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Nonequilibrium phases in rapidly quenched Co–C–Si and Ni–C–Si alloys

A. INOUE, S. FURUKAWA*, T. MASUMOTO
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

It has been found that the rapid quenching of Co–C–Si and Ni–C–Si alloys results in the formation of an amorphous phase in the range above 10 at% C and 12 to 23 at% Si in the Co–C–Si system, and a nonequilibrium ordered bcc β' phase with a lattice parameter of 0.2744 nm in the range above 4 at% C and 15 to 21 at% Si in the Ni–C–Si system. Since the interaction between cobalt and carbon is repulsive, the glass formation in the high metalloid concentration range in the Co–C–Si system is thought to be attributed to a strongly attractive interaction between metalloid atoms (carbon and silicon). Crystallization temperature and Vickers hardness of the amorphous alloys are in the range of 671 to 708 K and 833 to 942 diamond pyramid number (DPN) respectively. Furthermore, the amorphous alloys exhibit a soft ferromagnetism and the Curie temperature, saturated magnetization under an applied field of 100 Oe, coercive force and permeability at 1 kHz are 395 to 432 K, 4.33 to 5.50 kG, 0.031 to 0.210 Oe and 31 000, respectively, in the as-quenched state. The effective permeability of $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ amorphous alloy is higher than that of $Co_{67}Fe_4Si_{19}B_{10}$ amorphous alloy with zero magnetostrain at frequencies above 200 kHz. Accordingly, the Co–C–Si amorphous alloys newly found in the present work are very attractive as a soft ferromagnetic material with good characteristics in the high frequency range.

1. Introduction

Melt quenching of alloys has generally been known to result in the formation of supersaturated solid solution, nonequilibrium crystalline phase and amorphous phase. However, there is no report on the formation of nonequilibrium phases in Co–C–Si and Ni–C–Si alloys with high concentrations of carbon and silicon. This is presumably because these alloy systems can not be expected to have a great rapid quenching effect. The presumption results from the information that (i) silicon can dissolve into cobalt and nickel up to as much as about 10 to 12 at% [1]; and (ii) the formation energy of cobalt- and nickel-rich carbide has positive values [2], hence the interaction between these atoms is repulsive. Most recently, even in Ni–B–C systems with a repulsive interaction of Ni–C atoms, it has been found [3] that an amorphous phase is formed in a very wide composition range from 11 to 54 at% boron and 0 to 20 at% carbon. This unexpected finding has been interpreted [3] to originate from the enhancement of the glass-forming tendency through a strongly attractive interaction between the metalloid atoms (boron and carbon). From the various properties of SiC compound [4], the C–Si bonding in Co–C–Si and Ni–C–Si alloys is also thought to be attractive and rather strong. It is therefore expected that a nonequilibrium phase, such as amorphous, is formed in a high metalloid concentration region in rapidly quenched Co–C–Si and Ni–C–Si alloys. The aims of this paper are (i) to clarify the compositional dependence of structure in rapidly quenched Co–C–Si and Ni–C–Si alloys and the mechanical properties, thermal stability and magnetic properties of nonequilibrium phases, especially an amorphous phase, produced by rapid quenching, and (ii) to investigate the feature of properties of the present nonequilibrium phases by comparing with the data of the other alloy systems.

2. Experimental procedures

The specimens used in the present work were $Co_xC_ySi_z$ and $Ni_xC_ySi_z$ ternary alloys. The subscripts are nominal atomic percentages of weighed values. Mixtures of electrolytic pure metals (99.9 wt% Co and 99.97 wt% Ni), pure charcoal and Si (99.99 wt%) were melted in a purified argon atmosphere using an arc furnace. Ribbon specimens of 1 mm width and about 0.02 mm thickness were prepared by directing a stream of molten alloy onto the outer surface of a rapidly revolving copper roller.

The rapidly quenched phases were examined by X-ray diffractometry, transmission electron microscopy (TEM) and differential thermal analysis (DTA). The TEM samples were electrolytically thinned in an electrolyte consisting of 90 parts ethyl alcohol and 10 parts perchloric acid, the electrolyte being cooled to approximately 273 K. Hardness and fracture strength were measured with a Vickers microhardness tester using a 100 g load and an Instron-type tensile testing machine at a strain rate of 8.3×10^{-4} sec^{-1}. Ductility

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*Permanent address: Unitika Research and Development Center, Unitika Ltd., Uji 611, Japan.

