Production and Properties of Functionally Gradient Films Varying from Amorphous Al(Ti, N) to Hexagonal Al(Ti)N Phase

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The application of sputtering in a mixed gas of argon (Ar) and nitrogen (N_2) to $Al_{80}Ti_{20}$ resulted in the formation of compositionally and structurally gradient film consisting of amorphous Al(Ti, N) and hexagonal Al(Ti)N phases. By continuously changing the partial pressure (P_N) of N_2 from 0.02 to 0.1 Pa in a total Ar + N_2 pressure of 1 Pa, the resulting phase is an amorphous Al(Ti, N) in the P_N range below 0.06 Pa and changes to an Al(Ti)N through coexistent amorphous plus Al(Ti)N phases in the higher P_N range. The average sputtered rate of the film was $0.9 \mu m/ks$ and the N_2 concentration along the film thickness increases to 63 at% with an increase in P_N to 0.1 Pa. As P_N increases, the wave vector at the peak position of the amorphous halo in the X-ray diffraction patterns decreases continuously and crystallization temperature increases from 662 to 728 K. The Knoop hardness and the electrical resistivity measured along the film thickness increase from 325 to 2310 and from $2.4 \times 10^{-7} \Omega m$ to an infinite value, respectively, with an increase in N_2 content in the amorphous phase and the subsequent phase transition to Al(Ti)N. The load leading to a failure in the film is 0.44 N which is about twice as large as that (0.24 N) for the Al(Ti)N phase. Thus, the sputtered amorphous-hexagonal phase film is concluded to have functionally gradient characteristics resulting from the compositional and structural gradients.

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I. Introduction

It has recently been reported that a number of amorphous alloys are formed by rapid solidification in Al-based alloy systems such as Al-Si-TM⁽¹⁾, Al-Ge-TM⁽¹⁾, Al-ETM-LTM⁽²⁾, Al-Ln⁽³⁾ and Al-Ln-LTM⁽⁴⁾. Here, TM, ETM, LTM and Ln represent transition metals, early (IVA-VIA group) transition metals, late (VIIA-VIIIA group) transition metals and lanthanide metals, respectively. These amorphous alloys have attracted great interest because of their high tensile strength combined with low density and good corrosion resistance. However, the thermal stability of these Al-based amorphous alloys is rather low and the crystallization begins to occur at about 550 K in the case of annealing for 3.6 ks. In addition, the glass-forming ability is not always high and the critical sample thickness for glass formation by the conventional melt spinning method is usually less than $40 \mu m$. As trials to improve the thermal stability and glass-forming ability for the Al-based amorphous alloys, the optimization of alloy components has been carried out for the last several years⁽⁵⁾⁽⁶⁾. Besides, the compositional and structural gradience along the thickness of the sample is also thought to be one of the methods leading to the increase in the thermal stability and critical thickness of Al-based amorphous alloys. Although a large number of data have been reported⁽⁷⁾ on the production and properties of functionally gradient materials,

the materials consist only of crystalline phases and little has been known about the production and properties of the functionally gradient materials consisting of amorphous alloy and crystalline or amorphous ceramics. This paper is intended to present the production of the compositionally and structurally gradient films consisting of amorphous Al-based phase and hexagonal AlN in an Al-Ti-N system by a sputtering method and the microstructure, mechanical strength and electrical resistivity of the Al(Ti)-Al(Ti)N films.

II. Experimental Procedure

An $Al_{80}Ti_{20}$ target with a disk shape of 75 mm in diameter and 6 mm in thickness was prepared from pure Al with a purity of 99.99 mass% and pure premelted Ti with a purity of 99.9 mass% by arc melting in a purified argon atmosphere. The premelted target was sputtered on a glass or aluminum substrate to form a film with a surface shape of $50 \times 50 mm^2$ and a thickness of about $6 \mu m$ using a DC magnetron sputtering apparatus. After evacuating the sputtering chamber mounted with the target material up to 6.0×10^{-5} Pa, mixed argon and nitrogen gases of 1.0 Pa were fed through an automatic gas-flow controller to make argon plasma in the chamber. The partial pressure of nitrogen to argon plus nitrogen (P_N) was changed at a rate of 0.01 Pa or continuously in the range of 0 to 0.1 Pa. The argon plasma was generated between the substrate cathode and

