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High Strength Al-Ti-Fe Alloys Consisting of Amorphous and fcc-Al Phases Prepared by Rapid Solidification

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Coexistent of amorphous and fcc-Al phases were formed in rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3, 5$ and 8 at%) alloys. The structure consists of equiaxed Al grains embedded in the network of an amorphous phase. The grain size of the Al phase is 20 to 30 nm and the interparticle spacing is about 7 nm for the $\text{Al}_{93}\text{Ti}_5\text{Fe}_2$ alloy. The volume fraction of the Al phase is evaluated to be 70 to 80%. The mixed structure is presumably formed through the solidification process of liquid $\rightarrow$ primary fcc-Al + remaining liquid $\rightarrow$ Al + amorphous phases. The further increase in Ti content to 10 at% causes the formation of an amorphous single phase. The crystallization temperature (T_x) of the amorphous phase increases from 641 to 701 K with increasing Ti content from 3 to 10%. It is to be noticed that the T_x values are much higher than that (≈ 573 K) for Al-TM-Ln (TM=transition metal, Ln=lanthanide metal) amorphous alloys because of the low diffusivity of Ti. The mixed phase alloys have good bending ductility and exhibit the highest tensile strength (σ_t) of 1200 MPa for $\text{Al}_{93}\text{Ti}_5\text{Fe}_2$. The ductility decreases with further increasing Ti content because of the transition from ductile to brittle nature for the amorphous phase and no high tensile strength exceeding 500 MPa is obtained for the amorphous single phase alloy. The formation of the finely mixed amorphous and Al phases with high σ_t and T_x values is important for the future development of Al-rich Al-Ti based alloys with high specific strength.

Keywords: high-strength aluminum base alloy, nanogranular aluminum phase, nanoscale mixed structure, amorphous network phase, low diffusivity, high crystallization temperature

I. Introduction

Rapidly solidified Al-based alloys with nonequilibrium phases have attracted great interest because of the expectation of achieving high mechanical strength with low density. An amorphous single phase with high tensile strength has been formed in rapidly solidified Al-rich alloys containing less than about 88 at%Al in Al-TM-Ln (TM=IV to VIII transition metals, Ln=lanthanide metal) systems⁽¹⁾⁽²⁾. It has subsequently been found⁽³⁾⁻⁽⁵⁾ that a further increase in Al content to 88 to 90 at% causes the formation of finely mixed fcc-Al and amorphous phases which exhibit higher tensile strength by about 1.4 times as compared with the corresponding amorphous single phase. More recently, the use of Al-Mn-Ln⁽⁶⁾⁽⁷⁾, Al-Mn-TM⁽⁸⁾⁽⁹⁾, Al-Cr-Ln⁽¹⁰⁾, Al-Cr-Ln-TM⁽¹¹⁾⁽¹²⁾, Al-V-TM⁽¹³⁾⁽¹⁴⁾ and Al-V-TM-Ln⁽¹⁵⁾ (TM=Fe, Co or Ni) alloys containing the icosahedral-forming elements Mn, Cr and V was found to cause the formation of nanoscale icosahedral particles surrounded by fcc-Al phase with an interparticle spacing of about 10 nm in a rapidly solidified state. The volume fraction of the icosahedral phase is as high as 60 to 70% and the tensile strength reaches as high as 1390 MPa even in the high Al concentration range of 92 to 94 at%. Since the nanoscale icosahedral particles have random orientations and are always surrounded by fcc-Al phase, the icosahedral particles have been presumed⁽¹⁶⁾⁽¹⁷⁾ to be formed as a primary phase from the liquid, followed by the solidification of

the Al phase from the remaining liquid. Furthermore, the replacement of Mn and Cr by V was found to cause the formation of a new nanogranular amorphous phase in the presence of the fcc-Al phase⁽¹³⁾⁻⁽¹⁵⁾. The nanogranular amorphous phase has also been presumed to result from the suppression of the phase transition from the supercooled liquid to nanoscale icosahedral particles. This presumption has also been supported from some results⁽¹³⁾⁻⁽¹⁵⁾ that the decomposition of the nanogranular amorphous phase takes place through two stages of amorphous $\rightarrow$ icosahedral $\rightarrow$ crystalline phases and the decrease in the rotation speed of a melt spinning wheel causes the transition from amorphous to icosahedral phases. The suppression of the development of the icosahedral phase is presumably because V has a lower diffusivity in Al⁽¹⁸⁾⁽¹⁹⁾, more multistage peritectic reactions⁽²⁰⁾ and higher icosahedral-forming tendency⁽²¹⁾ as compared with those for Mn and Cr elements in Al. It is known that Ti in Al has a much lower diffusivity than that of V⁽¹⁸⁾⁽¹⁹⁾ and does not have an icosahedral-forming ability⁽²¹⁾. Consequently, the examination of the microstructure and mechanical properties of rapidly solidified Al-Ti-Fe alloys and the subsequent comparison with those for the Al-V-Fe alloys give us a unique opportunity to investigate the roles of the diffusivity and icosahedral-forming ability in the formation of the nanogranular icosahedral base structure. This investigation is expected to cause the clarification of the mechanism for the formation of the nanogranular amorphous phase which was found for the

first time in the rapidly solidified Al-V-Fe alloys.

