Mechanical Properties and Thermal Stability of Ti- and Al-Based Amorphous Wires Prepared by a Melt Extraction Method

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The application of a melt extraction method to Ti- and Al-based alloys with highly reactive molten states was found to cause the formation of continuous amorphous alloy wires with good bending ductility. The wire diameter is in the range of 40 to 150 μm for $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and 40 to 100 μm for $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ and the difference reflects the difference in the glass-forming ability between both alloys. The glass transition temperature, crystallization temperature and heat of crystallization are 629 K, 691 K and 1.71 kJ/mol, respectively, for the Ti-based wire with the diameter of 100 μm and 530 K, 546 K and 0.37 kJ/mol for the Al-based wire with the diameter of 50 μm . The tensile strength is 2000 MPa for the former wire and 930 MPa for the latter wire. The thermal stability and mechanical strength are nearly the same as those for the melt-spun amorphous ribbons with the thickness of 15 μm . No appreciable concave resulting from the use of the copper wheel with a steep edge is seen in the cross section and the solidification is completed during the flight after extraction. The cooling rate of the Al-based wire with the diameter of 70 μm is estimated to be of the order $6 \times 10^4 \text{ K/s}$. Thus, the formation of the amorphous alloy wires with a circular cross section is due to the rapid solidification of the fine supercooled liquid stream in the suppression of heterogeneous nucleation during the high-velocity flight in the argon atmosphere. The combination of the solidification process with high cooling rate and the good formability into the wire shape allows us to expect that the present process develops as an alternative method to produce amorphous alloy wires in various kinds of alloy systems including reactive elements as main components.

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I. Introduction

It has recently been found that amorphous alloys with high tensile strength and good bending ductility as well as a supercooled liquid region before crystallization are formed in light metal base alloys such as Al-(1)(2), Mg-(3) and Ti-(4) based systems by the melt spinning method. The resulting samples have a thin ribbon shape with a thickness below about 50 μm . The utilization of the high specific strength is more favorable for the wire-shape sample with a circular cross section. It is well known that amorphous alloy wires in Fe-(5)(6), Co-(7), Ni-(8), Pd-(9) and Pt-(10) based systems are produced by the in-rotating-water melt spinning method(11) and the Fe- and Co-based amorphous wires have been used in various kinds of application fields by utilizing good mechanical properties, high corrosion resistance and unique soft magnetic properties. However, no successful result on the preparation of amorphous alloy wires has been obtained for Al-, Mg- and Ti-based alloys(12), though very active challenges for the preparation of their amorphous alloy wires were made by the in-rotating-liquid melt spinning method using various kinds of liquid mediums. This difficulty is

mainly due to the high reactivity of these molten alloys with the liquid coolants. In addition to the in-rotating-liquid melt spinning method, the use of the melt extraction method(13) without any liquid medium is expected to enable the formation of continuous amorphous alloy wires even in the Ti-, Al- and Mg-based alloys, when the cooling rate obtained by this technique exceeds the critical cooling rates for the formation of their amorphous alloys. That is, the glass formation by the melt extraction method is attributed to the cooling ability of the method and the glass-forming ability of their light metal base alloys.

It has recently been reported that the critical cooling rates for glass formation of Al-Ni-Ln alloys are of the order 10^3 to 10^4 K/s (14) and can be amorphized in a sheet form with the thicknesses below 0.2 mm even by a metallic mold casting method(15). As a result, the application of the melt extraction method to an $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloy was found to cause the formation of amorphous alloy wires with good mechanical properties in the diameter range of 40 to 70 μm . The outline of the formation and properties of the Al-Ni-Ce amorphous wire was presented in Ref. (16). It has subsequently been reported(4) that Ti-Zr-Cu amorphous alloys have the largest glass-forming ability in the Ti-TM systems and the critical maximum sample thickness is about 150 μm . The large glass-forming ability for the Ti-based alloys allows us to expect that an amorphous alloy wire is formed by the melt-extraction method. The first aim of this paper is to present the glass-

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forming ability of Ti–Zr–Cu and Al–Ni–Ce alloys, the preparation condition in which the Ti- and Al-based amorphous wires are formed by choosing alloy compositions with the largest glass-forming ability by the melt extraction method, and the structure, shape, thermal stability and mechanical properties of the resulting Ti- and Al-based amorphous wires. The second is to investigate the reasons for the formation of the wire shape with a circular cross section and for the achievement of the high cooling rates which enable the formation of the amorphous phase for the present preparation technique.

