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Transmission electron microscopy analysis of the interfaces of TiAlN/Mo multilayers

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Abstract: This paper focus on the analysis of the interfaces of nanocomposite TiAlN/Mo multilayers by high-resolution transmission electron microscopy (HRTEM). These thin films were deposited by reactive magnetron sputtering, with modulation periods below 7 nm. The structural disorder at the interfaces was probed by the analysis of the X-ray diffraction data, and afterwards correlated with the TEM observations on the cross-sections of the TiAlN/Mo multilayers. For specific deposition conditions, these structures can be prepared with relatively planar interfaces, revealing layer-by-layer growth. For modulation periods below 3 nm the intermixing acts a major role in the degradation of the multilayer chemical modulation.

Introduction

In specific engineering of multilayer coating design there is an important need of modelling in order to find the optimum conditions for the individual components of the bilayer. Nitride/metal multilayered coatings have attracted considerable attention because they combine properties of both hardness and elasticity; it has also been shown that nitride/metal multilayers [1] represent a promising category of coatings for improving surface mechanical properties due to the resulting hardness and elasticity, which is greater than that of the individual layers. The system that is studied in this work is a $Ti_{0.4}Al_{0.6}N$/Mo multilayer structure where the metal (bcc - body centered cubic) provides a softer and ductile layer while, the nitride (fcc – face centred cubic) accounts for the high hardness.

X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) are important tools for the study of the structural quality within the layers and at the interfaces since the microstructure is imaged with fine detail [2]. Atomic scale information on the structure of both the layers and the interfaces can be obtained as well as general features like columnar growth, grain size and orientation and interfacial roughness.

Experimental Details

The $Ti_{0.4}Al_{0.6}N$/Mo multilayer coatings were deposited on high-speed steel (AISI M2) substrates and (100) silicon wafers using a custom made reactive sputtering automated system operating in static mode. An automated gas inlet system enabled the continuous adjustment of the Ar/N_2 atmosphere, being the nitrogen only introduced during the nitride deposition. Additional information on these experimental techniques can be encountered elsewhere [3].

XRD θ-2θ scans were performed using a Bruker AXS D5005 diffractometer with Cu-Kα radiation, while for the TEM cross-section observation in high-resolution mode a JEOL 3010 equipment with accelerating voltages of 300 kV was used.

The XRD experimental profiles were calculated using the kinematical theory developed by Segmüller and Blakeslee [4,5]. Staring off with a set of interplanar spacing from the dominant crystalline texture growth, extracted from the XRD patterns of separate monolithic films of $Ti_{0.4}Al_{0.6}N$ and Mo, the number of atomic planes (monolayers) in each layer material was calculated, its standard deviation and the modulation period. After this, other structural parameters can be calculated such as an estimate for the grain size and the interface thickness due to either continuous layer thickness fluctuation or chemical intermixing.

Results and Discussion

This level of interfacial disorder, which is correlated with the overall rms roughness, can be viewed in figure 1, where a plot of both the XRD calculated rms interfacial roughness and interfacial intermixing is shown for several samples grown with 250 bilayers as a function of the modulation period (Λ). These roughness parameters are expressed in terms of monolayers, being the average monolayer equivalent to the average interplanar spacing (0.23 nm). It can be seen that as the period is reduced from 6 nm to 3 nm the structural disorder also decreases since the layers are growing thinner as is their thickness fluctuation. However, below 3 nm the roughness values increase again since in this periodicity range there is a strong chemical intermixing of the atoms, which grows stronger as the period is reduced to zero, where eventually it would turn into a composite film. This is in agreement with the fact that at low periods the rms roughness is practically similar to that amount of intermixing, being equal to two monolayers at the smallest period. It is important to note that the rms roughness values have a lateral validity that is linked with the coherency length of the X-rays, which in the high-angle mode is very small, about the size of a few grains.

HRTEM observation was used to image the fine structure within the cross-section of the $Ti_{0.4}Al_{0.6}N$/Mo multilayered coatings. Figure 2 corresponds to a micrograph of a sample grown with 250 bilayers, Λ=3.9 nm, revealing a high contrast layer-by-layer planar structure. The darker layers are associated with Mo due to the higher scattering factor of this constituent. The inset shows a selected area electron-diffraction pattern (SAD), which reveals that the dominant texture in the multilayered stacking growth is along [001], in agreement with the texture change from (111) to (002) that occurs when using a high negative bias voltage (–100 V). This has already been reported elsewhere [3] by the authors and results from the fact that for that for B1 NaCl structures the [111] direction possesses the densest array of atom columns while the [001] is the most open in the channelling direction. Moreover, the lowest surface energy for fcc (Ti,Al)N is (200) [6], therefore the preferred orientation should be along [001] when the ion bombardment is enhanced, as is the adatom mobility.

In figure 3 there is another HRTEM image now associated with a $Ti_{0.4}Al_{0.6}N$/Mo multilayer with 250 bilayers having Λ=1.6. By comparing it with figure 2, and bearing in mind the discussion from the XRD patterns, it is shown that for smaller periods the superlattice chemical modulation is degraded by the intermixing between the layers atoms species at the interfaces. On a larger lateral scale this structural disorder is noticeable as a waviness of the interfaces. Additionally, and from the inset SAD pattern, for this range of periodicity the texture is weaker and the crystalline growth is more random as proven by the several crystalline reflections present and by the distribution of the spots on those rings. The three-dimensional crystalline growth is more competitive in these conditions resulting in a stronger mixing at the interfaces. This factor lends a lesser contrast to the micrograph; however the modulation is still visible.

