Formation and Thermal Stability of Amorphous Ti-Si Alloys

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The crystallization behavior of amorphous Ti-Si alloys containing 10 to 100 at%Si, which was prepared by sputtering, has been investigated by measuring DTA curves, and observing microstructures of annealed sample in a hot stage using a electron microscope. The amorphous Ti-Si alloys usually pass through three stages during crystallization, although the alloys having the compositions corresponding to Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , $TiSi$ and $TiSi_2$ compounds show a single stage of crystallization and higher crystallization temperatures. The amorphous Ti-33.4 at%Si alloy crystallizes at the temperature of 748 K. Fine crystalline particles of Ti_5Si_3 with the diameters ranging diameter from 0.2 to 1 μm appear at a heating time of 300 s, and the number and size of these particles quickly increase at a heating time of 600 s. At the higher heating temperature of 888 K, the grains of crystalline Ti_5Si_3 phase grow quickly bigger.

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I. Introduction

Amorphous alloys are metastable materials, which crystallize upon annealing to stable crystalline phases. Several titanium-base alloy systems indicate good glass forming ability with a wide composition range⁽¹⁾, and their glass phases show superior corrosion resistance and high hardness⁽²⁾. Metalloids such as B and Si are known to stabilize the amorphous structure of Ti-alloys and change the composition range of glass formation. Naka *et al.*⁽³⁾ reported that the addition of B allows to make amorphous Ti-B alloys containing 8 to 50 at% boron. The aim of this work is to clarify the effect of Si on the crystallization behavior of amorphous Ti-Si alloys upon annealing, and also the microstructures of the crystallized alloys.

II. Experimental Procedure

The Ti-Si binary thin films were prepared on water-cooled aluminum substrates with 15 mm width, 15 mm length and 1 mm thickness by using a magnetron sputtering apparatus in a low pressure argon gas of 6.65 mPa. The composition of the films were varied by changing the target ratio of pure Ti to Si. The sputtering condition of 600 W and 10.8 ks was used, and the thickness of dense films without porosities was found 25 μm . The structure of the sputtered and annealed films peeled from the aluminum substrates was investigated by X-ray diffractometry and transmission electron microscopy. The crystallization behavior of the alloys peeled from the substrates was investigated by differential thermal analysis with a heating rate of 0.33 Ks⁻¹. The microstructures of the

Fig. 1 X-ray diffraction patterns of Ti-Si sputtered alloys using $CuK\alpha$.

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alloys were also observed by transmission electron microscopy with a hot stage.

III. Results and Discussion

Glass formation of Ti-Si alloys is confirmed in the composition range of 10–100 at%Si. Figures 1 and 2 show the X-ray diffraction patterns of a series of Ti-Si films with 0 to 100 at%Si. The films containing about 10 at%Si or more are amorphous by showing only a few diffuse diffraction peaks. The films with 60 at%Si or less show the main diffuse peak around 40 degrees, and the films with 80 at%Si or more show the main diffuse peak at the angle of 30 degrees or lower. This may indicate that the structure of the alloys with about 80 at%Si changes from the metallic side structure to the silicon side structure. The composition range of glass formation for the Ti-Si system is drawn in the Ti-Si phase diagram in Fig. 3. Thus the addition of silicon is more effective in inducing the glass formation, compared with the addition of boron, which produces glassy phase in the range of 8 to 50% B.

The crystallization behavior of Ti-Si amorphous alloys was investigated by using differential thermal analy-

Fig. 2 X-ray diffraction patterns of Ti-Si sputtered alloys using $\text{CuK}\alpha$.

sis. Figure 4 shows the crystallization temperature of the alloys plotted as a function of Si content. These data indicate that the amorphous Ti-Si alloys generally pass through three stages during crystallization, although the alloys having the compositions corresponding to Ti_3Si , Ti_5Si_3 , Ti_5Si_4 , TiSi and TiSi_2 compounds show a single stage of crystallization and higher crystallization temperatures. It is known that amorphous alloys with the compositions corresponding to compounds crystallize polymorphously to the corresponding crystalline compounds⁽⁴⁾.

The crystallization temperatures of Ti-Si amorphous alloys, in general, tend to decrease with an increase in Si content up to about 67 at% corresponding to the TiSi_2 composition, but the crystallization temperature of Ti-Si

Fig. 3 Phase diagram and glass forming range of Ti-Si alloys.

Fig. 4 Compositional dependence of crystallization temperature for sputtered Ti-Si amorphous alloys.

alloy with much higher Si contents apparently increases as shown in Fig. 4.

