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# Syntheses and properties of Ti<sub>2</sub>AlN MAX-phase films

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 $Ti_2AIN$  MAX-phase films were synthesized through the post-annealing process of as-deposited Ti-Al-N films. Near amorphous or quasi-crystalline ternary Ti-Al-N films were deposited on Si and  $Al_2O_3$  substrates by sputtering a  $Ti_2AIN$  MAX-phase target at room temperature, 300 °C and 450 °C, respectively. A vacuum annealing of those films at 800 °C for 1 hour changed those films to crystalline  $Ti_2AIN$  MAX-phase. The polycrystalline  $Ti_2AIN$  MAX-phase films exhibited very excellent oxidation resistance due to its characteristics microstructure (nanolaminates), which has potential applications for high-temperature protective coatings. The microstructure and composition of  $Ti_2AIN$  MAX-phase films were investigated using with a variety of characterization tools.

Key words: MAX-phase, Ti<sub>2</sub>AlN, Pulse DC magnetron sputtering, HRTEM, Oxidation behaviour.

#### Introduction

The  $M_{n+1}AX_n$  (n = 1, 2 or 3, abbreviated as MAX) phases are a family of ternary nanolaminates, where M is an early transition metal, A is an A-group element, and X is nitrogen and/or carbon. The structures consist of sheets of octahedral edge-sharing M-atoms separated from each other by layers of A-group elements. The carbon or nitrogen atoms are placed on the octahedral interstitial positions between the close-packed layers of transition metal atoms [1-3]. Due to alternating strong covalent M-X and relatively weak metallic M-A bonds along the c-axis of their hexagonal lattice, the MAXphases exhibit an unique combination of typical ceramic properties (e.g., high melting point, good oxidation and corrosion resistance) and typical metallic properties (e.g., good thermal and electrical conductivity, easy machinability, excellent thermal shock resistance and damage tolerance). This unusual combination of properties makes MAX-phases fascinating for potential application on high temperature components, e.g., protective coatings, electrical contacts, etc [4, 5].

As one member of nanolaminated MAX-phase groups,  $Ti_2AIN$  MAX-phase materials, especially films were not enough investigated. In recent years,  $Ti_2AIN$  has been synthesized by various techniques in bulk form or in thin film form. Lin et al. [6] and Yan et al. [7] fabricated single-phase bulk  $Ti_2AIN$  by hot isostatic

pressing (HIP) or spark plasma sintering (SPS) mixed powders of Ti, TiN and Al at high temperatures (1200 °C ~ 1400 °C). Joelsson et al. [8, 9] and Beckers et al. [10] reported epitaxially growing Ti<sub>2</sub>AlN thin films by reactive magnetron sputtering using Ti and Al dual-targets or Ti<sub>2</sub>Al compound target in an Ar + N<sub>2</sub> atmosphere at high temperature of 830 °C or 690 °C. More recently, Wang et al. [4] obtained Ti<sub>2</sub>AlN thin films by Ti and Al dual-target sputtering in an Ar + N<sub>2</sub> atmosphere at 540 °C and subsequent annealing at 800 °C.

The process window (with respect to N<sub>2</sub> partial pressure) for Ti<sub>2</sub>AlN deposition is extremely narrow [2, 9]. Nitrogen-deficient conditions typically yield phasemixed films composed of inverse perovskite Ti<sub>3</sub>AlN phase and intermetallic TiAl and Ti<sub>3</sub>Al phases, while nitrogen-rich conditions yield the binary nitride TiN and/or the solid solution (Ti, Al) N [5]. For this reason, Ti<sub>2</sub>AlN compound targets, rather than elemental targets or Ti-Al alloy target, can be used with more simplicity, repeatability and applicability in industrial PVD processes. Simultaneously, deposition of Ti<sub>2</sub>AlN thin film at low temperature is one of the main objectives of recent studies.

