Microstructure and Mechanical Properties of Rapidly Solidified Al-Cr-Ce-M (M=Transition Metal) Alloys Containing High Volume Fraction of the Icosahedral Phase

A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Coexistent icosahedral (I) and fcc-Al phase alloys exhibiting good bending ductility and high tensile strength (σ_t) were found to form in rapidly solidified $\text{Al}_{95.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_x$ ($x \leq 3$ at%) and $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ (M=Ti, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo or Hf) alloys. The particle size and interparticle spacing of the I-phase decrease down to about 40 and 10 nm, respectively, with increasing Ce content, accompanying the increase in the volume fraction of the I-phase. This microstructural change is interpreted to result from the increase in the quenching effect with increasing Ce content. The highest σ_t value is 1340 MPa for the $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy and 1330 MPa for the $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Ti}_1$ alloy. Even after annealing for 900 s at 673 K, the high σ_t values of 830 and 680 MPa are obtained for the Zr- and Fe-containing ternary alloys, respectively. The high σ_t values for these alloys are due to the high thermal stability of the I-phase against the grain growth and coalescence. The achievement of the high σ_t over 600 MPa and the high structural stability allows us to expect that high-strength bulk alloys by utilizing the I-phase as a strengthening medium can be prepared by extrusion at elevated temperatures. Furthermore, it was found from the high resolution TEM and EDX analyses that the Al base I-phase containing 7.2 at%Cr, 1.6%Cr and 2.6%Ce had a disordered structure on a short-range less than 1 nm. This is presumably because of the introduction of a high density of interface between I-phase and phason-induced approximant crystalline phase. The formation of the disordered structure is thought to be the reason for the good ductility which enables the achievement of high σ_t .

(Received June 13, 1994)

Keywords: aluminum base quasicrystalline alloy, icosahedral phase, rapid solidification, high mechanical strength, high ductility, phason-induced structure change, approximant crystalline phase, short-range disordered structure

I. Introduction

It is generally known that conventional Al-based alloys are strengthened by the precipitation from supersaturated solid solution. However, this strengthening mechanism has an upper bound because of the solid solubility limit in the fcc-Al phase. As one of the methods to overcome the upper bound, the utilization of an amorphous phase has been tried for the last five years. Al-based alloys in the Al-TM-Ln⁽¹⁾⁽²⁾, Al-ETM-LTM⁽³⁾ and Al-LTM-LTM⁽⁴⁾ (TM=IV-VIII group transition metal, ETM=IV-VI group transition metal and LTM=VII-VIII group transition metal) systems are amorphized by melt spinning or high-pressure gas atomization and the resulting melt-spun amorphous alloys exhibit high tensile strength reaching 1260 MPa⁽⁵⁾. Furthermore, the application of the powder metallurgy technique has enabled the production of bulk nanocrystalline alloys that exhibit a tensile strength reaching about 1000 MPa⁽⁶⁾ in the case of extrusions at temperatures above the crystallization temperature.

In addition to the strengthening mechanisms which utilize the crystalline, amorphous and nanocrystalline phases, one can consider the utilization of quasicrystal-

line phase in which the movement of dislocations is very difficult both at room temperature and at elevated temperatures because of the generation of planar faults⁽⁷⁾. More recently, Inoue *et al.* have succeeded in fabricating high-strength Al-based alloys consisting of nanocrystalline icosahedral phase surrounded by a thin Al phase in the Al-Mn-Ce⁽⁸⁾, Al-Mn-Ln⁽⁹⁾⁽¹⁰⁾ and Al-Cr-Co-Ce⁽¹¹⁾ systems, through the modified rapid solidification process. It is to be noticed that the nanocrystalline alloys have good bending ductility and high tensile strength exceeding 1300 MPa, in spite of a large volume fraction of the icosahedral phase reaching 60 to 70%. The origin of the noteworthy properties has been successfully explained on the basis of the microstructural data obtained by high-resolution transmission electron microscopy⁽¹²⁾. However, little is known about the effect of additional elements on the microstructure and mechanical properties of the icosahedral base alloys and also on the changes in the microstructure and mechanical properties upon annealing. The present work is intended to examine the microstructure and mechanical properties in as-quenched and annealed states of rapidly solidified Al-Cr-Co-Ce and Al-Cr-Co-Ce-M (M=transition metal) alloys and to investigate the strengthening mechanisms in the quasicrystalline base structure.

