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LUO, Quanshun <http://orcid.org/0000-0003-4102-2129>, RAINFORTH, W. Mark and MÜNZ, W. Dieter

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TEM studies of the wear of TiAlN/CrN superlattice coatings

Q. Luo[a], W.M. Rainforth[b]*, W.–D. Münz[a]
[a]Materials Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK
[b]Department of Engineering Materials, University of Sheffield, S1 3JD, UK

INTRODUCTION

Hard coatings produced by physical vapour deposition (PVD) are used to enhance the wear resistance of many tribological materials, particularly those operating in severe environments, such as cutting tools (e.g. Ref. [1]). Third generation coatings comprise multi-component constituents and, importantly, a multilayered structure (e.g. Ref. [2]). These coatings (often referred to as `superlattice') have exceptionally high hardness (hence the name `super-hard') and good thermal and chemical stability and consequently it is believed that they may be able to operate in unlubricated cutting operations. Laboratory and field studies (e.g. Ref. [3]) have shown that superlattice coatings offer significant improvements in wear resistance over first generation (e.g. TiN) and second generation coatings (e.g. TiAlCrN).

Third generation coatings have only recently been developed and little is known about their wear behaviour, in particular the effect the multilayer structure has on the wear mechanisms. Previous work [3], [4] and [5] has shown that surface plastic deformation during the initial stages of wear results in crack formation in two principal orientations. Firstly, for monolithically grown coatings, (i.e. the first and second generation) delamination cracks form within the deformed layer that eventually lead to spalling of this layer, leading to progressive loss of material. Secondly, the bending action associated with the plastic deformation leads to crack propagation along columnar grain boundaries. These cracks eventually branch and lead to catastrophic spalling of the coating and failure. This deformation was limited to the outer ~200 nm of second generation coatings and is therefore only detected through detailed TEM of longitudinal cross-sections of the worn surface. Our earlier work [3] comprehensively characterised the wear of second generation coatings, and provided some observations on the severe wear of third generation coatings. The present reports similar TEM techniques to characterise the early stages of wear of a third generation TiAlN/CrN multilayer coating to establish whether surface deformation plays a role in the wear of multilayer coatings.

EXPERIMENTAL

The TiAlN/CrN coating, consisting of alternating TiAlN and CrN layers of thickness 1.5–2 nm, was deposited onto a M2 high speed steel substrate (Vickers hardness 7.99±0.08 GPa) by PVD in a four target Hauzer HTC1000-ABS coating machine, using the combined cathodic arc etching and unbalanced magnetron sputtering process. Following Cr metal ion etching in the steered arc mode, a base layer of TiAlN was produced by unbalanced magnetron sputtering deposition for 30 min using three TiAlN targets operated at 8 kW. The multilayer coating was then deposited by unbalanced magnetron sputtering with the additional Cr target at 5 kW and the TiAl targets at 8 kW for 210 min.

Unlubricated wear tests were performed in a block-on-ring configuration at room temperature (21°C), using a normal load of 91N (applied by dead weight) and a sliding speed of 0.42 m/s for a total distance of 1000 m. The coating was applied to the 12 mm diameter flat face of the block. An M2 high speed steel counterface ring was used of diameter 60 mm and width 12 mm (i.e. the same as the substrate material). The wear rate was determined by measuring the wear scar dimensions using a micrometer attached to an optical microscope (accuracy±0.001 mm). The worn surface was examined by SEM (Jeol 6400) and TEM (Philips CM20 (operating at 200 kV)). Longitudinal cross-section TEM samples were then prepared from all the worn samples using argon ion beam milling, following standard procedures.

RESULTS

The thickness of the coating was measured at 3.13 μm and hardness (HK) was 29.7±6.1 GPa. The microstructure and crystallographic texture of the coating is described in detail elsewhere [2]. Briefly, it consisted of a 500 nm thick TiAlN base coat followed by the multilayer coating (of individual CrN and TiAlN layer thickness 1.5–2 nm), with a columnar structure, and a (111) preferred growth orientation.

