Thermal stability of wurtzite ZrAlN coatings studied by in-situ high-energy x-ray scattering during annealing

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Hard coatings are used to improve the wear resistance of many cutting tools. These hard coatings must withstand temperatures up to 1000 °C or above due to the high temperatures reached during a typical cutting operation. The most commonly used nitride coatings are based on the TiN system with TiAlN being the dominant coating material for wear resistant applications. The favourable high temperature mechanical properties of TiAlN are connected to the formation of nanostructured cubic (c)-TiN and c-AlN domains during decomposition of the unstable cubic structured TiAlN phase [1,2]. However, subsequent transformation of the metastable c-AlN into stable hexagonal-AlN at temperatures above ~900°C reduces the hardness of TiAlN coatings [3]. Therefore, other material systems that retain their hardness at temperatures exceeding 900 °C need to be considered. ZrAlN is one such material that shows promise for high temperature coatings. ZrAlN coatings are more difficult to stabilize in a cubic crystal structure while a wurtzite (w) solid solution phase can be grown when the Al-content is high [4]. Both cubic structured and hexagonal structured ZrAlN coatings have promising high temperature mechanical properties [4]. Further, semi-coherency between cubic and hexagonal phases in ZrAlN coatings may contribute to enhanced mechanical properties [5].

To study the thermal stability of w-ZrAlN, ~8 µm thick $Zr_{1-x}Al_xN$ coatings were deposited on WC-Co substrates using an industrial scale cathodic arc evaporation system. The coated substrates were then cut into 1 mm thick slices for in-situ synchrotron annealing measurements conducted in a tube furnace inside a vacuum chamber. The samples were heated at 20 K/min to a maximum temperature of 1100 °C and held at the maximum temperature for 3 hours. During annealing both small and wide angle x-ray scattering signals were recorded in transmission geometry by a two-dimensional detector (Perkin Elmer) (Figure 1). The beam size, defined by slits, was set to 10x100 µm^2 (vertical x horizontal) and a x-ray wavelength of 0.158 Å was used.

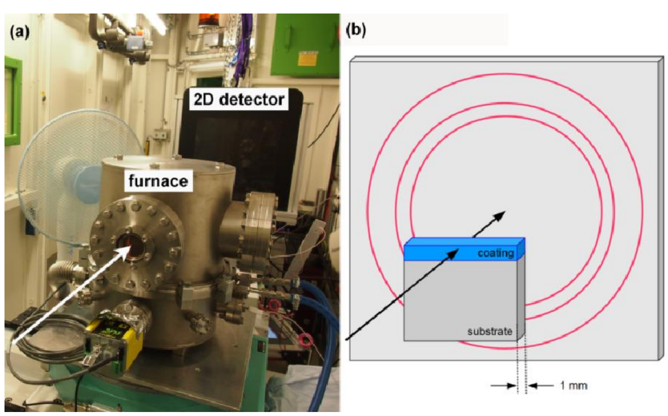

Figure 1: Experimental setup used during in-situ annealing experiments, (a) furnace and 2D detector with the x-ray beam direction indicated by the arrow and (b) a schematic illustration of x-ray transmission through the coating.

The wide angle scattering results (Figure 2) show that the lattice parameter of the wurtzite ZrAlN phase changes with Al-content, suggesting a solid solution. At ~800 °C the w-ZrAlN diffraction peaks broaden and with annealing time at 1100 °C, a new diffraction peak corresponding to a plane spacing of ~2.63 Å appears. The diffraction peak at ~2.63 Å belongs to a c-ZrN phase which forms with the 111-direction parallel to the wurtzite 002-direction. A small angle scattering signal is appearing at a similar temperature as the broadening of the w-ZrAlN 002-diffraction peak (not shown). The small angle scattering signal is observed only in the growth direction and suggests that a layered structure is formed during annealing. The layer period extracted from the small angle scattering signal is on the order of 2 nm and is constant with annealing time. The layer period changes with Al-content in the coating and is smaller for lower Al-content coatings.

The phase separation and formation of nanostructured layers result in retained or increased hardness of the annealed coatings compared to coatings in the as-deposited state.

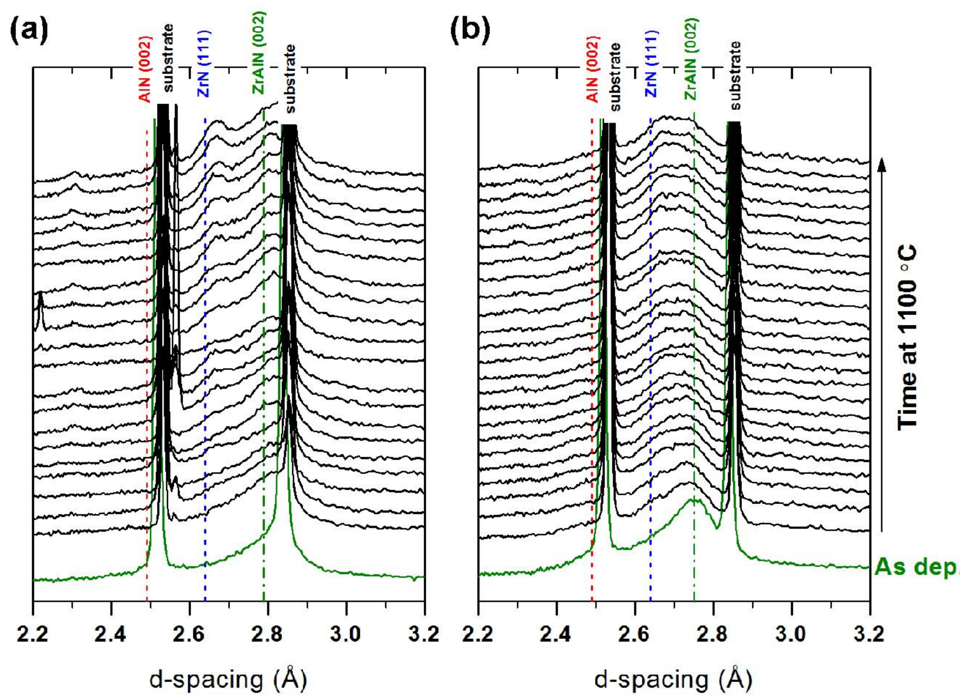

Figure 2: Lineouts in the coating growth direction from (a) $Zr_{0.49}Al_{0.51}N$ and (b) $Zr_{0.36}Al_{0.64}N$ showing the phase content evolution during 3 hours annealing at 1100 °C, the interval between each lineout being ~10 °C.

References

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