Fig. 2 Bright-field electron micrographs and selected-area electron diffraction patterns of rapidly solidified $\text{Al}_{95}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_{0.5}$ (a and b), $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ (c and d) and $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_2$ (e and f) alloys. The reflection rings of 1, 2 and 3 are identified to be $(11100)_i$, $(211100)_i$ and $(211111)_i$, respectively, of the icosahedral phase.

of the diffraction peaks corresponding to the icosahedral phase in the X-ray diffraction patterns shown in Fig. 1.

The finely mixed phase alloys have good ductility which is shown by a 180 degree bending without fracture, despite that the volume fraction of the icosahedral phase is as high as about 70% for the 1%Ce alloy and about 85% for the 2%Ce alloy. Consequently, these alloys are expected to exhibit high tensile fracture strength. Figure 3 shows the changes in the tensile fracture strength (σ_f) and Vickers hardness number (Hv) as a function of Ce content. As the Ce content increases, σ_f increases rapidly, reaching a maximum of 1340 MPa at 1%Ce and then decreases monotonously. The similar tendency is also seen for Hv . The 1%Ce alloy shows a maximum hardness number of 450. In comparison with the microstructure shown in Fig. 2, the mixed structure, in which spherical quasicrystals of the icosahedral phase are surrounded by an fcc-Al phase, seems to be optimum for the achievement of higher tensile strength. On the contrary, the precipitation of fine crystalline phase in the fcc-Al matrix is not. The decrease in σ_f in the Ce concentration range above 1.0% indicates the existence of an optimum volume fraction of the icosahedral phase for the attainment of the highest tensile strength.

2. Rapidly solidified $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ alloys

Figure 4 shows the X-ray diffraction patterns of the rapidly solidified $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ ($\text{M}=\text{Ti}, \text{Mn}, \text{Fe}, \text{Co}$,

Fig. 3 Tensile fracture strength (σ_f) and Vickers hardness number (Hv) as a function of Ce content for rapidly solidified $\text{Al}_{95.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_x$ alloys.

Fig. 4 X-ray diffraction patterns of rapidly solidified $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ ($\text{M}=\text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zr}, \text{Nb}, \text{Mo}$ or Hf) alloys.

Ni, Cu, Zr, Nb, Mo or Hf) alloys. The X-ray diffraction patterns consist of the icosahedral and Al phases for these pentenary alloys except the Al-Cr-Co-Ce-Cu alloy. Although no appreciable diffraction peaks corresponding to the icosahedral phase are seen for the Cu-containing alloy, the TEM observation indicates the formation of the coexistent icosahedral and Al phases. It therefore seems that there is no appreciable change in the mixed structure by the replacement of Al by 1 at% of transition element M. The formation of the mixed structure, with the icosahedral phase as a main phase, is

presumably due to the existence of 3%Cr and 1%Ce. Furthermore, the good bending ductility remains unchanged for all the alloys. Figure 5 shows the tensile fracture strength (σ_f) and Vickers hardness (H_v) for the rapidly solidified pentenary alloys. The tensile strength shows the highest value of 1330 MPa for the Ti-containing alloy and decreases in the order of $Zr > Co > Mo > Mn > Fe > Ni \equiv Cu > Nb > Hf$. It is to be noticed that the high tensile strength above 1000 MPa is obtained for the alloys containing Ti, Zr, Co, Mo, Mn, Fe, Ni or Cu as the M element. On the other hand, the hardness is in the range of 390 to 490 for the alloys except $M = Cu$. The absence of the complete agreement in the tendency between σ_f and H_v is thought to come from the differences in the ductility of the melt-spun ribbons and the smoothness of their outer surface and edge.

Figure 6 shows a bright-field electron micrograph and selected-area electron diffraction pattern of the rapidly solidified $Al_{93.5}Cr_3Co_{1.5}Ce_1Ti_1$ alloy with the highest tensile strength. The icosahedral phase has a spherical morphology with a particle size of about 25 nm and it is surrounded by an fcc-Al phase with a thickness of about 10 nm. The volume fraction of the icosahedral phase estimated by the image analyzer is as high as 80% and the distribution of the nanoscale icosahedral particles is rather homogeneous. Consequently, one can notice that the

Fig. 5 Tensile fracture strength (σ_f) and Vickers hardness number (H_v) of rapidly solidified $Al_{93.5}Cr_3Co_{1.5}Ce_1M_1$ ($M = Ti, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo$ or Hf) alloys.

