

Characteristics of Ti-Ni-N-O Thin Films Prepared by Pulsed Laser Deposition

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Abstract

Titanium nickel oxynitride (Ti-Ni-N-O) thin films have been successfully prepared by pulsed laser deposition (PLD) method. Experiments were carried out by changing surface area ratio of target ($S_R = S_{Ni} / (S_{TiN} + S_{Ni})$) from 0 to 20 %. From the analysis of X-ray diffractometer (XRD), the thin films prepared at the whole S_R range were found to be NaCl type (B1) structure. By using a transmission electron microscope (TEM) and an energy dispersive X-ray spectroscopy (EDS), it was found that the thin film prepared at $S_R = 10$ % contained a novel (Ti, Ni)(N, O) phase with B1 structure. The hardness of the Ti-Ni-N-O thin films did not improve due to the partial substitution of nickel atoms for titanium sites in B1 structure. In oxidation tests, it became clear that the oxidation resistance of Ti-Ni-N-O thin film is higher than that of Ti-N-O thin film.

Key words: Solid solution, Thin film, (Ti, Ni)(N, O) phase, Hardness, Oxidation resistance

1. INTRODUCTION

Titanium nitride (TiN) is one of the most widely used coating materials for cutting tools. However, to use TiN coated tools for harder material and/or high-speed cutting, it is necessary to develop coating materials having higher hardness and oxidation resistance than that of TiN. In recent years, the ternary compounds such as titanium aluminum nitride (Ti-Al-N) and titanium silicon nitride (Ti-Si-N) has been actively investigated to fulfill the demand [1-3].

In this study, we attempted to prepare solid solution thin films, in which nickel (Ni) atoms were partially substituted for titanium (Ti) sites of TiN. Although various cermet Ti-Ni-N thin films have been prepared, the solid solution titanium nickel nitride ((Ti, Ni)N) phase have never been obtained [4,5]. The authors thought that it is possible to substitute nickel atoms for partial titanium sites in TiN structure, because the ionic radius of Ti^{3+} and Ni^{2+} was almost same [6,7]. The hardness of (Ti, Ni)N was expected to increase due to solid solution hardening. In addition, the existence of nickel atoms in (Ti, Ni)N may lead to the improvement of oxidation temperature, since Ni has been known to have excellent oxidation resistance. However, there are no data in the literature not only for the preparation of (Ti, Ni)N thin film but also for synthesis of (Ti, Ni)N phase.

In addition, it is difficult to completely avoid the contamination of oxygen into nitride, as it has been reported that nitride thin films prepared by physical vapor deposition (PVD) contain oxygen of approximately 10 at. % [8-10]. It is therefore necessary to characterize material in titanium nickel

oxynitride (Ti-Ni-N-O) system.

The aim of this study is to reveal structure, hardness and oxidation resistance of Ti-Ni-N-O thin films, which are prepared by pulsed laser deposition (PLD).

2. EXPERIMENTAL SETUP

The thin films were prepared with a Nd : YAG laser ($\lambda = 355$ nm) of flash lamp excitation system. The laser can generate short pulse (7 ns) and high energy by an electro-optical Q switch. The deposition was performed by using a pulse repetition rate of 10 Hz. The laser fluence (F) at the target was set at 3 and 5 J/cm² by changing the focal area of laser on a target.

Figure 1 shows configuration of targets. The targets, which consisted of pure TiN (99.5 %) and pure Ni (99.7 %) plates, were used for the deposition. Cation compositions of the thin films were controlled by changing the irradiated area of TiN (S_{TiN}) and Ni (S_{Ni}) plates. Surface area ratio of the target (S_R) was defined by the following equation: $S_R = S_{Ni} / (S_{TiN} + S_{Ni})$.

Before the deposition, the chamber was evacuated to 4×10^{-6} Torr by using rotary and cryo pumps. The single-crystal Si (100) substrates were placed at the opposite position of 20 mm from the target. Substrate temperature was controlled at 400 °C by using a heater and a thermocouple. The experiments were done at the ammonia pressure of 0.2 Torr.

The crystal structure of the thin films was evaluated by X-ray diffractometer (XRD) using Cu K_α radiation of 1.5418 Å at the operating conditions of 50 kV and 300 mA. Microstructural observations were carried out

with a transmission electron microscope (TEM) at the operating conditions of 200 kV. Composition of the thin films was determined with an energy dispersive X-ray spectroscopy (EDS) that is attached to TEM. The sample for TEM observation was pulverized and fixed on a molybdenum (Mo) mesh. The hardness of the thin films measured with a Vickers hardness tester using the load of 10 gf. The measurements were carried out by seven times, and hardness was evaluated to extract the minimum and maximum values. In oxidation tests, using a electrical furnace, the thin films were held at temperature of 600 °C for 1 hour in air.