II. Experimental Procedure

Ternary Al-Ti-Fe alloys containing more than 85 at%Al were used in the present study. The ingots were prepared by melting a mixture of pure Al (99.99 mass%), Ti (99.8 mass%) and Fe (above 99.9 mass%) metals in an arc-furnace with a purified argon atmosphere. The compositions are nominally expressed in atomic percent. From the master alloy ingots, ribbons with a width of about 1 mm and a thickness of about 20 μm were prepared by a single roller melt-spinning technique in an argon atmosphere. The as-quenched and annealed structures of the melt-spun ribbons were examined by X-ray diffractometry and transmission electron microscopy (TEM). The TEM samples were prepared by electrolytically thinning the melt-spun ribbons in a solution of 25% nitric acid and 75% methanol at 243 K. The volume fractions of fcc-Al and amorphous phases were measured from the TEM images by an image analyzer (PIAS-III). The decomposition behavior of the as-quenched phase was also examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Tensile strength of the ribbon specimens was measured by an Instron-type testing machine operating at a strain rate of $8.3 \times 10^{-4} \text{ s}^{-1}$. Five tensile test data were used to determine the tensile fracture strength. Strips having a gauge dimension of 10 mm were cut from the melt-spun ribbon and used for the measurement of tensile fracture strength. Subsequent to tensile testing, the cross-sectional area at the fracture site of each specimen was measured by optical microscopy and scanning electron microscopy in order to minimize error in the estimation of the tensile strength.

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3, 5, 8$ and 10 at%) alloys. The diffraction patterns can be analyzed to consist of fcc-Al + $\text{Al}_{24}\text{Ti}_8$ phases at 3 at%Ti, Al + amorphous phases at 5 and 8 at%Ti and an amorphous phase at 10 at%Ti. The $\text{Al}_{24}\text{Ti}_8$ has been reported to be an ordered tetragonal superstructure of Al_3Ti and the lattice spacings of a and c axes are 0.3875 and 3.3835 nm, respectively⁽²²⁾. The increase in Ti content causes a significant increase in the glass-forming ability. The formation of the amorphous phase at the high Al concentration in Al-Ti-Fe system is believed to be the first evidence. Here, it is to be noticed that coexistent of amorphous plus Al phases are formed even at the high Al concentration of 95 at%. In order to confirm the existence of the amorphous phase, TEM examination was carried out. The bright-field electron micrographs and selected-area electron diffraction patterns of the rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3$ and 5 at%) alloys are shown in Fig. 2. These diffraction patterns consist of halo rings due to an amorphous phase and reflection spots due to an fcc-Al phase. From the change in the Bragg reflection contrast in the bright-

Fig. 1 X-ray diffraction patterns of rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3, 5, 8$ and 10 at%) alloys.

Fig. 2 Bright-field electron micrographs and selected-area electron diffraction patterns of rapidly solidified $\text{Al}_5\text{Ti}_3\text{Fe}_2$ (a and b) and $\text{Al}_{93}\text{Ti}_3\text{Fe}_2$ (c and d) alloys.

field image by tilting the specimen, the fine grains with bright contrast correspond to fcc-Al phase and the network phase with dark contrast results from an amorphous phase. The Al phase appears to have an equiaxed morphology. The morphology without dendrite shape is presumably because the Al phase precipitates from the highly supercooled liquid in the metastable state where the redistribution of the constituent elements and the preferential growth on a particular crystallographic plane are suppressed. In order to confirm the analyzed result, the dark-field image taken from a part of the main halo ring is shown in Fig. 3. The contrast in the dark-field image reveals clearly that the network phase is composed of an amorphous phase, in agreement with the result obtained from the change in the bright-field image contrast

Fig. 3 Dark-field electron micrograph taken from a part of main halo ring resulting from an amorphous phase for a rapidly solidified $\text{Al}_{93}\text{Ti}_5\text{Fe}_2$ alloy.

