1. Introduction

TiN has been widely used as a protective coating for cutting tools, forming tools, and dies because of its hardness and wear, corrosion, and oxidation resistance. Over the last several decades, ternary Ti-based nitrides such as Ti$_{1-x}$Al$_x$N, Ti$_{1-x}$Cr$_x$N, Ti$_{1-x}$Zr$_x$N, Ti$_{1-x}$Si$_x$N, and Ti$_{1-x}$Ni$_x$N have been developed by the incorporation of foreign metals into the basic TiN structure, resulting in microstructural transitions leading to improvements in physical and chemical properties as a function of time. For instance, the microhardness of Ti$_{1-x}$Al$_x$N gradually increases from 20 to 32 GPa between X = 0 and 0.6 while maintaining a NaCl-type cubic structure. Corresponding to the transformation or the precipitation of ZnS-type wurtzite structure beyond X = 0.6, the microhardness rapidly decreases down to 14 GPa. Similarly, in the case of Ti$_{1-x}$Si$_x$N and Ti$_{1-x}$Ni$_x$N, the maximum hardness is obtained due to the prevention of plastic deformation and the propagation of dislocations when the polycrystalline TiN changes to a nanocomposite comprising nanocrystallites and amorphous phases at certain X values.

Tungsten has been recognized as a key element in various tooling materials such as cemented carbide, cermet, and high-speed steel. To harden TiN, Ti$_{1-x}$W$_x$N has been prepared from various Ti$_{1-x}$W$_x$ alloy targets under a N$_2$-Ar atmosphere at different N$_2$/Ar partial pressures. Shaginyan et al. reported that the microhardness of the Ti$_{1-x}$W$_x$N deposited from a Ti$_{100-x}$W$_x$ target was dependent on the nitrogen concentration, crystal structure, morphology, and residual stress. Silva et al. prepared several Ti$_{1-x}$W$_x$N samples from a Ti$_{80}$W$_{20}$ target and showed that their hardness, friction coefficients, and wear coefficients change because the nitrogen content affects the ratio of Ti to W.

However, a comprehensive study of the microstructure, mechanical, and thermal properties of Ti$_{1-x}$W$_x$N with differing X values has not been reported to date. In this study, we synthesized Ti$_{1-x}$W$_x$N from Ti$_{100-x}$W$_x$ (0 ≤ X ≤ 1) alloy targets using the radiofrequency (RF) magnetron sputtering method using alloy targets of Ti$_{1-x}$W$_x$ with X = 0, 0.25, 0.5, 0.75, and 1.0. The Si wafers were used for X-ray analyses and hardness evaluations whereas the stainless-steel substrates were used for oxidation tests. These films were synthesized under pure N$_2$ and Ar atmosphere at a total pressure of 1.0 Pa, with a N$_2$ partial pressure of 0.1 Pa. The power density of the targets was 10.6 W/cm$^2$, and the deposition temperature was 250 °C. The substrate negative bias voltage and the target-to-substrate distance were fixed at ~50 V and 45 mm for all the depositions, respectively. The films thicknesses were adjusted to 1.0-3.0 μm to prevent the films from peeling off.

The metal compositions were measured using energy dispersive X-ray fluorescence analysis (EDXRF; Shimadzu Rayny EDX-800HS) after calibration using a standard specimen, Al (99.99% purity). The sample crystal structures and lattice parameters were evaluated by X-ray diffraction (XRD; Shimadzu XRD-7000) using Cu-Kα radiation at 40 kV and 30 mA. The microhardness of the samples was measured with a conventional micro-Vickers hardness tester (Mitutoyo HM-221) under a load of 98.0 × 10$^{-3}$ N. The isothermal oxidation tests were conducted in a thermogravimetric analyzer (TGA; Shimadzu TGA-51H). To eliminate the influence of the substrate material in the TGA measurements, the films were chemically removed from the stainless-steel substrates using a diluted hydrochloric acid solution. After filtering and cleaning, the films were reduced to powders. The mass gain of powders was recorded during isothermal oxidation at 600 °C as a function of time. The surface morphologies of films after atmospheric annealing at 600 °C for 1 h were observed using scanning electron microscopy (SEM; Hitachi SU-1500).

