The effect of layer architecture on the tribological behaviour of coatings

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Abstract. PEEK is a medical grade material which is increasingly used instead of titanium in osteosynthesis and joint replacement. However, its surface properties of PEEK lack on an adequate osteoconductivity. In this study, two coatings with different architectures composed of Ti, Mg and Ag were prepared by physical vacuum deposition to be used in spinal implants. The mechanical durability of the coatings is investigated in terms of their tribological behaviour.

1 Introduction

The semicrystalline polyether ether ketone (PEEK) polymer is as an alternative to metallic biomaterials due to its biocompatibility, chemical and radiation resistance, high mechanical strength and is approved as a medical grade material by U.S. FDA [1]. However, the adhesion of the bone tissue on the surface of PEEK proceeds slowly. This is attributed to low osteoconductivity which is a function of the surface properties of the biomaterial. An alternative technique for improving the surface properties of a material is coating it with a relevant material.

The scratch test is a fast and efficient method commonly used to determine critical loads, which are a measure of the adhesion strength of coatings. In scratch testing, a diamond tip (stylus) moves on a sample surface with a linearly increasing load. During this movement, different failure modes such as spalling, chipping and buckling occur at the interface of the coating-substrate material or between the layers forming the coating. Critical loads (L_c) of failure can be determined from the fluctuations in the acoustic emission signal at horizontal (tangential) power or from deformations in the surface determined by light microscopy. Normally, the lower critical load (L_{c1}) indicates the cohesive failure in the coating, while the higher critical load (L_{c2}) indicates the adherent failure between the coating and the substrate material [2, 3].

In this study, coatings with two different architectures, being preliminary developed for improving the osteoconductivity and antibacterial properties of PEEK, are investigated in terms of their tribological behaviour under progressive scratch loading. Crystallite sizes of the coatings are determined by x-ray diffraction studies (XRD, Rigaku RINT Ultima+) and their hardness values are also measured.

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In order to determine the mechanical behaviour of the coatings micron-scaled scratch test is performed using a NanoScratch Tester (NST, CSM-Instruments). The failure analysis of the coatings is carried out by examining the scratch tracks with scanning electron microscope (SEM, Jeol-JSM 6060).

2 EXPERIMENTAL

Two different types of coatings are prepared, namely multi-layered (ML) and gradient-layered (GL). The coatings are deposited at room temperature by an industrially-scaled vacuum coater using magnetron sputtering from pure Ti, Mg and Ag targets in Ar atmosphere. Initially the PEEK surfaces were pretreated before loading to the vacuum chamber by an industrially washing machine and subsequently dried. A plasma activation in high energetic, neutralized plasma occurred after pumping to high vacuum conditions (10^{-5} mbar) by an anode layer ion source, whereby during this step as well as during the next step (coating deposition) the substrate were rotated on 3-axis. In both finally achieved coatings types, a ~ 1000 nm titanium layer is adhesion layer on the PEEK substrate. In the multi-layer coating, the intermediate layer consists of ~ 250 nm Mg and the top layer consists of ~ 250 nm Ag layer, whereas in the gradient-layered coating, there is a functionally graded layer on the Ti where the concentrations of Mg and Ag change throughout the thickness. The concentration of Mg is 100% just above Ti and decreases along the thickness to the surface. On the contrary, Ag decreases from top to the interface.

The surface morphologies are investigated by atomic force microscope (AFM, NanoMagnetics Instruments, ezAFM) in tapping mode by choosing $2 \times 2 \mu\text{m}$ scanning area.

Phase analyses are performed on a Rigaku RINT Ultima + diffractometer with $\text{CuK}\alpha$ radiation. The Bragg-Brentano scanning geometry (theta-theta) is applied between 10° and 60° with a step width of 0.02° . The crystallite size of the coatings is calculated using the Scherrer formula [4, 5].

The mechanical characterization of the coatings is performed by using ultra-micro hardness indentation apparatus (Fischerscope HV100) with a Berkovich diamond indenter under 1.2 mN load and loading/unloading rate 0.12 mN/s.

NanoScratch Tester (NST, CSM-Instruments) is used to determine the failure behaviour under progressive load. The tests are carried out by a Rockwell diamond indenter with a $100 \mu\text{m}$ tip radius. The progressive scratch tests are performed between 0.03-3 N with a loading rate of 6000 mN/min along 3mm scratch track and critical load (L_{c1}) is determined. The failure analysis of the coatings is carried out by examining the scratch tracks with scanning electron microscope (SEM, Jeol-JSM 6060).

3 Results and discussion

The surface morphologies of ML and GL coatings, analysed by AFM, are given in Figure 1 and 2, respectively. GL shows a finer surface structure than ML.

Fig. 1. The AFM images of the multi-layered coating taken in (a) topography and (b) phase mode.

Fig. 2. The AFM images of the gradient-layered coating taken in (a) topography and (b) phase mode.

The crystallite size of the coatings are calculated from XRD data by using Sherrer formula. Crystallite size decreased by changing the architecture from ML (27.49 nm) to GL (16.23 nm).

