Transition in Microstructure, Mechanical and Oxidational Properties Induced by Phase Transformation of $\text{Zr}_{1-x}\text{Al}_x\text{N}$

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In this study, we evaluated the microstructure, microhardness, tribological properties, and oxidation behaviors of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ films, considering the requirements for their use as wear-resistant coatings. $\text{Zr}_{1-x}\text{Al}_x\text{N}$ films were synthesized by radio-frequency magnetron sputtering from $\langle\text{ZrN}\rangle_{1-x}\text{Al}_x$ targets. X-ray diffraction analysis indicated that the $\text{Zr}_{1-x}\text{Al}_x\text{N}$ film had a cubic phase when $X = 0.12$, being transformed into a mixture of cubic and hexagonal phases when $X = 0.26$. $\text{Zr}_{0.86}\text{Al}_{0.14}\text{N}$ displayed an average frictional coefficient of 0.3-0.5 and a minimum wear depth of 0.4 $\mu$m. The microhardness of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ decreased from 36.5 GPa for $X = 0.12$ to 16.9 GPa for $X = 0.43$. During dynamic oxidation, the exothermic peak in a differential thermal analysis curve shifted from 730 $^\circ$C for $X = 0.12$ to 835 $^\circ$C for $X = 0.43$. In accord with this behavior, the mass gain measured by thermogravimetric analysis for $\text{Zr}_{0.86}\text{Al}_{0.14}\text{N}$ exhibited minimum values at isothermal oxidation temperatures in the range of 600-700 $^\circ$C.

Keywords: ZrAlN, Microstructure, Microhardness, Coefficient Of Friction, Oxidation Resistance

1. Introduction

Transition metal nitrides such as TiN, CrN, and ZrN find extensive technological application in wear resistant, diffusion-barrier, optical, electrical, and decorative coatings. ZrN coatings, in particular, have attracted much attention because of their expected widespread industrial uses. Hence, their properties (e.g., chemical bonding behavior, electrochemical properties, thermal oxidation behavior, crystal structure, optical reflectivity, tribological properties, hardness, fracture toughness, and sheet resistance) have been investigated in several studies $^{1-4}$.

$\text{Zr}_{1-x}\text{Al}_x\text{N}$ films were deposited by doping Al atoms into ZrN structures on the basis of the successful coating of cutting tools with $\text{Zr}_{1-x}\text{Al}_x\text{N}$ and $\text{Cr}_{1-x}\text{Al}_x\text{N}$ to prevent tool wear; these surfaces demonstrated greater hardness and superior oxidation resistance, as compared to the undoped TiN and CrN coatings. Because $\text{Zr}_{1-x}\text{Al}_x\text{N}$ is known to contain metastable phases, with cubic-to-hexagonal phase transformations occurring, depending on the Al content, the maximum solubility of Al atoms in ZrN while maintaining the cubic structure has been explored via theoretical analyses and experimental methods. Makino et al. $^9$ predicted, from a structural map based on band parameters, that the maximum solubility of Al atoms in cubic $\text{Zr}_{1-x}\text{Al}_x\text{N}$ occurs when $X = 0.33$. Previous X-ray diffraction analyses indicated that the cubic structure of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ remained unchanged for values of $X$ up to 0.43 $^{10}$, 0.37 $^{11}$, and 0.36 $^{12}$. $\text{Zr}_{1-x}\text{Al}_x\text{N}$ has been prepared using a binary alloy target $(\text{Zr}_{1-x}\text{Al}_x)$, two metallic targets $(\text{Zr}$ and Al), and a ceramic target $(\langle\text{ZrN}\rangle_{1-x} \langle\text{AlN}\rangle_x)$, and its mechanical properties $^{13,14,15}$, thermal stabilities $^{16}$, wear behavior $^{17}$, and oxidation behavior $^{18}$ have been reported. These properties are indispensable for applications to cutting tools in order to protect against tool wear and cutting heat. However, a comprehensive study of the mechanical, tribological, and oxidation properties of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ having different values of $X$ has not been carried out to date. In the study reported herein, $\text{Zr}_{1-x}\text{Al}_x\text{N}$ films were deposited by radio-frequency (RF) magnetron sputtering in Ar discharges from several $(\text{ZrN})_{1-x} \langle\text{Al}\rangle_x$ targets that had been previously prepared by sintering ZrN and Al powders. After deposition, using X-ray diffraction, hardness and friction tests, and thermal analyses, we comprehensively evaluated several properties relevant to the application of the films as wear-resistant coatings.