Fig. 6 Bright-field electron micrograph and selected-area electron diffraction pattern of a rapidly solidified $Al_{93.5}Cr_3Co_{1.5}Ce_1Ti_1$ alloy.

high tensile strength of the Ti-containing alloy is probably due to the high volume fraction and the small particle size of the icosahedral phase and also to the high degree of homogeneity of the mixed structure.

3. Annealed $Al_{93.5}Cr_3Co_{1.5}Ce_1M_1$ alloys

Figure 7 shows the X-ray diffraction patterns of the rapidly solidified $Al_{93.5}Cr_3Co_{1.5}Ce_1M_1$ alloys subjected to annealing for 900 s at 673 K. This annealing condition was chosen on the basis of the previous results that extrusion of atomized quaternary Al-Cr-Co-Ce powder compacts is successfully made in the range of 573 to 623 K after pre-heating for 900 s and that the microstructure of the quaternary alloys corresponds to that of the pentenary alloys annealed for 900 s at 673 K. Almost all the diffraction peaks are identified as being of the icosahedral or Al phase for all the alloys. Furthermore, in comparison with those of the as-quenched alloys, the peak intensity of the icosahedral phase increases significantly, accompanying the increase in the number of the diffraction peaks of the icosahedral phase and the decrease in the peak intensity of the Al phase. The change in the X-ray diffraction pattern indicates that the annealing causes the precipitation of the icosahedral phase from the Al phase. In addition to the diffraction peaks of the Al and icosahedral phases, one can notice the extra diffraction peaks. The phase corresponding to the extra peaks is not identified in the present study. It is therefore concluded that the annealed structure consists of icosahedral, Al and unknown crystalline compound phases.

We measured the mechanical strength of the annealed

Fig. 7 X-ray diffraction patterns of rapidly solidified $Al_{93.5}Cr_3Co_{1.5}Ce_1M_1$ ($M = Ti, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo$ or Hf) alloys subjected to annealing for 900 s at 673 K.

alloys consisting of the different phases, with the aim of determining an appropriate alloy system exhibiting good mechanical properties in the extruded bulk state. All the annealed alloys have good bending ductility and no appreciable difference between alloys is detected. Figure 8 shows the tensile fracture strength (σ_f) and Vickers hardness (H_v) of the $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ alloys annealed for 900 s at 673 K. The tensile strength is the highest for the Fe-containing alloy and then decreases in the order of $\text{Zr} > \text{Cu} > \text{Ti} \approx \text{Mo} > \text{Ni} > \text{Co} \approx \text{Hf} > \text{Mn} > \text{Nb}$. Furthermore, H_v also shows higher values for the Fe- and Zr-containing alloys. This result implies the possibility that a bulk alloy exhibiting high tensile strength is obtained for the Fe- and Zr-containing alloy systems. The changes in σ_f and H_v of the $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ ($\text{M}=\text{Fe}$ or Zr) alloys by annealing for 900 s at 673 K are shown as a function of M content in Fig. 9. The data on the Ti-contain-

Fig. 8 Tensile fracture strength (σ_f) and Vickers hardness number (H_v) of rapidly solidified $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ ($\text{M}=\text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zr}, \text{Nb}, \text{Mo}$ or Hf) alloys subjected to annealing for 900 s at 673 K.

Fig. 9 Tensile fracture strength (σ_f) and Vickers hardness number (H_v) of rapidly solidified $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ ($\text{M}=\text{Ti}, \text{Fe}$ or Zr) alloys subjected to annealing for 900 s at 673 K.

ing alloy with the highest σ_f value in the as-quenched state are also plotted for comparison. The tensile strength (σ_f) is 515 MPa for the $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$, and it increases by the replacement of Al by the M elements, reaching a maximum value of 680 MPa at 1%Fe, 835 MPa at 2%Zr and 630 MPa at 2%Ti. On the other hand, H_v tends to increase gradually with increasing Fe and Zr contents and remains almost unchanged for the Ti-containing alloys. Furthermore, Fig. 10 shows the changes in σ_f and H_v with annealing temperature for the rapidly solidified $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Fe}_1$, $\text{Al}_{92.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Zr}_2$ and $\text{Al}_{92.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Ti}_2$ alloys which exhibit the highest σ_f by annealing for 900 s at 673 K, along with the data of the quaternary $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy. The σ_f and H_v values in the temperature range from 573 to 773 K have the highest values of 915 to 535 MPa and 340 to 230 for the Zr-containing alloy, and they decrease in the order of Fe and Ti. The results described above indicate the possibility that the highest tensile strength for the bulk alloy

