sliding properties in the piston-liner group [7]. The tribological properties of Cr_xN were studied with respect to the different phases [8], for multi-layer coatings [9], and fretting was investigated [10]. Because of its importance for applications, there have been attempts to model the wear behavior of this material system [11]. The synthesis of arc evaporated Cr_xN coatings has been described and microstructure and mechanical properties of these coatings were characterized [12] and the wear of arc deposited Cr_xN coatings was studied [13]. Therefore, Cr_xN was utilized as “standard” for the comparison with the other materials discussed in this work.

Metal–carbon and diamond-like coatings support the trend in automotive industry for better fuel efficiency [3,4,14,15]. Tungsten and carbon (a-C:H:W) containing coatings on gear surfaces lower the friction and increase engine efficiency. Diamond-like carbon layers on injection needles of common-rail diesel systems of cars help to keep clearances tight for the high injection pressures needed. Coatings of a-C:H:W and diamond-like coatings (a-C:H) are produced in a combination of reactive sputtering and plasma activated CVD (PACVD) processes while tetrahedral amorphous (hydrogen-free) carbon (ta-C) is often prepared by cathodic arc evaporation [16–19]. In PACVD, gaseous precursors are utilized which result in typical hydrogen contents between

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5 and 30 at% in the synthesized coatings. This limits the stability of the materials to temperatures of about 300 °C and was one reason to investigate the tribological properties of hydrogen-free carbon coatings [15]. Despite many existing applications, carbon containing coatings are still an important field of research which is well summarized in comprehensive reviews [20–22].

Future engine development needs the selection of new coating materials which support the functional design of complex tribological systems. Based on the demands for better fuel efficiency discussed above, PVD coatings may be utilized to control wear in low viscosity lubricants, to protect standard materials in high temperature and oxidizing environment and to adapt the wear between different materials. Based on the variation in deposition methods, diamond-like carbon coatings show a different triobological behavior for lubricants [23] indicating that chemical reactions with formulated oils and additives have to be considered for the optimization of the tribological contact for these materials [24–26].

Facing all the parameters influencing the performance of tribological systems, new coating materials have to be designed which improve the wettability for oils and their additives and with better chemical and thermal stability. MoN (with and without Cu doping) is one promising material which has been studied [27,28] and was already tested for piston ring applications [29]. A pre-selection of new coating materials by real engine tests is, however, too expensive. Therefore, materials and material modification may likely be neglected for cost issues and already existing coating materials may be utilized without challenging them for the real best solution. A pre-selection of the coating material by simple test methods would be beneficial to reduce the efforts in engine tests and PVD coating development and has the potential for a higher degree of optimization. A reciprocating wear test [30] was utilized to investigate the wear of substrate surfaces coated by very different materials utilizing cathodic arc evaporation and the wear of the uncoated steel counter-part. The response of the test to surface roughness and lubrication is discussed.

In this work, reactive cathodic arc evaporation was chosen for two reasons to produce the coating materials: (a) cathodic arc evaporation can be easily performed in reactive gases like nitrogen, oxygen or hydrocarbons without complex control of the reactive gases and (b) composite targets can be utilized which provide easy access to ternary and quarternary compounds. In addition, reactive arc evaporation offers lower production costs compared to reactive sputtering. The disadvantage of this technology consists in the formation of droplets which are generated by the cathodic arc during the evaporation of the target surface. These droplets are incorporated in the coating during layer synthesis. The number of droplets can be reduced or even avoided utilizing steered arc (magnetic field supported) or filtered arc technology. However, both technologies have drawbacks for production. The steered arc is difficult to stabilize in pure oxygen gas and the filtered arc results in decreased deposition rates. Therefore, the disadvantage of droplet generation by random arc was accepted knowing that under production conditions a polishing step is common. The investigations here intend to emphasize the straightforwardness to synthesize coating materials of very different properties by reactive arc evaporation and the possibility to classify their tribological and protective properties for sliding contacts by a simple test method, the reciprocating wear test.

2. Experimental

The deposition of the coatings was performed in an INNOVA production system of OC Oerlikon Balzers AG. The substrates (polished disks of hardened steel and polished tungsten carbide inserts) were wet-chemical cleaned before deposition. After evacuation of the process chamber below 10^{-5} mbar, standard heating and etching steps were performed to ensure a good layer adhesion to the substrate. Elemental or composite metallic targets were utilized in combination with the appropriate reactive gases which were fed to the chamber via gas flow controllers (Table 1). The chromium targets were produced by GfE Metalle und Materialien GmbH, the graphite targets by Steinemann AG, and the Mo, Al–Mo and Mo–Cu targets by PLANSEE Composite Materials GmbH. The coatings were mostly deposited on Cr_xN interfaces. This interface was utilized because it forms a good adhesion layer to steel. In addition, Cr_xN was also utilized as standard for the comparison with the other synthesized coatings because for this material many investigations had been accomplished in the past. The depositions of the coatings were performed under conditions similar to them described elsewhere [31]. The synthesized layers represent a wide spectrum of materials: very hard ta–C, soft Cr_xN and Mo-based coatings.

Surface roughness was characterized by measurements of the mean roughness depth R_z, the roughness average R_a, the reduced peak height R_{pk}, the reduced valley depth R_{vk} and the material portions Mr1 and Mr2 of the coated samples before and after polishing according to the EN ISO standards [32,33] utilizing a stylus instrument (Mahr Perthometer M1). The tip radius of the used stylus is 5 μm, the evaluation length was set with ln = 4 mm (lr = 0.8). The averaged surface roughness was calculated from three single measurements per sample and for the bare hardened steel substrate.

Optical microscopy (Olympus MX40) was utilized to investigate the wear track after SRV testing for identification of material transfer from the counter-part and removal of coating materials. The wear volume of the counter-part was calculated from the wear diameter of the counter-part [30].

A Zeiss LEO 1530 Gemini scanning electron microscope (SEM) equipped with a detector for Energy Dispersive X-ray (EDX) Analysis (from EDAX) was employed to examine the surface morphology and the fracture cross-section of the layers and to perform the compositional analysis of the material. EDX was also

Table 1
The most relevant deposition parameters, the chemical composition of the coatings and the mechanical properties of the coatings.

Sample	Cathode material	Process gases	T_{DEP} [C]	Thickness interface/ Functional layer [μm]	Compositional analysis of the coating		H_{IT} [GPa]	E_{IT} [GPa]
					RBS	EDX		
A	Cr	N_2	450	0/16.1	$Cr_{1.0}N_{1.0}$	Cr	14 ± 1	280 ± 12
B	Graphite	Ar	150	< 0.1/1.7	C (H < 1 at%)	C	52 ± 7	409 ± 31
C	$Al_{80}Mo_{20}$	N_2	450	5.2/10.6	$Al_{0.76}Mo_{0.24}N_{1.15}$	$Al_{74}Mo_{26}$	28 ± 2	257 ± 18
D	Mo	N_2	450	4.6/9.8	$Mo_{1.0}N_{1.0}$	Mo	19 ± 2	409 ± 58
E	Mo	N_2, O_2	450	4.8/11.2	$Mo_{1.0}N_{1-x}O_x$	Mo	29 ± 2	387 ± 15
F	$Mo_{85}Cu_{15}$	N_2	400	1.7/2.9	$Mo_{0.85}Cu_{0.15}N_{1.0}$	$Mo_{85}Cu_{15}$	28 ± 3	351 ± 34