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Characterisation of TiN and TiAlN thin films deposited on ground surfaces using focused ion beam milling

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TiN and TiAlN/TiN PVD coatings deposited onto as-ground surfaces have been characterised via direct cross-sectional imaging and transmission electron microscopy with the aid of a focused ion beam system. Cross-sections showed that the coatings exhibit consistent coverage, even in sheltered areas such as at the base of grooves resulting from prior grinding. A columnar grain structure was observed in all coatings. A number of defects were observed such as seams and voids resulting from coating onto the as-ground surface and macroparticles which were shown to be deposited during the metal ion etching stage. Cross-sections through nanoindents revealed that the coatings deform by through-thickness shear cracking.

The combination of the excellent coverage provided by PVD and the deformation mechanisms, which are related to the microstructure, contribute to the excellent performance of these coatings that has lead to their widespread application.

1. Introduction

Thin films of TiN and TiAlN deposited by physical vapour deposition (PVD) are widely used in industry to enhance the life of components in high wear applications. Of the two coatings, TiAlN is considered to have the better tribological performance at high temperatures because it forms a dense, passive Al_2O_3 layer at the surface of the coating [1, 2]. Coatings are typically 1–3 μm thick, and require good adhesion to the substrate, along with structural integrity and uniformity.

The properties of these PVD-coated tools are intricately related to the microstructure of the coating and therefore microstructural characterisation of coatings is extremely important. Characterising the structure of PVD thin film coatings can be performed using a number of techniques including X-ray diffraction and scanning and transmission electron microscopy (SEM and TEM). X-ray diffraction is an extremely useful technique, providing information about the structure of the coating, but its effectiveness is limited by the large penetration depth of the X-rays, and information from X-ray diffraction often needs to be empirically confirmed by direct observation using electron microscopy. However, the difficulty of specimen preparation for coated materials limits the usefulness of both scanning and transmission electron microscopy. Cutting, grinding and polishing cross-sections for analysis is cumbersome, and deformation of the surface layer or smearing of material across the interfaces can pose a problem.

Coatings regularly exhibit defects and inhomogeneities that are randomly distributed across the sample surface. The surface may be imaged using optical microscopy and SEM, and cross-sections, which are normally prepared by fracturing the sample, may also be examined using SEM. However surface imaging does not allow direct examination of the microstructure through the thickness of the coating and also does not allow investigation of defects, which often lie beneath the surface of the coating. In addition,

fractured cross-sections are randomly located, and therefore examination of specific areas or defects is difficult.

Focused ion beam (FIB) milling can be used to overcome many of these difficulties. The FIB miller uses a 30 kV beam of gallium (Ga^+) ions to sputter very precise sections of material. The secondary electrons yielded when the Ga^+ ions impact the surface can be collected to form secondary electron images. Details of the FIB technique are reported elsewhere [3–5]. The FIB can be used to prepare site-specific cross-sections from a surface, avoiding detrimental processes such as deformation, or the closing of existing cracks by mechanical abrasion. The FIB can also be used to prepare electron transparent sections for subsequent examination at high resolution using transmission electron microscopy (TEM) [6, 7].

In the current study, the microstructure of PVD coatings deposited onto ground surfaces was characterised using a focused ion beam miller. It is considered that such surfaces are more relevant to industrial practice than the polished, flat surfaces usually required for examination by nanoindentation and tribological tests. FIB cross-sections were used to examine TiN and dual-layer TiN/TiAlN coatings deposited on a number of ground steel substrates using a low voltage electron beam (LVEB) PVD system and a cathodic arc PVD process. Cross-sections were also prepared though indents, which were made using instrumented nanoindentation, to investigate the deformation mechanisms. In addition, the FIB technique was used to prepare a number of electron transparent membranes that were examined using TEM.

