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New Amorphous Alloys in Al-Ti Binary System

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An amorphous phase was found to be formed in coexistence with the fcc-Al phase for $\text{Al}_{92}\text{Ti}_8$ and with fcc-Al + Al_2Ti for $\text{Al}_{90}\text{Ti}_{10}$ by melt spinning with a circumferential velocity (V_f) of 40 m/s. The further increase in V_f to 50 m/s causes the formation of a mostly single amorphous phase at 10%Ti. The amorphous + fcc-Al and amorphous + fcc-Al + Al_2Ti alloys have good bending ductility and exhibit a high tensile fracture strength of 810 to 820 MPa and a high Vickers hardness of 300 to 310. Crystallization of the amorphous phase in the $\text{Al}_{90}\text{Ti}_{10}$ alloy takes place by two-stage reactions of $\text{Am} \rightarrow \text{fcc-Al} + \text{Al}_2\text{Ti} \rightarrow \text{fcc-Al} + \text{Al}_3\text{Ti}$. Considering that the as-quenched phase of the $\text{Al}_{95}\text{Ti}_5$ alloy consists of fcc-Al + Al_3Ti phases, it is interpreted that the formation of the amorphous phase in coexistence with the fcc-Al phase is due to the enrichment of Ti content in the remaining supercooled liquid to a critical solute concentration for glass formation and to the suppression of precipitation of Al-Ti compounds from the supercooled liquid with the enriched Ti contents. The enrichment phenomenon of the solute element in the remaining liquid seems to be hereafter utilized as a useful mechanism for the synthesis of an amorphous phase in the low solute concentration alloys where no amorphous phase is formed in the rapidly solidified state.

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I. Introduction

Since the first synthesis of Al-rich amorphous alloys with good bending ductility in the Al-Ni-Si system⁽¹⁾ by the melt-spinning technique, a large number of Al-based amorphous alloys with high tensile strength and good bending ductility have been prepared in the Al-TM-Si⁽²⁾, Al-TM-Ge⁽²⁾, Al-ETM-LTM⁽³⁾, Al-TM-Ln⁽⁴⁾⁽⁵⁾, Al-Ln⁽⁶⁾ and Al-Ca-TM⁽⁷⁾ (TM=IV-VIII group transition metals, ETM=IV-VI group transition metals, LTM=VII-VIII group transition metals, Ln=lanthanide metal) systems. The amorphous alloys in the Al-TM-Ln system exhibited the glass transition and a supercooled liquid region before crystallization⁽⁸⁾ and hence the consolidation of the amorphous phase in the supercooled liquid region was expected to enable the production of a high-strength bulk amorphous material⁽⁹⁾. Subsequently, a nanoscale mixed structure consisting of nanogranular icosahedral and fcc-Al phases was produced in melt-spun Al-rich Al-Mn-Ce⁽¹⁰⁾ and Al-Cr-Ce-Co⁽¹¹⁾ alloys. In the systematic study on the production of high-strength bulk alloys in the Al-based system by extrusion of these nonequilibrium alloy powders, various kinds of bulk alloys have been produced in different structures of amorphous single phase⁽⁹⁾, nanocrystalline phases consisting of fcc-Al and intermetallic compounds⁽¹²⁾ and nanoquasicrystalline phases of icosahedral and fcc-Al⁽¹³⁾. The nanocrystalline bulk alloy is named "GIGAS" and has been used as high-strength and superplastic materials in various application fields⁽¹⁴⁾. Further-

more, the bulk nanoquasicrystalline alloys prepared by the powder-metallurgy (P/M) method exhibit high mechanical strength combined with large elongation and high impact fracture energy⁽¹⁵⁾. More recently, we have also noticed that a mixed structure of nanogranular amorphous and fcc-Al phases is formed in melt-spun Al-V-(Fe, Co)⁽¹⁶⁾ and Al-Ti-(Fe, Co)⁽¹⁷⁾ alloys and their alloys exhibit high mechanical strength above 1000 MPa, though no successful data on the consolidation into a bulk form have been obtained. In the subsequent study on the formation of nanogranular amorphous structure, we have also found that an amorphous single phase is formed in melt-spun Al-Ti binary alloys. The clarification of the formation and properties of Al-Ti binary amorphous alloys is important as fundamental information for the development of high-strength material with light weight at elevated temperatures because Ti is a typical light metal with high melting temperature and has a low diffusivity in the Al phase⁽¹⁸⁾. This paper is intended to present the composition range in which an amorphous phase in the Al-Ti binary system is formed by melt spinning and their thermal stability and mechanical properties.

