Influence of phase transformation on the damage tolerance of Ti-Al-N coatings

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\textbf{ABSTRACT}

In contrast to earlier work, where we focused on the evolution of fracture toughness upon annealing of free-standing Ti-Al-N films using cantilever bending experiments, here we study the practically more relevant case of thin Ti-Al-N films firmly attached to a stiff substrate. We found - experimentally and by continuum mechanics modeling using the Transformation Field Analysis - that the formation of even tiny fractions of hcp (ZnS-wurtzite type) AlN during decomposition of supersaturated fcc (NaCl-type) Ti-Al-N gives rise to high in-plane compressive stresses in both the matrix and the precipitates. These eigenstresses impede the formation and propagation of cracks as evidenced by cube corner nanoindentation experiments – the measured fracture toughness ($K_{IC}$) increases from the as-deposited value of $\approx 4.4\text{ MPa}\sqrt{\text{m}}$ to $\approx 8.0\text{ MPa}\sqrt{\text{m}}$ when annealed at 900°C. The (apparent) toughening effects combine with less pronounced inherent toughening and concomitant age hardening effects to enhanced damage tolerance of annealed Ti-Al-N.

Limited atomic assembly kinetics during low temperature physical vapor deposition and extremely high local cooling rates in the film growth processes allow the synthesis of metastable phases \cite{1}. Even thermodynamically instable materials can be synthesized or stabilized as nanometer thick layers, especially when grown on lattice-matched template layers \cite{2–5}. In the latter case, the minimization of chemical, surface, and strain energy determines which crystal structure is preferred. If the resulting crystal structure has a smaller molar volume than the thermodynamically stable counterpart, the phase transformation into the stable configuration (under volume expansion) gives rise to the buildup of compressive stresses if the film is firmly attached to a stiff substrate. The compressive stresses can be expected to lead to an apparent increase in fracture toughness of the coating. Similar apparent toughening effects underlie, e.g., the transformation toughening due to martensitic-like phase transformations in the vicinity of crack tips or the Gorilla glass \cite{6} used for touchscreens of mobile devices and tablets, where intentionally implemented compressive stresses near the surface impede the formation of cracks. A low fracture toughness is usually the most restrictive property of ceramics and toughening by phase transformations offers an effective route towards reducing the susceptibility of ceramics to brittle failure.

Ti$_1-x$Al$_x$N is one of the best-established supersaturated materials in the field of hard protective coatings \cite{7}. Up to an AlN mole fraction ($x$) of $\approx 0.7$ (see for instance Ref. \cite{7}), Ti$_1-x$Al$_x$N crystallizes in a supersaturated NaCl-type face-centered cubic (fcc, B1, simply abbreviated here with c-) structured solid solution, where Al substitutes Ti on the metal sublattice. At temperatures typical for cutting tool operations, the solid solution iso-structurally transforms by spinodal decomposition into nanometer-sized fcc structured AlN- and TiN-rich domains resulting in age hardening effects \cite{8,9}. Recently, the authors found an – albeit slight (within the error bars) – increase in inherent fracture toughness for Ti-Al-N hard coatings upon vacuum annealing \cite{10} by testing free-standing film material in cantilever bending experiments. The aim of the present work, in contrast, is to study the fracture toughness evolution of Ti-Al-N upon annealing for the more practically relevant situation of thin Ti-Al-N coatings firmly attached to a stiff substrate.

We used continuum mechanics mean field theories to predict stresses due to the volume expansion associated with the cubic to hexagonal phase transformation in Ti-Al-N. Whereas standard Mori-Tanaka approaches can be used to determine phase averaged stresses in transforming two-phase systems, a Mori-Tanaka-based Transformation Field Analysis (TFA) \cite{11} framework allows handling multiple inclusions phases subjected to inelastic strains, e.g., due to thermal loads and/
or phase transformations, compare also Ref. [15]. Here, we applied this TFA framework to model the residual stress states due to the decomposition of c-Ti<sub>1</sub>-Al<sub>x</sub>N. The microstructure of the daughter phases was idealized as a two-phase system consisting of a c-Ti<sub>1</sub>-Al<sub>x</sub>N matrix with embedded wurtzite-type (hcp, B4, simply abbreviated here with h-) AlN precipitates in the shape of spherical particles. For simplicity, the matrix was assumed to be homogeneous (although atom-probe tomography [12] investigations have shown that the matrix phase is heterogeneous at the nanoscale as a result of the spinodal decomposition). The material parameters for c-Ti<sub>1</sub>-Al<sub>x</sub>N and h-AlN employed in the micromechanical model were taken from ab initio calculations [13,14].

