Surface Coating on Aluminum Flakes with Titanium Nitride Layer by Barrel-Sputtering Techniques

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Flake-shaped fine particles were modified with a thin TiN layer by a hexagonal-barrel-sputtering technique. To determine the optimum sputtering conditions, TiN films were deposited on a glass substrate by the reactive sputtering technique by varying the values of N2 percentage, total pressure, radio-frequency (RF) power, and substrate temperature. From the analysis of XRD patterns, it was determined that a N2 percentage of 25%, a total pressure of 1.2 Pa, a RF power of 200 W, and room temperature were suitable for the preparation of TiN films. Under these optimized conditions, Al flakes were modified with a TiN by the barrel-sputtering technique. The results of optical microscopy, X-ray diffraction measurements, scanning electron microscopy, and energy-dispersive X-ray spectroscopy measurements revealed that the surface of each Al flake was successfully coated uniformly with a TiN layer.

Keywords: barrel-sputtering system, powdery materials, titanium nitride, coating, thin films

1. Introduction

The surface coating of microparticles improves the physical and chemical properties of powdery materials. In order to develop improved powdery materials, a hexagonal-barrel-sputtering technique based on the radio-frequency (RF) sputtering method was developed for the surface coating of microparticles. In comparison to the commonly available techniques for coating microparticles, such as electroless plating and coating with finer particles, the barrel-sputtering technique has several advantages. It is a simple coating process that offers a wide range of choice of modification materials, prevents contamination from impurities, and carries a low environmental burden. We have previously reported that this technique could be applied to the surfaces of metals,1) ceramics,2) and polymer powders3,4) modified with a thin film of metal or alloys such as Pt or Pd–Pt. The barrel-sputtering technique was also used for the surface coating of particles with an oxide film such as TiO2, WO3 and SnO2.5–7) These coated particles can be used in several applications, for example, they can be used in hydrogen storage materials with high durability in air,1) electrochemical catalysts,2) and paint pigments.7)

Transition metal nitride films have interesting properties such as a high melting point, extreme hardness, and excellent thermal and chemical inertness, which make them useful materials in the industry. Titanium nitride (TiN), in particular, is one of the most successful materials for industrial applications such as coatings for high-speed steel cutting tools, diffusion barriers in semiconductors, and coatings for decorative.8–13) If the particle surface can be coated with TiN, the powder would gain new properties, and should find applications such as paint elements, polishing powders, and as diffusion barriers in metallurgy.

This study focused on the surface coating of Al flakes with a TiN layer by using a barrel-sputtering system. The TiN layer was prepared on the grass substrate under various sputtering conditions in order to optimize the conditions for preparing TiN layer by applying a reactive sputtering method. Further, Al flakes were coated with a TiN layer under these optimized conditions by using the barrel-sputtering technique, and analyzed for studying the structure of the TiN on Al flakes.

2. Experimental Details

Figure 1 shows a schematic view of the barrel-sputtering system. The system was characterized by a hexagonal barrel in a vacuum chamber. Powdery materials were placed in the barrel that could be rotated or swung in order to mix the materials. Before sputtering, the chamber was evacuated to 6.5 × 10−4 Pa by using a combination of a rotary pump and a turbo molecular pump. A mixture of Ar (purity: 99.9999%) and N2 (purity: 99.9998%) gases was then introduced into the chamber as the reactive sputtering gas. The gas ratio and total gas pressure in the chamber were regulated by a mass flow controller. A Ti metal target (Toshima Manufacturing Co. Ltd., purity: 99.999%) was placed in the center of the barrel. For coating the glass plate sample, the target was placed facing the glass plate that was positioned just below the target, and the barrel was fixed during sputtering. For coating powdery materials, the target face was tilted up to an...
angle of 30°, and the barrel was swung between −75° and +75° at a speed of 4 rpm during sputtering. Al flakes with an average diameters of 130 and 30 μm (Yamato Metal Powder Co. Ltd., purity: 99.75%, 6 g per batch) were used as the powdery materials. The preparation times for the glass plate sample and powdery sample were 1 h and 8 h, respectively. After sputtering, N₂ gas was carefully introduced into the chamber till the chamber pressure equaled the atmospheric pressure. The thickness of the TiN layer coated on the glass plate was evaluated using the cross-sectional image in a cut sample obtained by a scanning electron microscope (SEM). A sample for observing the cross section of the flake was prepared by the following method. Flakes were dispersed in a cold polymer (Marumoto Struers K.K., Specifix-20). After the polymer solidifies, it was cut into 1–2 mm thick slices, and the cut surface of each slice was polished and then analyzed. The prepared sample was analyzed by using an X-ray diffractometer (PHILIPS, PW1825/00), optical microscope (Nikon, ECLIPSE LV150), SEM (JEOL, JSM-5600LV and JSM-6701F), and energy dispersive X-ray spectrometer (EDS; JEOL, JED-2140).