2. Experimental details

2.1. Coating deposition

PVD coatings of TiN and TiAlN were deposited onto steel substrates of high-speed steel (M2), nitridable alloy steel (V820) and hot work die steel (H13). Two PVD techniques were used to deposit the coatings, namely, low-voltage electron beam (LVEB) evaporation for the deposition of TiN coatings and cathodic arc evaporation for the deposition of single layer TiN coatings and dual-layer TiN/TiAlN coatings. In the LVEB coating process, substrates were loaded into a coating chamber, which was pumped down to a base pressure of 2×10^{-3} Pa. The substrates were heated to approximately 450°C and argon ion etched for a period of fifteen minutes at a negative bias voltage of −200 V. An electron beam was then used to evaporate titanium, which was deposited on the substrates at a bias voltage of −100 V. After a few minutes, the reactive gas nitrogen was introduced into the chamber and TiN was deposited for a period of one hour.

In the cathodic arc coating process, a multi-source cathodic arc coating chamber was used. Substrates were loaded into the coating chamber which was pumped down to a base pressure of 5×10^{-3} Pa and heated to 250°C. They were initially biased at −1 kV and cleaned by argon ion etching at a pressure of 5 Pa. The bias voltage was then reduced to −800 V and the substrates metal ion etched using Ti ions generated from an arc source. For the single layer TiN, nitrogen was introduced to a chamber pressure of 7×10^{-1} Pa and a coating deposited for 40 min using a substrate bias of −200 V. For the TiAlN coatings a base coating of TiN was first deposited for a period of 20 min using the same deposition conditions as those used for the single layer TiN coating. The substrate bias was then reduced to −100 V for the TiAlN top coating which was deposited for a period of 40 min using two $Ti_{0.5}Al_{0.5}$ cathode targets.

2.2. Focused ion beam (FIB) milling

Focused ion beam (FIB) milling was performed using a FEI 200xP FIB system. Cross-sections were prepared according to Fig. 1 using apertures corresponding to a beam current of 2700 pA for the initial cuts, and 350 pA aperture for the final cleaning mills. Details of preparation of cross-sections using the FIB are provided elsewhere [8]. Due to geometric constraints, it is not possible to view the cross-section directly from above, so it is important to note the degree of tilt from the beam direction (θ). X-ray energy dispersive spectroscopy (XEDS) from some of the milled surfaces was performed using an Oxford instruments XEDS unit attached to a Hitachi 4500 field emission scanning electron microscope (FESEM). Nanoindentation was carried out using an Ultra-Micro Indentation System (UMIS) 2000, (CSIRO, Sydney, Australia).

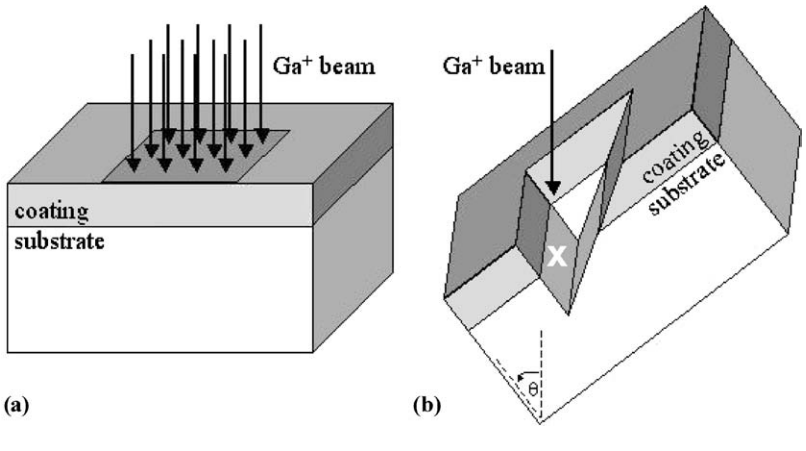

Figure 1 Preparing a cross-section using the FIB. The specimen is (a) milled using the ion beam and (b) tilted to an angle (θ) so that the newly created surface (labeled x) can be imaged.