Table I lists the orientation averaged Young’s moduli E and the Poisson’s ratios ν of the Ti<sub>1</sub>-Al<sub>x</sub>N matrix for a set of different Al mole fractions x (both taken from Ref. [14]) as well as the volume change δ (Ref. [13]) due to transformation of parent c-Ti-Al-N into daughter h-AlN. Note that the elastic constants listed here were orientation averaged. x represents the normalized Al mole fraction in the remaining matrix phase.

| x       | 1 − x | E<sub>c-Ti-Al-N</sub> [GPa] | E<sub>h-AlN</sub> [GPa] | ν<sub>c-Ti-Al-N</sub> | ν<sub>h-AlN</sub>
|---------|-------|-----------------------------|--------------------------|-----------------------|---------------------|
| 0.000   | 1.000 | 72.3429                     | 0.0000                   | 447.583               | 0.2078              |
| 0.5789  | 0.4211| 72.5469                     | 0.00282                 | 447.281               | 0.2079              |
| 0.5556  | 0.4444| 72.7736                     | 0.00595                 | 446.945               | 0.2080              |
| 0.5294  | 0.4706| 73.0173                     | 0.00932                 | 446.570               | 0.2081              |
| 0.5000  | 0.5000| 73.2885                     | 0.01307                 | 446.148               | 0.2082              |
| 0.4667  | 0.5333| 73.5811                     | 0.01712                 | 443.455               | 0.2115              |
| 0.4286  | 0.5714| 73.9067                     | 0.02162                 | 440.377               | 0.2151              |
| 0.3846  | 0.6154| 74.2685                     | 0.02662                 | 436.826               | 0.2194              |
| 0.3333  | 0.6667| 74.6720                     | 0.03219                 | 432.635               | 0.2243              |
| 0.2727  | 0.7273| 75.1256                     | 0.03847                 | 439.377               | 0.2269              |
| 0.2000  | 0.8000| 75.6428                     | 0.04561                 | 445.288               | 0.2247              |
| 0.1111  | 0.8889| 76.2353                     | 0.05381                 | 447.755               | 0.2218              |
| 0.0000  | 1.0000| 76.9354                     | 0.06348                 | 477.596               | 0.2316              |

Table 2

| a<sub>i</sub>[Å] | c<sub>i</sub>[Å] | E<sub>h-AlN</sub>[GPa] | ν<sub>h-AlN</sub> | ν<sub>c-Ti-Al-N</sub> | a<sub>h-AlN</sub>[Å] | c<sub>h-AlN</sub>[Å] | E<sub>c-Ti-Al-N</sub>[GPa] | ν<sub>c-Ti-Al-N</sub> |
|------------------|-----------------|------------------------|-----------------|------------------------|----------------------|-----------------------|--------------------------|----------------------|
| 3.1262           | 5.0233          | 85.81217               | 0.175404       | 292.5                  | 0.25                 |

The material parameters for c-Ti<sub>1</sub>-Al<sub>x</sub>N and h-AlN employed in the micromechanical model were taken from ab initio calculations [13,14]. Table I lists the orientation averaged Young’s moduli E and the Poisson’s ratios ν of the Ti<sub>1</sub>-Al<sub>x</sub>N matrix for a set of different Al mole fractions (x) as well as the volume change δ due to transformation of parent c-Ti<sub>1</sub>-Al<sub>x</sub>N into h-AlN, the material parameters used for the latter being given in Table II. Two sets of macroscopic boundary conditions were applied: “free boundary conditions” (FBC) and “layer boundary conditions” (LBC). Whereas the former directly correspond to the free-standing cantilevers, the latter describe a situation where a thin layer attached to a rigid substrate is able to deform only in the direction perpendicular to the film/substrate interface. Phase averaged stress tensors were evaluated for the phase volume fractions of the daughter phases, ξ, corresponding to given transformed Al mole fraction, x. Accordingly, the predictions do not account for details of the nucleation and growth of the AlN phase and, being based on mean-field micromechanical models, cannot resolve possible effects of the absolute size of the inclusions.