2. Experimental details

2.1 Film deposition

The films were deposited on polished (111)-oriented Si wafers and stainless-steel substrates by RF magnetron sputtering, using $(\langle\text{ZrN}\rangle_{1-x} \langle\text{Al}\rangle_x)$ and $(\text{ZrN})_{1-x} \langle\text{Al}\rangle_x$ targets. The Si wafer substrates were used for identifying the chemical composition, microstructure, microhardness, coefficients of friction, and wear depths, whereas the stainless-steel substrates were used for thermal analyses. The films were synthesized in an argon gas atmosphere at a total pressure of 1.0 Pa for 300 min. The power density of the targets was 10.6 W/cm$^2$, and the deposition temperature was 250 $^\circ$C. A negative bias voltage in the range between -100 and -300 V was applied to the substrate, and the distance between the target and substrate was 45 mm for all the deposition processes.

2.2 Film characterization

The chemical composition of the films was measured using energy-dispersive X-ray analysis (EDS; Oxford Instruments, X-Max80). Their crystal structures were evaluated by X-ray diffraction (XRD; Shimadzu XRD-7000), using Cu-K$_\alpha$ radiation at 40 kV and 30 mA in the $\theta$-2$\theta$ scan mode. The XRD pattern peaks were identified by comparison with International Center for Diffraction Data (ICDD) reference spectra. The cross-sectional structures of the films were observed by scanning electron microscopy (SEM; Hitachi High-Technologies SU-1500).

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The microhardness of the samples was measured from load-displacement curves obtained using a dynamic ultra-micro hardness tester (Shimadzu DUH-211S) under maximum depth-control mode. The maximum loads were 50–100 ± 10^−3 N, and the maximum indentation depth was <10% of the film thickness. Friction tests were performed with a ball-on-disc tribometer (Rhesea FPR-2100) under dry conditions; the temperature was 26 °C and the relative humidity of the atmosphere was 52%. SiC balls with a diameter of 4.8 mm were used as a counterpart material for predominately inducing abrasive wear, and rotational motion having a radius of 2.0 mm and speed of 300 rpm was used with test loads of 4.90 N. The surface roughness of the as-deposited sample and the wear depth after friction testing were determined using a surface-roughness tester (Mitutoyo SJ-301).

Dynamic oxidation and isothermal oxidation testing was conducted using differential thermal analysis (DTA; Shimadzu DTA-50) and thermogravimetric analysis (TGA; Shimadzu TGA-51H), respectively. To eliminate the effect of the substrate material on the DTA and TGA measurements, the films were chemically removed from the stainless-steel substrates using a dilute solution of hydrochloric acid. Then, after filtering and cleaning, the films were crushed into powders. For the dynamic oxidation tests, the powder samples were placed in a platinum crucible and heated from room temperature to 1400 °C in air at a heating rate of 15 °C/min. Al₂O₃ blocks were used as an inert standard sample for the DTA measurements. In the isothermal oxidation tests, the mass gain of each powder was recorded as a function of time during isothermal oxidation at 600 and 700 °C. The kinetic constants and activation energies of the powder samples were calculated from the TGA results.