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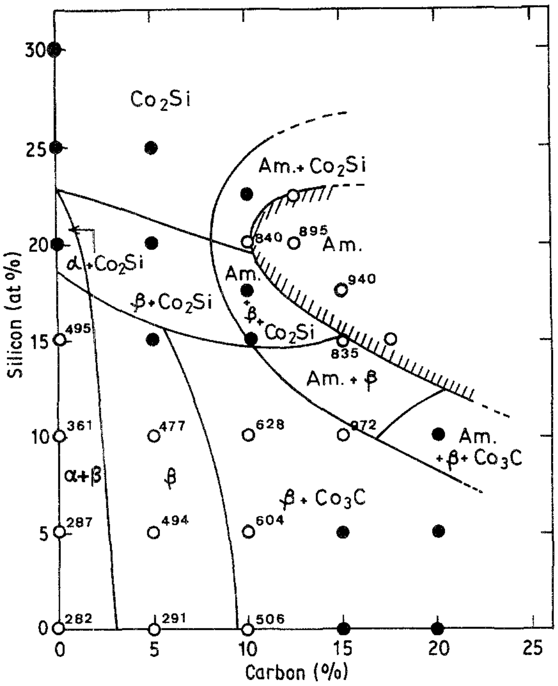

Figure 1 Compositional dependence of rapidly quenched structure in Co–C–Si alloys. The numbers in the figure represent the Vickers hardness. ○, Ductile; ●, brittle.

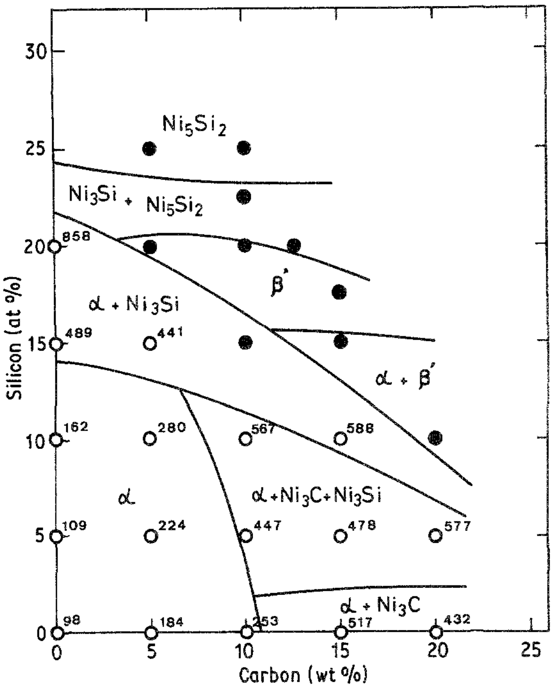

Figure 2 Compositional dependence of rapidly quenched structure in Ni–C–Si alloys. The numbers in the figure represent the Vickers hardness. ○, Ductile; ●, brittle.

was evaluated in a simple bend test. Magnetic properties of magnetization, Curie temperature, coercive force and permeability were measured using a magnetic balance, a B–H tracer and an impedance analyser.

3. Results

3.1. Rapidly quenched structure

Figs 1 and 2 illustrate the compositional ranges of phases in rapidly quenched Co–C–Si and Ni–C–Si alloys, respectively. The formation of nonequilibrium phases can be seen; an amorphous phase and an fcc β phase in the Co–C–Si system and an ordered bcc β′ phase in the Ni–C–Si system. Their formations are limited to the ranges of 12 to 23 at % Si and above 10 at % C for the amorphous phase, 0 to 16 at % Si and 4 to 9 at % C for the β phase and 15 to 21 at % Si and above 4 at % C for the β′ phase. Additionally, it is seen that the fcc Ni-based solid solution is extended up to the range of 14 at % Si and 11 at % C. No amorphous phase is formed in Ni–C–Si alloys and the β′ phase appears in the high carbon and high silicon range where an amorphous phase in the Co–C–Si system is formed. In Figs 1 and 2, the term "ductile" implies bending through 180° without breaking while "brittle" implies fracture during bending. Ductile samples are limited to the amorphous, β and β + X (X = hcp α-Co or Co$_3$C) phases in the Co–C–Si system and α and α + X (X = Ni$_3$C and/or Ni$_3$Si) phases in the Ni–C–Si system. The formation of an amorphous phase in the Co–C–Si system seen in the present work is a new finding.