2.3. Transmission electron microscopy (TEM)

TEM specimens were also prepared using the FIB workstation. Details of the use of the FIB for TEM specimen preparation are reported elsewhere [6, 7]. The H-type technique was used with an aperture corresponding to a beam current of 2700 pA employed for the initial cuts, followed by 1000 pA for finer cuts and finally 350 pA for the final cleaning mills. TEM specimens were examined in a Philips CM200 field emission gun TEM operating at 200 kV equipped with an EDAX energy dispersive X-ray spectroscopy (XEDS) unit.

3. Results and discussion

Fig. 2a–c are cross-sections of the three different types of coatings taken from a relatively flat area of the specimen surface. The LVEB coating and the TiN cathodic arc coating (Fig. 2a and b) were deposited on M2 high-speed steel, while the TiN/TiAlN coating (Fig. 2c) was deposited on V820 steel. The LVEB coating is $\sim$3.7 μm thick, while for the arc coatings, both the TiN and the dual-layer TiN/TiAlN coatings are $\sim$0.8 μm thick (note that the viewing angle, θ, is considered when the thickness of the coating is measured). The thicker coating on the LVEB sample is simply a result of a longer deposition time relative to the deposition rate.

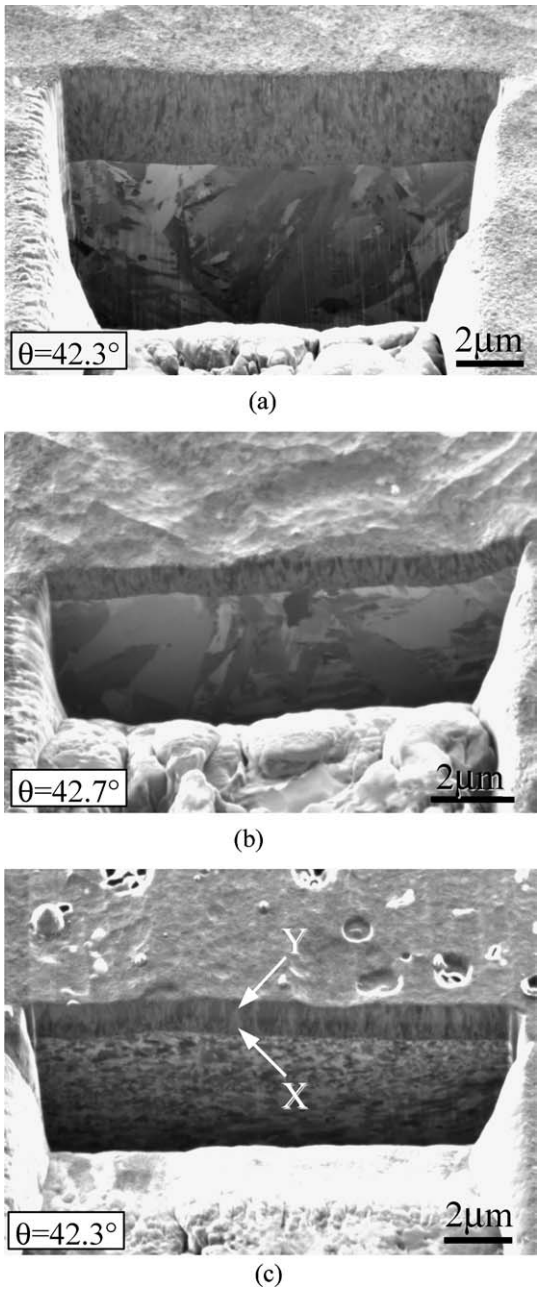

Figure 2 Secondary electron FIB image of cross-sections prepared from (a) a LVEB coating of TiN on a M2 steel substrate, (b) a cathodic arc coating of TiN also on a M2 steel substrate and (c) a TiN/TiAlN dual-layer coating on a V820 steel substrate.