3. Results and discussion

3.1 Morphology and crystal structure

The chemical compositions measured using EDS were Zr₁₋ₓAlₓN, ZrₓAl₀₂N, and Zrₓ₋₂AlₓN (Zr₁₋ₓAlₓN with \( x = 0.12, 0.26, \) and 0.43, respectively) for the films prepared from the three targets, with nitrogen contents of 51–53 at.% in each case. Fig. 1 shows the fractured cross-sectional micrographs of the as-deposited films. For all the films, the film thickness was 4–5 μm. The images reveal that columnar structures were not observed in the SEM photographs. Fig. 2 shows XRD patterns for the as-deposited Zr₁₋ₓAlₓN films, including peaks at the positions expected for ZrN (ICDD No. 00-035-0753) and AlN (ICDD No. 01-070-0354). Here, the prefixes “c-” and “h-” refer to the cubic and hexagonal structures of the metastable nitrides, respectively. The XRD spectrum of Zr₀.₉₃Al₀₂N resembles that of a single cubic (NaCl-type) polycrystalline structure. Comparing the XRD spectra for \( x = 0.12 \) and \( x = 0.26 \), the intensity of the peaks is smaller and slightly broader for the higher value of \( x \). Zrₓ₋₂AlₓN contains a mixture of the cubic and hexagonal (wurtzite-type) structures. In the case of Zrₓ₋₂AlₓN, the sharp peaks apparent in the XRD spectra of the other two films are absent, and the background intensity increases with respect to those exhibited in the \( x = 0.12 \) and 0.26 spectra. Additionally, the broad and shoulder peaks between 30–40° covered several c-ZrN and h-AlN peaks. This result suggests that the Zrₓ₋₂AlₓN films have an amorphous-like structure, comprising the cubic and the hexagonal phases, owing to lower crystal growth. Our XRD results show the weak h-peaks appeared for \( x = 0.43 \), while several researchers have detected definite h-peaks for \( x = 0.58^{14} \) and 0.74^{15}; XRD intensity of h-peaks would presumably be correlated to the Al fraction \( (X) \) in ZrN.

The phase boundary between the cubic and hexagonal structures of Zr₁₋ₓAlₓN has been explored using a combination of Zr and Al or Zr₁₋ₓAlₓ targets in several previous studies. Lamni et al.^{10} reported that a c-phase and a (c, h)-phase were observed for \( x \leq 0.43 \) and \( 0.43 < X \leq 0.73 \), whereas Rogström et al.^{12} reported

![Fig. 1](image1.png)

Cross-sectional micrographs of fractured films of Zr₁₋ₓAlₓN with \( x = 0.12, 0.26, \) and 0.43.

![Fig. 2](image2.png)

XRD patterns of as-deposited Zr₁₋ₓAlₓN (\( x = 0.12, 0.26, \) and 0.43) on Si wafers. The prefixes c- and h- refer to the cubic and hexagonal structures, respectively.
that a c-phase, a (c, h)-phase, and an h-phase were present for $X \leq 0.36$, $0.36 < X \leq 0.70$, and $X \geq 0.70$, respectively. Furthermore, $\text{Zr}_{1-x}\text{Al}_x\text{N}$ was studied by Franz et al. \cite{franz2001}, who suggested that a c-phase when $X = 0.15$ transformed to a (c, h)-phase when $X = 0.28$, and confirmed the existence of a single h-phase at $X = 0.58$ in the phase space.

### 3.2 Tribological behaviors and microhardness

Fig. 3 shows the coefficients of friction ($\mu$) for $\text{Zr}_{1-x}\text{Al}_x\text{N}$, with $X = 0.12$, 0.26, and 0.43, on the Si wafers versus sliding distance ($l$), obtained using a test load of 4.90 N in each case. The average surface roughness of the as-deposited films is less than 0.02-0.05 $\mu$m. For the films with $X = 0.12$ and 0.26, the $\mu$ values increase gradually up to $\mu = 0.5$ between the initial state ($l = 0$ m) and the transient state ($l = $ ca. 5 m) due to adhesion between the SiC ball and the films. The average steady-state ($l = $ beyond 5 m) frictional coefficients are $\mu = 0.3$-0.5 and $\mu = 0.4$-0.6, respectively. For the $X = 0.43$ film, a drop in the frictional coefficients to $\mu = 0.2$, which is a similar value to that of the Si wafer, is observed between the initial and steady states, after the coatings on the substrates are exposed to wear.