Bright-field electron micrographs, selected area electron diffraction patterns and X-ray diffraction patterns showing the rapidly quenched microstructure and crystal structure are shown in Fig. 3 for the β phase in Co$_{85}$C$_5$Si$_{10}$ alloy, Fig. 4 for the amorphous phase in Co$_{70}$C$_{10}$Si$_{20}$ alloy and Fig. 5 for the β′ phase in Ni$_{67.5}$C$_{15}$Si$_{17.5}$ alloy. The β phase consists of equiaxed grains with a size of about 0.4 μm and contains a number of stacking faults. The lattice parameter of the β phase is measured to be 0.3553 nm, being slightly larger than that (0.35447 nm) [5] at 298 K of the β-cobalt phase containing nitrogen and antimony of 0.1 to 1.0%. The increase in lattice parameter is presumably because of the dissolution of large amounts of carbon and silicon. As shown in Fig. 4, no contrast revealing the precipitation of a crystalline phase is seen in rapidly quenched Co$_{70}$C$_{10}$Si$_{20}$ alloy and the electron and X-ray diffraction patterns show only broad halo peaks, indicating the formation of an amorphous single phase. The β′ phase in Ni$_{67.5}$C$_{15}$Si$_{17.5}$ alloy has a grain size of about 0.5 μm and appears to contain a high density of internal defects. From the electron and X-ray diffraction patterns shown in Fig. 5, the β′ phase is identified to be an ordered bcc structure with a lattice parameter of 0.2744 nm. The crystal structure is the same as that of the β′-NiAl compound [6] and the alloy composition suggests that the aluminium site in NiAl compound may be occupied by silicon and/or carbon. Since no β′-type compound is seen in Ni–Si and Ni–C equilibrium phase diagrams [7], the simultaneous dissolution of silicon and carbon is thought to be essential for formation of the ordered bcc β′ compound.

3.2. Mechanical properties

As shown in Figs 1 and 2, H_v of Co–C–Si alloys is 475 to 495 diamond pyramid number (DPN) for the β phase and 835 to 940 DPN for the amorphous phase and that of Ni–C–Si alloys is 100 to 280 DPN for the α phase and 870 to 1215 DPN for the β′ phase. It is thus noticed that the amorphous phase exhibits high hardness combined with good bend ductility. The β′ phase has a high hardness of about 1200 DPN in spite of nonferrous alloys. The high hardness is thought to be attributed to the covalent-like bonding nature

