Crystallization of Sputter Deposited Amorphous Ti–52at%Al Alloy

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The crystallization process of amorphous Ti–52at%Al alloy was studied using sputter deposited materials. The crystallization occurred at about 800 K accompanying the abrupt drop in an electrical resistivity vs. temperature curve. From changes in X-ray and electron diffraction patterns due to annealing at 800 K, the crystallization sequence was represented as

From the analyses of lattice parameter, the crystallization was considered to be an isoconcentrational process. The formation of metastable phases in preference to the stable $\gamma(\text{L1}_0)$ one was well predicted by the kinetic analysis in terms of relative nucleation rate assuming that the free energy of amorphous phase was lower than that of undercooled liquid by 3.5 kJ/mol.

KEY WORDS: crystallization; amorphous; metastable phase; Ti–52at%Al alloy; driving force; nucleation frequency.

1. Introduction

Intermetallic titanium aluminide, γ -TiAl (L1_0) is of current interest for applications in the aerospace industry owing to its low density, high specific strength and good oxidation and corrosion resistance at least up to 1273 K.¹⁾ However, their poor ductility and low toughness at room temperature prevent their widespread use and much effort has been made to increase their ductility and toughness by alloying additions and microstructure modifications through thermal and mechanical treatments.^{2,3)}

Rapid solidification,^{4,5)} mechanical alloying,^{6,7)} sputtering and other non-equilibrium processing techniques have been employed during the past few years to improve mechanical properties of various materials by refining the microstructure and reducing the extent of deleterious segregation during solidification. In addition, rapid solidification may produce supersaturated solid solutions, metastable crystalline intermediate phases and amorphous phase and consequent improved properties. In the case of Ti–Al alloys, formations of amorphous phase have been reported for mechanical alloying^{6,7)} or sputtering.⁸⁾ For the effective utilization of these metastable phases to improve mechanical properties of titanium aluminide, it is necessary to reveal the transition process from metastable phase to stable one on the heat treatment. Thus, the present study is aimed to make clear the crystallization process of amorphous Ti–52at%Al alloy on heating.

2. Experimental Procedure

The Ti–52at%Al amorphous alloys were prepared by the magnetron sputtering with 99.999% pure aluminum and 99.99% pure titanium targets. The sputtering was performed at an argon pressure of 5×10^{-3} Torr. The composition of sputter deposited alloy was controlled by the discharge wattage for each target. The Al concentration of 51.9 at% was obtained for the sputter deposited alloy by compleximetric titration. Amorphous alloys of 1 to 2 μm thicknesses were prepared on water cooled quartz substrates for electrical resistivity measurements and X-ray analysis. For microstructural observations by transmission electron microscope, thin films of 0.05 to 0.2 μm thickness were prepared directly on collodion coated copper mesh. The isochronic electrical resistivity measurements were performed by the four probe technique at fixed heating rate of 0.167 K/s. In order to avoid oxidation effects, samples were annealed and measured in vacuum of 10^{-6} Torr.

3. Structure of Sputter Deposited Ti–52at%Al Alloy

Figure 1 shows a bright-field electron micrograph and an electron diffraction pattern of sputter deposited Ti–52at%Al alloy. The bright-field image shows no contrast revealing the precipitation of a crystalline phase and the diffraction pattern shows halo rings typical of an amorphous phase, indicating that the Ti–52at%Al alloy is composed of an amorphous single phase. Yan *et al.*⁸⁾ have reported the formation of amorphous phase for sputter deposited Ti–Al alloys containing 30 to

Fig. 1. (a) Bright-field electron micrograph and (b) electron diffraction pattern of a sputter deposited Ti-52at%Al alloy.

Fig. 2. Electrical resistivity vs. temperature for an amorphous Ti-52at%Al alloy.

75 at% Al. The present alloy is within the above concentration range for amorphous formation.