Amorphous alloys are likely to have a structure similar to the corresponding liquid alloys. Then the crystallization temperature should be normalized by the melting temperatures. Figure 5 shows that the crystallization temperature of amorphous Ti-Si alloys increases with the melting temperature. However, the alloys containing 67 at%Si or more differ from those straight line of such correlation. These alloys indicate a different behavior of their crystallization from the other alloys.

Figure 6 shows the thermal differential analysis curve of Ti-33.4 at%Si amorphous alloy, in which the Si content is close to that of Ti_5Si_3 . The alloy crystallizes at the temperature of 800 K with three stages. The crystallization microstructure of the alloy was also observed by successive heating in a transmission electron microscope. The amorphous Ti-33.4 at%Si is stable up to 748 K and shows diffuse diffraction patterns (see Fig. 7). The gener-

al feature of diffraction patterns of the alloy in Fig. 8 does not change with increasing heating temperature, where they were obtained by tracing the patterns. These results indicate that the amorphous Ti-33.4 at%Si alloy is stable before crystallization, although amorphous Ti-B alloys during heating decompose into two amorphous alloys before crystallization⁽³⁾.

Fig. 5 Relationship between crystallization temperature of amorphous Ti-Si alloys and melting point for Ti-Si crystalline alloys with equivalent compositions.

Fig. 6 DTA curve of Ti-33.4 at%Si amorphous alloy.

Fig. 7 Microstructures and selected area diffraction patterns for Ti-33.4 at% Si alloy at heating temperatures: (a) as prepared, (b) 689 K and (c) 748 K.

Fig. 8 Change in intensity of electron diffraction pattern for Ti-33.4 at%Si amorphous alloys with temperature.

Fig. 9 Microstructure (a) and selected electron diffraction pattern of zone axis $[3213]$ for Ti_5Si_3 (b) in Ti-33.4 at%Si alloy at 748 K for 300 s.

Fig. 10 Microstructure (a) and selected electron diffraction pattern of zone axis $[0001]$ for Ti_5Si_3 (b) in Ti-33.4 at%Si alloy at 748 K for 300 s.

The amorphous Ti-33.4 at%Si alloy crystallizes at temperature of 748 K. Fine crystalline particles of Ti_5Si_3 ranging diameter from 0.2 to 1 μm appear at a heating time of 300 s (Fig. 9), and the number and size of these particles quickly increase at a heating time of 600 s (Fig. 10). At the higher heating temperature of 888 K, the grains of crystalline Ti_5Si_3 phase grow bigger as shown in Fig. 11.

While the observation of microstructures of Ti-33.4 at% alloy shows two stages of crystallization, differential thermal analysis in Fig. 6 indicates three stages. The main peak and third peak in the DTA curve correspond to the crystallization of amorphous phase to Ti_5Si_3 phase, and the grain growth of Ti_5Si_3 , respectively. Small amounts of the crystalline Ti_3Si phase from the amorphous alloy

Fig. 11 Microstructure (a) and selected electron diffraction pattern of zone axis [0001] for Ti_5Si_3 (b) in Ti-33.4 at%Si alloy at 888 K.

expected from the Ti-Si phase diagram have not been observed during heating by electron microscopy. The Si content of Ti-33.4 at%Si alloy deviates a little from the stoichiometric composition of Ti_5Si_3 , and this amorphous alloy crystallizes with a primary crystallization process instead of a polymorphous crystallization.

IV. Conclusions

The amorphous Ti-Si alloys containing 10 at%Si or more were prepared by rf. sputtering in low pressure argon. The thermal stability of amorphous alloys have been investigated by thermal differential analysis and by observing the microstructure of crystallization using a electron microscope.

The amorphous Ti-Si alloys with higher melting temperatures indicate the higher crystallization temperatures. The amorphous alloys with silicon content corresponding to compounds show the relatively higher crystallization temperatures, as compared to other alloys

in the Ti-Si system. Although Ti-Si alloys in general show three stages of crystallization, the amorphous alloys having the Si content equivalent to stable crystalline compounds transform by a single stage crystallization.

Amorphous Ti-33.4 at%Si alloy corresponding to the Si content, near that of Ti_5Si_3 , crystallizes to the Ti_5Si_3 phase with a nucleation growth mechanism at the first stage of heating. The grains of crystalline Ti_5Si_3 grow during heating, but small amounts of Ti_3Si have not been observed by electron microscopy.

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