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Structural evolution of TaN-alloyed Cr–Al–Y–N coatings

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ABSTRACT

Substitutions of metallic elements in Al-containing ternary transition metal nitrides are a promising method for improving the alloy thermal stability and oxidation resistance. In this work, combined experimental and ab initio analysis of thermal stability and structural evolution of CrAlYN alloyed to tantalum nitride is presented. As-deposited reactively-sputtered $Cr_{1-x-y-z}Al_xY_yTa_zN$ coatings ($z = 0 \div 0.21$) exhibit single phase cubic sodium chloride (B1) structure identified as fcc-CrAlY(Ta)N solid solution. The presence of Ta in the solid solution shifts the decomposition process to higher temperatures (>1000 °C for Ta content of $z = 0.21$) compared to CrAlYN (~900 °C), thus enhancing the alloy thermal stability. Improved thermal stability of tantalum-containing solid solutions may be attributed to their higher cohesive energies, as revealed from ab initio calculations. X-ray diffraction and transmission electron microscopy investigation of the N_2-depleted structure after exposure at high temperature (1200 °C) in Ar + H_2 atmosphere revealed the presence of wurtzite AlN (w-AlN), cubic, hexagonal and tetragonal Cr- and Ta-containing binary or ternary nitrides (h-Cr_2N, h-TaN, h-Ta_2N, t-$Cr_{0.8}Ta_{1.2}N$) and metallic phases (bcc-Cr(AlTa), fcc-Cr_2Ta). First-principle calculations show negative values of mixing free energies for fcc-$Cr_{1-x}Ta_xN$ over the whole composition range at 1600 K indicating its enhanced thermodynamic stability compared to cubic $Al_{1-x}Ta_xN$ and $Al_{1-x}Cr_xN$.

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1. Introduction

Development of materials with characteristics optimized to the requirements of modern applications demands great efforts for understanding the intrinsic material properties and their suitable combinations. Improvement of hard coatings leads to achievement of new excellent properties such as high hardness combined with good oxidation resistance above 1000 °C [1], extremely low friction with high wear resistance and enhanced toughness, especially combined with high resistance to cracking [2,3]. A promising way to produce hard coatings with these desired properties is through the use of non-equilibrium thin film growth deposition techniques like sputtering, that allows synthesizing nanostructured (nanocomposite) metastable systems that often surpass the physical and chemical properties of their stable components [4,5]. Crucial factor that limits the unique properties of the nanostructure formed in the films is its temperature stability, which is strongly affected by the annihilation of structural defects, rearrangement of atoms leading to reduction of internal stresses, interdiffusion, recrystallization, decomposition mechanism and phase transformation during high temperature exposure and oxidation processes [6–8].

Typical representatives of nanostructured hard coatings are ternary and quaternary transition metal nitrides (TMNs — Transition Metal Nitrides, Ti, Cr-, Zr, Nb-, V-, Ta-, Y- and HfN), where their attractive mechanical and chemical properties arise mainly from strong interatomic bonds, which can generally be present as mixtures of metallic, ionic and covalent contributions [9]. The structures of common Al-containing ternary coatings, $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$, consist of metastable face-centered cubic NaCl-type (B1) *fcc*-TiAlN and *fcc*-CrAlN solid solutions. These supersaturated cubic structures remain stable due to large activation energies required for phase separation. However, at elevated temperatures, diffusion processes are sufficiently frequent to initiate decomposition and subsequent formation of nanostructured material. Spinodal decomposition is characteristic for $Ti_{1-x}Al_xN$. In its initial stage (~900 °C), spinodal decomposition is accompanied by an increase in hardness due to the formation of nanocomposites consisting of fcc-TiN and fcc-AlN-enriched coherent phases [4]. In the case of $Cr_{1-x}Al_xN$ precipitation of incoherent hexagonal ZnS-type (wurtzite) *w*-AlN nanograins occur within the solid solution at the temperature of about 700 °C. [4] The formation of this fine-grained nanocomposite is also accompanied by a slight increase in hardness. The continuing process of decomposition leads to the dual-phase structure

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containing stable *w*-AlN and *fcc*-TiN or *fcc*-CrN phases (stable up to ~1000 °C, then transformation to *h*-Cr_2N and Cr occurs), grain coarsening and degradation of mechanical properties.

