Elevated-Temperature Strength of an $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ Amorphous Alloy Containing Nanoscale fcc-Al Particles

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An $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ alloy with ultrahigh tensile fracture strength exceeding 950 MPa in the temperature range from room temperature to 573 K was found to be obtained by rapid solidification in the structural state where the nanoscale fcc-Al particles without internal defects disperse homogeneously in the amorphous matrix. The ultimate tensile strength is as high as 1560 MPa at room temperature and 970 MPa at 573 K. The high strength values were obtained in the mixed structure where the volume fraction of Al phase was about 25%. It is notable that the strength values at room temperature and 573 K are about 3 and 15 times, respectively, as high as those for conventional age-hardening type aluminum alloys. The extremely high strengths are presumably due to the dispersion strengthening resulting from the homogeneous dispersion of the nanoscale Al particles without internal defects. Furthermore, the excellent elevated-temperature strength is also presumed to originate from the high resistance of the defect-free Al particles against the softening as well as the particle growth.

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I. Introduction

Recently, light metal-based alloys in Al- and Mg-based systems have attracted increasing attention because of increasing social needs for lightweight high-strength materials. However, the elevated-temperature strength for the Al- and Mg-based alloys has been believed to be rather poor because of low melting and boiling temperatures of their base alloys. It has been reported⁽¹⁾ that high mechanical strength retention of 300 MPa at 573 K is one of the goal in the development of heat-resistant Al-based alloys. The present authors have found⁽²⁾⁽³⁾ that the tensile strength reaching 1560 MPa at room temperature is achieved for Al-based amorphous alloys containing fcc-Al particles with a particle size of 3 to 5 nm. Based on the experimental data⁽⁴⁾ on the absence of internal defects in the nanoscale fcc-Al particles in the high-resolution transmission electron micrographs, the achievement of the ultrahigh tensile strength has been presumed⁽⁴⁾⁽⁵⁾ to result from the dispersion strengthening due to the nanoscale fcc-Al particles without internal defects. It is to be expected that the dispersion strengthening due to the defect-free fcc-Al particles is effective even at elevated temperatures below the crystallization temperature of the amorphous matrix and the good elevated-temperature retention of strength is achieved in the mixed phase state.

This paper is intended to present the result that the ultrahigh tensile strength exceeding 950 MPa is obtained in the temperature range up to 573 K for an $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ amorphous alloy containing nanoscale fcc-Al particles without internal defects.

II. Experimental Procedure

An alloy ingot with composition $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ was prepared by arc melting of mixtures of pure Al, Ni, Ce and Fe metals in a purified argon atmosphere. Rapidly solidified ribbons with a width of 1.5 mm and various thicknesses ranging from 15 to 30 μm were prepared by a single roller melt-spinning technique and the volume fraction of fcc-Al phase (V_f) was controlled by changing either the rotation speed of copper roller with a diameter of 200 mm in the range of 25 to 83 s^{-1} (1500 to 5000 rpm) or the ejecting temperature of molten alloy. Rapidly solidified structure was examined by X-ray diffractometry, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The TEM samples were prepared by thinning electrolytically the melt-spun ribbons in a solution of 25% nitric acid and 75% methanol at 243 K. Crystallization temperature (T_x) and heat of crystallization were measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The V_f in the melt-spun ribbons was determined from the ratio of the amount of heat released during heating from room temperature to 850 K to the heat of crystallization in an amorphous single phase. Yield strength, tensile fracture strength and elongation were examined by an Instron-type tensile testing machine at an initial strain rate of $8.3 \times 10^{-4} \text{ s}^{-1}$.

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in the temperature range from room temperature to 573 K. The fracture morphology and fracture surface appearance were examined by scanning electron microscopy.

III. Results and Discussion

Figure 1 shows the change in the as-quenched structure of a melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ alloy with rotation speed of roller. As the rotation speed (cooling rate) decreases, the structure changes from an amorphous single phase to mixed phases consisting of a crystalline phase finely dispersed in an amorphous matrix. It is seen from the electron diffraction patterns that the crystalline phase has an fcc structure with a lattice parameter of 0.405 nm. The lattice parameter is nearly equal to that (0.4047 nm)⁽⁶⁾ of pure Al metal and hence the fcc phase is regarded as an Al-rich phase. The fcc-Al phase precipitates homogeneously as fine particles with diameters ranging from 3 to 30 nm and the particle size tends to increase with a decrease of cooling rate.