Fig. 1 shows the modelling results for the phase averaged stresses as functions of the transformed Al mole fraction (the c-Ti-Al-N matrix becomes depleted in AlN which transforms into h-AlN). The TFA predicts high compressive stresses in the h-AlN precipitates (Fig. 1(a), light blue curve) in the case of the FBC, but the specific volume expansion has to be accommodated by elastic deformation of the neighboring matrix, which is why the latter is subjected to tensile stresses (Fig. 1(a), dark yellow curve). With increasing transformed Al mole fraction from 0 to 0.6, the tensile stresses in the matrix increase from 0 to +8.8 GPa, while the compressive stresses in the precipitates decrease from −19.1 to −5.3 GPa. The transformed Al mole fraction of 0.6 corresponds to fully decomposed Ti<sub>0.4</sub>Al<sub>0.6</sub>N, that is, the film is a two-phase system comprised of c-TiN plus h-AlN. These results, which correspond to free-standing cantilevers from which the substrate material was removed, indicate that the formation of even tiny fractions of h-AlN results in tensile stresses in the matrix, which presumably lower the measured K<sub>C</sub> values for such a (free-standing pre-notched cantilever bending) configuration.

In contrast, the in-plane stresses predicted for LBC, corresponding to a thin film firmly attached to a thick substrate, are compressive for both the h-AlN particles and the matrix (Fig. 1(b), red and dark blue curves, respectively). Extrapolating the phase averaged stresses to x → 0 gives compressive stresses of −19.1 GPa for initially emerging h-AlN particles, which increase to −23.3 GPa for an Al mole fraction of 0.6. Simultaneously, the compressive in-plane stresses in the formerly stress-free matrix steadily increase to −14.0 GPa for the fully decomposed AlN matrix (Al mole fraction of 0.6). The stresses in out-of-plane direction (Fig. 1(b), green and purple curves), however, are similar to the ones predicted for the FBC case. Analogous results (not shown here) were obtained with TFA models based on the classical self-consistent scheme [11], which describe microstructures that are not necessarily of the matrix-inclusion type. Note that the version of the TFA used here does not account for the relaxation of residual stresses, e.g., by dislocations or migration of point defects. As a consequence, the model shows a tendency for overestimating stress levels.

As predicted by Density Functional Theory simulations and experimentally proven by in-situ high pressure experiments, the B1-structured AlN variant is favored for pressures above ~13–23 GPa [15]. Hence, high compressive stresses due to the formation of small amounts of h-AlN precipitates should stabilize the remaining cubic phase. Or, in other words, the compressive stresses enhance the thermal stability of c-Ti-Al-N coatings by shifting the formation of the thermodynamically stable (but softer) h-AlN to longer annealing time and/or higher temperature. The distribution and crystallographic orientation of the h-AlN precipitates can be controlled by film structure and orientation in the as-deposited state (cf. Ref. [16]).

To experimentally study the effect of compressive residual stresses on the fracture toughness of Ti<sub>1</sub>-Al<sub>x</sub>N in layer-substrate systems, we synthesized Ti<sub>0.4</sub>Al<sub>0.6</sub>N films with a thickness of about 1.8 μm on Al<sub>2</sub>O<sub>3</sub> (100) substrates using a modified Leybold Heraeus Z400 reactive magnetron sputter system. The films were grown in a mixed Ar/N<sub>2</sub> gas atmosphere (Ar/N<sub>2</sub> flow ratio = 4 sccm/6 sccm, total pressure = 0.35 Pa) by applying a constant current of 1 A to a 3″ Ti<sub>0.4</sub>Al<sub>0.6</sub>N target (99.5% purity, Plansee Composite Materials GmbH), while the temperature of the opposed substrates was kept constant at 500 °C. A negative bias voltage of −50 V applied to the substrate during film growth ensured a dense growth morphology. The as-deposited coated Al<sub>2</sub>O<sub>3</sub> substrates were vacuum annealed in a Centorr LF22-2000 vacuum furnace at a base pressure < 3 × 10<sup>−8</sup> Pa at maximum temperatures ranging from 750 to 900 °C using a holding time of 10 min.

