Thermal stability of metal nitride multilayer coatings; investigations using EELS and aberration corrected STEM

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It has been successfully demonstrated that nano-structured metal nitride multilayer surface coatings deposited by unbalanced magnetron sputtering (UBM) can provide extensive oxidation and tribological protection to a variety of substrates [1,2]. In this study, such a coating consisting of alternating CrAlYN and CrN layers with a periodicity of ~4nm plus a CrAlY(O)N/Cr(O)N oxy-nitride top coat (~0.5µm) was deposited to a total thickness of ~5µm on an intermetallic substrate the details of which are given elsewhere [3,4]. To assess the thermal stability under oxidative conditions the coating and substrate were subject to isothermal oxidation in laboratory air for 168 hours at 850°C. Cross sectional samples of the coating, post oxidation, for TEM/STEM analysis were prepared by conventional methods and examination was performed in a JEOL 2010F TEM/STEM. In addition, high spatial resolution EELS spectrum image line scans were performed in a modified VG-STEM equipped with a Nion spherical aberration corrector and Gatan (Enfina) electron energy loss spectrometer at 100 kV 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 an inner detector acceptance angle of 70mrad.

Fig. 1a shows a conventional BF-TEM image of the post-oxidation coating surface illustrating the zoned structure within the oxidized surface. The total extent of the oxidized zones appears to be confined to within a region originally occupied by the oxy-nitride topcoat. Fig. 1b shows the Al L₂,3 EELS spectrum from (i) the Al rich oxide region within the oxidized surface and (ii) the corresponding edge from the outermost surface layer. The associated O K edge and Cr L₂,3 edge is shown in Fig.1c (i) and (ii) respectively. The EELS data highlights the presence of a mixed Al/Cr oxide within the outermost surface layer below which a phase separated region is evident consisting Cr rich oxy-nitride and Cr depleted/Al rich regions. For the latter region the energy-loss near edge structure at the Al L₂,3 and O K edges reflect features similar to those observed in gamma or delta alumina rather than the alpha (corundum) phase [5].

In the as deposited coating below the oxy-nitride topcoat layer the N concentration fluctuates with a Cr/N ratio of almost unity in the nominal CrN layers (1.05±0.01) that is a slight excess of Cr while in the CrAlYN layers the N concentration is significantly higher with a Cr/N ratio of 0.59±0.02 [4]. Comparison of experimental EELS data with theoretically determined spectra has confirmed the structure of the individual CrN and CrAl(Y)N layers in the as deposited coating to be stoichiometric CrN and (Cr0.5xAl0.5-yYx+y)N respectively (where Yx+y in the latter case <0.01) [6].

In the same coating after oxidation, regions directly below the original oxy-nitride topcoat clearly show the CrAlYN/CrN multilayer structure is retained. The HAADF image in Fig. 2a illustrates the presence of the multilayer in the post-oxidation coating. A spectrum image line profile over several multi-layers is defined in the Fig. 2a and the relative N to Cr profiles presented in Fig 2b. The corresponding HAADF intensity profile shows the apparent CrN layers in brighter contrast. The relative proportions of Cr and N appear similar to that of the as-deposited coating with a slightly higher relative Cr content which is consistent with the initial stages of nitrogen out diffusion. These results confirm our previous reports that the surface oxy-nitride top-coat acts as an effective barrier to oxygen inter-diffusion and the bulk CrAlYN/CrN multilayer structure remains structurally stable even after prolonged exposure to air at 850°C.
References

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Figure 1. (a) Cross-sectional BF-TEM image of the surface region of the post-oxidation coating. EELS data from the oxidized surface region (b) Al L$_{2,3}$ edge from (i) Al rich oxide regions, (ii) very top surface layer and (c) corresponding spectral region showing N K, O K and Cr L$_{2,3}$.

Figure 2. (a) HAADF-STEM image of the retained multilayer structure just below the surface oxidized region after exposure to 850°C for 168hrs in air, (b) The relative Cr and N distribution and HAADF intensity profile across the multilayer region defined by the spectrum image line scan labeled in 2(a).