Figure 2 shows the DSC curves of melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbons having the amorphous or the mixed structure, along with the data of V_f . Two exothermic peaks are seen in each temperature range of 420 to 560 and 600 to 650 K. It was confirmed from the X-ray diffraction analysis that the two exothermic peaks are due to the precipitation of fcc-Al phase from the amorphous matrix and the transformation of the remaining amorphous phase to $\text{Al}_3(\text{Ni},\text{Fe})$ and $\text{Al}_{11}\text{Ce}_3$ phases, respectively. The magnitude of the first exothermic peak due to the precipitation of Al phase gradually decreases with decreasing rotation speed of roller, while that of the second exothermic peak remains unchanged, indicating that the volume fraction of the Al phase in the melt-spun ribbons

increases with a decrease of cooling rate. It is thus said that the precipitation amount of Al phase can be controlled by changing the rotation speed of the roller. In addition, the onset temperature (T_x) of precipitation of the Al phase increases with increasing V_f , suggesting that a part of elimination of Al content enhances the thermal

Fig. 2 Differential scanning calorimetric curves of melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbons with an amorphous single phase or coexistent amorphous and fcc-Al phases.

Fig. 1 Bright-field images and electron diffraction patterns showing the as-quenched structure of melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbons produced at different rotation speeds of roller.

Fig. 3 Hardness (H_v), Young's modulus (E), tensile fracture strength (σ_f), fracture elongation (ϵ_f) and lattice parameter of Al phase (a_0) as a function of V_f for melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ amorphous alloys.

stability of the remaining amorphous phase.

Figure 3 shows the hardness (H_v), Young's modulus (E), tensile fracture strength (σ_f), fracture elongation (ϵ_f) and lattice parameter of Al phase (a_0) as a function of V_f for the melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ alloy. The properties of σ_f and ϵ_f are the highest in the vicinity of $V_f=25\%$ and decrease with a further increase of V_f . Thus, the combined characteristics of good ductility and high tensile strength above 1200 MPa are achieved in the wide range of V_f from 10 to 30%. The highest σ_f attained is as high as 1560 MPa, being considerably higher than the highest value (1250 MPa)⁽⁷⁾ for Al-based amorphous alloys. On the other hand, E and H_v increase monotonously and a_0 decreases in the entire V_f range. The a_0 values are larger than that (0.4047 nm)⁽⁶⁾ of pure Al and hence the Al phase seems to be a supersaturated solution containing Ni, Ce and Fe. The change with V_f in the fracture surface appearance of the Al-Ni-Ce-Fe alloy is shown in Fig. 4. The fracture surface for the ductile samples with V_f below 25% consists of smooth and vein pattern regions. However, with increasing V_f in the range below 25%, the area fraction in the fracture surface occupied by the smooth area increases and the ledge pattern becomes significant. The changes with V_f in the E , σ_f , ϵ_f , H_v , a_0 and the fracture surface appearance for the Al-Ni-Ce-Fe alloy are very similar to those for the Al-Ni-Y⁽⁴⁾, Al-Ni-Y-M (M=Fe, Co or Mn)⁽²⁾ and Al-Ni-Y-Ce-Fe⁽³⁾ alloys with the same mixed structure.

The internal structure of the nanoscale fcc-Al particles was examined for the Al-Ni-Ce-Fe sample with $V_f=25\%$ by high-resolution electron microscopy. As shown in Fig. 5, no appreciable misfit in the fringe contrast in the Al particles is observed, suggesting that the Al

Fig. 4 Scanning electron micrographs showing the tensile fracture surface appearance of melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ amorphous ribbons with $V_f=12\%$ (a) and $V_f=25\%$ (b).

Fig. 5 High-resolution electron micrograph of a melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbon with $V_1=25\%$.

particles are composed of an fcc structure without internal defects. The absence of the internal defects in the nanoscale Al particles is also supported from the consideration that the annihilation of internal defects along the phase boundary between the nanoscale fcc-Al and amorphous matrix causes a decrease in internal energy of the mixed structure. Furthermore, since the Al-based amorphous matrix has a high tendency of structural relaxation at elevated temperatures where the precipitation of the Al particles takes place, the strain generated by the

precipitation of the Al particles can be easily relaxed through the relaxation of the amorphous matrix. In addition, the interface does not appear to have any facet planes and their particles have independent orientations in spite of the small interparticle spacing of 5 to 10 nm. Based on these microstructural data, it is presumed that the significant increase in σ_f is due to the dispersion strengthening of the defect-free Al particles embedded homogeneously in the amorphous matrix. The achievement of ultrahigh strength by the absence of internal

Fig. 6 Schematic illustration showing the mechanism for the shear deformation for an amorphous single phase (a) and coexistent amorphous and fcc-Ni phases (b).

defect is usually known from the previous data⁽⁸⁾ that the fracture strength of whiskers usually reaches theoretical fracture strengths of the corresponding components. In addition to the absence of the internal defects, the result that the particle size and interparticle spacing of the dispersed particles are also of the order of nanoscale is also thought to be an important factor for the achievement of the ultrahigh mechanical strength. As illustrated in Fig. 6, the deformation of an amorphous alloy at room temperature occurs inhomogeneously along the maximum shear plane and the atomic movement along the maximum shear plane⁽⁹⁾ is limited to a small region with a width of 10 to 20 nm. Accordingly, only when the dispersed Al particles have a particle size comparable to or smaller than the size of the shear deformation region, it is thought that the defect-free particles can act as an effective barrier to suppress the shear deformation of the amorphous matrix.