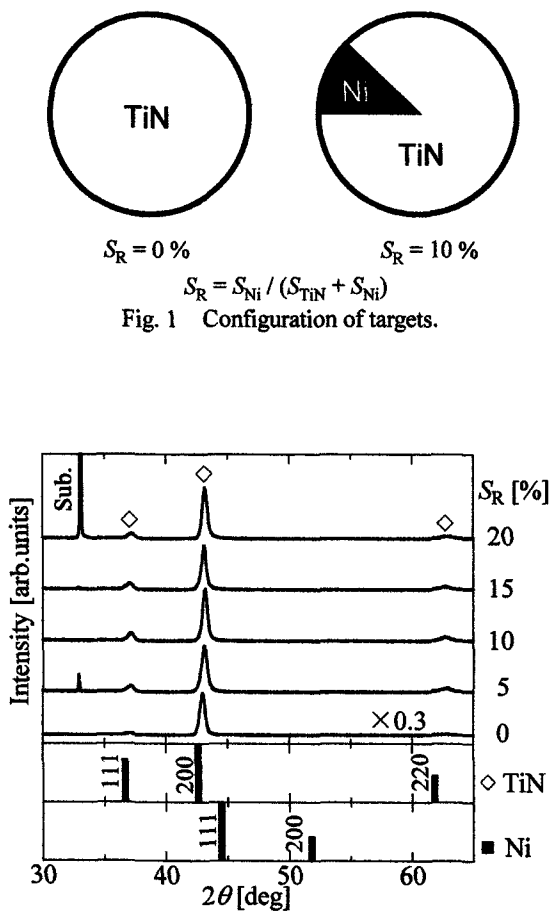


Fig. 2 XRD patterns of the thin films prepared by changing S_R from 0 to 20 %.

3. RESULTS AND DISCUSSION

3.1 Crystal structure of Ti-Ni-N-O thin films

Figure 2 shows XRD patterns of the thin films prepared by changing S_R from 0 to 20 %. The thin films were synthesized at the condition of $F = 3 \text{ J/cm}^2$ over the whole S_R range. In Fig. 2, JCPDS card data of TiN and Ni were shown under the XRD patterns for comparisons [11,12]. The diffraction peaks of the thin film prepared at $S_R = 0 \text{ %}$ appeared at the positions attributed to TiN (B1 structure), whereas such thin film considered to be composed of titanium, nitrogen and

oxygen atoms. In the S_R ranging from 5 to 20 %, the thin films had B1 structure, and did not indicate the diffraction peaks attributed to Ni. This fact seems to be a result of the substitution of nickel atoms for partial titanium sites in B1 structure.

Figure 3 shows lattice constant of the thin films prepared by changing S_R from 0 to 20 %. In Fig. 3, lattice constant of TiN and the thin films was expressed by filled square and diamonds, respectively. As a result, the thin film prepared at $S_R = 0 \text{ %}$ was found to have lower lattice constant than that of TiN. The result seems to be due to the dissolution of oxygen atoms and/or the composition deviation from the stoichiometry of TiN. In addition, the change of lattice constant due to the substitution of nickel atoms was not clearly obtained in Fig. 3, although lattice constant of solid solution thin films has been known to change with increasing solvent atoms [3,13].

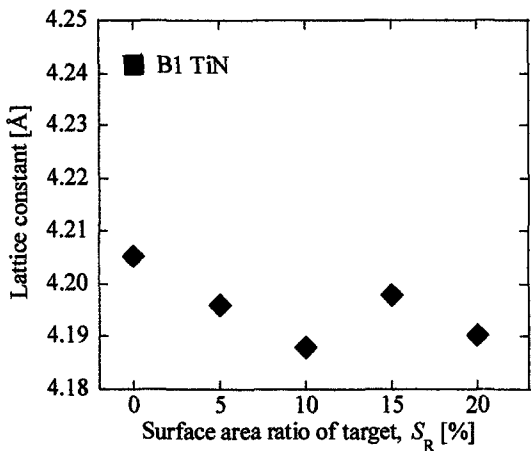
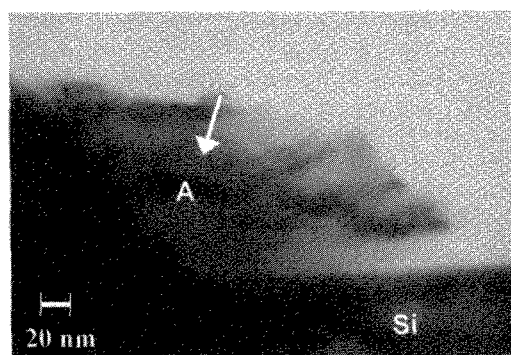


