Increase in Mechanical Strength of Ni-Si-B Amorphous Alloys by Dispersion of Nanoscale fcc-Ni Particles

A. Inoue, T. Shibata[†] and T. Masumoto

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

Ni-base amorphous alloys with the homogeneous dispersion of nanoscale fcc-Ni particles have been produced in the composition range of 5 to 14 at%Si and 7 to 15%B. The particle size and interparticle spacing are 10 and 20 nm, respectively. The alloys exhibit tensile fracture strength (σ_f), Young's modulus (E) and hardness (H_v) which are higher than those of the corresponding amorphous single phase alloys, accompanying an increase in fracture elongation (ε_f). The highest values of σ_f , E , H_v and ε_f in the mixed phase state of Ni-Si-B alloys, i.e., 3400 MPa, 130 GPa, 960 and 2.7%, respectively, are found for $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$. Addition of Cr increased σ_f and ε_f , their highest values being 3900 MPa and 3.8%, respectively for $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$. The increase in σ_f by the dispersion of the fcc-Ni particles is presumably because the fcc-Ni particles are higher in mechanical strength than the amorphous phase because of the absence of internal defects and can act as a barrier to suppress the shear deformation of the amorphous matrix. The increase in ε_f is due to the suppression of the inhomogeneous shear deformation. The effectiveness of Cr for the increase in σ_f and ε_f is presumably attributed to a further refinement of the fcc-Ni particle size due to the increase in glass-forming ability.

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I. Introduction

It is known⁽¹⁾ that amorphization of metallic materials by a liquid quenching technique causes a more significant increase in mechanical strength as compared with other strengthening mechanisms such as solid solution strengthening, dispersion strengthening, precipitation strengthening, strain-strengthening, etc. A number of high-strength metallic materials have been produced⁽²⁾⁽³⁾ by utilizing the quenching-induced amorphization for the last two decades. However, little has been obtained about the new strengthening mechanism exceeding the degree of the amorphization-induced strengthening. Most recently, the present authors have found that the homogeneous dispersion of nanoscale fcc-Al particles into the Al-base amorphous matrix gives rise to an increase in tensile strength by about 1.5 times as compared with that for the corresponding amorphous single phase⁽⁴⁾⁻⁽⁶⁾ and the highest tensile strength attained is as high as 1560 MPa for $\text{Al}_{88}\text{Ni}_9\text{Y}_2\text{Fe}_1$ ⁽⁷⁾. It has subsequently been reported⁽⁸⁾⁽⁹⁾ that a similar increase in tensile strength through the homogeneous dispersion of nanoscale hcp-Mg particles is also achieved for Mg-based amorphous alloys produced by melt spinning. We have carried out a systematic study on the confirmation of the new strengthening phenomenon in other alloy systems. This paper is intended to report the data of the increase

in mechanical strength of melt-spun Ni-Si-B amorphous alloys by the dispersion of nanoscale fcc-Ni particles.

II. Experimental Procedure

Ternary and quaternary alloy ingots with composition $\text{Ni}_{100-x-y}\text{Si}_x\text{B}_y$ ($x=5-15$ at%, $y=5-15$ at%) and $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{100-x}\text{M}_x$ ($\text{M}=\text{transition metal}$) were prepared by induction melting mixtures of pure Ni, M, silicon and crystal boron in a flowing argon atmosphere. Rapidly solidified ribbons with a width of 1.0 mm and a thickness of about 0.02 mm were prepared by a single roller melt spinning technique. The rotation speed of copper roller with a diameter of 170 mm was fixed to be 67 s^{-1} (4000 rpm). Rapidly solidified structure was examined by X-ray diffractometry, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM samples were prepared by thinning electrolytically the melt-spun ribbons in a solution of 10% perchloric acid and 90% methanol at 273 K. Crystallization temperature (T_x) and heat of crystallization (ΔH_x) were measured by differential scanning calorimetry (DSC) at a heating rate of 0.33 K/s. Hardness and tensile strength were examined at room temperature by a Vickers microhardness tester with 0.98 N (100 gf) load and an Instron-type tensile testing machine at a strain rate of $8.3 \times 10^{-3}\text{ s}^{-1}$, respectively. Young's modulus was measured by a forced oscillation method at a frequency of 10 Hz with a dynamic strain of 0.0015.

[†] On leave from Research and Development Division, Yoshida Kogyo K.K., Kurobe 938, Japan.