II. Experimental Procedure

Binary alloys with composition of $\text{Al}_{100-x}\text{Ti}_x$ ($x=3$ to 12 at%) were examined in the present study. Their alloy ingots were prepared by arc melting a mixture of pure Al and Ti metals in an argon atmosphere. The subscript numbers represent nominal alloy compositions of the

mixture. Rapidly solidified ribbons with different thicknesses ranging from 11 to 15 μm were produced by the melt spinning technique and the rotation speed of copper wheel was changed in the range of 20 to 50 m/s. The as-quenched and annealed structures were examined by X-ray diffractometry and transmission electron microscopy. The thermal stability was evaluated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Tensile strength and Vickers hardness were measured at room temperature by an Instron-type testing machine and a Vickers microhardness tester, respectively. The strain rate in the tensile test was fixed to be $8.3 \times 10^{-4} \text{ s}^{-1}$ and the hardness measurement was made under a load of 0.245 N.

III. Results and Discussion

Figure 1 shows X-ray diffraction patterns of the melt-spun $\text{Al}_{100-x}\text{Ti}_x$ ($x=3, 5, 8, 10$ and 12 at%) alloys prepared at 40 m/s. The structure is identified to consist of fcc-Al at 3 %Ti, fcc-Al+ Al_3Ti at 5%Ti, fcc-Al+amorphous at 8%Ti, amorphous+fcc-Al+ Al_2Ti at 10%Ti and fcc-Al+ Al_2Ti at 12%Ti. The lattice parameters of the fcc-Al phase are evaluated to be in the range of 0.4047 to 0.4027 nm which are slightly smaller than that ($a=0.40496 \text{ nm}$)⁽¹⁹⁾ for pure Al, in spite of the larger atomic size of Ti. The decrease in the lattice parameter of the fcc-Al phase by the dissolution of Ti agrees with the previous data⁽²⁰⁾ on the rapidly solidified Al-Ti binary alloys. The agreement indicates that the fcc-Al phase is a solid solution containing Ti. The Al solid solution with

various Ti contents depending on the coexistent phases in the as-quenched state is hereafter represented with the fcc-Al phase. The equilibrium phase in the Al-rich Al-Ti alloys consists of Al without appreciable solid solubility limit of Ti and tetragonal Al_3Ti ($a=0.385 \text{ nm}$ and $c=0.8596 \text{ nm}$)⁽²¹⁾ phases and hence the as-quenched phase including amorphous and tetragonal Al_2Ti ($a=0.3976 \text{ nm}$ and $c=2.4360 \text{ nm}$)⁽²²⁾ phases is concluded to be in a nonequilibrium state. Furthermore, it is seen that the peak intensity of the Al phase in the $\text{Al}_{90}\text{Ti}_{10}$ alloy is much lower than that in the $\text{Al}_{92}\text{Ti}_8$ alloy. This result indicates the possibility of forming an amorphous single phase in the case of a higher cooling rate for the $\text{Al}_{90}\text{Ti}_{10}$ alloy. With the aim of clarifying the mixed states of amorphous+fcc-Al and amorphous+fcc-Al+ Al_2Ti phases, the bright-field electron micrographs and selected-area electron diffraction patterns of the $\text{Al}_{92}\text{Ti}_8$ and $\text{Al}_{90}\text{Ti}_{10}$ alloys prepared at 40 m/s are shown in Fig. 2. Besides, Fig. 3 shows the enlarged bright- and dark-field electron micrographs and the selected-area electron diffraction pattern of the $\text{Al}_{92}\text{Ti}_8$ alloy. The dark-field image (Fig. 3(b)) was taken from a part of the halo ring due to an amorphous phase. Although the structure consists of amorphous and crystalline phases for both alloys, the coexistent state differs significantly. That is, the $\text{Al}_{92}\text{Ti}_8$ alloy has a nanoscale mixed structure of fine fcc-Al crystallites with a size of about 10 nm and the amorphous phase

Fig. 1 X-ray diffraction patterns of melt-spun $\text{Al}_{100-x}\text{Ti}_x$ ($x=3, 5, 8, 10$ and 12 at%) alloys prepared at a rotation speed of 40 m/s.

Fig. 2 Bright-field electron micrographs and selected-area electron diffraction patterns of melt-spun $\text{Al}_{92}\text{Ti}_8$ (a and b) and $\text{Al}_{90}\text{Ti}_{10}$ (c and d) alloys prepared at a rotation speed of 40 m/s.