stainless-steel anode. The supplied anode current was usually 300 mA and the anode voltage was changed from 0.4 to 0.5 kV. The sputtering time was changed to be in the range of 7.2 to 10.8 ks at each P_N . In addition, the continuously gradient films were produced by changing continuously P_N in the range of 0 to 0.1 Pa and the sputtering time was in the range of 7.2 to 10.8 ks. Prior to sputtering the target, the substrate was sputtered to clean its surface for 600 s by applying a negative bias against the substrate. The gap between the target and substrate was fixed at 60 mm. Analyses of constituent components in the sputtered films were made with an electron-probe microanalyzer for aluminum and titanium and an oxygen-nitrogen analyzer for nitrogen.

The as-prepared structures for the sputtered films were examined by thin-film type and conventional-type X-ray diffractometry using Cu- or Co-K α radiation, optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The 2θ angle in the X-ray diffractometry was calibrated with Si powder. The cross-sectional micrograph revealing the structural change along the sample thickness was taken from the sample subjected to mechanical cleavage, followed by polishing with emery papers and then chemical etching in a 5% hydrochloric acid for 2.4 ks at room temperature (≈ 290 K). Measurement of electrical conductivity was made at room temperature by the conventional four-probe technique. The changes in Knoop and Vickers hardness numbers with thickness of the films were examined by using a Vickers microhardness tester with a Knoop or a Vickers indenter and a load of 10 g. The critical load against exfoliation of the film was also examined in the condition of a down speed of load of 2 g/s and a moving velocity of 10 $\mu\text{m/s}$ by a scratch tester (SST101). The detection of exfoliation during the scratch test was made by measuring an output voltage through cartridge.

III. Results

Figure 1 shows the change with P_N in the thin-film type X-ray diffraction patterns of the sputtered films obtained in the condition where the incident angle (α) of the X-ray beam to the specimen surface is 2.5 degrees. Although the as-sputtered film consists mainly of an fcc-Al phase at $P_N=0$, the increase of P_N into 0.02 Pa causes the formation of a mostly single amorphous phase and the amorphous single phase remains unchanged up to $P_N=0.06$ Pa. The further increase in P_N to 0.07 and 0.09 Pa causes the formation of a mixed structure of amorphous and hexagonal AlN phase and the amorphous phase disappears at $P_N=0.1$ Pa. The wave vector (K_p) defined by $K_p=4\pi \sin \theta/\lambda$ at the position of the maximum on the X-ray diffraction patterns corresponding to the amorphous phase shown in Fig. 1 is plotted as a function of P_N in Fig. 2. K_p decreases gradually from 51.40 to 47.90 nm^{-1} with an increase in P_N from 0.02 to 0.07 Pa. This change indicates that the nitrogen content in the amorphous phase increases with P_N , leading to the increase in

Fig. 1 X-ray diffraction patterns of the films prepared by sputtering an $\text{Al}_{80}\text{Ti}_{20}$ alloy in the atmospheres in which the P_N was changed in the range below 0.1 Pa.

Fig. 2 Wave vector ($K_p=4\pi \sin \theta/\lambda$) of the peak position of an amorphous halo in the X-ray diffraction patterns shown in Fig. 1 as a function of P_N .

the atomic distance between Al and Al pairs.

Figure 3 shows a bright-field electron micrograph and an electron diffraction pattern of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N=0.02$ Pa. No contrast revealing the existence of any crystalline precipitates is seen in the bright-field image and the diffraction pattern consists

Fig. 3 Bright-field electron micrograph (a) and selected-area diffraction pattern (b) of an $\text{Al}_{80}\text{Ti}_{20}$ film prepared by sputtering at $P_N=0.02$ Pa.

only of halo rings, indicating the formation of an amorphous single phase. Figures 4 and 5 show a bright-field electron micrograph, a selected area diffraction pattern and a dark-field electron micrograph taken from the (100) and (002) reflection rings of the hexagonal AlN phase for the sputtered $\text{Al}_{80}\text{Ti}_{20}$ films prepared at $P_N=0.07$ and 0.1 Pa, respectively. The film prepared at

$P_N=0.07$ Pa has a mixed structure consisting of amorphous and hexagonal AlN phases and the very fine AlN particles with a size of about 4 nm disperse homogeneously at an interparticle spacing of about 4 nm. The increase in P_N to 0.1 Pa causes the formation of a mostly single hexagonal AlN phase with a grain size of about 8 nm, being consistent with the result derived from the X-ray

Fig. 4 Bright- and dark-field electron micrographs (a and b) and selected-area diffraction pattern (c) of an $\text{Al}_{80}\text{Ti}_{20}$ film prepared by sputtering at $P_N=0.07$ Pa.