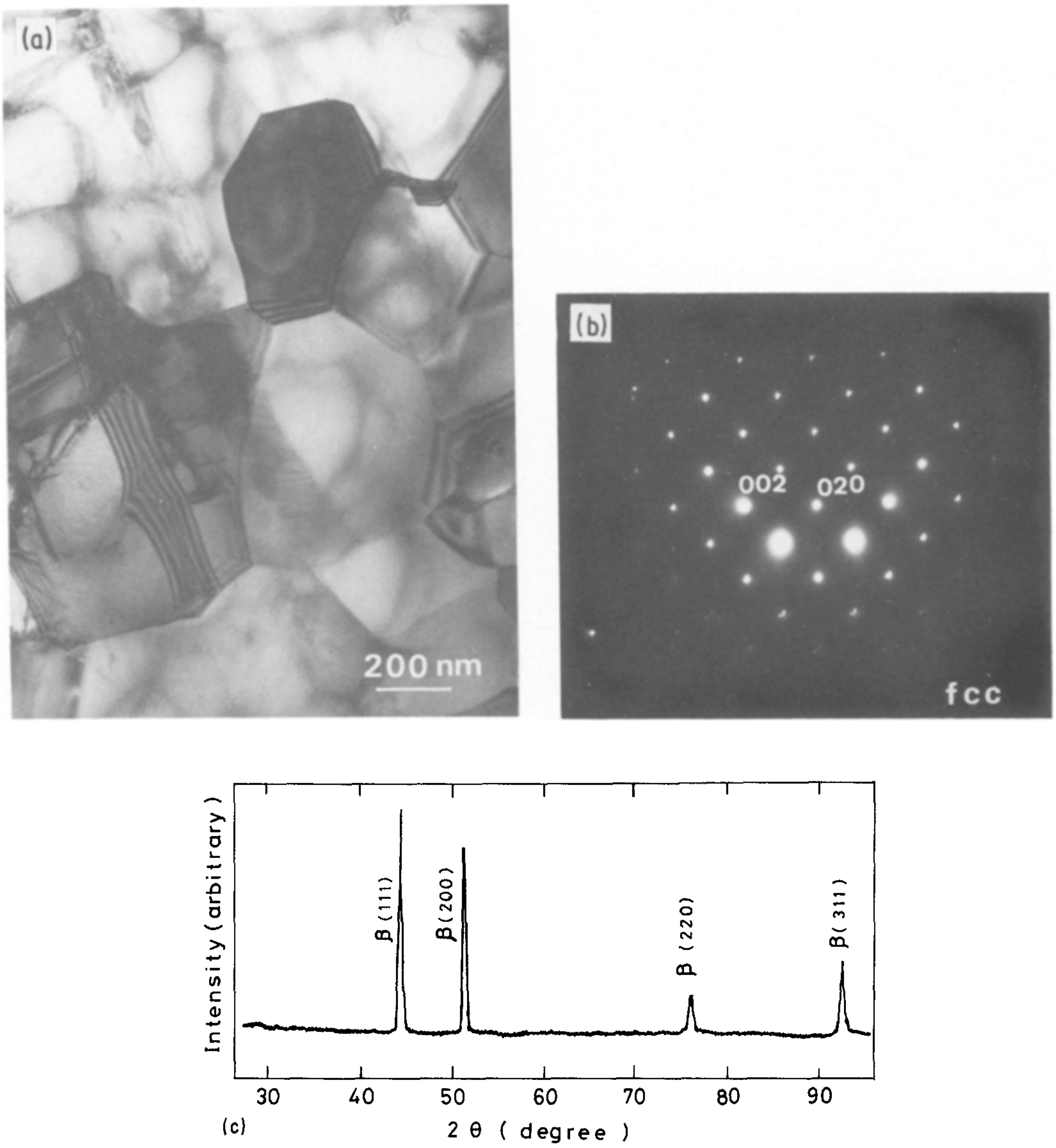

Figure 3 (a) Bright field electron micrograph, (b) selected area electron diffraction pattern and (c) X-ray diffraction pattern of rapidly quenched $Co_{85}C_5Si_{10}$ alloy, fcc phase (β).

of the constituent atoms which is inherent for the β'-NiAl compound with an ordered bcc structure [8].

Continuous wire samples with about 120 μm diameter were found to be prepared for the β phase in the Co–C–Si system and for the α phase in the Ni–C–Si system by melt spinning in rotating water. As an example, Fig. 6 shows stress–elongation curves of the rapidly quenched wires. Proof stress of 0.2% ($\sigma_{0.2}$), tensile fracture strength (σ_f) and elongation (ε_p) are 1190 MPa, 1340 MPa and 2.3%, respectively, for the β wire and 790 MPa, 1000 MPa and 2.9%, respectively, for the α wire. It is thus noticed that rapidly quenched materials with tensile strengths above 1000 MPa and rather good elongation are obtained even in the nonferrous alloys of Co–C–Si and Ni–C–Si systems. The high strength is thought to originate from the solid solution strengthening by carbon and silicon and the strengthening due to the grain size refinement.

3.3. Magnetic and electrical properties

Table I summarizes the magnetic properties of Curie temperature (T_c), residual magnetization (B_r), saturated magnetization under an applied field of 100 Oe (B_{100}), coercive force (H_c) and permeability at 1 kHz (μ'_{max}) and other properties of hardness (H_v), crystallization temperature (T_x) and electrical resistivity at room temperature ($\varrho_{R.T.}$) for Co–C–Si and Co–Fe–C–Si amorphous ribbons prepared newly in the present study. The data [9] for a Co–Fe–Si–B amorphous alloy with almost the same metalloid content are also shown for reference. T_c and B_{100} of Co–C–Si and $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ alloys are 395 to 423 K and 4.33 to 5.50 kG, being almost the same as those of the Co–Fe–Si–B amorphous alloy. However, the Co–C–Si and Co–Fe–C–Si alloys exhibit higher H_c and lower μ'_{max} as compared with the $Co_{65.7}Fe_{4.3}Si_{17}B_{13}$ alloy. The magnetic properties of $Co_{70}C_{10}Si_{20}$ and $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ alloys are hardly improved upon annealing for 1 h at 493 K higher than T_c, even though there remains a possibility that an improvement of soft magnetic properties may occur by choosing a higher annealing temperature close to T_x. Fig. 7 shows the frequency dependence of effective permeability (μ') of $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ amorphous alloy with nearly zero magnetostrain, along with the data [10] of $Co_{67}Fe_4Si_{19}B_{10}$ amorphous alloy