II. Experimental Procedure

Ti₄₀Zr₁₀Cu₅₀ and Al₈₅Ni₁₀Ce₅ ternary alloys were chosen because these ternary amorphous alloys exhibit rather large glass-forming ability, distinct glass transition and high mechanical strength. The ingots were prepared by arc melting a mixture of pure constituent metals in an argon atmosphere. The compositions are given in nominal atomic per cent. The master alloy ingots were remelted in a graphite or a boron nitride crucible in an argon atmosphere and Ti- and Al-based alloy wires with diameters ranging from 40 to 80 μm and the length of about 10 meters were prepared by melt extraction using a copper wheel with a steep edge in the inert gas atmosphere. The diameter of the copper wheel used for the melt extraction was 200 mm and the angle of the edge was fixed to 60 degrees. The rotation speed of the wheel was changed in the range of 16.7 to 66.7 turns s^{-1} . The temperature of the molten alloy in the crucible was fixed to be about 1300 K for the Ti–Zr–Cu alloy and about 1100 K for the Al–Ni–Ce alloy which are about 200 K higher than the corresponding melting temperatures. The temperature was measured with a radiative thermometer. We confirmed that the deviation of the extracted temperature from $T_m + 200$ K to the higher and lower temperature sides caused the difficulty of the formation of a continuous amorphous wire with a circular cross section. The extraction temperature was defined as the temperature of the molten alloy in the crucible just before extraction. Amorphous Ti₄₀Zr₁₀Cu₅₀ and Al₈₅Ni₁₀Ce₅ ribbons with the width of 1 mm and the thickness of about 15 and 60 μm were also prepared for comparison by a single roller melt spinning technique in an argon atmosphere. The amorphicity of the melt-extracted wires and the structural relaxation, glass transition and crystallization behavior of the amorphous phase were examined by X-ray diffraction using Cu K α radiation, transmission electron and optical microscopy (TEM and OM) and differential scanning calorimetry (DSC). The OM observation was made after etching for 15 s at 293 K in a 10% hydrofluoric acid aqueous solution for the Ti-based samples and for 30 s at 298 K in a 10% sodium hydroxide aqueous solution for the Al-based samples. The heating rate in the DSC measurement was fixed at 0.67 K/s. Ductility was evaluated by a simple bend test. Ductile sample means that the wire can be bent through 180 degrees without fracture. Hardness and tensile strength of the wire speci-

mens were measured by a Vickers microhardness tester with a 0.49 N load and an Instron-type tensile testing machine at a strain rate of $4.2 \times 10^{-4} \text{ s}^{-1}$, respectively. Fracture surface appearance and bent structure were examined by scanning electron microscopy.

III. Results

1. Preparation of amorphous alloy wires

Figures 1 and 2 show the composition range in which an amorphous phase with a supercooled liquid region before crystallization is formed in Ti–Zr–Cu and Al–Ni–Ce systems, respectively. The appearance of the glass transition and wide supercooled liquid region is recognized in the wide composition ranges of 10 to 40%Zr and 40 to 50%Cu for the former system and 8 to 12%Ni and 6 to 10%Ce for the latter system and the widest supercooled

Fig. 1 Composition range in which the glass transition in Ti–Zr–Cu amorphous alloys is observed and the compositional dependence of the supercooled liquid region defined by the temperature difference between crystallization temperature (T_x) and glass transition temperature (T_g).

Fig. 2 Composition range in which the glass transition in Al–Ni–Ce amorphous alloys is observed and the compositional dependence of the supercooled liquid region defined by the temperature difference between crystallization temperature (T_x) and glass transition temperature (T_g).

liquid region in each system is obtained for $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloys. Considering the previous relation⁽¹⁷⁾ that the critical cooling rate for glass formation decreases with an increase of the temperature interval of supercooled liquid region, it is concluded that the largest glass-forming ability in each system is obtained for the $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloy. Consequently, subsequent trials to prepare an amorphous alloy wire were made for the two alloys.