Fig. 5 Bright- and dark-field electron micrographs (a and b) and selected-area diffraction pattern (c) of an $\text{Al}_{80}\text{Ti}_{20}$ film prepared by sputtering at $P_N=0.1$ Pa.

diffraction patterns shown in Fig. 1. It is to be noticed that the particle size of the hexagonal AlN phase is as small as 8 nm and the nanoscale AlN phase is formed in the present sputtering condition.

It is shown in Fig. 2 that the K_p value of the amorphous phase decreases continuously with increasing P_N because of the change in the dissolution amount of nitrogen in the amorphous film. The change in the nitrogen content is expected to cause the changes in the crystallization temperature (T_x) and hardness number. Figure 6 shows the change in T_x with P_N for the sputtered

Al-based films. T_x increases from 662 to 728 K with increasing P_N from 0.02 to 0.07 Pa, indicating that the dissolution of nitrogen causes the significant increase in T_x . These T_x values are considerably higher than those (450 to 600 K)⁽⁸⁾ for Al-based amorphous alloys containing 80 at%Al. In addition, Fig. 7 shows the change in H_K with P_N for the sputtered Al-based films, along with the data of their structure. H_K increases from 325 for the fcc phase to 2310 for the hexagonal AlN phase through 430 to 910 for the amorphous single phase and the mixed amorphous plus hexagonal AlN phases. These results in-

Fig. 6 Crystallization temperature (T_x) as a function of P_N for the amorphous Al(Ti, N) films prepared by sputtering.

Fig. 7 Knoop hardness number (H_K) as a function of P_N for the fcc-Al(Ti), amorphous Al(Ti, N), amorphous plus hexagonal Al(Ti)N and hexagonal films.

indicate clearly that the functionally gradient properties resulting from the compositionally and structurally gradient structure are obtained in the sputtering condition where P_N is changed from 0 to 0.1 Pa.

Figure 8 shows the relation between P_N and sputtering time which is important to control the ramp rates. P_N was continuously changed in the range of 0 to 0.1 Pa for the sputtering time of 7.2 ks. Figure 9 shows the cleavage fracture surface and the concentration profiles of Al, Ti and N elements for the sputtered Al-AlN film prepared in the condition shown in Fig. 8. As shown in Fig. 9(b), the N_2 content increases continuously with an increase in the distance from the substrate, accompanying the gradual decrease in Al and Ti contents. The inaccuracy of the concentration profiles in the vicinity of the interface between the substrate and the film as well as in the vicinity of the top surface is induced because the diameter of the probe for the microanalysis is as large as $1\text{ }\mu\text{m}$. The cleavage surface shown in Fig. 9(a) is very smooth and neither appreciable distinction of the constituent phases nor any voids are seen over the whole cross section of the film. It is therefore concluded that the compositionally and structurally gradient film with a full density is formed in the present sputtering condition. Furthermore, the average sputtering rate of the film is evaluated to be 0.9 nm/s from the comparison between Figs. 8 and 9. In order to clarify the cross sectional structure of the film in more details, the deeply etched microstructure for the film produced by sputtering for 15 ks is shown in Fig. 10. Although no distinct contrast is seen in the amorphous single phase region marked with A, the degree of brightness decreases continuously with an increase of the distance from the substrate and becomes constant in the top-surface layer consisting of the hexagonal Al(Ti)N phase. The continuous variation in the degree of brightness also indicates that the component and structure in the film vary continuously along the film thickness. The variation of the contrast also implies that the corrosion resistance against the chemical solution is considerably higher for the amorphous layer than

Fig. 8 Variation of the partial pressure of nitrogen to nitrogen plus argon (P_N) with sputtering time.

Fig. 9 (a) Fracture surface appearance of the film sputtered in the condition shown in Fig. 8, and (b) changes in the concentration profiles of Al, Ti, N components in the sputtered film with film thickness.