Fig. 4 Change in the tensile fracture strength (σ_f) with Ti content for rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ alloys.

by controlling the Bragg reflection condition. The mixed structure allows us to presume that the granular Al phase precipitates as a primary phase from the liquid, followed by the solidification of the amorphous phase with the network morphology from the remaining liquid. This solidification mode is different from that⁽¹³⁾⁽¹⁴⁾ for the Al-V-Fe alloy where the solidification occurs through the process of the primary precipitation of amorphous phase, followed by the solidification of Al phase from the remaining liquid. The reason for the difference is discussed later.

Figure 4 shows the changes in the tensile fracture strength (σ_f) and as-quenched phases with Ti content for the rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ alloys. A distinct compositional dependence of σ_f is seen and the highest σ_f value of about 1200 MPa is obtained for the $\text{Al}_{93}\text{Ti}_5\text{Fe}_2$ alloy with the mixed amorphous and Al phases. The further increase in Ti content causes a significant decrease in σ_f , accompanying the increase in the volume fraction of the amorphous phase. The rapidly solidified $\text{Al}_{88}\text{Ti}_{10}\text{Fe}_2$ alloy consists of an amorphous single phase, as exemplified in Fig. 5. However, the amorphous alloy with the high Ti content of 10 at% has a brittle nature and hence no high σ_f value is obtained. Thus, the highest σ_f value is

Fig. 5 Bright-field electron micrograph and selected-area electron diffraction pattern of a rapidly solidified $\text{Al}_{88}\text{Ti}_{10}\text{Fe}_2$ alloy.

Fig. 6 DSC curves of the rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3, 5$ and 10 at%) alloys.

obtained in the finely mixed structure consisting of equiaxed Al grains and ductile amorphous phase containing low Ti contents below about 6 at%. Figure 6 shows the DSC curves of the rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3, 5$ and 10 at%) alloys. The exothermic peaks due to the crystallization of the amorphous phase are seen on all the DSC curves, though the peak is broad for the mixed phase alloys. The onset temperature of crystallization is 641 K at 3 at%Ti, 657 K at 5 at%Ti and 701 K at 10 at%Ti, indicating that the thermal stability of the amorphous phase increases with increasing Ti content. Considering that the precipitation temperature of Al-TM and Al-Ln intermetallic compounds is about 573 K for Al-TM-Ln amorphous alloys⁽¹⁾⁽²⁾, the amorphous phase in the Al-Ti-Fe system is concluded to have much higher thermal stability. The high stability is presumably because of the much lower diffusivity of Ti.

In comparison with the previous data⁽¹³⁾⁽¹⁴⁾ of Al-V-Fe alloys, we discuss the feature of the mixed structure for the present Al-Ti-Fe alloys. It is shown in Fig. 2 that the Al-Ti-Fe alloys have the mixed structure of equiaxed Al grains embedded in the network of the amorphous phase. We surmise that the solidification process in the Al-Ti-Fe alloys proceeds in the order of liquid $\rightarrow$ primary

equiaxed fcc-Al + remaining liquid $\rightarrow$ equiaxed Al + network amorphous phase. On the other hand, the Al-V-Fe alloys consist of nanogranular amorphous phase in coexistence with the network of the Al phase⁽¹³⁾⁻⁽¹⁵⁾. It has been presumed⁽¹³⁾⁻⁽¹⁵⁾ that the nanogranular amorphous phase is formed as a primary phase from the liquid, followed by the precipitation of Al phase from the remaining liquid. The difference in the solidification process is presumably due to the difference in the local atomic configurations of their liquid phase. That is, the liquid of the Al-V-Fe alloys containing the icosahedral-forming element (V) includes a high density of icosahedral clusters in which the atomic rearrangement on a long range scale during cooling is difficult. It is therefore thought that the icosahedral cluster region is solidified as the primary amorphous phase. On the other hand, it is thought that the Al-Ti-Fe alloy liquid without icosahedral-forming element does not include icosahedral clusters and hence the Al-Al pairs, which exist as a major component in the liquid, precipitate as a primary Al phase. As a result, the solute concentration in the remaining liquid increases significantly and the enrichment of the solute elements causes the increase in the amorphous-forming ability, leading to the formation of the network of the amorphous phase. The feature of the solidification process for the Al-Ti-Fe alloys is in agreement with that for the conventional metallic alloys.

The σ_f value is about 1400 MPa for the $\text{Al}_{94}\text{V}_4\text{Fe}_2$ alloy and about 1200 MPa for the $\text{Al}_{93}\text{Ti}_3\text{Fe}_2$ alloy. The significant difference in σ_f is presumably due to the difference in the grain sizes of the constituent phases. That is, the grain size of the former alloys is about 10 nm for the nanogranular amorphous phase and about 7 nm for the coexistent fcc-Al phase, while the size of the latter alloy is about 20 to 30 nm for the fcc-Al phase. Besides, the volume fraction of the amorphous phase is measured to be 60 to 70% for the nanogranular type and about 30% for the network type. It is therefore said that the lower σ_f value is due to the larger grain size of the fcc-Al phase and the lower volume fraction of the amorphous phase with high strength and good ductility. The finding that the mixed structure consisting of equiaxed fcc-Al grains embedded in the network of the amorphous phase is found in the rapidly solidified Al-rich Al-Ti-Fe alloys and exhibits high tensile strength combined with good ductility is important for the development of high-strength Al-based alloys.