Fig. 3 Enlarged bright-(a) and dark-(b) field electron micrographs and selected-area electron diffraction pattern (c) of the melt-spun $\text{Al}_{92}\text{Ti}_8$ alloy prepared at a rotation speed of 40 m/s.

at boundaries with a thickness of about 15 nm. On the other hand, the $\text{Al}_{90}\text{Ti}_{10}$ alloy includes heterogeneous precipitates of coarse fcc-Al and Al_2Ti phases with a size of about 700 nm in an amorphous matrix. The significant difference in the coexistent structure is presumably due to the difference in the solidification mechanism, *i.e.*, supercooled liquid $\rightarrow$ fcc-Al + remaining supercooled liquid $\rightarrow$ fcc-Al + amorphous for the $\text{Al}_{92}\text{Ti}_8$ alloy and supercooled liquid $\rightarrow$ amorphous $\rightarrow$ amorphous + fcc-Al + Al_2Ti for the $\text{Al}_{90}\text{Ti}_{10}$ alloy. It is further confirmed that the increase in Ti content to 12 at% induces the change from the amorphous matrix to the mixture of fcc-Al + Al_2Ti phases.

Figure 4 shows the X-ray diffraction pattern, bright-field electron micrograph and selected-area electron diffraction pattern of the melt-spun $\text{Al}_{90}\text{Ti}_{10}$ alloy prepared at 50 m/s. No distinct diffraction peaks due to a crystalline phase are seen in the X-ray diffraction pattern, but the bright-field image reveals very fine precipitates with a size of about 2 to 3 nm and weak reflection rings corresponding to the precipitates marked with arrows are seen, in addition to the broad reflection rings due to an amorphous phase. The increase in the rotation speed of the wheel induces the suppression of the growth reaction of the coexisting fcc-Al and Al_2Ti phases, though it is difficult to suppress completely the nucleation of fcc-Al and Al_2Ti phases.

Fig. 4 X-ray diffraction pattern (a), bright-field electron micrograph (b) and selected-area electron diffraction pattern (c) of a melt-spun $\text{Al}_{90}\text{Ti}_{10}$ alloy prepared at a rotation speed of 50 m/s.

Fig. 5 DSC curves of melt-spun $\text{Al}_{92}\text{Ti}_8$ and $\text{Al}_{90}\text{Ti}_{10}$ alloys prepared at a rotation speed of 40 m/s.

Figure 5 shows the DSC curves of the melt-spun $\text{Al}_{92}\text{Ti}_8$ and $\text{Al}_{90}\text{Ti}_{10}$ alloys consisting of amorphous + fcc-Al and amorphous + fcc-Al + Al_2Ti phases, respectively, prepared at the rotating speed of 40 m/s. These alloys exhibit two exothermic peaks, indicating that the amorphous phase crystallizes through two stages. We confirmed from the X-ray diffraction analyses that the first exothermic peak is due to the precipitation of fcc-Al + Al_2Ti and the second broad peak results from the transition of fcc-Al + Al_2Ti to fcc-Al + Al_3Ti . Furthermore, the crystallization temperature defined by the onset temperature of the first exothermic peak is measured to be 550 K for the 8%Ti alloy and 580 K for the 10%Ti alloy. The increase in Ti content increases the thermal stability of the amorphous phase. The preferential precipita-

Fig. 6 Changes in the as-quenched phase, bending ductility, tensile fracture strength (σ_f) and Vickers hardness (H_v) with Ti content for melt-spun $\text{Al}_{100-x}\text{Ti}_x$ alloys prepared at a rotation speed of 40 m/s.

tion of the Al_2Ti phase as an intermediate phase in as-quenched and partially crystallized states suggests that the supercooled liquid includes preferentially Al_2Ti -like clusters rather than Al_3Ti -like clusters.

Figure 6 shows the changes in the structure, bending ductility, tensile fracture strength (σ_f) and Vickers hardness (H_v) of the melt-spun $\text{Al}_{100-x}\text{Ti}_x$ alloys prepared at the rotation speed of 40 m/s. Here, the term "ductile" represents that the sample can be bent through 180 degrees without fracture and the "brittle" implies that the sample fractures during bending deformation. The ductile alloys are obtained in the structures of fcc-Al single phase, fcc-Al + Al_3Ti , amorphous + fcc-Al and amorphous + fcc-Al + Al_2Ti in the Ti concentration range up to 10 at% and the precipitation of a large amount of the Al_2Ti phase at 12%Ti induces the change to a brittle state. The σ_f is 210 MPa for the 3%Ti alloy with an fcc-Al single phase, increases significantly to 600 MPa for the 6%Ti alloy by the precipitation of Al_3Ti and further to 820 MPa for the 8%Ti and 10%Ti alloys by the coexistence of amorphous, fcc-Al and Al_2Ti phases, and then decreases rapidly for the 12%Ti alloy because of the increase in brittleness due to the precipitation of a larger amount of Al_2Ti phase in the absence of the amorphous phase. On the other hand, the H_v increases monotonously from 80 to 200 by the precipitation of Al_3Ti into the fcc-Al phase and the transition to amorphous + fcc-Al and amorphous + fcc-Al + Al_2Ti phases leads to a saturated hardness number of 330. No appreciable difference in