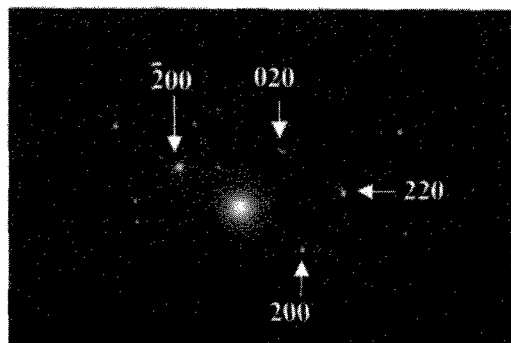
Fig. 3 Lattice constant of the thin films prepared by changing S_R from 0 to 20 %.

Figure 4 shows a bright field image (BFI) and a selected area diffraction (SAD) pattern of the thin film prepared at $S_R = 10 \text{ %}$. In BFI as shown in Fig. 4 (a), a part of the thin film where existed on Si, was observed to contain the crystallite (marked by white allow) having the size of approximately 80 nm. SAD pattern in Fig. 4 (b) was taken including the crystallite. As a result, the diffraction patterns were indexed by B1 structure. Thus, the crystallite with B1 structure was clarified to exist in the thin film prepared at $S_R = 10 \text{ %}$. This result was consistent with that of Fig. 2.

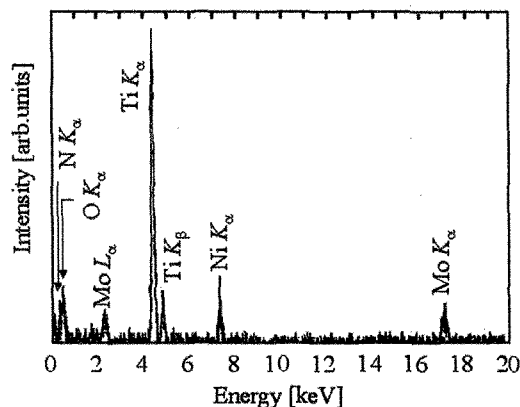
Figure 5 shows EDS spectrum of the thin film prepared at $S_R = 10 \text{ %}$. The spectrum was obtained with a 20 nm size electron beam focused on Point A in Fig. 4 (a). As a result, the peaks attributed to Ti K_{α} , Ni K_{α} , N K_{α} , O K_{α} and Mo K_{α} appeared. Among the peaks, Mo K_{α} was due to the Mo mesh, which fixed the pulverized thin films. Thus, from the results of Fig. 4 (b) and Fig. 5, the crystallite with B1 structure was found to be composed of titanium, nickel, nitrogen and oxygen atoms. This finding led to a conclusion that (Ti, Ni)(N, O) crystallite with B1 structure exists in the thin films prepared at $S_R = 10 \text{ %}$.



(a) BFI



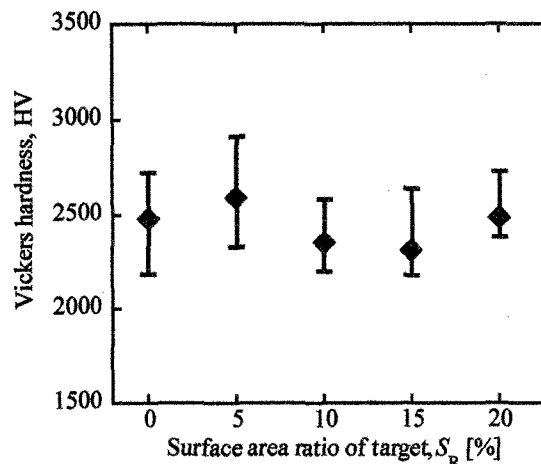
(b) SAD

Fig. 4 (a) bright field image and (b) selected area diffraction pattern of the thin film prepared at $S_R = 10\%$.Fig. 5 EDS spectrum of the thin film prepared at $S_R = 10\%$.

3.2 Hardness of Ti-Ni-N-O thin films

Figure 6 shows Vickers hardness of the thin films prepared at the S_R ranging from 0 to 20 %. The thickness of each thin film was approximately 2 μm , whereas the indenter penetrated approximately 0.3 μm into the thin films. Thus, the penetration depth of the indenter was found to be 15 % of thin film thickness. In the hardness measurement of the thin film, it has been required that the film thickness is more than 5 ~ 10 times of the penetration depth of the indenter.