4. Crystallization Characteristics

The electrical resistivity of Ti-52at%Al alloy decreases slightly with an increase in temperature up to about 800 K and abruptly drops to approximately 50% of the initial value at about 850 K due to the crystallization as shown in Fig. 2. Such a decrease in the electrical resistivity observed frequently in amorphous alloys is caused by the electron mobility rise when the long range order develops.⁹⁾ To reveal the crystallization process,

Fig. 3. Electrical resistivity vs. annealing time curves for an amorphous Ti-52at%Al alloy.

Fig. 4. Electron diffraction pattern of an amorphous Ti-52at%Al alloy annealed at 750 K for 8×10^3 s.

isothermal resistivity measurements were performed at various temperatures. The resistivity decreases with an increase in isothermal holding time at temperatures higher than 800 K as shown in Fig. 3. The higher annealing temperatures cause an increase in the decreasing rate and the amount of decrease suggesting the faster crystallization reaction. For annealing at 750 K, the resistivity increased gradually with an increase in holding time. Since no structural change was detected in TEM observation of the specimen annealed at 750 K for 8×10^3 s (Fig. 4), this increase could be attributed to formations of the crystallization nuclei as suggested by Pekala *et al.*⁹⁾ They observed the increase in electrical resistivity in the vicinity of crystallization temperature in the isochronic measurement of resistivity for amorphous Ni-Si-B alloys. From the effect of preannealing on the increase in resistivity, they concluded that the increasing density of crystallization nuclei lead to the increasing scattering of the conduction electrons. The absolute values of the resistivity in the amorphous phase depend on the actual density of crystallization nuclei and the kinetics of crystallite growth. Thus, the abrupt drops of the resistivity at temperatures higher than 750 K can be attributed to the faster crystallite growth. For annealing at 750 K, such a drop in the resistivity was not observed up to the annealing time of 8×10^3 s although the α phase was detected in the X-ray diffraction pattern for the annealing time of 1.08×10^4 s as shown in Fig. 5. This

suggests that the density of crystallization nuclei is still high even for the prolonged annealing time due to the slower crystallite growth at 750 K.

Figure 5 shows the X-ray diffraction patterns for an as sputter deposited materials and specimens annealed at various temperatures for 1.08×10^4 s. The pattern of as sputter deposited material clearly demonstrates an amorphous phase. The X-ray pattern of specimen after annealing at 750 K shows the presence of the hcp

Fig. 5. X-ray diffraction patterns of a sputter deposited Ti-52at%Al alloy annealed at various temperatures for 1.08×10^4 s.

structure. Specimens annealed at 800 and 843 K show X-ray patterns demonstrating the presence of both α (hcp) and γ (L1₀) phases. At higher annealing temperatures, the α phase disappears and only the γ phase is observed. For all annealing temperatures, the stable structure of Ti-52at%Al alloy is the γ phase, and the structures at lower annealing temperatures in Fig. 5 seem to demonstrate intermediate state in the crystallization reaction due to an insufficient diffusivity. Furthermore, there should be another possibility of changes in the

Fig. 6. X-ray diffraction patterns of a sputter deposited Ti-52at%Al alloy annealed at 800 K for various times.

Fig. 7.

(a) Bright-field electron micrograph, (b) dark field image taken by the $(\bar{2}10)$ reflection and (c) selected area electron diffraction pattern from the $[120]_{\alpha}$ direction of a sputter deposited Ti-52at%Al alloy annealed at 800 K for 1.5×10^2 s.

Fig. 8.

(a) Bright-field electron micrograph, (b) dark-field image of $\alpha_2(\text{DO}_{19})$ precipitates taken from the $(110)\alpha_2$ reflection, (c) and (d) selected area diffraction patterns taken from the $[110]\gamma$ and the $[010]\alpha_2$ directions of sputter deposited Ti-52at%Al alloy annealed at 800 K for 2×10^3 s.

Fig. 9. (a) Bright-field electron micrograph and (b) selected area diffraction pattern of a sputter deposited Ti-52at%Al alloy annealed at 800 K for 1.08×10^4 s.

crystallization sequence with annealing temperatures.