The wear coefficient after 1000 m sliding was 2.84×10^{-7} mm^3/Nm. After an initial value of 0.70, the friction coefficient rose gradually to a value of 0.77 at the end of the test. Fig. 1 gives a SEM image of the worn surface showing all the features observed. Because of the crowned nature of the

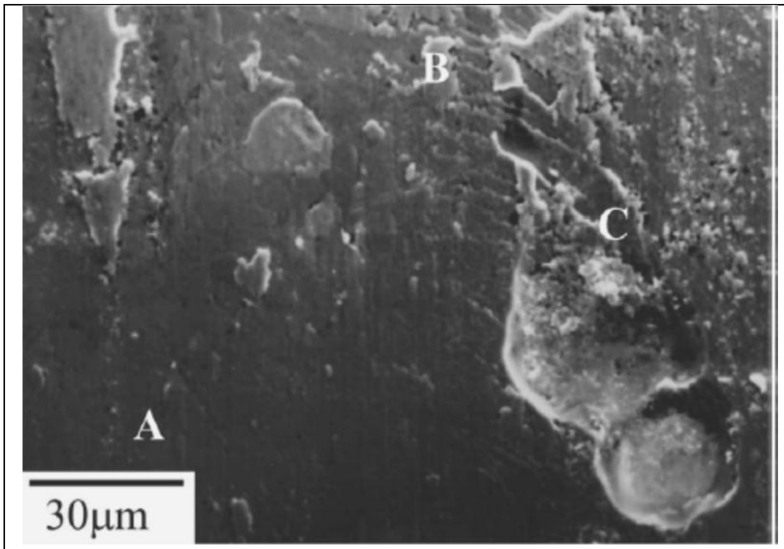

Figure 1. SEM micrograph showing thre worn surface of the multilayer. Labels A, B C are explained in the text.

counterface, the duration of contact varies across the micrograph, being least on the left and greatest on the right. The left-hand region of the micrograph (labelled A) shows the area of initial contact, which is smooth and relatively featureless. However, occasional prows are present on the surface, that energy dispersive spectroscopy (EDS) suggested were Fe based, but also contained oxygen. Adjacent to this, in a region that had undergone a longer contact period, cracks can be seen (labelled B), that ultimately lead to pitting (labelled C). Some loosely attached wear debris is present on the right of the micrograph.

Longitudinal cross-sections for TEM analysis were taken from the early stages of sliding, from region A in Fig. 1. Two characteristic microstructures were found. The first type is illustrated in the bright field TEM image in Fig. 2. In the lower region of the micrograph the original multilayer structure can be seen through Fresnel contrast. Plastic deformation in the superlattice region occurred at the surface, first detected at a depth of approximately 55 nm. Fig. 3 gives a higher magnification image of the deformed region. The image is taken slightly out of focus in order to maximise the Fresnel contrast from the multilayers. This, and a range of through-thickness images, suggests that the multilayer structure has been lost in the outer ~40 nm (labelled A). Below this, the multilayer structure had been rotated from a position of approximately parallel to the surface to approximately 30° to the surface in region B. Extensive microcracking was evident within the deformed region, but no evidence of delamination could be found.

The outer worn surface comprised a fine polycrystalline layer, Fig. 2 and Fig. 3. Fig. 4 gives a detail of this layer. Analysis of this and other diffraction patterns indicated that the film was predominantly Fe3O4 but with some Al2TiO5 and trace quantities of the components of the TiAlN/CrN. EDS confirmed that the layer consisted of components of both the counterface and the multilayer coating. The crystallite size within the layer was measured as 11±5 nm. The interface between this surface layer and the deformed substrate was sharp, with no transition region detected.

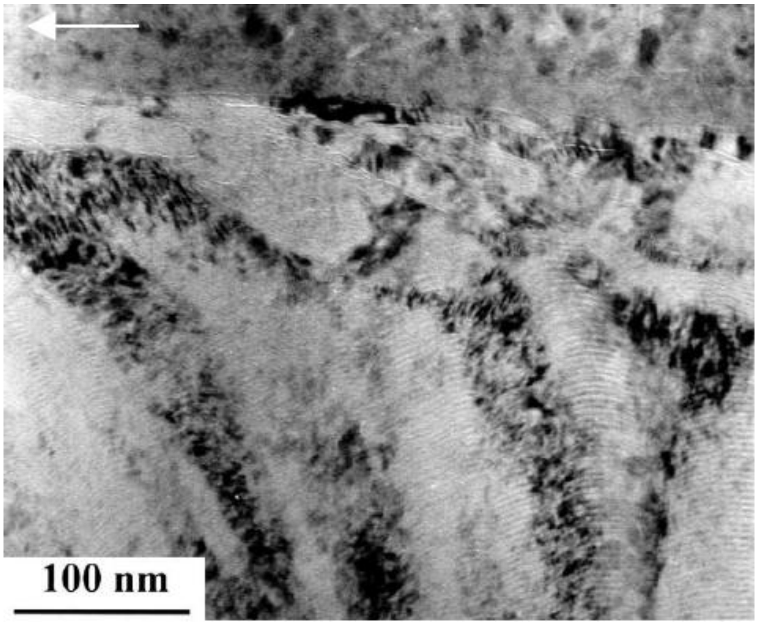

Figure 2. Bright field TEM micrograph from a longitudinal cross-section showing surface deformation and a surface transfer film. The arrow indicates the direction of movement of the counterface (the coated sample was static).