Fig. 10 Changes in the tensile fracture strength (σ_f) and Vickers hardness number (H_v) as a function of annealing temperature for rapidly solidified $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ ($\text{M}=\text{Ti}, \text{Fe}$ or Zr) alloys.

Fig. 11 Bright-field electron micrograph and selected-area electron diffraction pattern of a rapidly solidified $\text{Al}_{92.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Zr}_2$ alloy subjected to annealing for 900 s at 673 K.

prepared by extrusion of atomized powders in the temperature range of 573 to 673 K is obtained for the $\text{Al}_{92.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{Zr}_2$ alloy. As shown in Fig. 11, the annealed structure of the 2%Zr-containing alloy consists mainly of spherical icosahedral phases with a particle size of about 40 nm surrounded by fcc-Al phase and no distinct increase in the icosahedral particle size is seen, though very fine precipitates with a size of about 5 nm are observed in the fcc-Al phase. This microstructure also indicates that the icosahedral phase has a high thermal stability against the grain growth and coalescence caused by annealing. The high thermal stability of the icosahedral phase is thought to be the origin of the high tensile strength reaching 830 MPa even after annealing for 900 s at 673 K. A systematic study on the microstructure and mechanical properties of the bulk alloys prepared by extrusion at elevated temperatures is in progress.

4. Internal structure of nanoscale icosahedral phase

Considering that the volume fraction of the icosahedral phase is as high as 60 to 80% in the present mixed phase alloys, the good ductility is attributed to a highly ductile nature of the icosahedral phase itself. In order to investigate the reason for the good ductility for the icosahedral phase itself, we examined the internal structure of the icosahedral phase by the high-resolution transmission electron microscopy (TEM) technique. Figure 12 shows a bright-field electron micrograph and selected-area electron diffraction patterns taken from the regions A and B for the rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy. Diameter of the selected area is 1 nm. The diffraction pattern taken from region A can be identified as characteristic of an fcc-Al phase while that taken from region B consists of diffuse diffraction rings. The high-resolution TEM image of the region corresponding to the

Fig. 12 Bright-field electron micrograph and selected-area electron diffraction patterns of a rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy. The diffraction patterns (b) and (c) were taken from regions A and B.

Fig. 13 High-resolution transmission electron micrograph and selected-area electron diffraction patterns of a rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy. The diffraction patterns (b) and (c) were taken from regions A and B.

icosahedral phase is shown in Fig. 13, along with the selected-area diffraction patterns taken from regions A and B. Again, the selected area is 1 nm in diameter. The diffraction pattern taken from the region with periodic fringe contrast comes from the fcc-Al phase. On the other hand, no contrast with a periodic fringe and a long array of five-fold symmetric contrast is seen in the region B which covers almost all the area in the TEM image. Furthermore, the selected-area diffraction pattern appears to consist mainly of a halo ring. This result suggests that region B has a disordered structure on a short-range scale less than about 1 nm. However, the increase in the diameter of the selected area to 3 nm causes the diffraction pattern to appear in five-fold symmetry which is superimposed to the halo ring, as shown in Fig. 14. It is therefore concluded that the region B has an icosahedral atomic configuration on a long-range scale larger than 2 to 3 nm.