#### **Experiment details**

Fully dense Ti<sub>2</sub>AlN sputtering target with diameter of 80 mm and thickness of 1 cm was sintered from mixed powders using a spark plasma sintering technique. The starting material Ti (99.7% purity, ~11  $\mu$ m), Al (99.5% purity, ~18  $\mu$ m) and TiN (99.5% purity, ~20  $\mu$ m) powders with a designed molecule ratio of Ti : Al : TiN = 1 : 1 : 1

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was mixed by a 3D ball-mixing for 12 hours in Ar atmosphere. The sintering temperature was 1230 °C, holding for 10 minutes, under a pressure of 40 MPa (200 kN load). XRD result showed that the target consists of pure Ti<sub>2</sub>AlN MAX-phase, which has a atomic composition of Ti : Al : N : O = 0.471 : 0.224 : 0.245 : 0.06 (identified by EPMA).

The substrates used for depositing the Ti-Al-N films were (100) single crystalline Si wafers, polycrystalline and (0006) single crystalline Al<sub>2</sub>O<sub>3</sub> wafers which were cleaned and degreased by successive rinses in ultrasonic baths of acetone and alcohol for 30 minutes. A turbo based pumping system was used to achieve a base vacuum below  $5 \times 10^{-3}$  Pa. Pre-sputtering the Ti<sub>2</sub>AlN target was conducted in an Ar atmosphere of 0.6 Pa for 5 minutes in order to remove the surface oxide layer before the coating process. Prior to deposition, the substrates were at room temperature (RT) or heated to 300 °C or 450 °C. The substrates were further cleaned by an Ar ion bombardment at a bias voltage of -800 V for 5 minutes and sputter-etched at a bias voltage of -500 V and at an Ar gas pressure of  $1.0 \times 10^{-1}$  Pa for 5 minutes. The chamber pressure was 0.5 Pa by injecting the Ar gas near the target. The pulse DC power was kept at 0.8 kW and pulse ratio was 60%. A bias voltage of -50 V was supplied to the substrate which was fixed facing the sputtering target with a target-substrate distance of about 8 cm. The thin film was deposited at RT, 300 °C or 450 °C and the deposition time was 4 hours. After deposition, the thin films were vacuum annealed at 800 °C for 1 hour in a vacuum furnace. Oxidation tests were conducted in air atmosphere using a muffle furnace by heating the specimens which were deposited on (0006) single crystalline Al<sub>2</sub>O<sub>3</sub> substrate and vacuum-annealed at 800 °C.

The film thickness was measured by an  $\alpha$ -step stylus instrument. The film elementary composition was investigated by an electron probe micro-analysis (EPMA, Shimadzu, EPMA-1600). X-ray diffraction (XRD, D8-Discovery Brucker, Cu  $K_{\alpha}$  40 kV, 40 mA) was used to characterize the phase composition of the as-deposited and vacuum-annealed films. The cross-sections of the films were observed using a scanning electron microscopy (SEM, Hitachi, S-4800) operated at 15 kV. Samples for transmission electron microscopy (TEM) analysis were prepared by a focused ion beam (FIB) technique. Relevant cross-sectional TEM analysis was conducted in a field emission analytical electron microscope (JEOL-2010F) operated at 200 kV.

## **Results and discussion**

#### Syntheses of Ti<sub>2</sub>AlN MAX-phase films

Fig. 1 shows XRD patterns of Ti-Al-N films deposited at various temperatures by sputtering a target of  $Ti_2AIN$  MAX-phase. No peak corresponding to



Fig. 1. XRD patterns of Ti-Al-N films deposited at various temperatures from the sputtering target of  $Ti_2AIN$  MAX phase.



Fig. 2. (a) XRD pattern and (b) cross-sectional SEM images of RT-deposited film after post-annealing at 800 °C.