2. Experimental details

Ti$_{1-x}$W$_x$N films were deposited onto polished (111)-oriented Si wafers and stainless-steel substrates by the RF magnetron sputtering method using alloy targets of Ti$_{1-x}$W$_x$ with X = 0, 0.25, 0.5, 0.75, and 1.0. The Si wafers were used for X-ray analyses and hardness evaluations whereas the stainless-steel substrates were used for oxidation tests. These films were synthesized under pure N$_2$ and Ar atmosphere at a total pressure of 1.0 Pa, with a N$_2$ partial pressure of 0.1 Pa. The power density of the targets was 10.6 W/cm$^2$, and the deposition temperature was 250 °C. The substrate negative bias voltage and the target-to-substrate distance were fixed at ~50 V and 45 mm for all the depositions, respectively. The films thicknesses were adjusted to 1.0-3.0 μm to prevent the films from peeling off.

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3. Results and discussion

The Ti$_{1-x}$W$_x$N had W contents of X = 0, 0.34, 0.66, 0.84, and 1.0. Fig. 1 shows the XRD patterns of the Ti$_{1-x}$W$_x$N samples.
with the expected peak positions for TiN and W2N. Here, c- indicates the cubic structure of the metastable nitride. The XRD spectrum of TiN (X = 0) indicated a cubic (NaCl-type) polycrystalline microstructure with (111) and (200) preferred orientations. The relatively strong (111) peak and the small broad (200) peak were identified for X = 0.34, where the (111) peak shifted toward to lower diffraction angles while maintaining a NaCl-like structure. At X > 0.66, the peaks moved closer to the peak positions of c-W2N. From the obtained XRD results, it was determined that the microstructure of the Ti1-xWxN samples exhibited a NaCl-type substitutional solid solution with replacement of Ti atoms by W atoms.

The shifting of the diffraction angles indicates lattice shrinkage or expansion of TiN. Fig. 2 shows the lattice parameters of the Ti1-xWxN samples with X values ranging from 0 to 1.0. The lattice parameter in cubic structure increased from 0.422 nm (X = 0) to 0.427 (X = 0.34), and subsequently decreased to 0.423 nm (X = 1.0). These changes in lattice parameter likely arise from differences in the ionic radii of Ti and W atoms, e.g., Ti2+ (86 pm), Ti3+ (67 pm), Ti4+ (42 pm), W4+ (66 pm), W5+ (62 pm), and W6+ (42 pm).

The microhardness increased from 21 GPa at X = 0 to 28 GPa at X = 0.66 due to solid solution hardening, and then gradually decreased to 22 GPa at X = 1.0. The microhardness increased from 21 GPa at X = 0 to 28 GPa at X = 0.66 due to solid solution hardening, and then gradually decreased to 22 GPa at X = 1.0. The microhardness increased from 21 GPa at X = 0 to 28 GPa at X = 0.66 due to solid solution hardening, and then gradually decreased to 22 GPa at X = 1.0. The microhardness increased from 21 GPa at X = 0 to 28 GPa at X = 0.66 due to solid solution hardening, and then gradually decreased to 22 GPa at X = 1.0.

Fig. 2 Changes in lattice parameter and microhardness for Ti1-xWxN.

Fig. 3 Oxidation behaviors of Ti1-xWxN at 600 ℃. (a) Isothermal TGA curves and (b) surface micrographs after atmospheric annealing
progresses slowly and the incorporation of W atoms into TiN enhances this initial oxidation resistance. As shown in Fig. 3(b), the surface micrographs after atmospheric annealing at 600 °C indicated that several defects, such as pores and cracks, were formed in the oxide films with increasing X values. Because oxygen diffuses into the film through these defects, the films with X = 0.66-1.0 have higher mass gains than TiN (Fig. 3(a)).

4. Conclusions

Ti$_{1-X}$W$_X$N films with X = 0-1.0 were synthesized by the RF magnetron sputtering method, and their microstructure, microhardness, and oxidation behavior were studied. All the films exhibited solid solution properties with a cubic structure, and their lattice parameter increased from 0.422 nm (at X = 0) to 0.427 nm (at X = 0.34), and then decreased to 0.423 nm (at X = 1.0). The microhardness changed with the W content (X), and a maximum hardness of 28 GPa was obtained at X = 0.66. During isothermal oxidation at 600 °C, a minimum mass gain of 3% was observed for samples with X = 0.34. Our results suggest that the incorporation of W atoms into TiN was effective at enhancing the surface properties of the material, such as microhardness and oxidation resistance.

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