3. Results and Discussions

3.1 Study of sputtering conditions for the preparation of titanium nitride films

Figure 2 shows the XRD pattern of the films deposited on the glass substrate prepared by the conventional sputtering method with different percentage of N₂. The RF power, total pressure, and substrate temperature were set to 200 W, 1.2 Pa, and room temperature (≈300 K), respectively. In the sample prepared with a N₂ percentage of 0%, only reflection peaks from metallic Ti were observed in the XRD pattern as shown in Fig. 2(A). The XRD pattern of the sample prepared with a N₂ percentage of 5% did not show peaks from metallic Ti, and new diffraction peaks appeared at 2θ = 36.5° and 61.6°. These peaks originated from the crystalline TiN (111) and (220) planes, respectively. However, the peaks slightly shifted to a lower diffraction angle compared to those of the stoichiometric TiN thin films. This behavior probably suggests that a small ε-Ti₅N phase grew in the TiN film prepared with a N₂ percentage of 5%, and the diffraction peak shifted to a lower angle due to the small ε-Ti₅N (200) and (002) peaks. For samples prepared with a N₂ percentage of 10%, TiN (111) and (220) peaks were observed at 2θ = 36.6° and 61.7°, respectively—almost the same as the diffraction angles of the TiN thin films reported previously. The peak positions of TiN (111) and (220) did not change for the sample prepared with N₂ percentages between 10% and 35%, indicating that stoichiometric TiN films were prepared with these N₂ percentages. However, when the N₂ percentage in the sputtering condition was increased from 10% to 35%, the intensities of (111) and (220) peaks in the XRD pattern of the TiN films gradually reduced, further, the (200) peak was faintly visible in the XRD pattern for a N₂ percentage of 35%. For the sample prepared with a N₂ percentage of 50%, the (200) peak was clearly observed at 2θ = 42.6°, and the intensities of the (111) and (220) peaks were fairly reduced. This indicates that the crystalline orientation perpendicular to the deposited TiN film changed from (111) and (110) to (100) with the change of N₂ percentage from 35% to 50%. This behavior was qualitatively identical to that mentioned in previous reports. In addition, the full width at half maximum (FWHM) of the (220) peaks for the samples prepared with N₂ percentages of 35% and 50% were larger than that for a N₂ percentage of 25%, suggesting that the change in crystalline orientation caused large distortions in the TiN film. Consequently, it was found that crystallized stoichiometric TiN films were fabricated on the glass substrates by the reactive sputtering method when the N₂ percentages in the sputtering condition were above 10%.

