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# Influence of Zr on structure, mechanical and thermal properties of Ti–Al–N

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ABSTRACT

Multinary Ti–Al–N thin films are used for various applications where hard, wear and oxidation resistant materials are needed. Here, we study the effect of Zr addition on structure, mechanical and thermal properties of $Ti_{1-x}Al_xN$ based coatings under the guidance of ab initio calculations. The preparation of $Ti_{1-x-z}Al_xZr_zN$ by magnetron sputtering verifies the suggested cubic (NaCl-type) structure for x below 0.6–0.7 and $z \leq 0.4$. Increasing the Zr content from $z = 0$ to 0.17, while keeping x at ~0.5, results in a hardness increase from ~33 to 37 GPa, and a lattice parameter increase from 4.18 to 4.29 Å. The latter are in excellent agreement with ab initio data. Alloying with Zr also promotes the formation of cubic domains but retards the formation of stable wurtzite AlN during thermal annealing. This leads to high hardness values of ~40 GPa over a broad temperature range of 700–1100 °C for $Ti_{0.40}Al_{0.55}Zr_{0.05}N$. Furthermore, Zr assists the formation of a dense oxide scale. After 20 h exposure in air at 950 °C, where $Ti_{0.48}Al_{0.52}N$ is already completely oxidized, only a ~1 μm thin oxide scale is formed on top of the otherwise still intact ~2.5 μm thin film $Ti_{0.40}Al_{0.55}Zr_{0.05}N$.



## 1. Introduction

Components like valves, tappets, and camshafts used in automotive industry, as well as tools for advanced machining processes (e.g., high-speed and dry cutting) are exposed to severe tribological and thermal conditions. Aluminum based ternary transition metal nitrides Me–Al–N hard coatings (e.g., Ti–Al–N, Cr–Al–N, and Zr–Al–N) with cubic NaCl (c) structure, where Al substitutes for Me in the MeN based lattice (i.e., $Me_{1-x}Al_xN$), are in favor for such industrial applications due to their high hardness and wear resistance, together with good thermal stability, and oxidation resistance [1–11]. Among them, Ti–Al–N coatings are the most widely used to reduce tool wear. The crystal structure and mechanical properties of Ti–Al–N are depending on the Al content. Single phase cubic Ti–Al–N films with high Al contents exhibit excellent mechanical properties, age-hardening and oxidation resistance. For Al contents exceeding the maximum solubility (AlN mole fraction $x_{max}$ ~0.7, depending on the deposition conditions, see Ref. [12]) in the cubic phase, a mixed cubic-NaCl and wurtzite-ZnS (w-AlN) structure is formed. The wurtzite configuration exhibits lower hardness, bulk-, elastic-, and shear-moduli, as well as wear resistance [13–17].

High thermal stability and oxidation resistance of hard films are the key requirements of many industrial applications. Ti–Al–N films form a bi-layered $Al_2O_3/TiO_2$ oxide scale, if exposed to air at elevated temperatures [18,19]. The oxidation resistance of Ti–Al–N films, with a reported onset temperature for oxidation of up to ~850 °C [19], is a result of the formation of dense $Al_2O_3$ scales, which retard the corresponding diffusion processes (simultaneous outward diffusion of Al and inward diffusion of O). However, the high growth rate of porous $TiO_2$, when Ti–Al–N is exposed to temperatures exceeding 850 °C, results in crack formation also within the dense and protective $Al_2O_3$ outer-scale [18,19]. Consequently, break away oxidation occurs. In addition to the oxidation resistance also the age-hardening ability of Ti–Al–N films, which originates from spinodal decomposition to form cubic Al-rich and Ti-rich domains during annealing at temperatures below 1000 °C, [4–7,20] is attractive for industrial applications. Similar properties have led to the introduction of $Zr_{1-x}Al_xN$, where the reported metastable solubility limit for AlN in the c-$Zr_{1-x}Al_xN$ is at 42–47 mol% [9,10,21–23]. Annealing of c-$Zr_{1-x}Al_xN$ results in decomposing into their stable phases c-ZrN and w-AlN via the formation of cubic Al-rich domains and concomitant age-hardening up to an annealing temperature of 600 °C [21,22]. The transformation of the cubic Al-rich domains into the stable structure w-AlN for annealing treatments (or exposure during operation) above 1000 °C results in a rapid decline of the mechanical properties [4–6]. Furthermore, with increasing time of the exposure the corresponding transformation can occur already at lower temperatures.

