Effect of Y addition and thermal treatment on the phase stability of PVD deposited TiAlN coatings

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$Ti_{1-x}Al_xN$ coatings are well known for their excellent mechanical properties and thus used extensively as wear protection in various applications [1]. The deposition by low-temperature plasma-assisted vapor deposition (PVD) allows the preparation of a supersaturated $Ti_{1-x}Al_xN$ solid-solution with a cubic (c) NaCl structure for $x < 0.70$. Higher mole fractions lead to the formation of an additional hexagonal phase having a wurzite (w) structure [2]. The mechanical and tribological behavior of this hexagonal phase is inferior to the cubic modification and thus unwanted in industrial applications [3]. The addition of Y and Cr to TiAlN coatings was shown to improve the mechanical properties by grain refinement during film growth as well as the oxidation resistance as a result of the strong affinity of Y to O [4]. The effect of varying amounts of Y on the grain structure and phase composition of $(Ti_{1-x}Al_x)_{1-y}Y_yN$ coatings was recently investigated by means of conventional transmission electron microscopy (TEM) and X-ray diffraction [5], where reduction in the solubility limit due to the Y addition was reported.

In the current study, we investigate the local microstructure of the grain boundaries and the phase composition for films without Y (cTiAlN_0Y) and with 2 at% Y (cTiAlN_2Y) at room temperature (RT) and after annealing to 1050 ºC. Details on the film deposition can be found in [5]. Plan view TEM samples were prepared by lift-off of the film from the substrate and subsequent low energy Ar^+ ion thinning with energies ranging from 3 keV down to 0.3 keV. Sample investigation was carried out using a FEI Titan operated at 300 keV.

Selected area diffraction analysis confirmed the desired cubic structure for all investigated samples. In case of the sample containing no Y (cTiAlN_0Y_RT), grain sizes of about 20 nm were determined. High resolution (HR) images revealed that the grain boundaries were abrupt (Fig. 1b). For a sample containing 2 at% Y (cTiAlN_2Y_RT), a reduced grain size of about 5 nm and a more extended grain boundary phase with a width of about 2-3 nm was observed, as shown in Figure 2. This latter appears dark in the high angle annular dark field (HAADF) images indicating a lower average atomic number. This is further supported by EDS measurements indicating a higher Al and a lower Ti content in the grain boundary phase. EELS spectra document no significant differences in the N-K edge between grain interior and boundary, but pronounced changes of the Al-$L_{2/3}$ edge were seen. Annealing a cTiAlN_2Y sample at 1050 ºC (cTiAlN_2Y_1050) resulted in a microstructure with grain sizes of about 10-20 nm and very sharp boundaries, see Figure 3. No variations in Al content by EDS or changes in the EELS edges could be measured between grain interior and boundary region. Surprisingly, the Al-$L_{2/3}$ edge of the cTiAlN_2Y_1050 grains look similar to those of the grain boundary phase of sample cTiAlN_2Y_RT while the N-K edge more or less resemble the shape observed for the grains in cTiAlN_0Y_RT. To understand these results ab-initio calculations are required which are currently ongoing.

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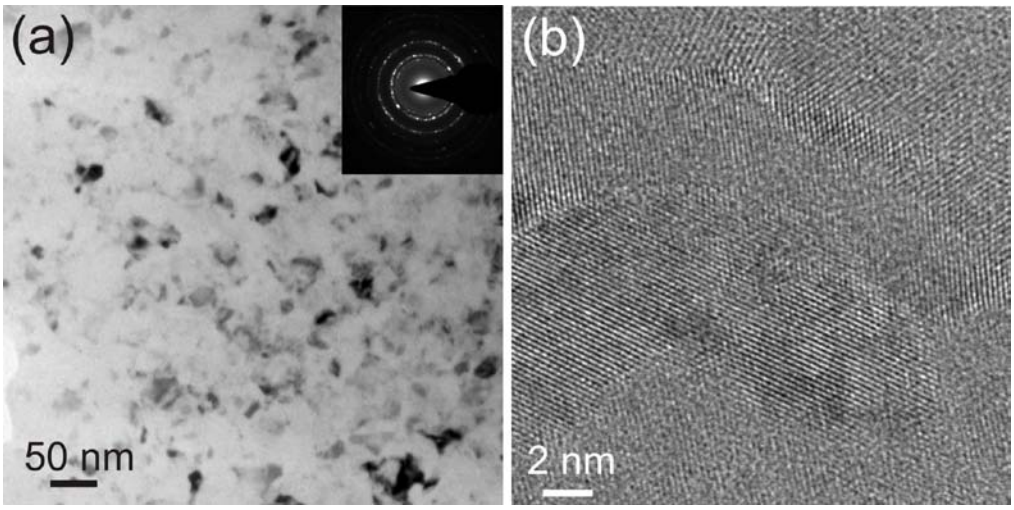

Figure 1. Sample cTiAlN_0Y_RT containing no Y and without heat treatment. (a) BF image showing grain morphology. The according SAD diffraction pattern confirms the cubic structure of the matrix. (b) HR image showing several grains and rather abrupt grain boundaries.