Figures 3 and 4 show scanning electron micrographs of the outer surface appearance and optical micrographs of their transverse cross sections after etching for the melt-extracted $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ wires, respectively. Their wires have a circular cross section of about $55\text{ }\mu\text{m}$ in diameter. The outer surface is smooth and has a good white luster. The uniformity of the wire diameter was measured and the fluctuation was found to be less than 6% for both the wires. No contrast corresponding to the precipitation of a crystalline phase is seen over the cross sectional area as well as on the outer surface, indicating the formation of an almost single amorphous phase in the Ti- and Al-based alloys. The diameter of the

Fig. 3 (a) Scanning electron micrograph revealing the outer surface appearance of a $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ wire, and (b) optical micrograph revealing the transverse cross sectional structure in an etched state.

Fig. 4 (a) Scanning electron micrograph revealing the outer surface appearance of an $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ wire, and (b) optical micrograph revealing the transverse cross sectional structure in an etched state.

wires produced in the present extraction condition is in the range of 40 to $150\text{ }\mu\text{m}$ for the Ti-based alloy and 40 to $80\text{ }\mu\text{m}$ for the Al-based alloy and tends to decrease with increasing rotation speed of the wheel.

In order to confirm the formation of an amorphous structure in their wires, X-ray diffraction patterns of the $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ wires with $70\text{ }\mu\text{m}$ in diameter are shown in Fig. 5, in comparison with those of their melt-spun amorphous ribbons with a thickness of $15\text{ }\mu\text{m}$. The X-ray diffraction patterns taken from the Ti- and Al-based wires consist only of broad peaks with the largest intensity at $K_p (=4\pi \sin \theta / \lambda) \approx 28.74$ and 24.98 nm^{-1} , respectively. This result indicates that these as-quenched wires are composed of an amorphous single phase, in agreement with the results of the scanning electron and optical micrographs shown in Figs. 3 and 4. It is further seen that the wave vectors at the peak position of the broad peaks for both wires agree with those for the melt-spun ribbons, indicating the similarity of the disordered structures between the wire and the ribbon samples.

2. Thermal stability

Figure 6 shows the differential scanning calorimetry curve of the melt-extracted $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ wire, along with that of the melt-spun ribbon. The glass transition phenomenon is seen for both samples and the glass transition temperature (T_g), the onset temperature of crystallization (T_x) and the heat of crystallization (ΔH_x) are 629 K, 691 K and 1.71 kJ/mol , respectively, for the wire, and 629 K, 691 K and 1.72 kJ/mol , respectively, for the rib-

Fig. 5 X-ray diffraction patterns of $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ wires with diameters of 130 and 70 μm , respectively. The results of melt-spun Ti–Zr–Cu and Al–Ni–Ce ribbons with a thickness of about 15 μm are also shown for comparison.

Fig. 6 Differential scanning calorimetric curve of a $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ wire with a diameter of about 130 μm . The result of the melt-spun ribbon is also shown for comparison.

bon. No distinct difference in these parameters representing the thermal stability is seen between both the samples, in spite of the significant difference in the sample thickness. It is to be noticed that the Ti–Zr–Cu amorphous wire has the very wide supercooled liquid region reaching 62 K which is defined by the temperature interval between T_g and T_x . The agreement of the thermal properties between the wire and the melt-spun ribbon is

Fig. 7 Differential scanning calorimetric curves of $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ wires with diameters of about 30, 50 and 100 μm . The result of the melt-spun ribbon is also shown for comparison.

also recognized for the $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ amorphous alloy, as shown in Fig. 7. The T_g , T_x and ΔH_x values of the Al–Ni–Ce amorphous alloy are 531 K, 546 K and 0.37 kJ/mol, respectively, for the wire and 529 K, 544 K and 0.39 kJ/mol, respectively, for the ribbon. The melting temperatures (T_m) of the $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloys are measured to be 1107 and 889 K, respectively, and hence the reduced glass transition temperature (T_g/T_m) were evaluated to be 0.57 and 0.60, respectively.