Figure 6 shows the change of X-ray diffraction pattern with an increasing annealing time at 800 K. In the specimen annealed for 1.5×10^2 s, the X-ray pattern shows the presence of the hcp structure. At annealing

time of 2×10^3 s, both α and γ structures are detected in the X-ray pattern. At longer annealing time, the X-ray pattern shows an increasing peak height for the γ phase.

Microstructural changes during isothermal annealing at 800 K were examined by TEM observations. At annealing time of 1.5×10^2 s, disordered α (hcp) precipitates were observed as shown in a darkfield electron micrograph of **Fig. 7**. At annealing time of 2×10^3 s, fine spherical precipitates with a diameter of about $0.1 \mu\text{m}$ are observed (**Figs. 8(a), 8(b)**). **Figures 8(c) and 8(d)** show selected area diffraction patterns of γ and $\alpha_2(\text{DO}_{19})$ structures, respectively, in the above specimens. At longer annealing time of 1.08×10^4 s, a fine equiaxed microstructure was observed as shown in **Fig. 9** suggesting the proceeded crystallization. In the X-ray diffraction patterns of **Figs. 5 and 6**, the α and α_2 phases can not be distinguished because the peaks peculiar to the α_2 phase such as $\alpha_2(100)$ and $\alpha_2(101)$ peaks are not detected. However, the presence of the α_2 phase is confirmed at annealing time of 2×10^3 s at 800 K by TEM observations. Thus, from results of TEM observations, the crystallization sequence in the Ti-52at%Al amorphous alloy can be represented as

Amorphous(Ti-52at%Al)– $\alpha(\text{hcp})$ – $\alpha_2(\text{DO}_{19})$ – $\gamma(\text{L1}_0)$.

The lattice parameters of observed structures are obtained from X-ray diffraction patterns and they are compared with those reported for equilibrium phases¹⁰⁾ in **Fig. 10**. The lattice parameters of γ phase in **Fig. 6** agree well with those for equilibrium phase. Equilibrium lattice parameters a and c for α and α_2 phases tend to decrease with an increase in Al content as shown by dotted curves in **Fig. 10**. The lattice parameters of metastable α and α_2 phases can be plotted on these lines extrapolated to the Al concentration of 52 at% suggesting

Fig. 10. Lattice parameters for the α (hcp), α_2 (DO₁₉) and γ (L1₀) phases in a sputter deposited Ti-52at%Al alloy annealed at 800 K compared to reported values for equilibrium states as a function of composition. The lattice parameter, a , of the α_2 phase is plotted by $a/2$.

that no compositional change occurs during the above crystallization sequence. For the solid solution forming alloys, Ishihara *et al.*¹¹⁾ suggested that the isoconcentration nucleation from the undercooled liquid would be possible by large undercoolings based on the thermodynamic analysis in terms of relative nucleation rates. This might be true to the present case since the structure of amorphous phase is close to the largely supercooled liquid.

5. Discussion

From X-ray and electron diffractions, it was found that the crystallization in the amorphous Ti-52at%Al alloy initiates by the formation of disordered α (hcp) phase. Figure 11 shows the free energy hierarchy for possible phases at the concentration of 52 at% Al. The free energies were calculated by the sublattice model using parameters reported by Kattner *et al.*¹²⁾ which could reproduce phase constitutions in the equilibrium Ti-Al system. The assumption here is the free energy of amorphous phase (G_{Am}) is the same as that of the supercooled liquid (G_L). The Ostwald's step rule¹³⁾ seems to be valid in the present crystallization sequence from the free energy hierarchy of possible phases in Fig. 11. However, the relative magnitude of driving force does not tell which phase is more likely to nucleate. Thus, the kinetic analysis was performed for this nucleation process according to the method adopted by Ishihara *et al.*¹²⁾