5. Alloy compositions of nanoscale icosahedral phase

The alloy compositions of the icosahedral and fcc-Al phases in the rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy

were examined by the EDX spectrometer. Figure 15 shows the EDX profiles taken from three different regions. The profile (a) was taken from the mixed phase region with a large diameter of 10 μm , while the profiles (b) and (c) were obtained from the icosahedral and fcc-Al phases, respectively, and the diameter of the electron beam was as small as 5 nm. The average values of analytical compositions obtained from five different regions are 94.50 at%Al, 3.01%Cr, 1.50%Co and 0.99%Ce for the mixed phase region, in good agreement with the nominal alloy composition. However, their values are 88.71 at%Al, 7.15%Cr, 1.59%Co and 2.56%Ce for the icosahedral phase and 97.16%Al, 1.01%Cr, 1.66%Co and 0.18%Ce for the fcc-Al phase. One can notice that Cr and Ce are significantly concentrated into the icosahedral phase while no distinct difference in Co concentration between the icosahedral and fcc-Al phases is seen. Since the Cr concentration of the stoichiometric icosahedral phase in the Al-Cr binary system is 15.4 at%⁽¹⁴⁾⁽¹⁵⁾, the measured Cr concentration of the icosahedral phase deviates significantly from the stoichiometric composition to the lower concentration side. This tendency is in agreement

Fig. 14 High-resolution transmission electron micrograph and selected-area diffraction pattern of a rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy.

with that for rapidly solidified Al-Mn-Ce alloys⁽⁸⁾⁻⁽¹⁰⁾ consisting of a similar mixed structure. The low solute concentration is presumed to result from the suppression of the redistribution of Cr and Ce elements between the icosahedral and fcc-Al phases caused by rapid solidification, leading to the high volume fraction of the icosahedral phase reaching 80%. It is to be noticed that the icosahedral phase forms as a main constituent phase even at the low solute compositions which are far away from the stoichiometric alloy composition by rapid solidification of the present multicomponent alloys with appropriate alloy compositions.

IV. Discussion

It is shown in Fig. 2 that the increase in Ce content to about 1% for the $\text{Al}_{95.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_x$ alloys causes the decrease in the particle size and the increase in the volume fraction of the icosahedral phase. Here, we discuss the reason for the structural effect caused by the ad-

dition of Ce. Considering that no icosahedral phase is formed in rapidly solidified Al-Ce binary alloys⁽¹³⁾, Ce element itself does not have an essential effect on the formation of the icosahedral phase. The formation of the icosahedral phase in the Al-Cr-Co-Ce alloys is considered to be due to the existence of the Cr element, because an icosahedral single phase is formed in a rapidly solidified $\text{Al}_{84.6}\text{Cr}_{15.4}$ alloy⁽¹⁴⁾⁽¹⁵⁾. It is therefore presumed that the effect of Ce occurs through the increase in the degree of supercooling ability of the liquid. The significant effect of Ce on the increase in the degree of quenching is supported by the previous result⁽¹⁶⁾ that an amorphous single phase is obtained for Al-Ln binary alloys. It is reasonable to consider that the increase in the degree of quenching causes the decrease in the particle size of the icosahedral phase. Furthermore, it is shown in Fig. 15 that the solute content in the icosahedral phase shifts significantly to the Al-rich side. This tendency increases with increasing supercooling ability⁽⁸⁾⁽¹⁵⁾. The deviation of the solute content of the icosahedral phase also implies that the

Fig. 15 Energy dispersive X-ray profiles taken from the mixed phase region with a diameter of $10\ \mu\text{m}$ (a), the icosahedral phase region with a diameter of $5\ \text{nm}$ (b) and the fcc-Al phase region with a diameter of $5\ \text{nm}$ (c) in a rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy.

further decrease in the solute content, with increasing supercooling ability, leads to the increase in the volume fraction of the icosahedral phase. The interpretation of the structural change by the increase in the quenching effect caused by Ce is consistent with the present results shown in Figs. 1 and 2. In addition, the decrease in Al content caused by the increase in Ce content for the $\text{Al}_{95.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_x$ alloys is also another reason for the increase in the volume fraction of the icosahedral phase.

It was demonstrated in the high-resolution TEM images shown in Figs. 12 to 14 that the nanoscale icosahedral phase in the rapidly solidified $\text{Al}_{94.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1$ alloy had the disordered structure on a short-range scale less than about $1\ \text{nm}$. Here, it is important to discuss the reason for the formation of the short-range disordered structure. It is generally known⁽¹⁷⁾⁽¹⁸⁾ that the icosahedral quasicrystal contains phonon deviations and linear phasons as defects inherent to the quasiperiodic structure. Their defects are generated by thermal fluctuation, by the deviation of alloy composition from the stoichiometric composition and by the introduction of applied strains⁽¹⁹⁾. The phonon deviations come from the deviation of atoms from the ordinary sites by the thermal fluctuation,