III. Results

1. Formation of coexistent fcc-Ni and amorphous phases

Figure 1 shows the compositional dependence of the rapidly solidified structure in the Ni-Si-B alloys. The structure changes from an fcc-Ni to an amorphous phase through a mixed state of fcc-Ni and amorphous phases. It should be noticed that the mixed structure is formed in a wide composition range of 5 to 14 at% Si and 7 to 15%B. The alloys with the amorphous single phase and the coexistent amorphous and fcc-Ni phases have good bending ductility and can be bent through 180 degrees without fracture. Figure 2 shows the X-ray diffraction patterns of rapidly solidified $\text{Ni}_{90-x}\text{Si}_{10}\text{B}_x$ alloys with various boron contents. It is seen that the intensity of the diffraction peaks corresponding to the fcc-Ni phase increases with decreasing B content, indicating that the precipitation amount of the fcc-Ni phase increases with decreasing B content. The change in the lattice parameter of the fcc-Ni phase with metalloid composition is shown in Fig. 3. The lattice parameter (a_0) decreases with increasing Si and B contents because of the smaller atomic sizes of Si and B as compared with the atomic size of Ni. Furthermore, the decrease in a_0 as a function of B content indicates that B is dissolved substitutionally in the fcc phase. The a_0 value at 0%Si and 0%B extrapolated from the result shown in Fig. 3 is considerably larger than that ($a_0=0.3524\text{ nm}$)⁽¹⁰⁾ of pure Ni metal. The significant difference indicates that the solute concentration in the fcc-Ni phase is much lower than that of the nominal solute concentration.

The particle size and dispersed state of the fcc-Ni phase in the rapidly solidified Ni-Si-B alloys were examined by the high-resolution transmission electron microscopy technique. As exemplified for $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$ alloy in Fig. 4, the fcc particles with periodic fringe contrast disperse

Fig. 1 As-quenched phase field in Ni-Si-B alloys rapidly solidified at a rotation speed of 67 s^{-1} (4000 rpm); amorphous; amorphous + fcc; crystalline.

Fig. 2 X-ray diffraction patterns of rapidly solidified $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$, $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$ and $\text{Ni}_{83}\text{Si}_{10}\text{B}_7$ alloys having an amorphous single phase or coexistent amorphous and fcc-Ni phases.

Fig. 3 Change in the lattice parameter (a_0) of fcc-Ni phase as a function of Si content for rapidly solidified $\text{Ni}_{93-x}\text{Si}_x\text{B}_7$ and $\text{Ni}_{92-x}\text{Si}_x\text{B}_8$ alloys with the coexistent amorphous and fcc-Ni phases.

homogeneously over the entire micrograph. The size of the particles and the interparticle distance are measured to be about 10 and 20 nm, respectively. The orientation of fringe contrast varies randomly from particle to particle, suggesting that each fcc-Ni particle has a random orientation in spite of the small interparticle distance. In addition, it is seen that the boundary between the fcc-Ni particle and the amorphous phase shows a complicated morphology, indicating that the interface does not lie on a fixed facet plane.

Fig. 4 High-resolution transmission electron micrograph of a rapidly solidified $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$ alloy.

2. Mechanical properties of coexistent fcc-Ni and amorphous phases

Figure 5 shows the compositional dependence of Vickers hardness (H_v) and Young's modulus (E) for the Ni-Si-B alloys with the coexistent fcc-Ni and amorphous phases, along with the data for the amorphous single phase and crystalline single phase alloys. It is clearly seen that the homogeneous dispersion of the nanoscale fcc-Ni particles causes significant increases in H_v and E , e.g., in the $\text{Ni}_{92-x}\text{Si}_8\text{B}_x$ alloys, from $H_v=700$ and $E=110$ GPa for the amorphous single phase to $H_v=950$ and $E=130$ GPa for the mixed phase. The optimum composition where the maximum values of H_v and E are found shifts to a lower B content with increasing Si content. A similar compositional dependence is also recognized for tensile fracture strength (σ_f) and tensile fracture elongation (ϵ_f) as shown in Fig. 6. The σ_f of the Ni-Si-B alloys containing 8%B increases from 2800 MPa for the amorphous single phase to 3200 MPa for the mixed structure. A similar increase in σ_f from 2400 MPa to 3400 MPa is also recognized for the $\text{Ni}_{90-x}\text{Si}_x\text{B}_{10}$ alloys. It should be noticed that the highest σ_f value (3400 MPa) attained for the mixed structure is about 1.4 times as high as the previously reported highest value (2500 MPa)⁽¹¹⁾ for the amorphous single phase in the Ni-Si-B system. In addition to the increase in σ_f , ϵ_f also increases in the mixed structure and the alloy composition where the maximum ϵ_f value is

Fig. 5 Changes in Young's modulus (E) and Vickers hardness (H_v) as a function of B content for rapidly solidified $\text{Ni}_{95-x}\text{Si}_5\text{B}_x$, $\text{Ni}_{92-x}\text{Si}_8\text{B}_x$, $\text{Ni}_{90-x}\text{Si}_{10}\text{B}_x$ and $\text{Ni}_{88-x}\text{Si}_{12}\text{B}_x$ alloys. Open, semiclosed and closed marks represent an amorphous single phase, coexistent amorphous and Ni phases and a crystalline phase, respectively.

found agrees with that for σ_f . It is thus concluded that the homogeneous precipitation of the nanoscale fcc-Ni particles causes the increase in ϵ_f as well as in mechanical strength. This tendency agrees with that for Al-(4)(5) and Mg-(8)(9) base amorphous alloys containing nanoscale fcc-Al and hcp-Mg particles, respectively.