Table 2

Material properties of h-AlN (Ref. [14]).

| α<sub>i</sub>[Å] | α<sub>i</sub>[Å] | E<sub>h-AlN</sub>[GPa] | ν<sub>h-AlN</sub> | ν<sub>c-Ti-Al-N</sub> | α<sub>h-AlN</sub>[Å] | α<sub>h-AlN</sub>[Å] | E<sub>c-Ti-Al-N</sub>[GPa] | ν<sub>c-Ti-Al-N</sub> |
|----------------|-----------------|------------------------|-----------------|------------------------|----------------------|-----------------------|--------------------------|----------------------|
| 3.1262         | 5.0233          | 85.81217               | 0.175404       | 292.5                  | 0.25                 |

Table 2

Material properties of h-AlN (Ref. [14]).
Further details of the film synthesis and annealing treatment can be found in Ref. [10].

Fig. 2(a) shows integrated Debye-Scherrer diffraction patterns of our Ti-Al-N coatings recorded at the Nanofocus Endstation of the Beamline P03 of the light source PETRAIII [17]. The diffraction patterns were collected in transmission geometry by applying a cross-sectional X-ray nanodiffraction approach [18,19] using monochromatic X-ray radiation with a wavelength of \( \sim 0.82 \) Å. In line with our previous X-ray diffraction analyses reported in Ref. [10], the data show that built-in structural point and line defects (originating from the film growth) heal out above the deposition temperature in the single phase c-Ti\(_{1-x}\)Al\(_x\)N. This is indicated by the shift of the diffraction peaks to higher 2\( \theta \) angles (corresponding to a smaller lattice constant) and the decrease in peak breadths when comparing the as-deposited sample with the sample annealed at 750 °C. Iso-structural spinodal decomposition into c-TiN- and c-AlN-rich domains occurs above 850 °C (evidenced by the formation of a shoulder close to the (200) peak at 2\( \theta \) \( \sim \) 23°) and becomes more pronounced for the 900 °C annealed sample. Hexagonal structured AlN is hardly detectable at 850 °C, but becomes evident at 900 °C (see in particular the emerging 00.2 diffraction peaks at 2\( \theta \) \( \sim \) 19° marked with orange arrows). Hence, increasing the temperature from 850 to 900 °C leads to an increase in volume fraction of h-AlN. The presence of h-AlN in the 900 °C annealed sample can be clearly seen when using high resolution transmission electron microscopy (see Fig. 2(b) and Ref. [10]).

The evolution of residual stress in c-Ti\(_{1-x}\)Al\(_x\)N upon annealing was determined from the elliptical distortion of the (200) Debye-Scherrer diffraction rings according to the sin\(^2\)\( \phi \) method [18] (we assumed ideally circular Debye-Scherrer rings in the case of a stress-free sample). The X-ray elastic constants of Ti\(_{0.4}\)Al\(_{0.6}\)N were calculated from single crystal elastic constants taken from Density Functional Theory simulations [13] using the Hill grain interaction model [20]. The analysis shows that high compressive stresses of \( \sim \) −3.9 \( \pm \) 0.3 GPa in the as-deposited c-Ti-Al-N matrix decrease to −2.5 \( \pm \) 0.1 GPa at 750 °C before steeply increasing to −5.2 \( \pm \) 0.3 GPa (Fig. 3(a)). The compressive stresses in the as-deposited state can be mainly ascribed to ion bombardment during film growth (driven by the negative bias voltage of −50 V applied to the substrates) [21]. In addition, thermal stresses due...
to the mismatch in the coefficients of thermal expansion [5,22] of film and substrate materials contribute to the overall stress state. The decrease of the compressive stresses results from recovery of built-in structural point and line defects above the deposition temperature (here 500 °C) and iso-structural spinodal decomposition of the c-Ti-Al-N solid solution into c-AlN- and TiN-rich domains, as the lattice parameter of the supersaturated c-Ti1-xAlxN has a positive deviation from the linearly interpolated lattice parameters of c-TiN and c-AlN [14,23]. The effect of spinodal decomposition in Ti-Al-N on the residual stress state was studied in detail by Rogström et al. [24] by in-situ X-ray scattering experiments and phase field simulations. Along with the formation of h-AlN, high compressive stresses form and increase with increasing volume fraction, in qualitative agreement with our TFA simulations (Fig. 1(b), dark blue curve) and earlier continuum mechanics modelling [14] and an in-situ high-temperature X-ray diffraction study [25].