In order to investigate the difference in the quenched-in structures due to different quenching conditions between wires prepared by melt extraction and ribbons prepared by melt spinning, the temperature dependence of the apparent specific heat (C_p) of $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ and $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ amorphous alloys in the shapes of wire and ribbon was examined with a DSC. Figures 8 and 9 show the thermograms of the Al–Ni–Ce and Ti–Zr–Cu amorphous wires, together with the data on the corresponding ribbons. The specific heat ($C_{p,q}$) of the as-quenched Al–Ni–Ce sample begins to decrease at about 405 K, in comparison with the specific heat ($C_{p,s}$) of the sample heated once for 60 s at 510 K. The decrease of $C_{p,q}$ indicates that appreciable relaxation occurs. As the temperature rises further, $C_{p,q}$ decreases gradually in the range below about 520 K and then increases rapidly in the region of glass transition. In the temperature range of 405 to 520 K, the apparent specific heat of the as-quenched samples is lower in the order of ribbon with the thickness of 15 μm (a), wire with the diameter of 60 μm (b), ribbon with the thickness of 60 μm (c) and wire with the diameter of 100 μm (d). These results indicate the following two points: (1) the temperature at which the structural relaxation begins (T_r) also decreases in the same order as that for $C_{p,q}$

Fig. 8 Change in the apparent specific heat (C_p) of an amorphous $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloy in wire (≈ 60 and $100 \mu\text{m}$ diameter) and ribbon (≈ 15 and $60 \mu\text{m}$ thick) shapes upon heating at a rate of 0.67 K/s . The $C_{p,q}$ and $C_{p,s}$ represent the specific heats of the samples in as-quenched state and annealed state for 60 s at 510 K, respectively.

in the range of 405 K to 520 K; (2) the integrated heat of relaxation, ΔH_r , is 0.90 kJ/mol for the ribbon (a), 0.71 kJ/mol for the wire (b), 0.63 kJ/mol for the ribbon (c) and 0.51 kJ/mol for the wire (d). There is a tendency for ΔH_r to increase with decreasing T_r and $C_{p,q}$ values. Thus, the amorphous wire with $60 \mu\text{m}$ in diameter is said to have a slightly more disordered structure as compared with the amorphous ribbon with the same thickness. This result indicates that the amorphous wire produced by the melt extraction method has been subjected to a cooling rate which is lightly higher than or almost comparable to that for the melt spinning method. However, as shown in

Fig. 9 Change in the apparent specific heat (C_p) of an amorphous $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ alloy in wire (≈ 100 and $150 \mu\text{m}$ diameter) and ribbon ($\approx 15 \mu\text{m}$ thick) shapes upon heating at a rate of 0.67 K/s . The $C_{p,q}$ and $C_{p,s}$ represent the specific heats of the samples in as-quenched state and annealed state for 60 s at 660 K, respectively.

Fig. 7, the Ti-Zr-Cu amorphous wires with diameters exhibit much higher T_r , smaller ΔH_r and higher $C_{p,q}$ as compared with the amorphous ribbon with a thickness of $15 \mu\text{m}$, indicating that the amorphous wires have much relaxed atomic configurations.

3. Mechanical properties

The Ti- and Al-based amorphous wires have a good bending ductility and can be bent through 180 degrees without fracture. Figure 10 shows the outer surface ap-

Fig. 10 Scanning electron micrographs revealing the deformed structure of amorphous $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ (a) and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ (b) wires which were bent through 180 degrees.

pearance of the Ti-Zr-Cu and Al-Ni-Ce amorphous wires with diameters of 100 and 50 μm , respectively, which were bent through 180 degrees. Although a number of deformation markings are observed in the severely bent region, no appreciable cracks are seen for both wires. The feature of the deformation markings in the bent region is the same as that for Pd⁽⁹⁾, Pt⁽¹⁰⁾, Fe⁽⁵⁾⁽⁶⁾, Co⁽⁷⁾ and Ni⁽⁸⁾ based amorphous alloy wires produced by the in-rotating-water melt spinning method.

Table 1 summarizes the Young's modulus (E), tensile fracture strength (σ_f), fracture elongation including elastic elongation (ϵ_f) and Vickers hardness (H_v) for the Ti₄₀Zr₁₀Cu₅₀ and Al₈₅Ni₁₀Ce₅ amorphous wires, along with the tensile fracture strain ($\epsilon_t = \sigma_f/E$), compressive fracture strain ($\epsilon_c = 3H_v/E$) and wire diameter. The data on the melt-spun ribbon with a thickness of 15 μm are also shown for comparison. The tensile strength is as high as 2000 MPa for the Ti-based wire and 930 MPa for the Al-based wire. It is notable that these strength values are about 1.5 times as high as the highest values for conventional Ti- and Al-based crystalline alloys, respectively. Although there is no distinct difference in E , σ_f , ϵ_f , H_v , ϵ_t and ϵ_c between the wire and the ribbon for the Al-

