EELS and STEM analysis of metal nitride/substrate interfaces

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Abstract. Nitride based protective coatings produced by physical vapour deposition offer a promising means to extend the oxidation and wear performance of $\gamma$-TiAl. Metal ion pre-etching of the substrate surface has been shown to significantly enhance the adhesion between the coating and substrate. In this study we have applied spectroscopic imaging and advanced STEM analysis to study such interfaces. For a conventional Cr cathodic arc discharge Cr ion implantation of $\sim$6nm into the substrate was observed. For an etch using high power impulse magnetron sputtering the metal ion implantation depth was reduced to $\sim$2-3nm. In both cases a corresponding depletion zone of Ti and Al was observed. In addition, nitrogen diffusion into the substrate during coating deposition was also revealed to a similar depth respectively.

1. Introduction

A requirement of protective surface coatings, designed for high temperature and wear resistance applications is an excellent adhesion between the substrate and coating. For coatings produced by physical vapour deposition (PVD) the principal technique to enhance adhesion usually involves the application of a substrate pre-treatment using an Ar glow discharge plasma. Previous studies have shown that the Ar glow discharge can sometimes result in poor adhesion due to insufficient removal of surface contaminants or coalescence of implanted Ar at the interface. On the other hand, etching with a metal arc discharge has resulted in an improvement in coating adhesion compared to glow discharge [1]. Such a pre-treatment process utilizes a cathodic arc discharge to generate the metal ion plasma. Cathodic arc discharges produce a high flux of metal ions effectively removing surface contamination such as oxide films while metal ion implantation helps to reduce the lattice mismatch between the substrate and coating, reducing interface stresses [2]. One drawback however of cathodic arc etches is the production of droplets on the coating surface which can lead to the formation of detrimental growth defects. A recent solution to this problem is the development of High Power Impulse Magnetron Sputtering (HIPIMS) which significantly reduces the formation of such growth defects resulting in dense coatings with a high adhesion to the substrate [3]. Potential alloys for aerospace and automotive applications such as $\gamma$-TiAl required protective coatings to extend component life times particularly at elevated temperatures. Knowledge of the structure of the interface between the applied coating and $\gamma$-TiAl substrate is therefore important in the evaluation of the coating/component performance. Hence, in this work, we present the application of electron energy-loss spectroscopy...
2. Experimental methods
Deposition of the nitride coating was performed in a Hauzer HTC 1000-4 PVD coater at the Nanotechnology Centre for PVD Research using unbalanced magnetron sputtering (UBM). Polished samples of γ-TiAl of composition Ti-45Al-8Nb-0.17C (at%) were subjected to either a Cr cathodic arc discharge or a Cr based HIPIMS etch prior to the UBM deposition of a TiAlN [2] or CrAlN [4] base layer respectively. The cathodic arc etching was performed with a substrate bias voltage of -1200V [1,2] whereas the HIPIMS etch utilized a substrate bias of -600V [5]. In both cases etching was performed in an Ar atmosphere (0.1 Pa) with a substrate temperature of 400°C.

Analysis of the coating and interface was performed using a JEOL 2010F TEM/STEM operating at 200kV equipped with an Oxford Instruments ISIS EDS system and a Gatan image filter (GIF). EDS analysis was performed in STEM mode across the interface between the base-layer and γ-TiAl substrate using a ~1nm probe at probe intervals of ~1.9nm and a spectrum acquisition time of 15 seconds per probe position. HAADF images of the interface were recorded before and after the line scan to assess specimen drift. Energy filtered images of the TiAlN/γ-TiAl interface were acquired at the Al L₂,₃ (73eV), N K (401eV), Ti L₂,₃, (456eV) and Cr L₂,₃ (575eV) edges. A slit width of 10eV was used for the Al L₂,₃ and 20eV for the N K, Ti L₂,₃ and Cr L₂,₃ each with an exposure time of 3x5 seconds.

Aberration corrected STEM was performed on the CrAlN/γ-TiAl interface in a modified Vacuum Generators STEM equipped with a Nion spherical aberration corrector and a Gatan Enfina EELS spectrometer. The EELS data was acquired at 100kV with a beam convergence half-angle of 24 mrad and a spectrometer collection angle of 19 mrad. High angle annular dark-field (HAADF) images were recorded with a detector acceptance angle of 70-210 mrad. Spectrum image EELS line scans were obtained across the interface with a nominal 0.15nm probe, a step size of 0.5nm and a spectrometer dispersion of 0.5eV/channel.