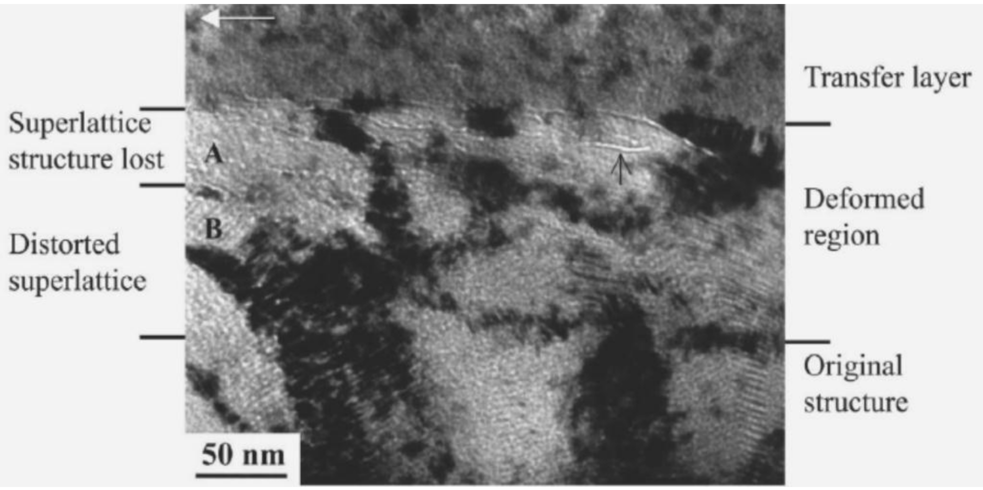

Figure 3. Bright field TEM micrograph from a longitudinal cross-section showing surface deformation in more detail. The Fresnel contrast reveals the position of the multilayer structure and the microcracks (e.g. arrowed). The arrow is the same as in Figure 2.

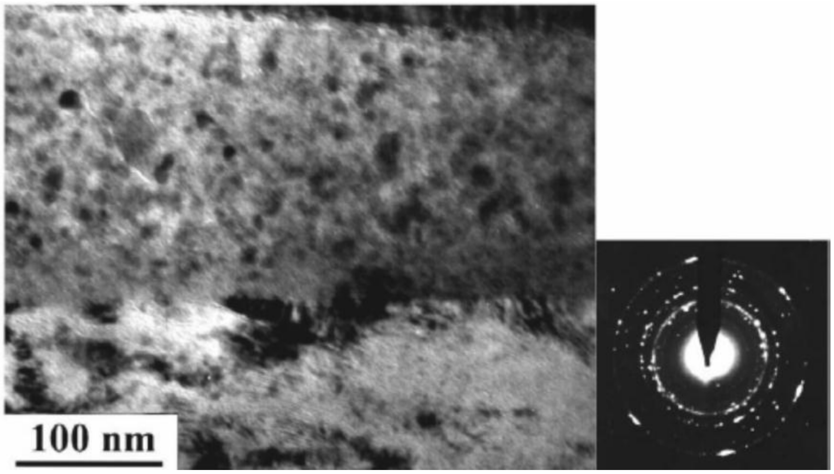

Figure 4. Bright field TEM micrograph from Fig. 2 showing the transfer film, predominantly made up of Fe3O4. The thin feature at the top of the micrograph is a gold coating used to label and protect the original surface.

Close to the edge of the wear scar, the second type of worn surface microstructure was identified (Fig. 5). In this case, no plastic deformation could be detected at the surface of the multilayer. However, a thin transfer layer, of thickness ~25 nm was observed, spread uniformly across the surface. Electron diffraction and EDS suggested that this layer had the same structure, composition and grain size to that observed in Fig. 4.

DISCUSSION

The wear coefficient recorded is lower than that found for TiN and similar to TiAlCrYN coatings both under identical test conditions [3]. Moreover, the wear coefficient during initial sliding was substantially less (the value quoted was averaged over the total 1000 m sliding, and included