Ti<sub>2</sub>AlN MAX-phase appears for the as-deposited Ti-Al-N films regardless of deposition temperature. Instead, the films deposited at room temperature and 300 °C were composed of FCC-TiN and AlTi intermetallic phases, while the film deposited at 450 °C was composed of Ti<sub>3</sub>AlN, TiN, and Ti<sub>2</sub>N phases. The MAX-phases are usually high temperature form, normally synthesized at high temperature. Thus, high deposition temperature is a most important factor to synthesize MAX-phase film. The deposition temperature in this study is believed not high enough to form crystalline Ti<sub>2</sub>AlN MAX phase films.

Fig. 2(a) shows XRD pattern for the RT-deposited

film (of Fig. 1) after post-annealing treatment in vacuum at 800 °C for 1 hour. Pure  $Ti_2AIN$  MAX-phase was observed in films. It was considered the following reaction major occurred.

$$AlTi + TiN = Ti_2 AlN \tag{1}$$

Fig. 2(b) shows cross-sectional SEM images of the  $Ti_2AIN$  MAX-phase films, which were deposited on polycrystalline  $Al_2O_3$  substrates at RT and post-annealed at 800 °C. The reason why  $Al_2O_3$  substrate was used for this work is because it has similar thermal expansion coefficient to  $Ti_2AIN$  MAX-phase. The fractured cross-sectional SEM images revealed that the  $Ti_2AIN$  MAX-phase film was very dense and composed of fine equiaxed crystals (less than 0.2 µm in size).

Film composition is an important factor for Ti<sub>2</sub>AlN MAX-phase film formation. The EPMA result shows the Ti<sub>2</sub>AlN film deposited at RT and post-annealed at 800 °C has a chemical compositions of Ti : Al : N : O = 0.498 : 0.308 : 0.13 : 0.06. Small amount of oxygen was incorporated into the MAX-phase films, which must be derived from oxygen contamination during target fabrication. However, the oxygen in the films should also contribute to the formation of Ti<sub>2</sub>AlN MAX-phase. Persson et al. [11] had reported the MAX-phase oxynitride Ti<sub>2</sub>Al(O,N) formed by solid-state reaction between substoichiometric TiN thin films and Al<sub>2</sub>O<sub>3</sub> (0001) substrates. Therefore, the crystalline Ti<sub>2</sub>AlN MAX-phase films could be obtained even some incorporation of oxygen in this work.

Fig. 3(a) shows a high-resolution TEM (HR-TEM) image and FFT (fast Fourier transformation) pattern of the Ti<sub>2</sub>AlN MAX-phase film obtained in Fig. 2(b). From the observations of lattice fringe and the corresponding FFT patterns, the film was revealed to have well-crystallized Ti<sub>2</sub>AlN MAX-phase. The d values of the (104) and (103) planes were perfectly matched with those of the Ti<sub>2</sub>AlN MAX-phase. The schematic illustration for the structure of Ti<sub>2</sub>AlN MAX-phase unit cell is shown in Fig. 3(b) [12]. Ti<sub>2</sub>AlN MAX-phase possesses a hexagonal structure in



Fig. 3. (a) HRTEM image and FFT pattern (inset) of the film obtained from Fig. 2 and (b) schematic diagram of its unit cell of  $Ti_2AIN$  MAX-phase.

which covalent TiN layers are intercalated with metallic Al layer. Due to weak Ti-Al bands and high activity of Al atoms, Al atoms can easily diffuse.

## Characteristic oxidation resistance of Ti<sub>2</sub>AlN MAXphase films

Excellent oxidation resistance is one of the characteristics of Ti<sub>2</sub>AlN MAX-phase [13]. Oxidation tests were conducted in air atmosphere using a muffle furnace by heating the specimens which were deposited on (0006) single crystalline  $Al_2O_3$  substrate and vacuum postannealed at 800 °C for 1 hour. Fig. 4 shows crosssectional SEM images and the corresponding EDX line-scanning profiles of Ti<sub>2</sub>AlN MAX-phase films after oxidation at 900 °C for 1, 10, and 20 hours, respectively. Continuous and dense  $Al_2O_3$  scales were formed on the surface of Ti<sub>2</sub>AlN film. In addition, very low oxygen signals were observed in the remained Ti<sub>2</sub>AlN films.