Nowadays, research activity is focused on improvement of thermal stability and oxidation resistance of ternary nitrides via a concept of alloying TMNs with nitrides or other elements [10]. Many articles [11–19] report mainly on quaternary systems based on $Ti_{1-x}Al_xN$ and alloyed with nitrides of elements from group III–VI (Y, Zr, Hf, V, Nb, Ta, Mo, W), where alloying is realized by substitution of Ti and Al atoms in the metallic sublattice. This allows for a huge variety of size and bonding types, due to different electronic configurations of constituting atoms (e.g., additional d- and f-states) [4]. Investigations of several authors [20–22] showed that Ta alloying (a pentavalent element) results in a pronounced increase in thermal stability of $Ti_{1-x-y}Al_xTa_yN$ by shifting the onset of the nitride phase decomposition by ~200 °C. Additionally, alloying Ta into $Ti_{1-x}Al_xN$ is also very beneficial for oxidation resistance [20]. Unlike for $Ti_{1-x}Al_xN$, effects of alloying TM elements on the improvement of $Cr_{1-x}Al_xN$ coatings are much less investigated. Rovere [23–25] reported enhanced oxidation resistance of $Cr_{0.30}Al_{0.68}Y_{0.02}N$ with very small content of yttrium (~1 at.%.). In such coatings, Y promotes the formation of a dense and adherent mixed $Al_2O_3 + Cr_2O_3$ scale which results in a very promising oxidation resistance up to temperatures exceeding 1000 °C [25].

In this study, we investigate the influence of tantalum addition on the phase stability and structural evolution of $Cr_{1-x-y-z}Al_xY_yTa_zN$ coatings prepared by reactive magnetron co-sputtering. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA) were used to analyze thickness, morphology, chemical composition and mass changes of the coatings, respectively. Thermal stability and decomposition route after annealing at temperatures up to 1200 °C were examined using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Ab initio calculations were performed to support experimental data and to predict thermodynamical phase stabilities of quaternary solid solutions and products of their decompositions.

2. Methods

2.1. Experimental details

Cr–Al–Y–Ta–N coatings were reactively deposited using unbalanced magnetron co-sputtering from powder metallurgically prepared CrAlY target (49.5/49.5/1 at.%, 100 mm dia., 99.5% purity) and Ta target (100 mm dia., 99.99% purity) in Ar + N_2 discharge. The magnetrons were tilted with the angle of ~50° between their axes; see Ref. [26] for more details. The substrates were mounted on the sample holder at different positions with respect to the targets, yielding variable tantalum content in Cr–Al–Y–Ta–N.

The magnetron power densities were fixed at 6.5 W cm^{-2} and 1.4 W cm^{-2} for the CrAlY and the Ta targets, respectively. The base pressure in the chamber was below 1×10^{-3} Pa and the total working gas pressure during depositions was kept at 0.53 Pa with a N_2-partial pressure at ~0.17 Pa. All depositions were carried out at a negative substrate bias of $U_s = -50$ V. No additional heating of samples was used during deposition.

The as-deposited Cr–Al–Y–Ta–N coatings were annealed in Ar + 5% H_2 (99.999% purity) atmosphere (10^{-1} Pa) at the temperatures of 900 °C, 1000 °C, 1100 °C and 1200 °C for 3 min using a heating rate of 50 K min^{-1} and self-limiting cooling rate. Heating chamber base pressure was 1×10^{-4} Pa before each heat treatment. Mirror-polished Al_2O_3 plates (sapphire, c-cut, $8 \times 8 \times 0.5$ mm^3) were chosen to avoid interdiffusion of substrate and coating material at the high annealing temperatures. Prior to the deposition, all substrates were ultrasonically cleaned in acetone and isopropyl alcohol.

