| ROBL-CRG | **Experiment title:** Decomposition process and thermal stability of metastable fcc-(Ti,Al)N in Ti-Al-N based multilayers | **Experiment number**: 20-02-720 |
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**Report:**

In the TiN/(Ti,Al)N/AlN and TiAlN/AlTiRuN multilayers deposited using cathodic arc evaporation (CAE), the decomposition of metastable fcc-(Ti,Al)N into the Ti- and Al-rich nitrides was studied by using *in situ* high-temperature glancing angle X-ray diffraction (HT-GAXRD) and *in situ* high-temperature small angle X-ray scattering (HT-SAXS) at ROBL BM 20 using an energy of E=11.5 keV ($\lambda$=0.10781 nm). The samples were annealed in a high temperature chamber at a pressure of $10^{-4}$Pa. *In situ* HT-GAXRD and HT-SAXS patterns were recorded at several temperatures between 550 and 950 °C as well as at 100°C after each annealing step. From the analysis of the HT-GAXRD patterns, the phase composition, the macroscopic lattice strain and the stress-free lattice parameter $a_0$ of the fcc-(Ti,Al)N phases were determined. The analysis of the SAXS measurements yielded the electron density, the interface roughness and the thickness of individual layers in the multilayer stack.

The as-deposited CAE TiAlN/AlTiRuN multilayers with the overall composition of $Ti_{0.45}Al_{0.53}Ru_{0.02}N$ that were deposited at the bias voltages of $U_B$= -40 V (coating I) and $U_B$= -80 V (coating II) contained fcc-(Ti,Al)N as major phase and traces of w-AlN. Additionally, the coating II was characterized by pronounced local concentration fluctuations resulting in Ti- and Al-rich fcc-(Ti,Al)N regions that were concluded from an asymmetric peak shape of the fcc-(Ti,Al)N diffraction lines. The *in situ* HT-GAXRD revealed the following thermal behaviour. After annealing at 650 °C a decrease of this asymmetry and $a_0$ (see Fig. 1) indicated the intermixing of Ti and Al in fcc-(Ti,Al)N. At 850°C the fcc-(Ti,Al)N phase started to decompose into Al-rich and Ti-rich fcc-(Ti,Al)N phases in both coatings. During annealing at 900°C this process continued and the phase fraction of Ti-rich fcc-$Ti_{1-x}Al_xN$ increased significantly permitting the determination of its $a_0$ which revealed an Al content of x~0.4 in the Ti-rich fcc-$Ti_{1-x}Al_xN$ phase of coating I and nearly Al-free fcc-TiN in

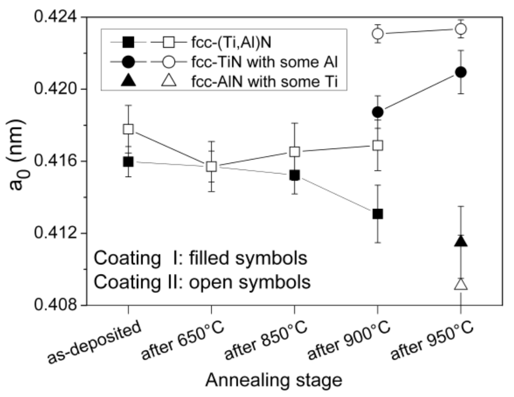


Fig. 1: Development of $a_0$ of the fcc-phases after different annealing steps in the coatings I and II.

coating II. Additionally, the amount of w-AlN increased in both coatings. During the thermal treatment at 950°C the separation of Ti and Al was nearly completed; the Al content in the Ti-rich fcc phase decreased further to x~0.2 in coating I. Furthermore, a considerable amount of fcc-AlN of ~(33±5) mol.% and (44±5) mol.% was stabilized in coating II and I, respectively. The phase fraction of w-AlN increased to ~(20±5) mol.% in sample II and almost 10 mol.% in coating I. These results revealed the influence of $U_B$ on the thermal stability of TiAlN/AlTiRuN multilayers, since the decomposition was accelerated in coating II as compared to sample I, although the chemical composition and the annealing conditions were indentical. In contrast to that, *in situ* HT-GAXRD experiments of the $Ti_{0.48}Al_{0.52}N$, $Ti_{0.47}Al_{0.53}Ru_{<0.01}N$, $Ti_{0.45}Al_{0.53}Ru_{0.02}N$ coatings deposited at $U_B$=-40 V did not indicate any significant influence of the Ru addition on their thermal stability.