For the LVEB coating, the microstructure clearly consists of columnar grains typically 50–100 nm in width, oriented approximately parallel to the direction of growth. The columnar grains do not extend all the way though the cross-section of the thin film, indicating that not all grains grow from the base of the coating, some are nucleated during the coating growth. Close inspection of the thinner coatings deposited using the cathodic arc process revealed that these too, consist of columnar grains $\sim$50–100 nm wide. In the TiN/TiAlN specimen, the two layers can be seen, labeled x and y, which are the TiN and TiAlN respectively, and the grains extend through the interface across the thickness of the coating.

Careful examination of the coatings on each of the different substrates throughout this study revealed no discernable difference between the coatings prepared in the same way on the different substrates.

Interestingly, the microstructure of the substrate, as well as that of the coating, can be clearly seen in the FIB secondary electron images due to both compositional and channeling contrast mechanisms. The grains of differing orientation can be quite clearly discerned. Secondary electron images generated in a scanning electron microscope exhibit only topographic and compositional contrast. As a result, the individual grains in a polished cross-section of a coating cannot be discerned as the surface is flat, and there is no compositional difference between the grains. Fig. 3 is a SEM image of a polished cross-section included for comparison. Channeling contrast is unique to secondary ion microscopy and arises from channeling of the ion beam [4]. When the specimen is oriented closer to a low index crystallographic direction the positive ions are 'channeled'

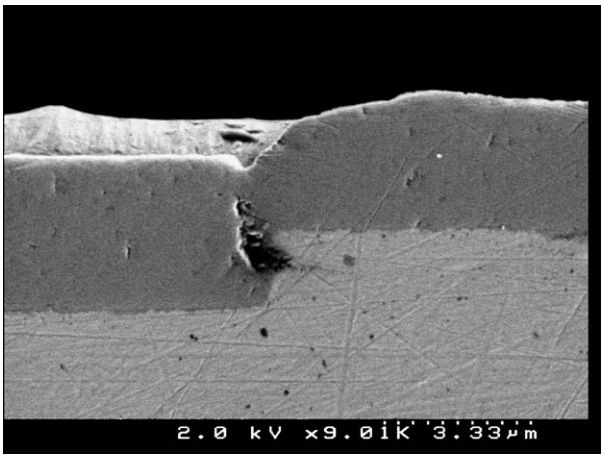

Figure 3 Secondary electron SEM image of cross-sections prepared from a LVEB coating of TiN on a V820 nitridable steel substrate.

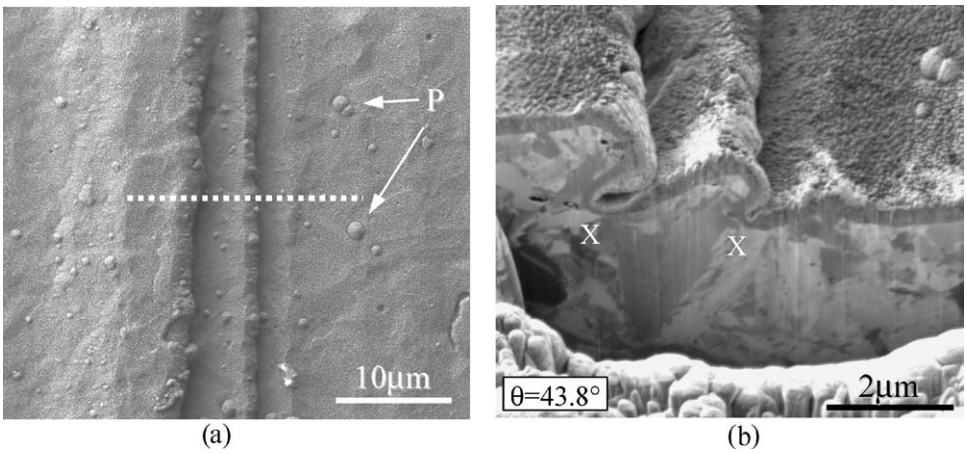

Figure 4 (a) Top view of ground, coated sample and (b) Cross-section of grooves resulting from grinding in a cathodic arc coating deposited using the cathodic arc process onto M2 high speed steel.

between the positive nuclei of the atoms and may travel a considerable distance into the sample, making particle escape more difficult. Grains of differing orientations therefore have different secondary electron yields, resulting in the orientation contrast between the grains which is commonly known as channeling contrast.