In order to increase the mechanical strength of the Ni-Si-B alloys with the coexistent amorphous and fcc-Ni phases, the effect of the addition of the transition metal ($M=\text{Ti, Zr, V, Nb, Cr, Mo, Mn, Fe}$ or Al) on the mechanical properties was investigated for $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{M}_3$ alloys. As summarized in Table 1, the effectiveness on the increase in the glass-forming ability, σ_f and ϵ_f is the highest for Cr and the next highest for Nb. No appreciable effect is recognized for the other M elements. Figure 7 shows the tensile stress-elongation curves for $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$ and $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$ alloys with the coexistent amorphous and fcc-Ni phases, along with the result for $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ with an amorphous single phase. In comparison with the amorphous single phase alloy, σ_f of the Ni-Si-B ternary alloy increases to 3400 MPa by the homogeneous precipitation of nanoscale fcc-Ni particles, accompanying the increase in E to 130 GPa. The further increase in σ_f to 3900 MPa as well as the increase in ϵ_f to 3.8% is recognized for the Cr-containing alloy,

Fig. 6 Changes in σ_f and ϵ_f as a function of B content for rapidly solidified $\text{Ni}_{95-x}\text{Si}_5\text{B}_x$, $\text{Ni}_{92-x}\text{Si}_8\text{B}_x$, $\text{Ni}_{90-x}\text{Si}_{10}\text{B}_x$ and $\text{Ni}_{88-x}\text{Si}_{12}\text{B}_x$ alloys. Open, semi-closed and closed marks represent an amorphous single phase, coexistent amorphous and Ni phases and a crystalline phase, respectively.

Table 1 Glass-forming ability evaluated from the critical ribbon thickness for formation of an amorphous phase, σ_f and ϵ_f for rapidly solidified $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{M}_3$ ($\text{M} = \text{Ti}, \text{Zr}, \text{V}, \text{Nb}, \text{Cr}, \text{Mo}, \text{Mn}, \text{Fe}$ or Al) alloys.

M element	Glass-forming ability	Tensile fracture strength, σ_f	Tensile fracture elongation, ϵ_f
Ti	no change	decrease	no change
Zr	increase	decrease	no change
V	no change	decrease	increase
Nb	increase	no change	increase
Cr	no change	increase	increase
Mo	increase	decrease	no change
Mn	increase	decrease	increase
Fe	no change	decrease	decrease
Al	no change	decrease	no change

but the E value decreases to 116 GPa. The decrease in E is presumably due to the decrease in the volume fraction of the fcc-Ni particles because the dissolution of Cr causes an increase in the glass-forming ability⁽¹²⁾. The significant increase in σ_f is presumably due to the decrease in the particle size of the fcc-Ni particles resulting from the increase in the glass-forming ability. In addition to the formation of the finer mixed structure, the increase in σ_f seems to be attributed to the more attractive bonding force⁽¹³⁾ between Cr and Si or B atoms as

Fig. 7 Stress-elongation curves of $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ alloy with an amorphous single phase and $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$ and $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$ alloys with coexistent amorphous and fcc-Ni phases.

compared with that between Ni and Si or B atoms. The highest σ_f value attained in the present study reaches 3900 MPa which is about 1.6 times as high as the highest value⁽¹¹⁾ of the Ni-base amorphous alloys. The possibility of enhancing mechanical strength of amorphous wires in Ni-Si-B systems through the structural modification is under investigation with the aim of developing high-strength wires without ferromagnetism. Figure 8 shows the tensile fracture surface appearance of the $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ alloy with the amorphous single phase and the $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$ alloy with the coexistent amorphous and fcc-Ni phases. Although the fracture surface of the former alloy consists of smooth and vein regions, that of the latter alloy contains a remarkable ledge pattern as well as the smooth pattern, indicating an increase in the degree of viscous flow at the final fracture stage. The increase in the viscous flowability is presumably because of the increase in the fracture strength by the precipitation of the nanoscale fcc-Ni particles which causes the increase in the degree of adiabatic deformation at the final instantaneous fracture stage.