Therefore, during severe industrial applications reaching or exceeding working temperatures of 1000 °C, or to increase the lifetime of these coatings, further optimization of the oxidation resistance and the thermal stability in general is needed. An improvement of their properties can be achieved by the incorporation of large (substitutional) atoms (e.g., Nb, Ta and Y) into Ti–Al–N [24–28], as

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they effectively retard diffusional driven processes resulting in an increased thermal stability as well as improved mechanical properties. Alloying Zr to TiN and Ti–Al–N is reported to improve their hardness due to solid solution strengthening [29,30]. However, a detailed literature survey revealed that the impact of Zr incorporation on thermal stability and oxidation resistance of Ti–Al–N has not yet been explored.

In the present work we use differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), stress measurements, X-ray diffraction analysis (XRD), and nanoindentation measurements to investigate the thermal stability, structure evolution, and mechanical properties of magnetron sputtered Ti–Al–Zr–N films for annealing temperatures up to 1500 °C. The effect of Zr-incorporation on the oxidation resistance of Ti–Al–N films is studied by means of DSC measurements in synthetic air, subsequent XRD, and cross-sectional scanning electron microscopy (SEM) investigations of coated polycrystalline $Al_2O_3$ substrates after isothermal oxidation for 20 h at 850 and 950 °C.

For a better understanding and explanation of the observed results we use density function theory (DFT) to calculate the energy of formation, bulk moduli and lattice parameters of cubic and wurtzite modifications of the $Ti_{1-x-z}Al_xZr_zN$ solid solution with x between 0 and 1, and z between 0 and 0.3.

## 2. Experimental and calculation details

$Ti_{1-x-z}Al_xZr_zN$ films were deposited onto various substrates (see next paragraph) by unbalanced magnetron sputtering from a powder-metallurgically prepared $Ti_{0.5}Al_{0.5}$ compound target (diameter of 152 mm, thickness of 5 mm and purity of 99.9%, PLANSEE) in a mixed $Ar+N_2$ (both of 99.999% purity) glow discharge. $Ti_{1-x-z}Al_xZr_zN$ films with different compositions were obtained by placing Ti and Zr platelets on the target race track (diameter of 5 mm and thickness of 1 mm). Prior to the deposition with a constant substrate temperature ($T_a$) of 500 °C, a base pressure ≤0.8 mPa, a bias potential of −60 V, a $N_2$-to-total pressure ratio of 17%, and a substrate-to-target distance of 85 mm, the substrates were etched for 20 min using an $Ar^+$ glow discharge with −1250 V and 25 mA, at a pressure of 3.0 Pa. More details on the magnetron sputtering system used are given in Ref. [31].

Different substrates were used for the individual investigations: austenitic stainless steel for hardness measurements of as deposited films; polished MgO (100) plates ($10\times10\times1$ mm$^3$) for hardness measurements of as deposited and annealed films; Si stripes ($20\times7\times0.3$ mm³, both sides polished) for residual stress measurements; low alloyed steel for DSC and X-ray diffraction measurements of as deposited and annealed films and polycrystalline $Al_2O_3$ plates ($10\times10\times1$ mm3) for oxidation resistance measurements. Before loading the deposition chamber, the substrates were ultra-sonically cleaned in acetone and ethylene.

DSC with TGA was performed in a Netzch-STA 409C from room temperature (RT) to 1500 °C with a heating rate of 20 K/min in flowing He (99.9% purity and 20 sccm flow rate) and synthetic air (79% $N_2$, 21% $O_2$, and 20 sccm flow rate). Prior to these measurements, the Ti–Al–Zr–N films were removed from their low alloyed steel substrates by chemical etching in 10 mol% nitric acid, in order to avoid substrate interference. For isothermal oxidation experiments, coated polycrystalline $Al_2O_3$ substrates were isothermally oxidized at 850 and 950 °C for 20 h in a conventional tube furnace, and afterwards investigated by fracture cross-sectional scanning electron microscopy (SEM) studies.