In order to investigate the structural integrity of the coatings; their thickness consistency, microstructure and also the origin of any subsurface inhomogeneities, cross-sections were prepared not only through relatively flat areas of the specimen surface (Fig. 2a–c) but also through surface sections which contain irregularities on the ground surface such as grooves resulting from prior grinding (Figs 4–6) and macroparticles (Fig. 8a and b).

Fig. 4a is a secondary electron micrograph, taken using the FIB, of the surface of the sample prior to milling. The white dotted line represents the area from which the cross-section was prepared. Fig. 4b is secondary electron micrograph of a cross-section revealing both the coating and the substrate. In Fig. 5 the surface from which the cross-section is prepared is shown in the image inset in the bottom right of the figure. Again, the dotted white line indicates the region from which the cross-section was prepared.

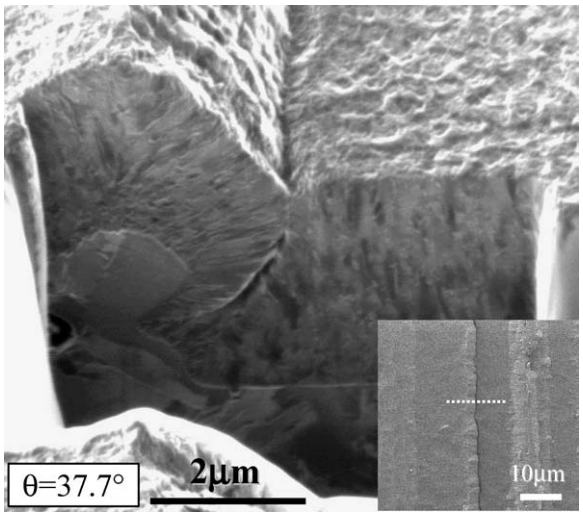

Figure 5 Cross-section of grooves resulting from grinding in a cathodic arc coating deposited using the LVEB process onto M2 high speed steel. The top view is shown in the inset image.

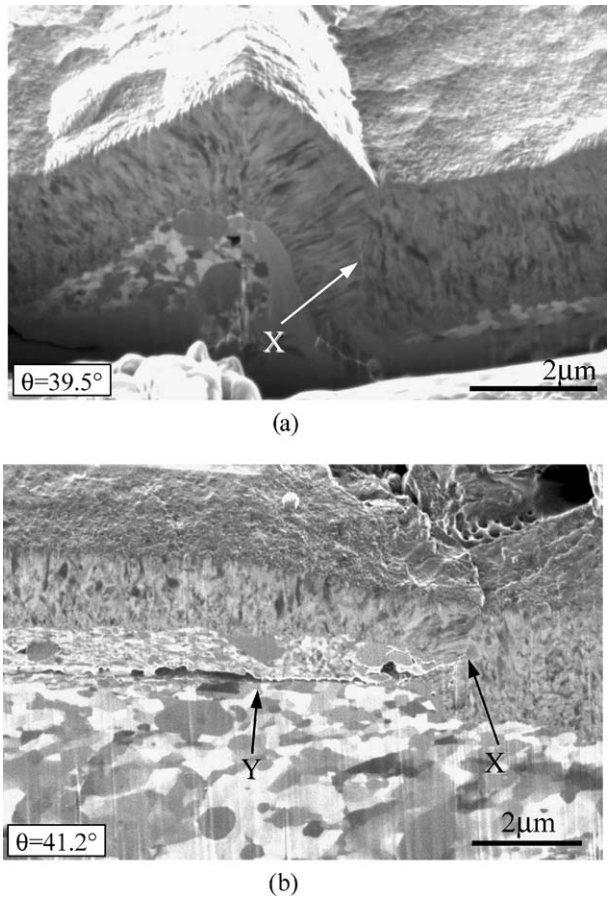

Figure 6 FIB cross-sections taken from rough areas on the coating deposited using the LVEB process onto a H13 steel substrate.