IV. Summary

The microstructure and mechanical properties of rapidly solidified $\text{Al}_{98-x}\text{Ti}_x\text{Fe}_2$ ($x=3$ to 10 at%) alloys were examined, with the aim of obtaining a high specific strength combined with good ductility through the formation of a nonequilibrium phase. The results obtained are summarized as follows:

(1) The as-quenched structure consists of amorphous + fcc-Al phases in the concentration range of 3 to 8 at%Ti and an amorphous phase at 10 at%Ti. The mix-

ed structure is composed of equiaxed Al grains embedded in the network of an amorphous phase. The fcc-Al phase has an average grain size of about 25 nm and the interparticle spacing is about 7 nm.

(2) The finely mixed structure appears to be formed through the process of primary fcc-Al phase, followed by the solidification of the amorphous phase with network morphology from the remaining liquid.

(3) The crystallization temperature increases from 641 to 701 K with increasing Ti content from 3 to 10 at%. The T_x is higher by about 70 to 130 K than those for Al-TM-Ln amorphous alloys, presumably because of the much lower diffusivity of Ti.

(4) The finely mixed nanogranular Al and amorphous phase alloys exhibit σ_f of about 1200 MPa for the $\text{Al}_{93}\text{Ti}_3\text{Fe}_2$ alloy and the further increase in Ti content causes a significant decrease in σ_f to 600 MPa because of the lack of good ductility for the amorphous phase containing more than 7 at%Ti. The formation of the finely mixed amorphous and Al phases with high tensile strength is important as a fundamental information for the development of a new type of high specific strength material.

REFERENCES

- (1) A. Inoue, K. Ohtera, A. P. Tsai and T. Masumoto: Jpn. J. Appl. Phys., **27** (1988), L479.
- (2) A. Inoue and L. Arnberg: *The Encyclopedia of Advanced Materials*, Vol. 1, ed. by R. W. Cahn, Pergamon, (1994), p. 217.
- (3) Y. H. Kim, A. Inoue and T. Masumoto: Mater. Trans., JIM, **32** (1991), 331.
- (4) A. Inoue: Mater. Sci. Eng., **A179/A180** (1994), 57.
- (5) A. Inoue: Nanostructured Mater., **6** (1995), 53.
- (6) A. Inoue, M. Watanabe, H. M. Kimura, F. Takahashi, A. Nagata and T. Masumoto: Mater. Trans., JIM, **33** (1992), 723.
- (7) M. Watanabe, A. Inoue, H. M. Kimura, T. Aiba and T. Masumoto: Mater. Trans., JIM, **34** (1993), 162.
- (8) A. Inoue, Y. Horio and T. Masumoto: Mater. Trans., JIM, **34** (1993), 85.
- (9) Y. Horio, A. Inoue and T. Masumoto: Mater. Sci. Eng., **A179/A180** (1994), 596.
- (10) A. Inoue, M. Watanabe, H. M. Kimura and T. Masumoto: Sci. Rep. Res. Inst. Tohoku Univ., **A38** (1993), 138.
- (11) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: Mater. Trans., JIM, **35** (1994), 85.
- (12) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: Mater. Trans., JIM, **36** (1995), 6.
- (13) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: Nanostructured Mater., **7** (1996), 363.
- (14) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: Mater. Trans., JIM, **37** (1996), 1343.
- (15) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: Int. J. Rapid Solidification, **6** (1996), 103.
- (16) A. Inoue and H. M. Kimura: *Synthesis and Processing of Nanocrystalline Powder*, ed. by D. L. Bourell, TMS, Warrendale, (1996), p. 91.
- (17) A. Inoue and H. M. Kimura: Mater. Sci. Forum, in press.
- (18) *Metals Databook*, ed. by Japan Inst. Metals, Maruzen Tokyo, (1983), p. 24.
- (19) J. M. Sater, S. C. Jha and T. H. Sanders, Jr.: Treatise on Mater. Sci. and Tech., **31** (1989), 409.
- (20) *Binary Alloy Phase Diagrams*, ed. by T. B. Massalski, ASM Intern., Materials Park, Ohio, (1990).
- (21) A. Inoue and A. P. Tsai: Bulletin Japan Inst. Metals, **29** (1990), 782.
- (22) V. L. Rieck: Acta Metall., **21** (1973), 61.