Therefore, the hardness measurements would be reasonably correct. Although the improvement in hardness was expected to occur due to dissolved nickel atoms, the thin films had Vickers hardness (HV) of approximately 2500 in the S_R ranging from 0 to 20 %. In titanium aluminum nitride (Ti-Al-N) thin films, in which aluminum atoms were substituted for partial titanium sites in TiN structure, the highest hardness value was obtained in a thin film with composition close to the solubility limit [1,13]. Thus, to understand the change in hardness of Ti-Ni-N-O thin films, it is necessary to clarify the solubility limit of such thin films.

Fig. 6 Vickers hardness of the thin films prepared by changing S_R from 0 to 20 %.

3.3 Oxidation resistance of Ti-Ni-N-O thin films

Figure 7 shows XRD patterns of Ti-N-O and Ti-Ni-N-O thin films (a) before and (b) after the oxidation tests. The thin films were prepared at $S_R = 0$ and 12.5 % under the condition of $F = 5 \text{ J/cm}^2$. From Fig. 7 (a), Ti-N-O and Ti-Ni-N-O thin films obey to the B1 structure. In addition, since the diffraction peaks attributed to Ni were not observed in the Ti-Ni-N-O thin film, the Ni atoms in such a thin film seem to exist at the Ti sites in the Ti-N-O phase with B1 structure. In Fig. 7 (b), JCPDS card data of TiN, titanium oxide (TiO) and titanium dioxide (rutile TiO_2) were shown under the XRD patterns [14,15]. In the Ti-N-O thin film held in air at 600 $^\circ\text{C}$, most part of the thin film was oxides such as TiO and TiO_2 . On the other hand, the Ti-Ni-N-O thin film held at 600 $^\circ\text{C}$ was clarified to consist mainly of B1 structure. These results indicated that the oxidation resistance of Ti-Ni-N-O thin film seems to be higher than that of Ti-N-O thin film.

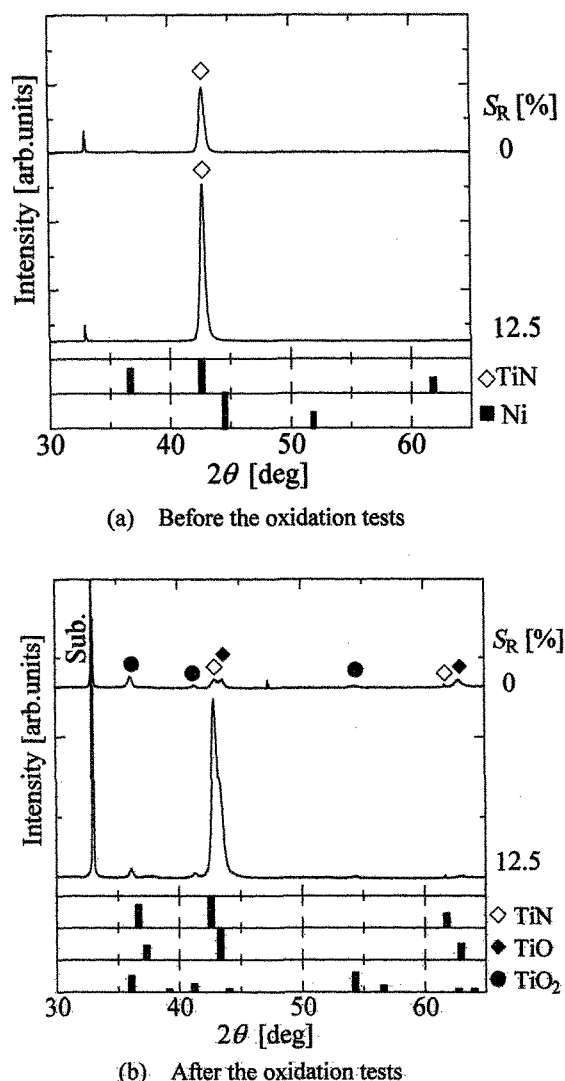


Fig. 7 XRD patterns of Ti-N-O and Ti-Ni-N-O thin films before and after the oxidation tests.

4. CONCLUSIONS

From these experimental results, we have obtained the following conclusions.

- 1) Ti-Ni-N-O thin films have been successfully prepared by PLD.
- 2) A novel (Ti, Ni)(N, O) phase with B1 structure existed in Ti-Ni-N-O thin films prepared at $S_R = 10\%$.
- 3) The Vickers hardness of the thin films were approximately 2500 over the whole S_R range.
- 4) The oxidation resistance of Ti-Ni-N-O thin films was much better than that of Ti-N-O thin films.

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