The homogeneous nucleation frequency (I) at a temperature (T) given by the classical nucleation theory is expressed as¹⁴⁾

$$I = K \exp(-\Delta G^*/kT), \quad \dots\dots\dots(1)$$

where K is the kinetic parameter, k is the Boltzmann's constant. ΔG^* is the excess free energy of a critical nucleus expressed as

$$\Delta G^* = 16\pi(\sigma^3 v^2 / \Delta G^2) / 3, \quad \dots\dots\dots(2)$$

Fig. 11. Calculated relative Gibbs free energies of amorphous, α (hcp), α_2 (DO₁₉), γ (L1₀) and α -Al(fcc) referred to liquid-Ti and Liquid-Al for the Ti-52at%Al alloy.

Fig. 12. Calculated ΔG^* as a function of temperature for α (hcp), β (bcc), α_2 (DO₁₉), γ (L1₀) and α -Al(fcc) phases of the Ti-52at%Al alloy assuming that G_{Am} is equal to G_L .

where σ is the surface energy between the amorphous and the crystalline phases, v is the molar volume, ΔG is the free energy difference between the two phases.

σ can empirically be expressed as a function of the latent heat (L) and molar volume¹⁵⁾

$$\sigma = 0.065Lv^{-2/3}, \quad \dots\dots\dots(3)$$

Assuming that the latent heat is the same as the enthalpy difference (ΔH) between the two phases, ΔG^* for each possible phase was calculated by the sublattice model using Kattner's parameters.¹¹⁾ At 800 K, the bcc phase is the most probable phase to nucleate and the hcp phase is the second probable one as shown in Fig. 12. This discrepancy may be due to too simple approximations used in the present analysis. The free energy of amorphous phase (G_{Am}) cannot be precisely expressed by that of undercooled liquid (G_L) as clearly seen from the experimental facts¹⁶⁾ that the structure of amorphous phase varies depending on the cooling rate. In the present

Fig. 13. Calculated ΔG^* as a function of temperature for α (hcp), β (bcc), α_2 (DO₁₉), γ (L1₀) and α -Al(fcc) phases of the Ti-52at%Al alloy assuming that G_{Am} is equal to $G_L - 3.5$ kJ/mol.

case, the hcp phase becomes to be the most probable phase to nucleate when G_{Am} is lowered by 3.5 kJ/mol ($G_{Am} = G_L - 3.5$ kJ/mol) as shown in Fig. 13. Furthermore, Fig. 13 can well predict the present results that the stable γ phase is more dominant at higher annealing temperature as shown in Fig. 5. The assumptions in the present analysis seem to be too simple but they can predict very well the tendency of the metastable phase formation in preference to the stable γ phase.

6. Conclusion

The crystallization process of sputter deposited amorphous Ti-52at%Al alloy was examined by electrical resistivity measurements, X-ray diffraction and transmission electron microscopy. From these results, the following conclusions have been obtained.

- (1) The crystallization occurs at about 800 K accompanying abrupt drop of electrical resistivity.
- (2) For annealing at 750 K, the electrical resistivity increases with an increase in holding time. Since no structural change was detected in TEM observation, this increase can be attributed to formations of the crystallization nuclei.
- (3) The X-ray pattern of specimen after annealing at 750 K for 1.08×10^4 s shows the presence of the α (hcp)

phase. At 800 and 843 K, both α (hcp) and γ (L1₀) phases are detected. At higher annealing temperatures, only the γ phase is detected.

(4) From the changes in X-ray and electron diffraction patterns due to annealing at 800 K, the crystallization sequence can be represented as

Amorphous(Ti-52at%Al)– α (hcp)– α_2 (DO₁₉)– γ (L1₀).

(5) From the analyses of lattice parameter, it is concluded that the crystallization is an isoconcentration process.

(6) The formation of metastable phase in preference to the stable γ phase can be well predicted by the kinetic analysis in terms of relative nucleation rate, assuming that the free energy of amorphous is lower than that of undercooled liquid by 3.5 kJ/mol.

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