based alloy, the Ti-based amorphous wire has higher values of E , σ_f and H_v and lower values of ϵ_f , ϵ_t and ϵ_c as compared with those for the melt-spun ribbon. The difference is evaluated to be 40% for E , 20% for σ_f , 5% for H_v , 10% for ϵ_f , 15% for ϵ_t and 30% for ϵ_c . This result indicates that the Ti-based amorphous wire has higher strength and lower ductility as compared with those for the melt-spun ribbon, though the wire has a good bending ductility. These differences are in good contrast to the result for the Al-based amorphous alloy that no distinct difference in the strength and ductility is detected between the wire and ribbon. The difference is presumably due to the difference in the degree of structural relaxation resulting from the fact that the Ti-based amorphous wire has much higher T_g and larger diameter as compared with those for the Al-based amorphous wire. The detailed discussion will be given in Section IV.

The tensile fracture of the Ti- and Al-based amorphous wires takes place along the maximum shear plane, which is declined by about 45 degrees to the direction of tensile load, and the fracture surface consists of smooth and vein regions, as shown in Fig. 11. The features of the fracture behavior and fracture surface appearance also agree with those for the melt-spun ribbons. The agreement in the tensile fracture behavior is presumably because the wires have good ductile nature which is nearly the same as that for the melt-spun ribbons with a thickness of 15 μm .

IV. Discussion

As described above, the present melt extraction method was found to cause the formation of amorphous wires with high tensile strength and good bending ductility. Here, it is important to discuss the reason why the Ti- and Al-based wires with thicknesses of 50 to 150 μm exhibit nearly the same thermal and mechanical properties as those for the melt-spun ribbons with a thickness of

Table 1 Mechanical properties of amorphous Ti₄₀Zr₁₀Cu₅₀ and Al₈₅Ni₁₀Ce₅ wires with diameters of 60 and 50 μm , respectively, prepared by the melt extraction method. The data of the melt-spun amorphous ribbons with a thickness of 15 μm are also shown for comparison.

	E / GPa	σ_f / MPa	ε_f (%)	Hv	ε_t (%)	ε_c (%)	Diameter or thickness/ μm
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Ti ₄₀ Zr ₁₀ Cu ₅₀							
wire	102	2000	2.2	615	2.0	1.8	60
ribbon	73	1650	2.5	585	2.3	2.4	15
<hr/>							
Al ₈₅ Ni ₁₀ Ce ₅							
wire	62.0	930	1.5	295	1.5	1.4	50
ribbon	60.5	920	1.6	270	1.5	1.3	15

Fig. 11 Scanning electron micrographs revealing the tensile fracture surface appearance of amorphous Ti₄₀Zr₁₀Cu₅₀ (a) and Al₈₅Ni₁₀Ce₅ (b) wires.

about 15 μm . It has previously been shown that the formation of amorphous ribbons with good bending ductility by the use of the single-roller melt spinning method is limited to a thickness range below about 150 μm for the $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ alloy⁽¹⁸⁾ and about 65 μm for the $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloy⁽¹⁵⁾. The maximum thickness of the ductile amorphous wire obtained by the present melt extraction process is approximately 150 μm for the Ti-based alloy and 70 μm for the Al-based alloy. The approximate agreement of the maximum thickness for the formation of ductile amorphous alloys clearly indicates that the present melt extraction process enables the achievement of a high cooling rate comparable to that of the conventional melt-spinning method.

In order to confirm this presumption, we estimated the cooling rate by measuring the lamellar spacing in an $\text{Al}_{67}\text{Cu}_{33}$ (mass%) crystalline wire with a diameter of 50 μm prepared at the same preparation condition by the melt extraction method. Figure 12(a) and (b) shows the TEM image taken from the central region in the Al-Cu wire sample and the SEM image of its outer surface. The SEM image was taken after etching for 10 s at 298 K in the Keller's solution. The lamellar spacing is measured to be about 300 nm in the central region and about 100 nm in the outer surface. Based on the previous empirical relation between lamellar spacing and cooling rate for the Al-Cu alloy⁽¹⁹⁾, the cooling rate of the Al-Cu wire is estimated to be about 2×10^4 K/s in the central region and about 2×10^5 K/s in the outer surface.