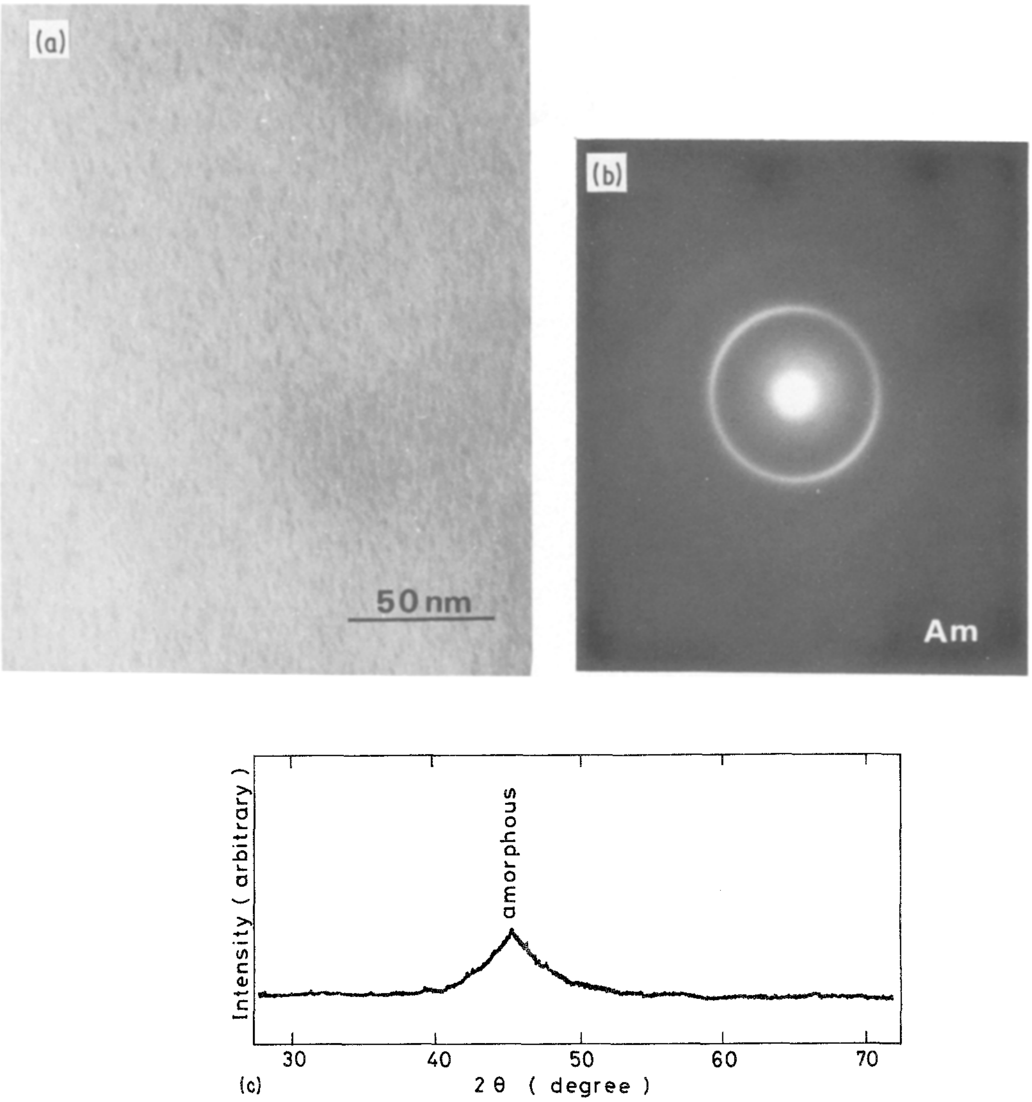

Figure 4 (a) Bright field electron micrograph, (b) selected area electron diffraction pattern and (c) X-ray diffraction pattern of rapidly quenched $Co_{70}C_{10}Si_{20}$ alloy, amorphous phase.

exhibiting zero magnetostrain. The μ' of the Co–Fe–C–Si alloy is almost the same as that of as-quenched $Co_{67}Fe_4Si_{19}B_{10}$ alloy at frequencies below about 200 kHz, and is lower than that of appropriately heat-treated $Co_{67}Fe_4Si_{19}B_{10}$ alloy. However, the μ' values of the Co–Fe–C–Si alloy at frequencies higher than about 200 kHz are considerably higher than those of the Co–Fe–Si–B alloy in as-quenched and heat-treated states, indicating that the magnetic properties of the present Co–Fe–C–Si alloy are rather good in the high frequency range. Although the reason for such good high frequency characteristics for the Co–Fe–C–Si alloy remains unknown at present, a more appropriate heat treatment is expected to result in a further improvement of high-frequency characteristics of Co–Fe–C–Si alloys.