Fig. 4 shows the wear depth after sliding against SiC balls and the microhardness of the $\text{Zr}_{1-x}\text{Al}_x\text{N}$ ($X = 0.12$, 0.26, and 0.43) samples. The measured wear depths increase with $X$, from 0.4 $\mu$m for $\text{Zr}_{0.18}\text{Al}_{0.82}\text{N}$ to 2.8 $\mu$m for $\text{Zr}_{0.25}\text{Al}_{0.75}\text{N}$. The wear track on $\text{Zr}_{0.57}\text{Al}_{0.43}\text{N}$ had a depth of up to 6.9 $\mu$m because the SiC ball penetrated the substrate through the films. Consistent with the increasing wear depths, the microhardness of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ decreases from 36.5 GPa ($X = 0.12$) to 24.9 GPa ($X = 0.26$) and 16.9 GPa ($X = 0.43$) (Fig. 4). These results show that the incorporation of Al atoms into ZrN enhanced its conventional hardness, and a maximum value for the hardness of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ was obtained at an Al content corresponding to the phase boundary between the cubic and mixed or hexagonal phases. Previous studies concerning $\text{Tl}_{1-x}\text{Al}_x\text{N}$ and $\text{Cr}_{1-x}\text{Al}_x\text{N}$ suggest that similar hardening phenomena can be attributed to solid-solution hardening and crystal-grain refinement\cite{franz2001,whittaker2003}.

### 3.3 Dynamic and isothermal oxidation

Fig. 5 shows DTA curves for the $\text{Zr}_{1-x}\text{Al}_x\text{N}$ ($X = 0.12$, 0.26, and 0.43) samples that were acquired during dynamic oxidation, from room temperature to 1400 °C. The first small DTA peak is observed at 350-550 °C, the temperature at which exothermic reactions occur via the recovery process and recrystallization\cite{franz2001,whittaker2003}. In general, the recovery process is strongly correlated with the relaxation of deposition-induced lattice defects and residual stress at elevated temperatures. The intensity of the DTA signal for $\text{Zr}_{0.26}\text{Al}_{0.74}\text{N}$ increases at temperatures above 600 °C.

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**Fig. 3** Coefficients of friction, $\mu$, for $\text{Zr}_{1-x}\text{Al}_x\text{N}$ ($X = 0.12$, 0.26, and 0.43) as a function of sliding distance, $l$, at a test load of 4.90 N.

**Fig. 4** Wear depth, after friction testing, and microhardness of $\text{Zr}_{1-x}\text{Al}_x\text{N}$ ($X = 0.12$, 0.26, and 0.43). The error bars represent the standard deviations of the measurements.

**Fig. 5** DTA curves for $\text{Zr}_{1-x}\text{Al}_x\text{N}$ ($X = 0.12$, 0.26, and 0.43) during dynamic oxidation from room temperature to 1400 °C.
and exothermic peaks are observed at 730 °C. The corresponding exothermic DTA peaks for Zr_{70}Al_{30}N and Zr_{65}Al_{35}N are shifted toward higher temperatures, appearing at 775 and 835 °C, respectively, suggesting that adding large amounts of Al to ZrN delays the complete dynamic oxidation. According to previous reports of Zr_{1-x}Al_{x}N oxidation behavior studies\(^{31,32,33}\), the formation of oxidative products, such as ZrO_2 and Al_2O_3, was confirmed by X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopic analyses. The ZrN oxidation behavior studies of Krusin-Elbaum et al.\(^{33}\) and Wu et al.\(^{31}\) indicated that monoclinic- and tetragonal-ZrO_2 were present after atmospheric oxidation at 600-650 °C. Meanwhile, Franz et al.\(^{32}\) describe the probable presence of amorphous-like Al_2O_3 together with tetragonal-ZrO_2 after oxidizing Zr_{1-x}Al_{x}N at 900 °C.