3. Results and Discussion
3.1. TiAlN/γ-TiAl with cathodic arc etch
A conventional STEM HAADF image of the lower region of the nitride coating and substrate is given in figure 1a revealing a band of bright contrast at the interface boundary. The results of EDS probe analysis across the interface (defined in figure 1a) is shown in figure 1b. A number of key features are evident, firstly an obvious Cr peak is observed within the substrate surface clearly demonstrating the effective ion implantation process during cathodic arc etching. Secondly a corresponding decrease in the Al signal and slight decrease in the Ti signal are also detected at the interface. The presence of significant Cr and reduction in the Al and Ti signal are therefore consistent with the observed bright contrast in the HAADF STEM image (figure 1a) since the average atomic number at the interface has clearly increased. However, due to the limitations with the detector efficiency it was not possible to record the relative nitrogen signal using EDS. Therefore additional energy filtered imaging was performed. The results of this investigation are presented in figure 2. A clear Cr signal is observed with a sharp onset in the intensity profile, tailing off with an implantation depth of 5-8nm into the substrate. Likewise the regions of Al and Ti depletion appear to correlate well with the region of Cr implantation. Interestingly, the N map exhibits the distinct presence of nitrogen diffusion into the substrate to a similar depth to that observed for the Cr implantation. Titanium aluminides are known to have a high affinity for nitrogen, forming nitrides preferentially during the initial stages of oxidation in air. Since the etch process was performed in Ar atmosphere the observed N diffusion region must have developed during the deposition stage of the nitride base-layer most likely during the very initial stages when significant nitrogen species would be present in the reactive atmosphere [1,2].
Figure 1. a) ADF-STEM image of the interface between the substrate and nitride coating, b) EDS line profile across the interface between the substrate (left hand side) and base-layer (right hand side).

Figure 2. EFTEM maps and corresponding intensity profiles across the interface between the TiAlN base-layer and Cr ion cathodic arc etched γ-TiAl substrate.

3.2. CrAlN/γ-TiAl with HIPIMS etch

A bright field aberration corrected STEM image of the interface between the substrate and base-layer of the HIPIMS etched sample is shown in figure 3a. The image illustrates the presence of coherent lattice fringes across the interface supporting previous reports of localized epitaxy between the coating and substrate after HIPIMS treatment [5]. A HAADF STEM image of the same region is shown in figure 3b indicating the position of the EELS and EDS line scans. The interface imaged in dark contrast in the BF-STEM image (figure 3a) is clearly observed in bright contrast in figure 3b suggesting a significant increase in the average atomic number at the interface as previously observed for the cathodic arc etched substrate. The result of EDS STEM analysis, shown in figure 4a, reveals a significant decrease in the Al content at the interface and a slight segregation of Nb (from the bulk substrate towards the substrate surface) both consistent with the HAADF image contrast. However, in this instance there is little evidence for any major Cr implantation compared to the cathodic arc treatment. The EELS spectrum image profile shown in figure 4b however confirms the presence of shallow Cr implantation with a slight increase in the Cr concentration at the substrate surface. As observed for the TiAlN cathodic arc etched sample, N diffusion is also revealed to a depth of 4-5nm into the substrate surface, most likely during the initial deposition of the nitride base-layer. It was not possible to record the Al EELS signal during the acquisition of the data shown in figure 4b (due to limitations with the coupling optics between the microscope and spectrometer). However, subsequent studies of the Al K edge (1560eV) across the interface boundary likewise showed a similar decrease at the interface supporting the previous EDS data.
4. Conclusions
We have successfully performed EELS, EFTEM and advanced STEM imaging of the interface between two nitride coatings and a γ-TiAl substrate. Regions of localised epitaxy were observed between the coating and substrate in each case. For a conventional Cr ion cathodic arc discharge and TiAIN coating a Cr ion implantation of ~6nm was observed into the substrate surface. For a Cr based HIPIMS etch and CrAlN coating the metal ion implantation depth was reduced to ~2-3nm. In both samples a corresponding depletion zone of Ti and Al was observed within the substrate surface. The diffusion of nitrogen into the substrate during coating deposition was also revealed to a similar depth to that corresponding to the ion implanted region.

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