TABLE I Comparison of properties of Co–C–Si and Co–Fe–C–Si amorphous alloys with reference to $Co_{65.7}Fe_{4.3}Si_{17}B_{13}$ amorphous alloy: Vickers hardness (H_v), crystallization temperature (T_x), Curie temperature (T_c), electrical resistivity at room temperature ($\varrho_{R.T.}$), residual magnetization (B_r), saturated magnetization under an applied field of 100 Oe (B_{100}), coercive force (H_c) and permeability at 1 kHz (μ'_{max}).

Alloy (at %)	H_v (DPN)	T_x (K)	T_c (K)	$\varrho_{R.T.}$ ($\mu\Omega$ m)	Condition	B_r (kG)	B_{100} (kG)	H_c (Oe)	μ'_{max} (1 kHz)
$Co_{70}C_{10}Si_{20}$	840	683	423	2.03	As-quenched Water-quenched*	1.81 1.89	5.35 5.50	0.162 0.160	– –
$Co_{67.5}C_{12.5}Si_{20}$	900	671	395	2.24	As-quenched	2.10	4.86	0.210	–
$Co_{67.5}C_{15}Si_{17.5}$	940	708	–	1.85	As-quenched	–	–	–	–
$(Co_{94}Fe_6)_{67.5}C_{12.5}Si_{20}$	840	682	432	1.83	As-quenched Water-quenched*	3.10 2.94	4.34 4.33	0.038 0.031	26.000 31.000
$Co_{65.7}Fe_{4.3}Si_{17}B_{13}$	–	803	420	–	Water-quenched†	–	5.30	0.006	55.000

*Water quenching after annealing for 1 h at 493 K.
†Water quenching after annealing for 1 h at 723 K.