Morphological and thickness characterization of the coatings was obtained from imaging of their cross section by a dual-beam scanning electron microscope Tescan Lyra (SEM). The chemical composition of as-deposited and annealed samples was determined during the electron microscopy studies by means of the energy-dispersive X-ray analysis (EDX, INCA Wave, Oxford Instruments Analytical). Mass changes associated with changes in the chemical composition of the coatings during annealing were monitored by thermogravimetric analysis (TGA) in Thermal Analysis Apparatus Netzsch STA 409 CD using a heating rate of 10 K min^{-1}, 10 sccm flow of high pure Ar (99.9999% purity), and a maximum temperature of 1400 °C. Prior to TGA the coatings were chemically removed, cleaned in acetone and isopropyl alcohol, rinsed with distilled water, grounded and then inserted into the Al_2O_3 crucible. Structural investigations of the as-deposited and annealed samples were performed by Bragg–Brentano X-ray diffraction (XRD) measurements using PANalytical X'Pert PRO MRD diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). Patterns of as-deposited and annealed samples were fitted by Rietveld refinement in order to determine more detailed information, such as grain size and lattice parameters. Detailed studies of the nanostructure of selected samples were conducted with transmission electron microscopy (TEM) using JEOL 2100 operated at 200 keV. Elemental distribution in the observed structure was determined with EDX during investigations in scanning mode (STEM). Specimen preparation was performed using a Tescan Lyra focused ion beam (FIB) work station.

2.2. Computational details

Ab initio density functional theory (DFT) calculations were performed with the VASP 5.3 code [27,28] employing projector

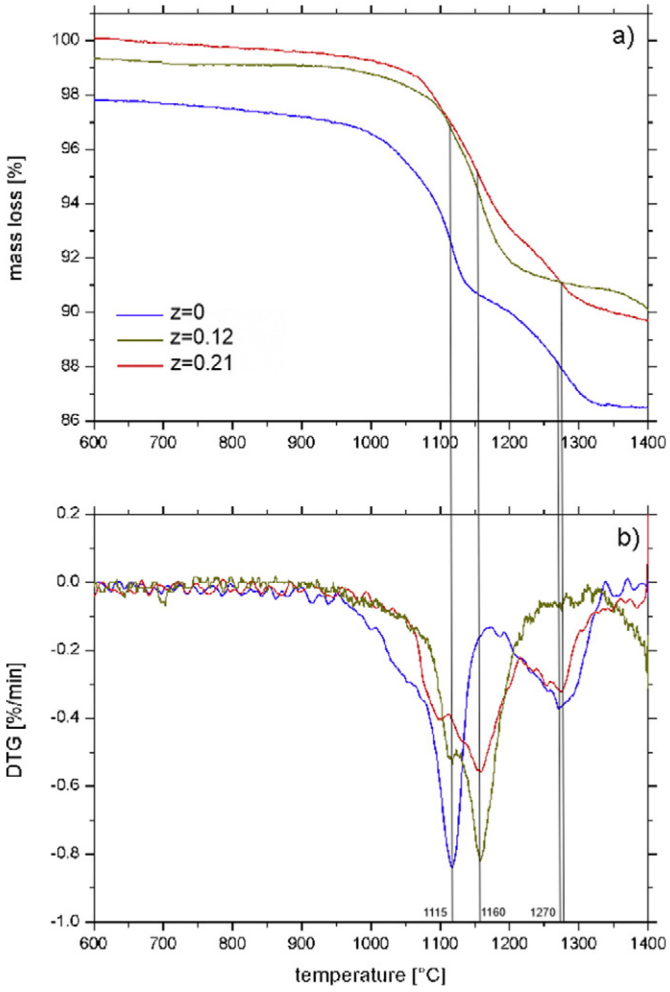

Fig. 1. TGA and DTGA analysis of annealed Cr–Al–Y–Ta–N coatings in Ar atmosphere.

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