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# Interface-directed spinodal decomposition in TiAlN/CrN multilayer hard coatings studied by atom probe tomography

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**Abstract**

Microstructural and compositional changes in TiAlN/CrN multilayered films occurring at temperatures up to 1000 °C were studied at different length scales by a combination of atom probe tomography, transmission electron microscopy and X-ray diffraction. We observe the onset of decomposition of the multilayer structure at 700 °C via the mechanism of interface-directed spinodal decomposition of TiAlN layers, where Al atoms preferentially move toward the nearest interface and segregate there. The interface-directed mechanism later transforms into isotropic spinodal decomposition and is accompanied by intense interdiffusion between the constituting layers. Distinct compositional gradients across columnar grain boundaries (extending perpendicular to the multilayers) are detected at this stage of decomposition. Drastic differences in decomposition behavior across the film depth were observed at elevated temperatures (800–1000 °C): the layered structure completely dissolves in the near-surface part but persists in the regions distant from the surface. The influence of residual stresses caused by the sputter deposition process on the thermally induced evolution of the multilayer thin films is discussed.


*Keywords:* Multilayer thin films; Nitrides; Atom probe tomography (APT); Spinodal decomposition; Residual stresses

## 1. Introduction

Many tribological loading situations require materials with an excellent combination of mechanical contact strength and corrosion resistance that is often not attainable for conventional bulk materials. A promising approach to meet these requirements is the "bottom-up" synthesis of nanostructured materials, e.g. preparation of compositionally modulated nanoscale multilayers by physical vapor deposition (PVD) techniques [1–10]. The properties of such multilayers (both metallic and ceramic) often deviate strongly from those of the corresponding bulk materials and are essentially controlled by the high interface density. The strength and hardness of multilayer hard coatings can be substantially increased by reducing the layer thickness to the nanometer range, where in-grain deformation is size limited, and the layer interfaces act as highly effective obstacles against dislocation motion [11]. The composition, elastic constants, thicknesses of the constituent layers as well as the interfacial widths are important parameters in this context, as they determine the critical shear stress across the layer interfaces. By carefully controlling these properties, hardness values up to 5000 kg mm$^{-2}$, which are comparable to cubic BN and only exceeded by diamond, can be achieved in many nitride multilayer systems such as TiN/AlN [5], TiN/NbN [6] and CrN/AlN [9]. Nitride hard coatings with high Al and Cr contents also exhibit good corrosion and oxidation resistance due to the formation of a passivation layer on the surface [12–14]. Such nitride multilayers have high potential as protective coating materials of cutting tools and machine parts. However, multilayers are typically in a metastable state due to the high interface density and hence

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possess only limited thermal stability [15]. The operation temperatures in dry-cutting applications can reach 1000 °C [16], leading to interdiffusion and dissolution of the nanolayered structure, which usually gives rise to a substantial deterioration of the mechanical properties.

One high-performance coating systems that shows an outstanding combination of wear and oxidation resistance is multilayered TiAlN/CrN [17]. Although the microstructure and mechanical properties of TiAlN/CrN multilayers as well as their thermal evolution have been studied before [17–21], the structure–property relationships of these coatings are not well understood. First, studies of the thermal stability have been usually carried out in air, which makes it difficult to distinguish between thermal and oxidation effects. Second, almost no information is available for nitride multilayer hard coatings regarding the elemental distribution at atomic scale. However, such compositional data are necessary for understanding diffusion and decomposition phenomena occurring at elevated temperatures.

Previous studies of TiAlN/CrN coatings revealed that short-range diffusion at interfaces starts already at 500 °C, but a decrease in hardness and pronounced compositional changes begin at a temperature as high as 700 °C [17,22]. The current study is focused on the nanolayered $(Ti_{0.75}Al_{0.25})N$/CrN hard coating synthesized by means of sputter deposition. The chosen Ti:Al ratio yields a coating with single-phase face-centered cubic (fcc) structure and superior mechanical properties [21,23]. To elucidate both structural and chemical changes in TiAlN/CrN multilayers under elevated temperatures, we employ atom probe tomography (APT) in conjunction with transmission electron microscopy (TEM) and X-ray diffraction (XRD). To reveal only thermally induced changes in multilayers and distinguish them from oxidation-related phenomena at high temperatures, multilayers were heat treated in a purified Ar atmosphere (i.e. oxidation was completely excluded). The current study focuses on temperatures up to 1000 °C, which is a typical operating range for cutting tools.