Fig. 10 Optical micrograph revealing the cross-sectional structure of the $\text{Al}_{80}\text{Ti}_{20}$ film prepared by sputtering in the condition shown in Fig. 8.

for the hexagonal Al(Ti)N layer. Besides, no contrast revealing the existence of pores is seen, indicating the formation of the fully dense film, in consistent with the

Fig. 11 Knoop hardness number (H_K) of the compositionally gradient film consisting of amorphous Al(Ti, N)-hexagonal Al(Ti)N phase. The Knoop indentations are also shown for reference.

interpretation derived from the cleavage fracture surface shown in Fig. 9.

Figure 11 shows the Knoop hardness (H_K) on the cross section of the sputtered film as a function of the distance from the substrate, along with the photograph revealing the change in the size of the Knoop indentations. H_K increases almost linearly from 325 to 2310 with an increase in the distance from the substrate, namely with an increase in the nitrogen content. The distinct change in H_K indicates clearly that the present film belongs to the functionally gradient material (FGM).

Furthermore, the critical load leading to the failure of the compositionally gradient films with the same film thickness of about $6 \mu\text{m}$ was measured by detecting the output voltage through the cartridge during the scratch test. As shown in Fig. 12, the critical applied load at which the initiation of the crack is observed is 0.24 N for the hexagonal Al(Ti)N film, 0.3 N for the FGM film and 0.44 N for the FGM film coated with the Al(Ti)N surface layer. Thus, the critical applied load leading to the initiation of the crack increases significantly through the compositional and structural gradient as compared with

Fig. 12 Relation between the output voltage of the cartridge which is sensitive to the generation of failure and the applied load for the compositionally gradient film consisting of amorphous Al(Ti, N)-hexagonal Al(Ti)N phase.

that for the ceramic Al(Ti)N layer itself.

Figure 13 shows the electrical resistivity between the bottom fcc-Al(Ti) layer prepared at $P_N=0$ Pa and the amorphous Al base layer prepared at $P_N=0.02$ or 0.05 Pa or the hexagonal Al(Ti)N layer prepared at $P_N=0.1$ Pa through the amorphous Al base layer. The electrical resistivity increases gradually from 2.4×10^{-7} to $2.4 \times 10^{-5} \Omega\text{m}$ with increasing nitrogen content in the Al base amorphous phase and the transition of the amorphous phase to the Al(Ti)N phase causes the change of electricity from the conductive to insulative state. The steep increase in T_x , H_K and electrical resistivity allows us to conclude that the compositionally and structurally gradient amorphous Al(Ti, N)-hexagonal Al(Ti)N film also has functionally gradient characteristics.

Fig. 13 Electrical resistivity between the fcc-Al(Ti) layer and the amorphous Al(Ti, N) or hexagonal Al(Ti)N layer in the sputtered film.

IV. Discussion

The formation of the amorphous layer in the present functionally gradient film and the significant variations of T_x , H_K and electricity with nitrogen content in the amorphous layer are the most important point in the present results. Consequently, we shall consider the role of nitrogen in the glass-forming ability, thermal stability and mechanical strength of the Al-based amorphous alloy. As shown in Fig. 1, the sputtered structure of the $\text{Al}_{80}\text{Ti}_{20}$ alloy consists of an fcc supersaturated solution in the case of argon sputtering and hence the dissolution of nitrogen is concluded to be very effective for the increase in the glass-forming ability for the Al-based alloy. Although the nitrogen-induced amorphization has been reported to be obtained by mechanical alloying⁽⁹⁾⁻⁽¹¹⁾, little has been obtained about the information on the effect of nitrogen on the thermal stability, mechanical strength and electrical resistivity of amorphous alloys. As shown in Figs. 6, 7 and 11, T_x and H_K in the amorphous Al (Ti, N) phase are in the range of 660 to 730 K and 420 to 900, respectively, depending on the nitrogen content. The T_x and H_K values are considerably larger than those (520 to 580 K and 370 to 410)⁽²⁾⁽⁸⁾ for $\text{Al}_{80}\text{Ti}_{10}\text{M}_{10}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$ or Cu) amorphous alloys with the same solute content prepared by melt spinning. Accordingly, the significant difference in T_x and H_K is concluded to be due to the dissolution of nitrogen. There is a clear tendency for T_x and H_K to increase with an increase in the magnitude of negative heat of mixing among the constituent elements⁽¹²⁾. The negative heat of mixing is 37 kJ/mol for Al-Ti pair, 11 to 38 kJ/mol for Al-M pairs, 20 to 44 kJ/mol for Ti-M pairs, 158 kJ/mol for Al-N pair and 169 kJ/mol for Ti-N pair⁽¹³⁾⁻⁽¹⁵⁾, being much larger for the nitrogen-containing pairs. It is therefore reasonable to consider that the bonding nature among the constituent elements is much stronger for the nitrogen-containing pairs than for the other pairs and the stronger bonding nature among the constituent elements in the Al-Ti-N system causes the much higher T_x and H_K values for the Al(Ti, N) amorphous alloy. It is also presumed that the number of the nitrogen-containing pairs in the amorphous layer increases with increasing nitrogen content, resulting in the significant and continuous increase in T_x , H_K and electrical resistivity with film thickness.