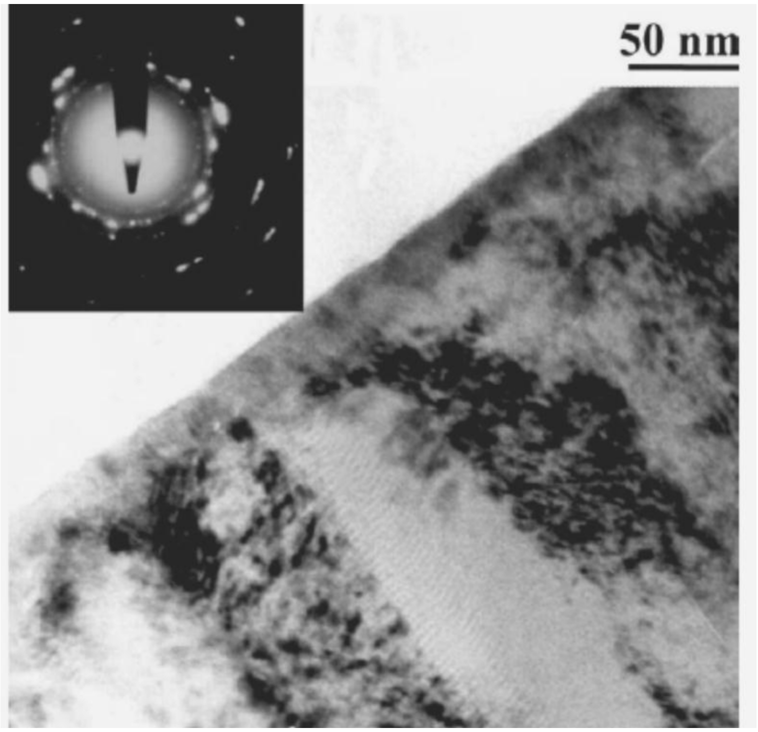

Figure 5. Bright field TEM micrograph from an area near to Fig. 2 showing the earlier stages of wear. Note the thin (~25 nm) transfer layer and the absence of surface deformation (as shown by the orientation of the multilayer structure).

coating failure). In the early stages of sliding the worn surface became smoother than in the as-deposited state. Subsequently, prows on the surface developed as a result of transfer of material from the counterface, demonstrating that adhesive wear was at least one component of the wear mechanism. Later in the sliding process, macroscopic cracking was observed which rapidly led to spalling and catastrophic loss of the coating. The TEM investigation was focused on the early states of wear (region A of Fig. 1), since it constituted the majority of the coating life.

Fig. 4 and Fig. 5 show the transfer layer at the surface. The presence of both coating and counterface material in the transfer layer indicates significant adhesion between the two. The presence of Fe_3O_4 but without Fe_2O_3 or FeO suggests that the surface temperature was in the range 500–600°C [6]. Interestingly, there was no evidence of direct oxidation of the coating itself, i.e. the sharp interface between transfer layer and coating suggests the surface layer did not form by progressive oxidation of the coating. This is consistent with other studies show that oxidation of the coating can only be detected at ≥ 900°C [2].

The extent of plastic deformation was less than that observed at the surface of second generation coatings [3], reflecting the superior resistance to plastic deformation offered by the multilayer structure. Nevertheless, substantial strain had occurred. An estimate of the equivalent tensile strain was made using the well-known equation [7]:

$$\bar{\delta} = \left(1 - \frac{\tan \varsigma}{\tan \theta}\right) \frac{\tan \theta}{\sqrt{3}}$$

where δ is the equivalent tensile strain, ς is the angle of inclination of the unstrained feature to the worn surface normal and θ is the angle of inclination of the strained feature to the worn surface normal. This indicated an equivalent tensile strain of 2.5. While this is much less than found for metals [8], it nevertheless represents a substantial strain that led to widespread microcracking. Thus, the surface plastic deformation leads directly to wear through delamination initiated by the microcracks that are formed (Fig. 3). Interestingly, the deformation process led to bending of the multilayer structure and subsequently to its destruction within ~40 nm of the surface. There was no clear evidence of shear within the multilayer structure, as the uniformity and spacing of the layers was largely preserved as they were rotated by deformation. Therefore, the loss of the multilayer structure was presumably through diffusion between the CrN and TiAlN layers, aided by plastic deformation arising through the temperature rises in the range 500–600°C (as shown by the type of oxide in the transfer layer).

CONCLUSIONS

(1) Plastic deformation to an equivalent tensile strain of 2.5 was detected at the worn surface of a TiAlN/CrN multilayer following sliding against an M2 high speed steel. The extent of plastic deformation was less than that found for TiAlYCrN coatings worn under the same conditions [3]. Plastic deformation led to microcracking, providing a mechanism for subsequent wear through surface delamination.

(2) A transfer layer formed, predominantly of Fe3O4, but also containing components of the coating. The presence of Fe_3O_4 without Fe_2O_3 or FeO suggests temperatures in the range ~500–600°C. The loss of the multilayer structure in the outer ~40 nm is consistent with diffusion and deformation processes occurring at this temperature.

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