hardness by the transition from the amorphous + fcc-Al + Al_2Ti to fcc-Al + Al_2Ti is seen, in good contrast to the compositional dependence of σ_f . Considering that the densities of the melt-spun $\text{Al}_{92}\text{Ti}_8$ and $\text{Al}_{90}\text{Ti}_{10}$ alloys are 2.85 and 2.89 Mg/m^3 , respectively, the specific tensile strength is evaluated to be as high as $2.81 \times 10^5 \text{ N}\cdot\text{m/kg}$ and $2.80 \times 10^5 \text{ N}\cdot\text{m/kg}$, respectively, which are much higher than that ($2.14 \times 10^5 \text{ N}\cdot\text{m/kg}$) for the superduralumin (7075-T6) alloy.

Here, it is important to discuss the reason why the Al-Ti binary amorphous alloys are formed in the range of 8 to 10%Ti. It has previously been pointed out⁽²³⁾ that the significant difference in atomic size between the major and solute elements is an important factor for the formation of an amorphous phase. However, considering that the atomic radius is 0.143 nm for Al and 0.147 nm for Ti, the difference in atomic size is very small and hence the glass formation cannot be interpreted in the framework of the atomic size rule. Furthermore, the equilibrium phase diagram in Al-Ti binary system⁽²¹⁾ indicates that the eutectic reaction does not exist in the vicinity of 10% Ti and the equilibrium 10%Ti alloy solidifies to Al + Al_3Ti phases by the complex peritectic reaction. Besides, the coexisting liquid/solid temperature region is as large as 585 K⁽²¹⁾. This result suggests that the formation of the amorphous phase is not attributed to the ease of supercooling of the liquid phase. It was shown in Figs. 1 to 3 that the change in the as-quenched structure of the $\text{Al}_{100-x}\text{Ti}_x$ alloys with increasing Ti content takes place in a series of the fcc-Al single phase, fcc-Al + Al_3Ti , fcc-Al + amorphous, amorphous, amorphous + fcc-Al + Al_2Ti and fcc-Al + Al_2Ti phase. The systematic change allows us to presume that the Ti-enriched Al-Ti liquid in coexistence with Al phase has changed to the amorphous phase. As described above, the Al_3Ti and Al_2Ti phases have the tetragonal structures with large unit volumes⁽²¹⁾⁽²²⁾. Although no amorphous phase is formed in the vicinity of the stoichiometric Al_3Ti and Al_2Ti compositions by melt spinning, it is well known that the mechanical alloying of the Al_3Ti and Al_2Ti alloys causes the formation of an amorphous phase⁽²⁴⁾⁽²⁵⁾. These results suggest that if one can suppress the direct formation of Al_3Ti and Al_2Ti phases with high melting temperatures (T_m) from the liquid, there is a high possibility of obtaining an amorphous phase. The Ti content in the $\text{Al}_{92}\text{Ti}_8$ alloy liquid is 8 at% at temperatures above T_m and increases rapidly by the precipitation of fcc-Al with decreasing temperature. However, the rapid decrease in temperature can suppress the nucleation of the Al_3Ti and Al_2Ti phases even after the Ti content in the remaining liquid reaches a critical Ti content which enables the precipitation of their compounds. That is, the glass formation in coexistence with fcc-Al phase and the precipitation of fcc-Al and Al_2Ti phases from the amorphous phase are attributed to the enrichment of Ti content in the remaining liquid to the critical solute content in the low temperature range where the nucleation and growth reactions of crystalline Al_3Ti and Al_2Ti phases are difficult. It is therefore said that the formation of the

solute-enriched liquid phase by the use of the exclusion of solute elements from the primary crystalline phase is useful for the formation of an amorphous phase at the new Al-rich alloy composition where no amorphous phase has not been found up to date. It is subsequently expected that the use of the new concept for glass formation enables the formation of a number of amorphous alloys in a coexistent primary crystalline phase. Furthermore, the formation of the mostly single amorphous phase in the Al₉₀Ti₁₀ alloy prepared at the higher rotation speed of 50 m/s suggests that the minimum critical Ti content for formation of the amorphous phase lies around 10%Ti. However, the further increase in Ti content increases rapidly the melting temperature, leading to the significant decrease in the melt-quenching effect of the Al-Ti binary alloys.

In conclusion, coexistent amorphous and fcc-Al phases and a mostly single amorphous phase having good bending ductility and high specific tensile strength were found to be formed in the limited composition range of 8 to 10 at%Ti in the melt-spun Al-Ti binary alloys. Considering that the formation of an amorphous phase in Al-rich binary alloys containing 90 at%Al had been limited to Al-Ln (Ln=lanthanide metal) system⁽²⁶⁾, the finding of forming the amorphous phase in the simple light-metal system is important for future development of a higher specific strength material at low cost.

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