Conclusions

The interfacial roughness and intermixing was monitored and calculated using the XRD kinematical theory for multilayers. HRTEM cross-sectional observations further unveiled the interfacial quality of these coatings and revealed the structural coherency of the multilayers constituents at the interface. At the lower limit of Λ intermixing destroys the chemical modulation at the interfaces and contributes mostly to the rms roughness that was determined by the XRD profile calculation.

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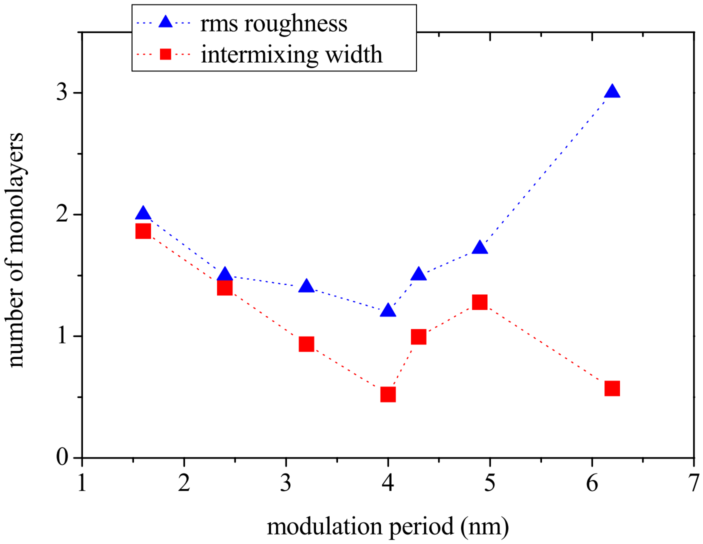

Fig. 1 – Evolution of structural disorder parameters with respect to the modulation periodicity for a set of $(Ti_{0.4}Al_{0.6}N/Mo)\times 250$ bilayers, resulting from the calculation the XRD patterns.

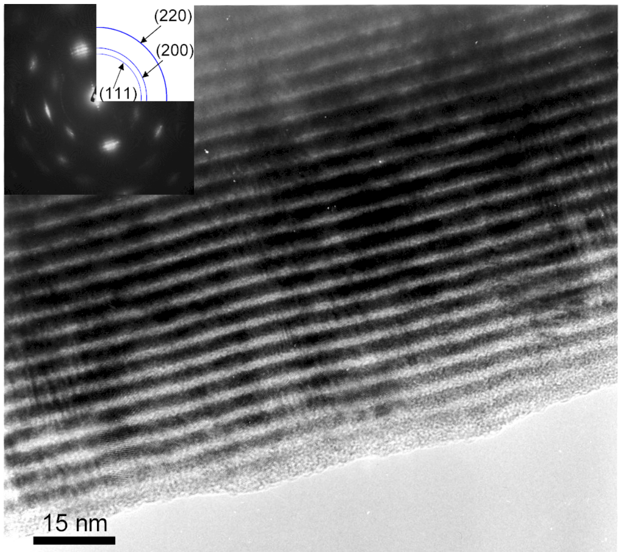

Fig. 2 – HRTEM micrograph from the cross-section of a ($Ti_{0.4}Al_{0.6}N$/Mo)×250 multilayer with Λ=3.9 nm, revealing the planar laminar growth. In the inset a SAD pattern evidences that the dominant crystalline texture (002) is along the multilayers direction of growth.

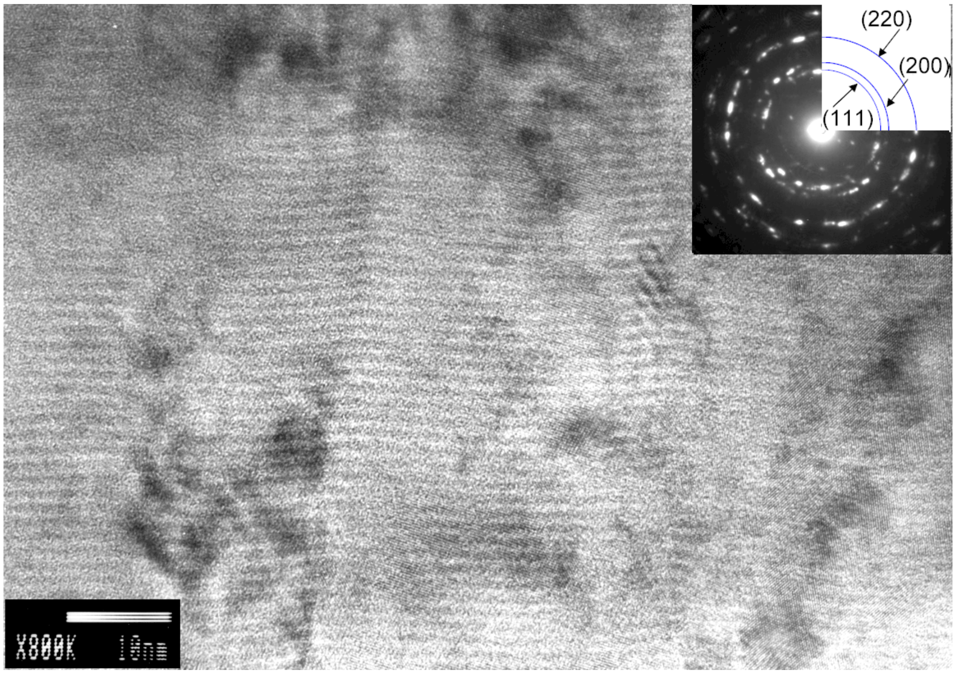

Fig. 3 - HRTEM micrograph from the cross-section of a ($Ti_{0.4}Al_{0.6}N$/Mo)×250 multilayer with Λ=1.6 nm, revealing a wavy laminar growth due to the intermixing present at the interfaces. The inset selected SAD reveals that the grains have a less textured growth and are distributed more randomly.