## 2. Experimental details

$Ti_{0.75}Al_{0.25}N$/CrN multilayers were prepared by means of reactive DC sputter deposition on a M2 HSS (high-speed steel) substrate attached to a rotating sample holder. The substrate was polished, cleaned with acetone and ethanol, and subsequently cleaned in a deposition chamber by $Ar^+$ bombardment. $Ti_{0.75}Al_{0.25}$ alloy and pure Cr were used as target materials. After deposition of a Cr buffer layer on the substrate, an Ar(60 vol.%)/$N_2$(40 vol.%) gas mixture was supplied to the chamber for deposition of the metal nitride layers. Prior to the deposition of multilayers, a 100 nm TiAlN buffer layer was deposited, where the bias voltage and temperature of the substrate were kept at −150 V and 300 °C, respectively. Additional information about the deposition procedure can be found in Ref. [21]. The total thickness of the multilayers after deposition was about 2 μm. The Ti:Al ratio of the as-sputtered TiAlN layers determined by wavelength-dispersive electron probe microanalysis (JEOL, JXA-8500F) was found to be 2.8:1.

The substrate plate with deposited coating was cut into pieces using spark erosion to avoid undesirable heating. The cut samples were sealed into quartz ampoules with purified Ar (>99.99%) and a Ti getter and annealed at different temperatures up to 1000 °C. Further APT analyses showed no oxygen contamination of the film due to annealing. Structural characterization of the film was performed using transmission electron microscopy in scanning mode (JEOL JEM-2200FS, 200 kV) and wide-angle XRD (Co $K_\alpha$ radiation) operating in Bragg–Brentano geometry. APT analyses were carried out with a Cameca LEAP™ 3000X HR system, applying laser pulses of 532 nm wavelength with 250 kHz pulse frequency, ~12 ps pulse length and 0.4 nJ pulse energy. The specimen base temperature and detection rate were kept at ~60 K and 0.5%, respectively.

TEM and APT specimens were prepared using a dual-beam focused-ion beam (FIB) (FEI Helios Nanolab 600) following the lift-out procedure [24,25]. To avoid analyzing near-surface regions of the film, which might have been damaged by spark erosion, APT specimens were prepared from the region 100–300 nm below the surface unless otherwise stated. To reduce the amount of Ga implantation during FIB preparation, TEM and APT specimens were milled using 5 keV ion energy for the final preparation step. The resulting Ga contamination as analyzed by APT was <0.01 at.% for all specimens. The level of other impurities in the as-sputtered coating (predominantly oxygen stemming from the residual atmosphere inside the sputtering chamber) was directly determined from the APT mass spectra and did not exceed 0.1 at.%.

## 3. Results

### 3.1. X-ray diffraction

The as-sputtered film shows single-phase fcc (B1-type) structure according to the XRD data (Fig. 1). Only (1 1 1) and (2 2 2) Bragg peaks of the B1 structure appear in the XRD patterns. Since weak XRD peaks from the steel substrate appear as well, the pattern obviously yields structural information from the entire thickness of the film. The coating in the as-sputtered state has a fiber structure where all grains have ⟨1 1 1⟩ crystallographic orientation in the direction of film growth. The lattice parameter of the fcc phase determined from the positions of the Bragg peaks is 0.427 nm, which is slightly higher compared to bulk fcc CrN (0.414 nm) and TiN (0.424 nm) phases [26], indicating dilatation of the lattice in the growth direction. The dilatation is associated with the sputter-deposition process, which causes introduction of numerous defects due to intensive ion bombardment. As the film is attached to the substrate and is not free to expand in the in-plane direction, dilatation creates residual compressive stresses parallel to