**Fig. 6** TGA curves for Zr_{1-x}Al_{x}N (X = 0.12, 0.26, and 0.43) during isothermal oxidation at (a) 600 °C and (b) 700 °C. (c) Arrhenius plots for X = 0.12, 0.26, and 0.43.

and 0.43) samples for isothermal oxidation at 600 and 700 °C. The TGA curves reveal parabolic oxidation kinetics, with the oxidation behavior changing drastically with temperature. The final measured mass gain Δm at 600 °C decreases from 10.2% for X = 0.12 to 9.5% for X = 0.26 and 7.4% for X = 0.43 (Fig. 6 (a)). For Zr_{65}Al_{35}N, the mass gain at 700 °C is almost constant at 9.4-9.7% after 4 h, because of its complete oxidation (Fig. 6 (b)), which is in accord with the appearance of the exothermic DTA peaks at 730 °C (Fig. 5). In contrast, the oxidation of Zr_{1-x}Al_{x}N with X = 0.26 and 0.43 proceeds for 10 h at 700 °C, and the parabolic curves are observed, without any plateau (Fig. 6 (b)). Zr_{65}Al_{35}N displays a smaller mass gain (Δm = 16.3%) than that of Zr_{1-x}Al_{x}N (Δm = 21.5%) in Fig. 6 (b). The parabolic rate constants \(k_p\) were calculated based on the assumption that the oxidation kinetics for Zr_{1-x}Al_{x}N conformed to a parabolic law, and the logarithm of \(k_p\) was plotted versus the reciprocal of the absolute temperature \(1/T\) (Fig. 6 (c)). The activation energies obtained from the associated Arrhenius equations are 27.5 kJ/mol for Zr_{65}Al_{35}N, 49.8 kJ/mol for Zr_{1-x}Al_{x}N, and 47.1 kJ/mol for Zr_{65}Al_{35}N. Although the activation energies for the cases of X = 0.26 and 0.43 are similar, our results show that the Zr_{65}Al_{35}N film exhibited the highest oxidation resistance among the studied films. This difference in oxidation behavior probably occurs because of the suppression of oxygen diffusion by Al-rich protective oxide products.

Our study revealed that better wear resistance was obtained at the small Al fraction (X = 0.12), whereas adding the large Al fraction (X = 0.43) into ZrN enhanced oxidation resistance. This result means that there is a trade-off relationship between the both properties. We suggest that wear resistance is significant rather than oxidation resistance for an application to cutting tools because superior wear resistance prevent an exposure of cutting edge and protect thermal damage arising from cutting heat.

### 4. Conclusions

Zr_{1-x}Al_{x}N films were deposited by RF magnetron sputtering in Ar discharges from several (ZrN)_{1-x}Al_{x} targets. Their microstructures, microhardness, coefficients of friction, wear depths, and oxidation behaviors were examined. Zr_{1-x}Al_{x}N was shown to have a cubic structure when X = 0.12, and mixtures comprising cubic and hexagonal phases were observed for X = 0.26 and 0.43. Zr_{65}Al_{35}N exhibited a minimum wear depth of 0.4 μm after the friction test with a load of 4.90 N and displayed a maximum hardness of 36.5 GPa. The exothermic DTA peaks measured during dynamic oxidation shifted from 730 °C, for X = 0.12, toward higher temperatures, up to 835 °C for X = 0.43. The TGA analyses at 700 °C indicated that complete oxidation of Zr_{65}Al_{35}N occurred, and the measured mass gain decreased with X, from 21.5% for X = 0.26 to 16.3% for X = 0.43.

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