The mechanical properties of the coatings, in terms of hardness, are determined from the indentation test, using samples coated on silicon wafer to eliminate the substrate compliance of the soft polymers. The GL with finer surface microstructure and smaller crystallite size has higher hardness than ML. Hardness values of the coatings are measured as 1.59 GPa and 2.55 GPa for ML and GL coatings, respectively.

Fig. 3: SEM images of scratch track for multi-layered coating after progressive scratch test.

Fig. 4: SEM images of scratch track for gradient-layered coating after progressive scratch test.

SEM images of the scratch tracks for ML and GL coatings are given in Figure 3 and 4, respectively. As can be seen from these images, the tribological wear mechanism for both coating types start with asperity deformation at lower loads. The asperities are structures resulting from the protruding large crystals or droplets formed during coating process. In case of the multi-layer coating, some Ag layer is detached from the top of the asperities (black spots in Fig. 5) resulting in adhesive wear during the plastic deformation of the asperities. On the other hand, the coating surface becomes smoother with increasing load and shows a polishing effect.

The critical loads (L_{c1}) indicating the cohesive failure in the coating are determined as 1.07 N and 2.01 N for multi-layered and gradient-layered coatings, respectively. In the case of multi-layered coating, the failure mechanism is adhesive wear, whereas an abrasive deformation can be attributed to the gradient-layered coating.

Figure 5: SEM images showing the asperity deformation on ML coating, at different magnifications.

The first angular cracks are starting to form at the edge of the scratch track behind the indenter with increasing load as seen in Figure 3b. The load at which the coating damage is first observed is the critical load (L_{c1}) and gives the adhesion strength of the coating. The first local coating failure for ML is seen at 1.07 N. However, in an earlier study carried out by SEM and EDS mapping analysis it has been shown that only the Ag top layer is delaminated in this coating [6]. With further progress of the indenter at higher loads, the surface at the center of the track becomes smoother whereas more angular cracks appear at the edges. Finally, high plastic strains and strain hardening in the surface resulting due to the increased scratch load and contact zone cause plastic deformation of the surface. Thus, exceeding the load support of the coating accompanied with the propagation of interfacial cracks lead to proceeding of transverse semicircular cracks towards plastic pile-up regions and finally, spallation of the layer. Generally, these transverse semicircular cracks arise

from the intrinsic stresses, which result during coating at low temperature and form due to the compressive stress in front of the indenter progressing. Besides, some of the Ag layer is embedded in the soft Mg layer. Mg possesses a high deformation ability due to its low hardness. Therefore, only transverse semicircular cracks could form at this load region (Figure 3g). In the final load region, the transverse semicircular cracks become more visible. Eventually, a large portion of the Ag layer delaminates and causes adhesive failure.

The deformation ability and failure behaviour of GL vary from that of ML because of its finer structure and higher hardness. Similar to ML, the tribological wear mechanism on GL, starts with asperity deformation (Figure 4). However, the traces left after deformation of the asperities reveal a different appearance on the GL coating (Figure 4). The top layer of GL layer has smaller crystallite size and higher hardness than ML due to the architecture of the layers and thus, affects the deformation behaviour of the top layer. Consequently, the micro-cutted debris from the top of asperities are introduced into the contact zone and cause abrasive deformation resulting in deeper grooves. This phenomenon is known as third body wear [2]. The enhanced load bearing capacity of the coating due to its higher hardness hinders the ploughing of the coating. As a result, the stresses are reduced in the substrate and thus, prevent the deformation of the substrate [7]. Angular cracks behind the indenter at track edges become visible with increasing load. The first crack, L_{c1} , is seen at 2.01 N (Figure 6).

Fig. 6: The first cracks seen on GL coating taken by SEM at different magnifications.

As it seen from Figure 4e and 7, transverse semicircular cracks are formed by merging of the angular cracks with each other, with increasing load. These transverse semicircular cracks, also known as tensile cracks, originate from the tensile stress behind the indenter.

Fig. 7: SEM images of transverse semicircular cracks formed by merging of angular cracks.

At ultimate scratch load, the coating is no longer able to carry the load and causes the deformation of the substrate. Finally, the coating starts buckling in a concentric manner to the indenter due to the compressive stress in front of the indenter and simultaneous plastic pile-up effect. All of the individual semicircular cracks propagate along the scratch track. The coating is fully damaged during the propagation of the indenter over these semicircular cracks formed in front of the indenter and some of the coating is embedded in the substrate while some is spalled off (Figure 4e-f and Figure 8).

Fig. 8. (a) SEM image and (b) EDX mapping of final failure in GL coating.

4 Conclusion

In this study, the effect of the coating architecture on the deformation behaviour under progressive load is investigated. Two different coating types are chosen, namely a multi-layered and gradient-layered. Two different wear and failure mechanisms are observed depending on the coating architecture.

A series of microstructural analysis performed by SEM and EDS on scratch tracks after progressive scratch test show that the GL with higher hardness and finer microstructure (smaller crystallite size) has higher adhesion strength than ML (1.07 N vs. 2.01 N). The failure mechanism in ML is seen as adhesive wear whereas abrasive wear is dominant in GL. The increased stiffness due to the coating architecture has changed the deformation ability and failure mechanism of the gradient-layered coating.

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