leading to the generation of elastic strains⁽²⁰⁾. The phonon deviations can annihilate rather easily by annealing treatment and hence they do not affect the formation of the disordered structure in the icosahedral phase. On the other hand, the elimination of the linear phasons is very difficult at room temperature and at elevated temperatures where the atomic diffusion of the constituent elements is difficult. A high density of linear phasons are introduced by the deviation of alloy composition from the stoichiometric composition to the Al-rich composition and by quenching-induced strains, leading to the generation of various types of approximant crystalline phases on a subnanoscale⁽¹⁹⁾. The approximant crystalline phases have a periodic structure with large unit cells containing icosahedral atomic configurations on a short-range scale⁽²¹⁾. The existence of a great number of approximant crystalline regions on a subnanoscale also causes the introduction of a high density of interface boundaries between icosahedral and approximant crystalline phases. The interface regions are thought to have a disordered atomic configuration on a subnanoscale which is similar to that for an amorphous phase. That is, the formation of the short-range disordered structure is attributed to the unique defect structure resulting from the quasi-periodic atomic configuration.

Finally, we investigate the reason for the high strength and good ductility for the Al-Cr-Co-Ce and Al-Cr-Co-Ce-M alloys containing high volume fractions of icosahedral phase. As described above, the icosahedral phase which occupies the volume fraction of 60 to 80% in the Al-based alloys has the disordered atomic configurations on a short-range scale less than about $1\ \text{nm}$. The feature of the disordered structure can be summarized as follows; (1) the existence of attractive bonding nature between major (Al) and other minor atoms, (2) the absence of slip planes on a long-range scale, (3) the existence of voids which enable the local movement of the constituent atoms, (4) the unfixed atomic configurations which lead to the structural relaxation, and (5) the existence of Al-Al bonding pairs because of the Al-rich concentrations. These features in the short-range disordered structure are similar to those⁽²²⁾ for amorphous metallic materials exhibiting higher strength and better ductility as compared with those for the corresponding crystalline alloys. It is therefore presumed that the high tensile strength and good ductility for the quasicrystalline base Al-Cr-Co-Ce and Al-Cr-Co-Ce-M alloys are due to the formation of the similar short-range atomic configuration as that for the metallic amorphous alloys. This presumption is consistent with the present result that the tensile strength increases with increasing volume fraction of the icosahedral particles and with decreasing particle size. In any event, it is to be noticed that the formation of the disordered structure on a short-range scale leading to the high strength and good ductility is due to the phase transition of icosahedral to approximant crystalline phase caused by the linear phason defects inherent to the icosahedral phase. The new method in the structural modification on a short-range scale less than about $1\ \text{nm}$ is expected to

give rise to new unexpected properties which are not obtained for stoichiometric icosahedral alloys.

V. Summary

In order to search an optimum alloy system exhibiting high strength and good ductility through the formation of coexistent icosahedral (I) and fcc-Al phases, the microstructure and mechanical properties were examined in the as-quenched and annealed states for rapidly solidified $\text{Al}_{95.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_x$ ($x \leq 3$ at%) and $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ (M=Ti, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo or Hf) alloys. The results obtained are summarized as follows.

(1) The as-quenched structure consists of the I and Al phases in the Ce concentration range below 3 at%. The increase in Ce content causes the decrease in the particle size and the spheroidization of the particle morphology of the I phase, accompanying the increase in the volume fraction. The Cr and Ce concentrations in the I-phase were analyzed to be 7.15% and 2.56%, respectively. There is a tendency for Cr and Ce elements to concentrate into the I-phase.

(2) The Al-Cr-Co-Ce alloys remain ductile in the whole Ce range tested and the highest tensile strength (σ_t) of 1340 MPa is obtained for the 1%Ce alloy.

(3) The coexistent I and Al phases were obtained for all the $\text{Al}_{93.5}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_1$ alloys. The mixed phase alloys also have good bending ductility and the highest σ_f of 1330 MPa is obtained for the Ti-containing alloy.

(4) The annealing for 900 s at 673 K caused the formation of the mixed structure of I, Al and compound phases. The volume fraction of the I phase increases by the precipitation of the I and compound phases from the Al phase.