To evidence impeded or even mitigated crack formation upon annealing, we carried out cube corner nanoindentation experiments using a UMIS nanoindenter. Per sample, at least 5 indents for each of 3 different maximum loads (130, 150, 200 mN) were made. The threshold loads at which surface cracking occurred was determined from pop-in events in the indentation load-displacement curves and from top-view scanning electron micrographs of the indents. The fracture toughness ($K_{IC}$) was estimated from the length of radial cracks, $c$, following Ref. [26]:

$$K_{IC} = \sqrt{\frac{ Eh}{c^{3/2}}} \left( \frac{P}{c^{1/2}} \right)$$

(1)

In Eq. (1), $\alpha$ denotes an empirical constant that depends on the geometry of the indenter (for the cube corner $\alpha \sim 0.04$, Ref. [26]), $E$ is the Young's modulus, $H$ the hardness, and $P$ the peak indentation load. The values for $E$ and $H$ were determined using the UMIS nanoindenter equipped with a Berkovich tip (30 indents per sample, applying increasing maximum loads from 3 to 45 mN). The data were evaluated using the Oliver and Pharr method [27] taking into account only indents with indentation depths below 10% of the coating thickness to avoid substrate interference (see Ref. [10]).

When evaluating the fracture toughness using formula (1), one finds that $K_{IC}$ decreases from \( \sim 4.4 \) MPa$\sqrt{m}$ in the as-deposited state to \( \sim 3.8 \) MPa$\sqrt{m}$ after annealing to 750 °C, before it increases again to \( > 8 \) MPa$\sqrt{m}$ for the sample annealed at 900 °C (Fig. 3(b)). The trend is in agreement with our previously reported results [10] (dark grey full symbols). However, in the present study the “inherent” toughness evolution of Ti-Al-N as a function of temperature (influenced by concomitant spinodal decomposition and formation of tiny amounts of h-AlN precipitates) is overlaid by pronounced apparent toughening effects due to the presence of residual stresses. Note that we had to use relatively high loads and thus high indentation depths (\( \sim 60-90\% \) of the film thickness) to create cracks. Yet, the crack lengths, $c$, were \( \leq 2a \) for all samples tested, see Fig. 4, with $a$ being the characteristic dimension of the “plastic” impression. As the conditions for using Eq. (1) are not fulfilled (these are $c \gg a$ and indentation depths \( \leq 0.1 \) film thickness, cf. Ref. [28]), the presented $K_{IC}$ data should be interpreted in a qualitative rather than in a quantitative manner. Especially the absolute $K_{IC}$ values of the samples annealed at 850 and 900 °C presented in Fig. 3(b) may be subject to errors due to the short crack lengths.

Interestingly, the maximum in measured fracture toughness of our Ti-Al-N coatings coincides with the peak in hardness (which is 37 ± 2 GPa at 900 °C in comparison with 34 ± 1 GPa in the as-deposited state) and the peaks in elastic (H/E ratio) as well as plastic (H$^3$/E$^2$) strain to failure. Hence, Ti-Al-N becomes a hard yet tough and, hence, damage tolerant thin film upon annealing. We propose that besides the “self-toughening” ability of Ti-Al-N in application (e.g., when machining leads to high temperature loads), post-deposition annealing treatments can be used to effectively tailor age hardening,
residual stresses, and (apparent) toughening effects. However, care has to be exercised as excessively high compressive stresses in the in-plane directions (and the corresponding tensile stresses in the out-of-plane direction) can threaten the integrity of the film/substrate composite.

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