IV. Discussion

In this section, we shall discuss the mechanism for the increase in the mechanical strength of the Ni-Si-B alloys with the coexistent amorphous and fcc-Ni phases, in comparison with that for the amorphous single phase. Considering that all the mechanical strengths of σ_f , H_v and E increase in the mixed structure, the nanoscale fcc-Ni particles are presumed to have a mechanical strength higher than that of the amorphous single phase. It has recently been reported⁽⁵⁾ that no appreciable internal defects are observed in the nanoscale fcc-Al particles with a particle size of 3 to 7 nm embedded in the amorphous matrix for $\text{Al}_{88}\text{Ni}_{10}\text{Y}_2$ and $\text{Al}_{88}\text{Ni}_9\text{Y}_2\text{Fe}_1$ alloys as well as in nanoscale hcp-Mg particles in rapidly solidified $\text{Mg}_{85}\text{Zn}_{12}\text{Ce}_3$ and $\text{Mg}_{85}\text{Zn}_{12}\text{La}_3$ alloys⁽¹⁴⁾. No definite evidence of the absence of internal defects in the fcc-Ni particles is obtained even in the high-resolution electron micrograph shown in Fig. 4. However, considering the

Fig. 8 Tensile fracture surface appearance of rapidly solidified Ni-Si-B alloys. (a) $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ with an amorphous single phase, (b) $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$ with coexistent amorphous and fcc-Ni phases.

similarities of the particle size among the fcc-Al, hcp-Mg and fcc-Ni particles as well as the structural control method, it is reasonable to consider that the nanoscale fcc-Ni particles also have a defect-free structure. It is well known⁽¹⁵⁾ that the formation of a defect-free phase gives rise to an ultra-high mechanical strength comparable to a theoretical strength value of each constituent element. It may be therefore concluded that the achievement of the ultra-high mechanical strengths exceeding that of the corresponding amorphous phase is due to the homogeneous dispersion of the defect-free fcc-Ni particles which have mechanical strengths higher than that of the amorphous single phase. Furthermore, the size of the dispersed fcc-Ni particles also seems to have an important meaning for the mechanical properties. As illustrated in Fig. 9, the deformation of an amorphous alloy at room temperature

occurs inhomogeneously along the maximum shear plane, i.e., in the so-called shear bands⁽¹⁶⁾ with a thickness of 10 to 20 nm⁽²⁾. Accordingly, the present results seem to suggest that the defect-free dispersed particles can act as an effective barrier to suppress the shear deformation of the amorphous matrix when the size of the dispersed particles is comparable to or smaller than the thickness of the shear bands. In this case, propagation of shear deformation along the same shear plane may be suppressed giving an increase in the total elongation of the specimens. The above-described model can well explain the observed fact that the homogeneous dispersion of defect-free fcc-Ni particles with nanoscale particle size gives rise to the simultaneous increase in σ_f , E , H_v and ε_f of the Ni-Si-B amorphous alloys.

V. Summary

Microstructure and mechanical properties of rapidly solidified Ni-Si-B ternary and $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{M}_3$ (M=transition metal) quaternary alloys have been examined in order that of investigating the possibility that the high mechanical strength exceeding that of the amorphous single phase may be obtained in the coexistent amorphous and fcc-Ni phases. The results obtained are summarized as follows.

(1) The mixed phase consisting of homogeneously dispersed fcc-Ni particles and the amorphous matrix is obtained in a wide composition range of 5 to 14 at%Si and 7 to 15%B. The composition range is located at the lower solute concentration side as compared with that for the amorphous single phase.

(2) The fcc-Ni particles have a spherical or an ellipsoidal morphology and the particle size and interparticle distance are as small as 10 and 20 nm, respectively.

(3) The mixed phase alloys are higher in mechanical strength than the corresponding amorphous single phase,

Fig. 9 Schematic illustration showing the mechanism for the shear deformation for an amorphous single phase (a) and coexistent amorphous and fcc-Ni phases (b).

accompanying an increase in fracture elongation, and the highest values of σ_f , E , H_v and ε_f are 3400 MPa, 130 GPa, 960 and 2.7%, respectively, for $\text{Ni}_{81}\text{Si}_{10}\text{B}_9$. The increase in mechanical strength is presumably because the nanoscale fcc-Ni particles are in a defect-free state.

(4) The addition of Cr is very effective for the further increase in σ_f and ε_f , and the highest values of σ_f and ε_f , attained are as high as 3900 MPa and 3.8%, respectively, for $(\text{Ni}_{0.81}\text{Si}_{0.1}\text{B}_{0.09})_{97}\text{Cr}_3$. The effectiveness is presumably due to the further refinement of the nanoscale fcc-Ni particles resulting from an increase in the glass-forming ability by the dissolution of Cr, in addition to the increase in bonding force between Cr and Si or B atoms as compared with that between Ni and Si or B atoms.

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