We also estimated the solidification time of the extracted supercooled liquid stream with a diameter of about 70 μm after the extraction with the copper wheel by measuring the minimum distance at which the shape of the extracted melt stream changes by the collision against the ceramic plate. The measurement of the melt stream results from the result that the collision before the completion of solidification causes the change in the trans-

verse cross sectional shape. At the optimum extraction condition for the Al-Ni-Ce wire with the diameter of 60 μm , the minimum distance was measured to be about 150 mm. Here, it is assumed that the flight velocity of the extracted melt stream within the short distance of 150 mm is the same as the circumferential velocity of the copper wheel, and the temperature of the melt stream just after the extraction is approximately the corresponding melting temperature from the measurement of the temperature of the molten alloy during melt extraction. We can also assume that the solidification is completed at a temperature near T_g . Consequently, the cooling rate of the Al-Ni-Ce supercooled liquid stream is estimated to be 6×10^4 K/s. The cooling rate estimated thus agrees with the average cooling rate obtained from the lamellar spacing in the Al-Cu wire extracted at the same preparation condition. The good agreement of the cooling rates estimated by the different methods allows us to conclude that the present extraction method can yield the cooling rate of the order 6×10^4 K/s which is high enough to cause an amorphous single phase in the Ti- and Al-based alloy wires. Furthermore, one can notice that the cooling rate is comparable to those for the single roller melt spinning and the in-rotating-water melt spinning methods.

Finally, we discuss the reason why the present melt extraction method causes the formation of the continuously long amorphous wires with a circular cross section. It is shown in Figs. 3 and 4 that the transverse cross section has a circular shape and one cannot see any appreciable concave resulting from the use of the copper wheel with a steep edge. This result indicates that the completion of the solidification to the amorphous wire takes place during the flight in an argon atmosphere after the melt extraction. This solidification mode is different from the previous result⁽²⁰⁾ that the solidification into a melt-spun amorphous ribbon is almost completed during the contact with the copper roll. The reason why the fine melt

Fig. 12 Bright-field electron micrograph taken from the central region (a) and scanning electron micrograph taken from the outer surface region (b) of an $\text{Al}_{67}\text{Cu}_{33}$ wire with a diameter of 50 μm prepared by the melt extraction method.

stream can be solidified into the amorphous solid with a circular cross section during the flight in the argon atmosphere may be due to the solidification from supercooled liquid with high viscosity in the non-contact state against other solid substances leading to the suppression of heterogeneous nucleation of a crystalline phase. The solidification process of the fine melt stream is different from those for the conventional melt spinning and the in-rotating-liquid spinning processes. It is thus concluded that the formation of the Ti- and Al-based amorphous alloy wires by the present melt extraction method is attributed to the rapid solidification of the fine supercooled liquid stream in the suppression of heterogeneous nucleation during the high-velocity flight in the argon atmosphere.

V. Summary

Amorphous $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{50}$ and $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ alloy wires with high tensile strength and good bending ductility were found to be formed by a melt extraction method using the copper wheel with a steep edge of 60 degrees. The extraction temperature is approximately 200 K higher than the melting temperature and the circumferential speed of the wheel is 42 m/s. The diameter of the resulting amorphous alloy wires is in the range of 40 to 150 μm for the Ti-based wire and 40 to 100 μm for the Al-based wire and the length is as long as 10 m. No appreciable concave in the transverse cross section is seen in spite of the use of the copper wheel. The solidification is thought to be completed during the flight after the extraction. The thermal stability and tensile strength of the Al- and Ti-based amorphous alloy wires are nearly the same as those for the melt-spun amorphous ribbon with a thickness of about 15 μm . The cooling rate by the present technique is estimated to be about $6 \times 10^4 \text{ K/s}$ for the Al-based wire with the diameter of 70 μm . The formation of the amorphous wires with the circular cross section is due to the rapid solidification of the fine supercooled liquid stream in the suppression of heterogeneous nucleation during the high-velocity flight in the argon at-

mosphere. The solidification process, which is different from those for the conventional melt-spinning and the in-rotating-liquid spinning methods, is promising for the subsequent development of amorphous alloy wires in various kinds of alloy systems containing reactive metals as a main component.

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