Fig. 4b is a cross-section prepared from the sample coated with TiN deposited by the cathodic arc process onto M2 high-speed steel. The surface of the specimen contained many parallel grooves running across the entire specimen surface resulting from prior grinding of the uncoated surface. Fig. 4a shows two deep grinding grooves side by side. Fig. 4b is a cross-section prepared through these two grooves in the area indicated. All surfaces were coated by TiN, even at the base of the grooves, indicating that the plasma manages

to penetrate even the most apparently inaccessible areas. However, the coating appears to be thinner at the base of the grooves (for example in the area labeled *X* in Fig. 4b), indicating the deposition rate is slower in these less accessible areas.

Fig. 5 is taken from the sample where TiN was deposited onto M2 high-speed steel using the LVEB process. This relatively thick coating has again deposited on all surfaces, but a crack-like elongated void can be seen, labeled *X*, between sections of the coating growing from different parts of the specimen surface. From the orientation of the columnar grains it is clear that in both areas the coating is growing, as expected, in a direction perpendicular to the specimen surface. The two regions of the coating have met, and closed resulting in the formation of a void, so that no further deposition can occur in this area. Voids, such as the one observed in Fig. 5, may act as points of weakness in the specimen surface, which under an applied stress might act as an initiation point for some wear mechanisms and/or fatigue cracking, which could eventually lead to spalling and failure. In other cases, the coatings growing in different directions meet up, creating a plane along which the differently oriented columnar grains meet, which may also act as a plane of weakness. Examples are labeled *X* in Fig. 6a and b. (Both Fig. 6a and b are taken from a sample in which TiN is deposited using the electron beam process on H13 steel). Inhomogeneities such as these have not previously been observed due to the difficulty of specimen preparation.

In some cases, subsurface cracking was observed (for example in the area labeled *Y* in Fig. 6b). This cracking is thought to be present in the sample prior to coating, resulting from the grinding process. FIB examination of specimens, which had either failed, or spent considerable time in service, may provide a unique method to reveal the actual degradation mechanisms.

A preliminary investigation of specimens which had been subject to nanoindentation was also performed in an attempt to elucidate the deformation mechanisms. FIB cross-sections were prepared through the nanoindents; an example is shown in Fig. 7, where the TiN/TiAlN arc coating has been indented at 100 mN with a 1 μm radius spherical diamond indenter. Cracks were observed at the columnar grain boundaries, indicating that the coatings deform via through-thickness grain boundary cracking. Even at extremely high loads (up to 500 mN), which result in large amounts of strain, the coating retains its integrity. For example, the coating shown in Fig. 7 has been deformed to a depth more than twice the thickness of the coating, yet still remains intact. Nanoindentation combined with FIB analysis, using both cross-sectioning and TEM, is the subject of continuing studies; detailed results and analysis will be published in a later work.

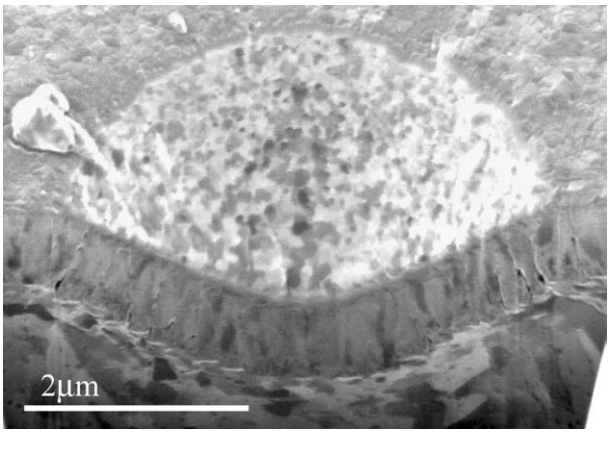

Figure 7 FIB cross-sections through an indent made with a 1 μm radium indenter at a 200 mN load on the TiN/TiAlN cathodic arc-coated sample showing that deformation occurs via grain shear cracks along the columnar grain boundaries.