The chemical compositions of the films in their as deposited state and after the oxidation experiments were determined using energy dispersive X-ray analysis (EDX) with an Oxford Instruments INCA EDX unit attached to a SEM operated with 25 kV. The error of measurements for the metal atoms is below 2 at.%. Phase identification and structural investigations of the layers (after removal from their low alloy steel substrates) in their as deposited state and after thermal treatment with the DSC equipment in He or synthetic air were conducted by XRD with $CuK_\alpha$ radiation using a Brucker D8 diffractometer in Bragg/Brentano mode. For classification of XRD peak, the JCDPS database was used [32]. Nanoindentation measurements of as deposited films and after vacuum annealing to 1100 °C were conducted with a CSIRO ultra-micro-indentation system (UMIS) using a Berkovich indenter. With respect to a proper statistic, at least 30 indents were performed for each sample with maximum loads ranging from 8 to 30 mN. Hardness and indentation moduli were calculated from the loading and unloading curves employing the Oliver–Pharr method [33]. Residual stresses σ of as deposited films were obtained using the substrate-curvature method. Detailed information on the measurement and the calculation of σ is described in Ref. [34].

Vacuum annealing of our films on MgO substrates was conducted in a vacuum furnace (pressure ≤0.1 mPa) to temperatures up to $T_a = 1100$ °C, using a heating rate of 20 K/min (corresponding to the DSC measurements).

DFT calculations were performed using the VASP code [35] and employing the projector augmented wave pseudopotentials based on the generalized gradient approximation as parametrized by Perdew and Wang [36]. We used 500 eV for the plane wave cut-off energy and approximately 320 k-points/atom. Such parameters guarantee the calculation accuracy in the order of meV/atom. Special quasi-random structure (SQS) [37] based supercells ($3\times3\times2$ (36 atoms) for the cubic and $2\times2\times2$ (32 atoms) for the wurtzite modification) were generated to model the ternary and quaternary alloys. This methodology allows to randomize the Ti and Al atoms on the metallic sublattice with respect to their short-range order (SRO) parameters. We used our own scripts for generating the supercells which are in detail described for the wurtzite phase elsewhere [38]. The resulting supercells used for the calculations in the present work are summarized in Appendix A (Tables A1 and A2). The deviation from ideal random-like behavior can be quantified by Warren–Cowley SRO parameters which are given in Table A3 in Appendix A. One can see that compared with a similar approach by Alling et al. [39], our cells exhibit in general worse SRO parameter values. This is likely to be cased by using considerably smaller supercells (36 and 32 atoms in the cubic and wurtzite phase, respectively compared with 64 atoms used by Alling et al. to model the cubic structure [39]). Nevertheless, even these rather small supercells have proved to be able to provide useful information on the structure and energetics of other similar ternary systems [40,41]. To obtain quaternary alloys we replaced one or two Ti or Al atoms by Zr. Thereby, we obtained cubic $Ti_{1-x-z}Al_xZr_zN$ structures with $z=0.056$ and 0.111, and wurtzite $Ti_{1-x-z}Al_xZr_zN$ structures with $z=0.0625$ and 0.125. Additionally, we also optimized an ad hoc cubic $Ti_{0.33}Al_{0.39}Zr_{0.28}N$ structure (the metal sublattice is composed of 6 Ti, 7 Al, and 5 Zr atoms).

## 3. Results and discussion

### 3.1. Structure and mechanical properties

Elemental analysis by EDX reveals that our $Ti_{1-x-z}Al_xZr_zN$ films are stoichiometric with N/metal ratios of $1\pm0.1$. As mentioned in the experimental section the composition of the metal sublattice is varied by adding Ti or Zr platelets at the race track of the $Ti_{0.5}Al_{0.5}$ compound target. Thereby the following films are obtained: $Ti_{0.48}Al_{0.52}N$ with 21 Ti platelets, $Ti_{0.40}Al_{0.55}Zr_{0.05}N$ with 10 Zr platelets, $Ti_{0.39}Al_{0.51}Zr_{0.10}N$ with 20 Zr platelets, $Ti_{0.36}Al_{0.47}Zr_{0.17}N$ with 40 Zr platelets, and $Ti_{0.34}Al_{0.37}Zr_{0.29}N$ with 80 Zr platelets. XRD investigations of these as deposited films, as shown in Fig. 1, reveal a single phase cubic structure, which is in agreement with ab initio calculations. Fig. 2a presents the energy of formation, $E_f$, of the cubic and wurtzite