The thicknesses of the TiN films prepared with different N₂ percentages were estimated by SEM measurements. Figure 3(A) shows the SEM image of the cross section of the TiN film on a glass substrate prepared with a N₂ percentage of 25%. The surface of the TiN film did not show any large bumps or steps, and the structure of the film was a columnar with a thickness of 270 nm. The thicknesses of the TiN films prepared with different N₂ percentages are shown in Fig. 3(B). The thickness of the film was sharply decreased with an increase in the N₂ percentage from 0% to 5%. This decrease was probably due to the formation of titanium nitride on the surface of a Ti target, thereby reducing the sputtering efficiency of a Ti atom. The film thickness gradually decreased from 400 to 200 nm as the N₂ percentage increased from 5% to 50%, probably due to the difference between the ionization rates of Ar and N₂ gas. Considering the results of the XRD measurements and the analysis of film thickness, an N₂ percentage of 25% was used for the following prepared TiN films.
Figure 4 shows the XRD patterns of the films prepared under different total gas pressures. The RF power and the substrate temperature were fixed at 200 W and room temperature, respectively. TiN (200) peak was observed clearly, while TiN (111) and (220) peaks were faintly visible in the XRD patterns of the film prepared under total pressures of 0.42 and 0.71 Pa. For the XRD patterns of the film prepared under a total pressure higher than 1.2 Pa, TiN (111) and (220) peaks appeared, while the (200) peak diminished, indicating that the preferred orientation in the film was changed. The thickness of the film prepared under a total pressure of 0.42 Pa was 120 nm, whereas the thickness of the film prepared under a total pressure of 1.7 Pa was 380 nm, as shown in the inset of Fig. 4. The relationship between the film thickness and the preferred orientation in the film was consisted with the result reported by Li et al. 21) Considering these results, the total pressure was fixed at 1.2 Pa for the remaining preparations.

Figure 5 shows the XRD patterns of films prepared using different values of RF power. The substrate temperature was fixed at room temperature. The TiN (111) and (220) peaks were appeared in all the XRD patterns, demonstrating that the crystalline TiN film was formed at each RF power. In the XRD pattern of the film prepared using an RF power of 100 W, the TiN (200) peak also appeared. This indicated that the preferred orientation in the film changed from (200) to (111) with changing the RF power from 100 to 200 W. An increasing in the RF power led to a proportional increase in the film thickness, as shown in the inset of Fig. 5. The preferred orientation in the film was related to the film thickness, as mentioned above. In the measurements of the XRD pattern
and the thickness of the films prepared under the different N\textsubscript{2} percentages and the total pressures, the (200) peak appeared when the film thickness was below 200 nm, which was consistent with the results on changing the RF power. Therefore, the change in the preferred orientation was due to the change in the thickness of the TiN film. When the RF power was increased up to 500 W, it was observed in the XRD pattern of the prepared film that the FWHM of the (111) and (220) peaks was large and the peak position of the TiN (220) slightly shifted to a high diffraction angle. This suggests that point defects or internal stresses in the film affected the XRD pattern of the film prepared using a high RF power. In the remaining preparations, an RF power of 200 W was used.

Figure 6 shows the XRD patterns of the films prepared at different substrate temperatures. All the diffraction patterns showed three diffraction peaks assigned to the TiN crystal, and these peak positions did not change. It should be noted that the XRD pattern of the film prepared at a temperature of 300 K (Fig. 6(D)) was different from the pattern as shown in Fig. 2(E), regardless of the fact that same preparation condition were employed in both the cases. This difference in the XRD pattern originated due to the heater attached in front of the target, which decreased the deposition rate. When the substrate temperature during the preparation of the film was increased from 348 to 423 K, the XRD pattern of the film showed a decrease in the intensity of the (111) peak from 310 to 90 cps, while there was a steep increase in the intensity of the (200) peak from 190 to 590 cps. The film thickness, however, did not change significantly with an increase in the substrate temperature during the preparation of the films. This change in the preferred orientation change due to a variation in the substrate temperature was consistent with that in previous report by Kajikawa et al.\textsuperscript{24} The peak intensity decreased as the substrate temperature during the preparation of the film increased from 423 to 498 K. This behavior was not clearly understood. A probable cause for this might be the formation of a film with a TiN\textsubscript{x}O\textsubscript{y} crystal structure because of a small amount of oxygen that might have been released from the vacuum chamber or the target heater during the heating of the substrate.\textsuperscript{27}