It is well known that macroparticles also known as 'macros,' 'droplets' or 'growth defects' are regularly observed in coatings deposited using the cathodic arc process [1] and can affect the properties of the coating [9]. These macroparticles result from the explosive emission of droplets/particles from the arc sources during evaporation. The effect is particularly prevalent when depositing from materials of low melting point [1]. These particles are normally observed in the SEM as round protrusions on the surface of the sample. However it is extremely difficult to establish their exact size and shape in three dimensions, and their position through the thickness of the coating, which may reveal at which stage of the coating process they were deposited.

In the specimens deposited using the cathodic arc process, numerous macroparticles, up to several microns in size, were observed on the coating surface. Some of these particles are labeled *P* in Fig. 4a. Fig. 8a and b show cross-sections prepared from these particles on cathodic arc coated H13 steel. A particle is shown prior to milling in the bottom right inset image, where the dotted white line indicates the region from which the FIB cross-section was prepared. Fig. 8a shows that the particle lies below both the TiN and TiAlN layers, which can be distinguished in this image. XEDS analysis, performed in a SEM, of the bigger particle shown in Fig. 8b showed that it was composed of primarily titanium. It is therefore concluded that these particular Ti macroparticles are formed during the Ti ion etching process, and the coating grows over the top of these particles. This is in agreement with observations made by Aharonov *et al.* [10], who noted that 'droplets' seen on the surfaces of arc deposited nitride coatings growth are TiN, reproducing the shape of macroparticles made of the cathode material buried under the surface of the coating. From the elongated shape of the particles seen in Fig. 8, it can be concluded that the particles were in the liquid state when they were deposited onto the substrate.

TEM examination of the coatings was performed using specimens prepared by the FIB. This technique allows the production of large, uniformly thin, electron transparent areas. Fig. 9a–c are bright field TEM micrographs of the three different coating types (Fig. 9a) is a LVEB coating on a M2 high speed steel substrate, 9b is a TiN cathodic arc coating on a H13 steel substrate and 9c is the TiN-TiAlN multi-layer coating on

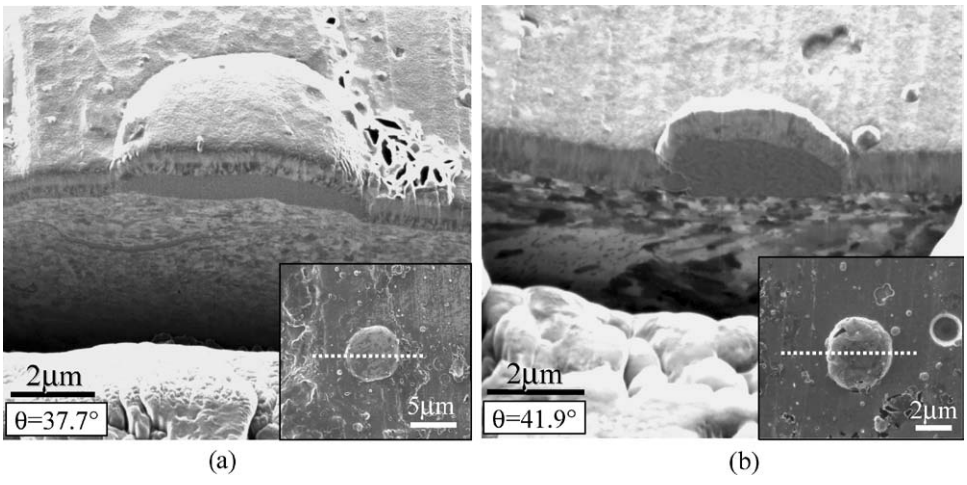

Figure 8 FIB cross-section prepared through macroparticles observed in the TiN/TiAlN cathodic arc coating deposited onto H13 steel. In each case the top view is shown in the inset image, with the position from which the cross-section was prepared indicated by the white dotted line.