Figure 7 shows the temperature dependence of nominal yield strength (σ_y), nominal ultimate tensile strength (σ_B) and elongation (ϵ_f) for the $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ alloy containing fcc-Al particles of 20 vol%. As the testing temperature rises, σ_B decreases significantly from 1440 MPa at room temperature to 1050 MPa at 373 K. However, the σ_B value of about 950 MPa remains almost unchanged in the temperature range below 573 K, though a slight decrease in σ_B is observed at about 423 K. σ_y shows a minimum value of 700 MPa at 423 K, increases with further increasing temperature and reaches a maximum value of about 840 MPa at about 523 K. Furthermore, the existence of the significant difference between σ_y and σ_B in the temperature range of 373 to 573 K indicates clearly that the alloy with the mixed structure has a work-hardenability resulting from the dispersed particles. On the other hand, σ_f shows a distinct maximum phenomenon at 423 K. The significant increase in elongation has been reported⁽¹²⁾ to occur through the propagation of deformation region resulting from the hardening

Fig. 7 Temperature dependence of nominal tensile yield strength (σ_y), nominal ultimate tensile strength (σ_B) and fracture elongation (ϵ_f) for a melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbon with $V_f = 20\%$.

Fig. 8 Bright-field image taken from the fracture surface edge in a melt-spun $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ ribbon with $V_f = 20\%$ subjected to tensile fracture at 425 K.

in the deformation region due to the precipitation of the Al particles during the tensile deformation. It is notable that the present Al-based alloy keeps σ_B and σ_y of 970 MPa and 770 MPa, respectively, even at a high temperature of 573 K. The high thermal stability of the nanoscale Al particles is presumably due to the absence of internal defects in the particles as well as the high thermal stability of the amorphous matrix resulting from the high solute concentration above the nominal solute concentration of the alloy.

In addition, Fig. 8 shows the bright-field electron micrograph of the ledge region which generated on the tensile fracture surface of the Al-Ce-Ni-Fe alloy subjected to tensile fracture at 425 K. The particle size and in-

terparticle spacing of the Al particles are about 5 to 10 nm and 4 to 8 nm, respectively, and no distinct increase of the particle size and interparticle spacing is seen even in the severely deformed area at the elevated temperature. The appearance of the significant ledge also indicates that the mixed phase alloy with the good elevated-temperature strength keeps a ductile nature which enables the development of the distinct ledge pattern. At any event, the achievement of the high strengths at elevated temperatures indicates clearly that the nanoscale Al particles without internal defects can act as an effective barrier against plastic deformation even at elevated temperatures. It is therefore concluded that the nanoscale Al particles have a high heat-resistance against mechanical strength as well as the high thermal stability against the coalescence and growth of the particles at elevated temperatures.

IV. Summary

The mixed structure consisting of fcc-Al particles with a size of 3 to 10 nm embedded in an amorphous matrix was found to form by controlling the cooling rate of an $\text{Al}_{88}\text{Ni}_9\text{Ce}_2\text{Fe}_1$ alloy from the melt. No contrast revealing the existence of internal defects in the fcc-Al particles is seen in the high-resolution electron micrograph, indicating the formation of the defect-free particles. When the volume fraction of the homogeneously dispersed Al particles is about 25%, the σ_f increases to 1560 MPa which is about 1.5 times as high as the highest value for the amorphous single phase, accompanied by an increase of elongation, E and H_v . The significant increase in σ_f is presumably due to the dispersion strengthening of the nanoscale Al particles without internal defects. The

ultimate tensile strength (σ_B) also shows high values at elevated temperatures and keeps a high level of 970 MPa even at 573 K. It is notable that the σ_B at 573 K is about 15 times as high as that for conventional age-hardening type Al-based alloys. There were no appreciable increases in particle size and interparticle spacing of the Al particles even in the ledge area which was deformed at 425 K. It is therefore presumed that the extremely high elevated-temperature strength for the mixed phase alloy is due to the high structural stability and the high mechanical property retention at elevated temperatures for the nanoscale fcc-Al particles without internal defects.

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