In nanoscaled TiN/(Ti,Al)N/AlN multilayers deposited by CAE, the *in situ* HT-GAXRD and HT-SAXS experiments were used to determine the influence of the local lattice strains on the thermal stability of the fcc-(Ti,Al)N phase. In the as-deposited state, the TiN/(Ti,Al)N/AlN multilayers contained fcc-(Ti,Al)N as the major phase, which was surrounded by nearly Ti-free and Al-free regions that resulted from the periodic variation of the Ti and Al concentration. The concentration variations in the as-deposited coating were confirmed by X-ray reflectivity (XRR), which revealed a mass density of 5.4 g/cm³, 5.0 g/cm³ and 4.15 g/cm³ of the TiN, the intermixed (Ti,Al)N and the AlN layers, respectively. An additional sign of the concentration variations was a high roughness of the (Ti,Al)N/TiN and (Ti,Al)N/AlN interfaces. The thickness of the periodic motif in the TiN/(Ti,Al)N/AlN multilayers was calculated to be 7.8 nm. The thicknesses of the individual layers were approx. 5 nm for the TiN, 1.2 nm for the (Ti,Al)N and 1.9 nm for the AlN layers. The as-deposited multilayers were under high compressive residual stress (see Fig. 2). The multilayer structure was preserved up to an annealing temperature of 950°C. The spinodal decomposition of the (Ti,Al)N phase and the formation of fcc-AlN were observed at the annealing temperatures above 650°C via formation of fcc-AlN peaks and via increase of the stress-free lattice parameter of fcc-(Ti,Al)N, which arrived at the intrinsic lattice parameter of fcc-TiN (see dotted line in Fig. 2). In this temperature range, no subsequent transition of fcc-AlN into w-AlN was observed. The decomposition of fcc-(Ti,Al)N was accompanied by a gradual decrease of the compressive residual stress (σ) from -10 GPa to ~ 0 after the annealing at 950°C. The decomposition of fcc-(Ti,Al)N into fcc-TiN and fcc-AlN was seen by the XRR through an decrease of the mean thickness of the TiN layers to approx. 4 nm and through an increase of the AlN layer thickness to approx. 2.9 nm, whereas the total layer thickness and the thickness of the periodic motif remained constant. The layer thickness of the diffuse intermixing layers decreased to from 1.2 nm to 0.9 nm, their mass density from 5.0 g/cm³ to 4.32 g/cm³. The XRR experiments confirmed the phase decomposition of the fcc-(Ti,Al)N phase by spinodal decomposition into fcc-TiN and fcc-AlN without the formation of w-AlN due to the assistance of the high local lattice strains in the as-deposited state.

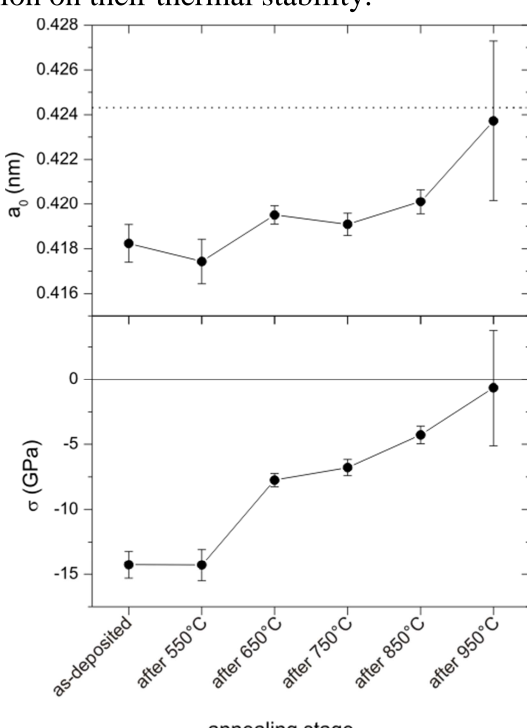

Fig. 2: Development of $a_0$ and σ of the fcc-phases after different annealing steps in a TiN/(Ti,Al)N/AlN multilayer.