In addition, we shall investigate the reason for the formation of the amorphous single phase in the Al-Ti-N system. It has been reported that no amorphous phase is formed in binary Al-N⁽¹⁶⁾, Ti-N⁽¹⁷⁾ and $\text{Al}_{80}\text{Ti}_{20}$ alloys even by sputtering and the sputtering-induced phase consists of fcc-Al plus hexagonal AlN, fcc TiN and fcc-Al solid solution, respectively. This result suggests that the supersaturated dissolution of nitrogen into the non-equilibrium fcc phase with optimum Al and Ti concentrations so as to suppress the precipitation of AlN and TiN is important for the formation of the amorphous phase. That is, the existence of Al-Ti bonding pairs seems to be essential for the construction of the metallic amorphous

structure containing nitrogen, in addition to the existence of Al-N and Ti-N pairs which results from the dissolution of nitrogen. When the nitrogen in the film does not cause the formation of nitrides, the dissolved nitrogen atom can act effective roles in the generation of misfit strain resulting from the significant difference in the atomic sizes between nitrogen and aluminum or titanium and in the suppression of diffusivity of the constituent atoms resulting from the formation of strongly attractive Al-N and Ti-N pairs. It is well known that both the significant misfit strain among the constituent elements and the low diffusivity of the constituent atoms are important factors for glass formation⁽¹²⁾⁽¹⁸⁾. Further detailed structural analyses on the amorphous Al-Ti-N alloys will shed some light in more clear interpretation on the roles of nitrogen in the amorphization of the fcc Al(Ti) supersaturated solution and the significant increase in thermal stability and mechanical strength.

V. Summary

The compositionally and structurally gradient films in the amorphous Al(Ti, N)-hexagonal Al(Ti)N system have been prepared by using a reactive sputtering method. By changing the partial gas pressure of nitrogen to nitrogen plus argon (P_N) in the range of 0 to 0.1 Pa in a total pressure of 1 Pa, the resulting film consists of an fcc Al(Ti) phase at $P_N=0$ Pa, an amorphous Al(Ti, N) phase in the P_N range of 0.02 to 0.06 Pa, coexistent amorphous plus hexagonal Al(Ti)N at 0.07 Pa and a hexagonal Al(Ti)N phase in the P_N range of 0.09 to 0.1 Pa. The nitrogen concentration changed continuously from 0 at% to about 63 at% along the sample thickness. The lattice parameters are 0.3985 nm for the fcc-Al phase and $a=0.3114$ nm and $c=0.4979$ nm for the hexagonal Al(Ti)N phase, being different from those for pure Al and stoichiometric AlN because of the dissolution of titanium and nitrogen. Furthermore, T_x of the amorphous Al(Ti, N) phase increases from 662 to 728 K with increasing nitrogen content. The Knoop hardness number (H_K) also increases steeply from 325 for the fcc Al(Ti) layer to 2310 for the hexagonal Al(Ti)N layer through 430 to 910 for the amorphous Al(Ti, N) and the coexistent amorphous plus Al(Ti)N layers. The critical load at which a failure generates is 45 g which is much larger than that (24 g) for the Al(Ti)N layer itself. The electrical resistivity also increases significantly from 2.4×10^{-7} to $2.4 \times 10^{-5} \Omega\text{m}$ with increasing nitrogen content in the amorphous phase and changes to an infinite value in the Al(Ti)N phase. The steep changes in T_x , H_K and electrical resistivity along the sample thickness indicate that the compositionally and structurally gradient films also have the functionally gradient characteristics.

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