3.2 Surface coatings of powdery materials

On the basis of these results, Al flakes were modified with TiN under the following deposition conditions: a N\textsubscript{2} percentage of 25%, a total pressure of 1.2 Pa, an RF power of 200 W, and room temperature (~300 K) as the substrate temperature. Figure 7(A) and (D) shows the photographs of the mod-
ified Al flakes with average diameters of 130 and 30 µm, respectively. For comparison, unmodified Al flakes are shown on the left side in each figure. The unmodified Al flake had a metallic color, while the modified samples of flakes with 130 and 30 µm diameters (the right side in each figure) were light brown which was similarly to the color of TiN powder. Optical microscopy observations showed that the unmodified flakes (B, E) had a sharp edge and an almost flat surface with a metallic color. On the other hand, each modified flake with a diameter of 130 µm (C) was uniformly gold in color. The color of the modified flakes with a diameter of 30 µm (F) was identical to that with a diameter of 130 µm.

The XRD patterns of the unmodified and modified samples with diameters of 30 µm are shown in Fig. 8. The strong peak assigned to Al metal was detected around 2θ = 38° and 45° in both the XRD patterns, and a weak peak attributed to the TiN (111) and (200) was detected around 2θ = 36° and 42° in the modified powder. No other peak was detected in the diffraction pattern. The XRD pattern of the modified Al flakes with a diameter of 130 µm also showed the peak attributed to the TiN (111) and (200). These results confirmed that the Al flakes were modified with crystallized TiN.

SEM and EDS measurements were performed on Al flakes before and after the modification with TiN. Figure 9 shows the SEM images (A) of Al flakes with a diameter of 130 µm before (I) and after (II) modification, and flakes with a diameter of 30 µm after modification (III). The Al (B) and Ti (C) elemental mapping images were obtained by EDS. The SEM images of an uncoated flake (A-I) showed a smooth surface with some irregularities and spots. The EDS measurement of the uncoated flakes detected the Al element (B-I), although the Ti element (C-I) was not detected. The SEM image of the modified flakes (rows II and III) was similar to that of the surface of the unmodified flakes; the surface did not show an island structure or cracks. The Ti element was uniformly detected for modified Al flake with a diameter of 130 (C-II) and 30 µm (C-III). XRD measurements and SEM observations confirmed that the surface of the Al flakes was uniformly coated with TiN.

In order to confirm the thickness of the coating, and its adhesion to Al flakes, the cross-sectional area of the modified Al flakes with a diameter of 130 µm was observed by an SEM, as shown in Fig. 10(B). For comparison, the cross-
The thickness of the TiN layer on the Al flake was approximately 1/6 to 1/10th of the thickness of the film on a glass plate for the same sputtering conditions. In a separate experiment using this technique, the thickness of the TiN layer was 200 nm. In a cross-sectional image of an unmodified Al flake is shown in Fig. 10(A). In this figure, the Al flake could be distinguished from the polymer matrix; the supporting matrix and the Al flake were shown on the right and the left sides of this figure, respectively. No layer was observed between the uncoated Al flake and the matrix. On the other hand, a layer was observed along the contour of the Al flake surface, as shown in Fig. 10(B). The layer was only detected on the surface of the modified Al flake, suggesting that the observed layer was TiN. The thickness of the TiN layer was 200 nm. In a separate experiment using this technique, the thickness of the layer on the particles was approximately 1/6 to 1/10th of the thickness of the film on a glass plate for the same preparation time. The thickness of the TiN layer on the Al flakes was almost the same as that obtained in the separate experiment. Consequently, it was revealed that the entire surface of each Al flake was uniformly coated with a TiN layer by using the barrel-sputtering system.

4. Conclusions

The surface coating of Al flakes with a thin TiN layer was achieved by using a hexagonal-barrel-sputtering technique. Suitable conditions for preparing the TiN layer were determined by sputtering on a glass substrate under various sputtering conditions. XRD measurements were used to optimize the conditions for preparing the TiN layer, and the optimized conditions were as follows: a N₂ percentage of 25%, a total pressure of 1.2 Pa, an RF power of 200 W, and room temperature as the substrate temperature (~300 K). Subsequently, the surface of Al flakes was modified with a TiN layer under these conditions by the barrel-sputtering technique. From the results of optical microscopy, SEM, and EDS observations, it was concluded that the surface of each Al flake was uniformly coated with the TiN layer.

REFERENCES

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