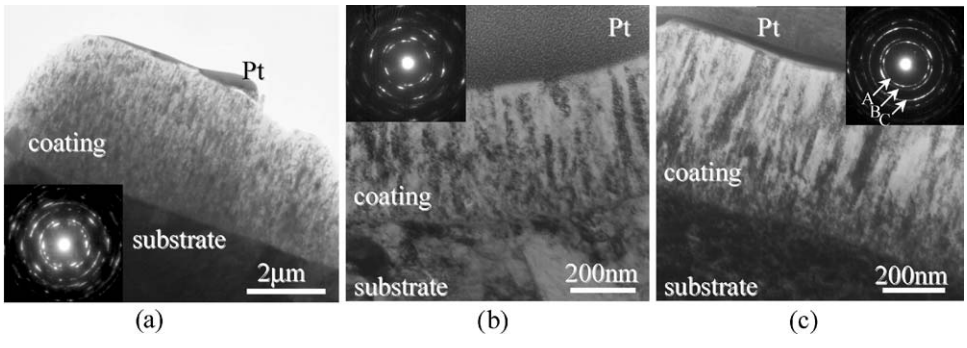

Figure 9 TEM bright field images of (a) the LVEB TiN coating on the M2 steel substrate, (b) the TiN cathodic arc coating on the H13 steel substrate and (c) the TiN/TiAlN coating on the V820 steel substrate. In each case, the respective diffraction pattern is inset.

a V820 steel substrate. In each figure the substrate and the coating are labeled, along with the remnants of a platinum layer applied in the FIB prior to thinning to protect the top edge of the sample. In addition, selected area diffraction patterns are provided, taken from an area near the middle of the cross-section of the coatings. The three Debye-Scherrer rings (labeled A, B and C in Fig. 9c) belong to the (111), (200) and (220) Bragg reflections of cubic TiN. The other rings belong to the higher (h, k, l) reflections. The measured lattice parameter closely corresponds to the to the reported lattice parameter of TiN (0.42 nm) [1]). TEM observations confirmed that all coatings displayed a columnar grain structure with grain-size 50–100 nm. Further, the samples prepared using the cathodic arc process displayed a finer, more equiaxed grain structure progressing toward a coarser, columnar structure toward the top of the coating. No obvious substrate modification was observed near the coating/substrate interface, nor was a Ti interlayer observed. In the dual-layer coating, growth continued epitaxially across the TiN/TiAlN boundary. A detailed TEM study of these materials is the subject of another report [11].

The excellent performance of PVD-coated TiN and TiAlN, which has lead to their widespread application over many years, is attributed to their structural integrity and even and consistent coverage, as evidenced by FIB cross-sections. In addition, deformation via grain boundary shear cracking and sliding allows the coatings to remain intact, even after deformation.

4. Conclusions

Cross sections prepared and imaged using the focused ion beam showed a columnar grain structure for TiN coating deposited using the LVEB process, and for both TiN and TiAlN dual-layer coatings deposited using a cathodic arc process. The grains grew through the TiN/TiAlN interface in the dual-layer coating.

Cross-sections taken from areas of the sample with an irregular surface confirmed that the columnar grains were oriented in the direction of growth, which is perpendicular to the specimen surface. The PVD coatings were deposited on all areas of the specimen surface, even in difficult to reach areas such as deep grinding grooves, though the deposition rate was lower in these hard-to-reach areas. Where the coatings growing from differently oriented surfaces met, they formed seams at the interface between the columnar grains of different orientations. In some cases, crack-like voids were observed along these seams. Cross-sections through a coating following nanoindentation showed that deformation occurs via through-thickness grain boundary shear cracking. In addition, macroparticles observed in the coatings deposited using the cathodic arc process were shown to be Ti-rich droplets deposited during the Ti ion etching stage.

Acknowledgements

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