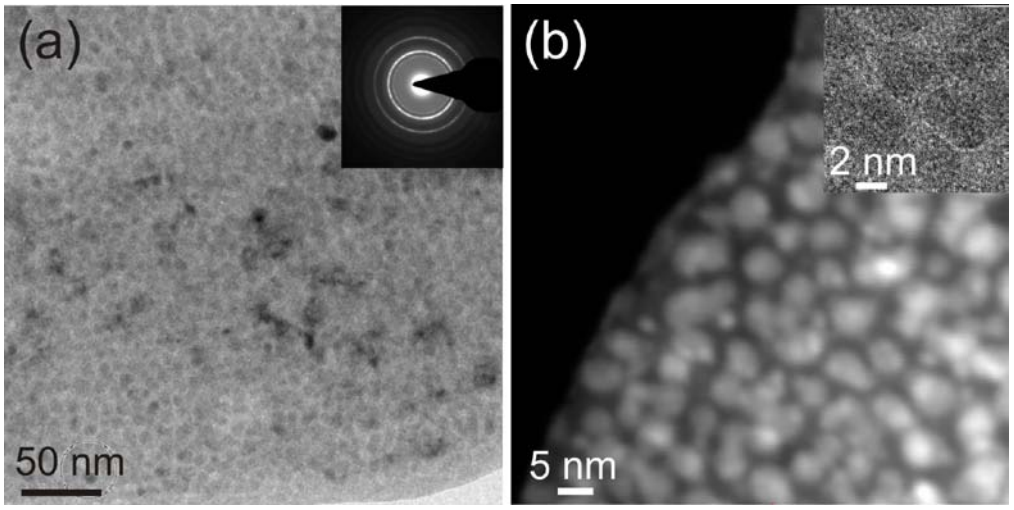

Figure 2. Sample cTiAlN_2Y_RT containing 2 at% Y and without heat treatment. (a) BF image showing grain morphology. The according SAD diffraction pattern depicts the cubic structure of the matrix and a high amorphous background associated with the existing grain boundary phase. (b) HAADF image and HR image showing an about 2-3 nm thick grain boundary phase.

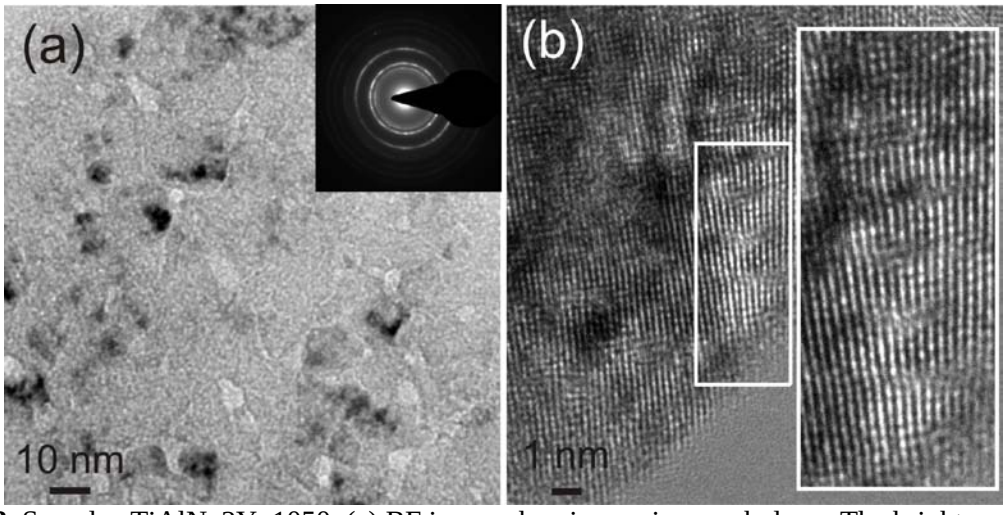

Figure 3. Sample cTiAlN_2Y_1050. (a) BF image showing grain morphology. The bright areas were most probably precipitates lost during preparation. (b) HR image showing a tilt boundary.

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