(5) The high σ_f above 600 MPa for the annealed $\text{Al}_{94.5-x}\text{Cr}_3\text{Co}_{1.5}\text{Ce}_1\text{M}_x$ alloys is obtained for the Fe- and Zr-containing alloys and the highest value is 830 MPa for the 2%Zr alloy and 680 MPa for the 1%Fe alloy. These results allow us to expect that the bulk alloys exhibiting high σ_f by utilizing the I phase as a strengthening phase are obtained for the Fe- and Zr-containing alloys by extrusion at elevated temperatures.

(6) The high-resolution TEM image reveals that the I phase has a disordered atomic configuration on a short range less than 1 nm and an I atomic configuration on a long range above 2 nm. The disordered structure is

presumably due to the introduction of a high density of interfaces between I and approximant crystalline phases resulting from the phase transition to approximant crystalline phases caused by the phason defects. The generation of the phason defects is due to the deviation of alloy compositions from the stoichiometric composition and the quenching-induced strain. The formation of the disordered structure on the short-range scale is thought to be the origin of the high strength through the achievement of good ductile nature.

REFERENCES

- (1) A. Inoue, K. Ohtera, A. P. Tsai and T. Masumoto: *Jpn. J. Appl. Phys.*, **27** (1988), L280.
- (2) Y. He, S. J. Poon and G. J. Shiflet: *Science*, **241** (1988), 1640.
- (3) A. P. Tsai, A. Inoue and T. Masumoto: *Met. Trans.*, **19A** (1988), 1369.
- (4) A. Inoue, Y. Horio and T. Masumoto: *Mater. Trans.*, **JIM**, **34** (1993), 85.
- (5) A. Inoue, N. Matsumoto and T. Masumoto: *Mater. Trans.*, **JIM**, **31** (1990), 493.
- (6) K. Ohtera, A. Inoue, T. Terabayashi, H. Nagahama and T. Masumoto: *Mater. Trans.*, **JIM**, **33** (1992), 775.
- (7) S. Takeuchi: *Tetsu-to-Hagane*, **78** (1992), 1517.
- (8) A. Inoue, M. Watanabe, H. M. Kimura, F. Takahashi, A. Nagata and T. Masumoto: *Mater. Trans.*, **JIM**, **33** (1992), 723.
- (9) M. Watanabe, A. Inoue, H. M. Kimura, T. Aiba and T. Masumoto: *Mater. Trans.*, **JIM**, **34** (1993), 162.
- (10) A. Inoue, M. Watanabe, H. M. Kimura and T. Masumoto: *Sci. Rep. Res. Inst. Tohoku Univ.*, **A-38** (1993), 138.
- (11) A. Inoue, H. M. Kimura, K. Sasamori and T. Masumoto: *Mater. Trans.*, **JIM**, **35** (1994), 85.
- (12) A. Inoue: *J. Japan Soc. of Powder and Powder Metallurgy*, **41** (1994), 899.
- (13) A. Inoue, K. Ohtera, T. Zhang and T. Masumoto: *Jpn. J. Appl. Phys.*, **27** (1988), L1583.
- (14) A. Inoue, L. Arnberg, B. Lehtinen and T. Masumoto: *Met. Trans.*, **17A** (1986), 2077.
- (15) A. Inoue, H. M. Kimura and T. Masumoto: *J. Mater. Sci.*, **22** (1987), 1758.
- (16) A. Inoue, K. Ohtera and T. Masumoto: *Jpn. J. Appl. Phys.*, **27** (1988), L736.
- (17) P. Bak: *Phys. Rev. Lett.*, **54** (1985), 1517.
- (18) D. Levine, T. C. Lubensky, S. Ostlund, S. Rawaswamy, P. J. Steinhardt and J. Toner: *Phys. Rev. Lett.*, **54** (1985), 1520.
- (19) Y. Ishii: *Phys. Rev.*, **B39** (1989), 11862.
- (20) T. C. Lubensky, S. Rawaswamy and J. Toner: *Phys. Rev.*, **B32** (1985), 7444.
- (21) F. Spaepen, L. C. Chen, S. Ebarland and W. Ohashi: *Proc. of the Adriatic Research Conf. on Quasicrystals*, ed. by M. V. Jaric and S. Lundqvist, World Scientific, Singapore, (1990), p. 1.
- (22) H. S. Chen: *Rep. Prog. Phys.*, **43** (1980), 353.