Fig. 5 shows the XRD diffraction pattern of  $Ti_2AIN$  films after oxidation at 900 °C for 1, 2, 5, 10 and 20 hours, respectively. No peak corresponding to oxide phase was detected after oxidation of  $Ti_2AIN$  film oxidized for 1 hour. This reflects that the oxide



**Fig. 4.** Cross-sectional SEM image and the corresponding EDX line-scanning profiles of the  $Ti_2AIN$  MAX-phase films after oxidations at 900 °C for (a) 1 hour, (b) 10 hours and (c) 20 hours.



Fig. 5. X-ray diffraction pattern of  $Ti_2AIN$  MAX-phase films after oxidation at 900 °C for 1, 10 and 20 hours.



Fig. 6. The thickness of the oxide layers formed on the  $Ti_2AIN$  MAX-phase films after oxidation at 900 °C as a function of oxidation time.

layer is very thin and the Ti<sub>2</sub>AlN MAX-phase has a strong resistance against oxidation. Peaks of α-Al<sub>2</sub>O<sub>3</sub> were detected after oxidation for 2 hours, while few peaks of TiO<sub>2</sub> were detected after oxidation for 5 hours. Fig. 6 shows the thickness of oxide layer formed on the surface of Ti<sub>2</sub>AlN MAX-phase film after oxidation at 900 °C as a function of oxidation time (hour). The oxide layer thickness formed on Ti<sub>2</sub>AlN MAX-phase film after oxidation for 1 and 20 hours were  $\sim 0.7\,\mu m$ and  $\sim 2 \mu m$ , respectively. The oxidation kinetic showed a parabolic behaviour with respect to oxidation time, indicating that the oxidation proceeds by the diffusion process through a dense oxide layer. The Ti<sub>2</sub>AlN MAXphase film obtained in our work was found to have very high oxidation resistance compared to previous Ti-Al-N films [14].

Due to the nanolaminated structure of  $Ti_2AIN$  MAXphase [15] where metallic Al layers positioned between strong Ti-N layers, the Al atoms are much more active and have higher diffusivity than the Ti atoms. Therefore, Al atoms in the  $Ti_2AIN$  MAX-phase diffuse out to the film surface to form a pure  $Al_2O_3$  oxide layer on the film surface as soon as the oxidation starts, and the formed dense  $Al_2O_3$  oxide layer prohibits the ingress of oxygen into the films. This is explained to be a reason why Ti<sub>2</sub>AlN MAX-phase had a strong resistance against oxidation. This film can be available as protective coatings against oxidation for various high-temperature components of Ti alloys.

### Conclusions

Ti<sub>2</sub>AlN MAX-phase films could be synthesized through the post-annealing process of as-deposited Ti-Al-N films. Near amorphous or quasi-crystalline ternary Ti-Al-N films were deposited on Si and Al<sub>2</sub>O<sub>3</sub> substrates by sputtering a Ti<sub>2</sub>AlN MAX-phase target at room temperature, 300 °C and 450 °C, respectively. A vacuum annealing of those films at 800 °C for 1 hour changed those films to crystalline Ti<sub>2</sub>AlN MAX-phase. The polycrystalline Ti<sub>2</sub>AlN MAX-phase films exhibited very excellent oxidation resistance. The oxidation of Ti2AIN MAX-phase films showed a parabolic behaviour with respect to oxidation time, and the mechanism was explained with a fast formation of Al<sub>2</sub>O<sub>3</sub> layer on the top of films due to fast diffusion of Al atoms, which is derived from a characteristic microstructure of MAX phase.

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