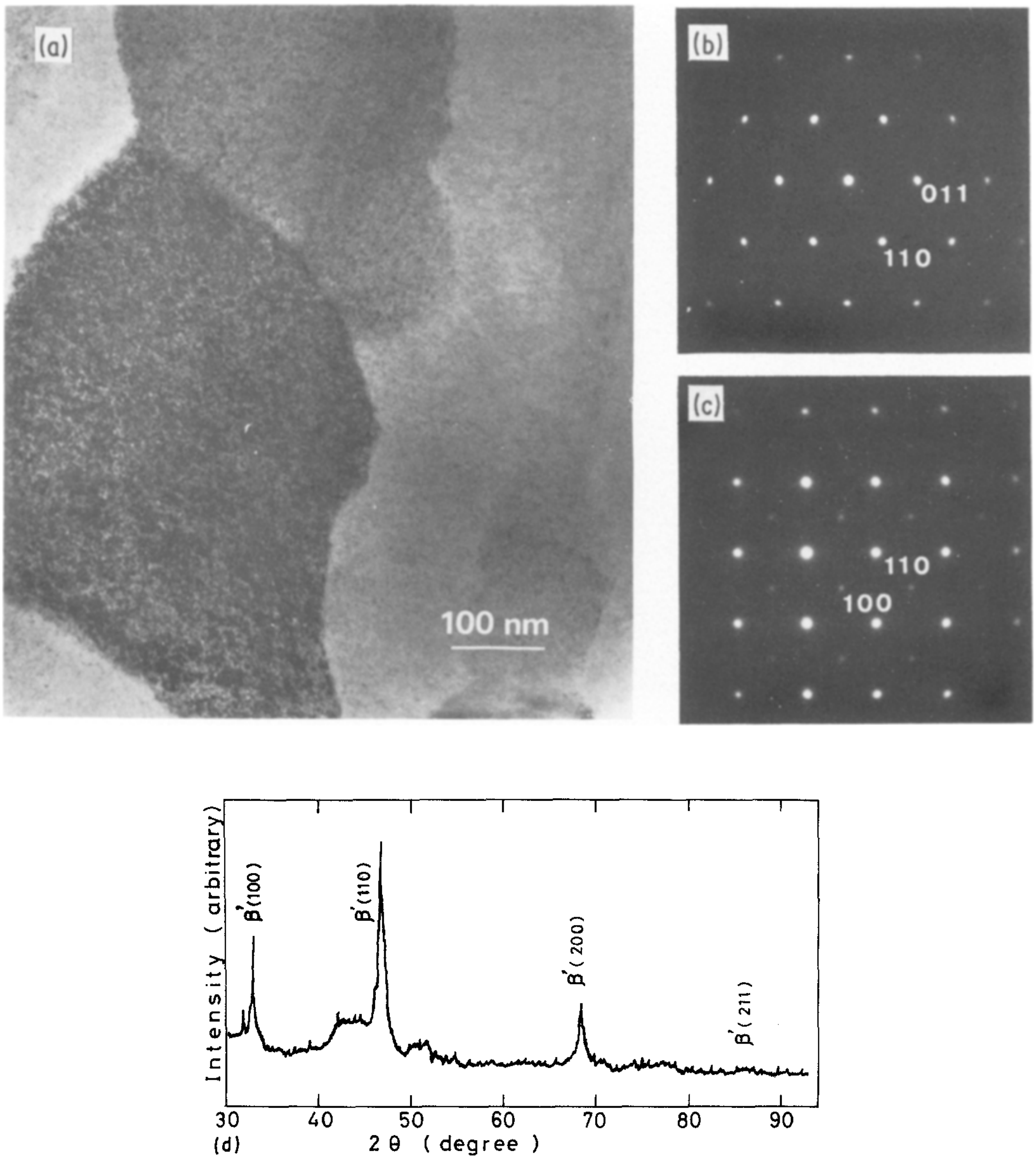

Figure 5 (a) Bright field electron micrograph, (b and c) selected area electron diffraction patterns and (d) X-ray diffraction pattern of rapidly quenched $Ni_{67.5}C_{15}Si_{17.5}$ alloy, ordered bcc phase (β').

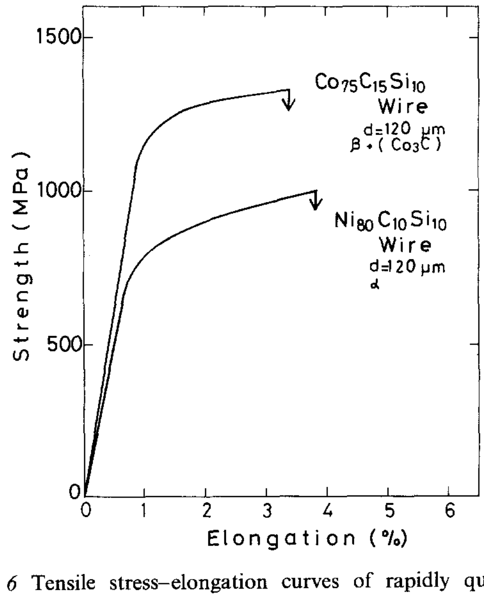

Figure 6 Tensile stress–elongation curves of rapidly quenched $Co_{75}C_{15}Si_{10}$ and $Ni_{80}C_{10}Si_{10}$ wires.

4. Discussion

It was shown in Section 3 that an amorphous single phase of the Co–C–Si system is formed in the high metalloid concentration range of 12 to 23 at % Si and above 10 at % C. Here we discuss the reasons for the formation of the new amorphous phase. An amorphous phase in Co–metalloid systems has been known to be formed in Co–P [11] and Co–B [12, 13] binary, and Co–Si–B [14] and Co–P–B [15] ternary alloys. The free energy of the formation of Co–metalloid compounds in these alloy systems is negative and the bonding nature has a strongly attractive interaction. However, for the Co–C–Si alloys, the Co–C bonding has a positive formation energy [2] and the addition of carbon into Co–Si alloys is thought to result in decrease of attractive interaction between metal and metalloids through the increase of the number of the repulsive bonding between cobalt and carbon. As shown in Fig. 1, the simultaneous dissolution of silicon and carbon is essential for the formation of an amorphous phase in Co–C–Si alloys and the lack of either carbon or silicon causes a disappearance of the amorphous phase. The enhancement of the glass-forming ability of Co–C–Si alloys

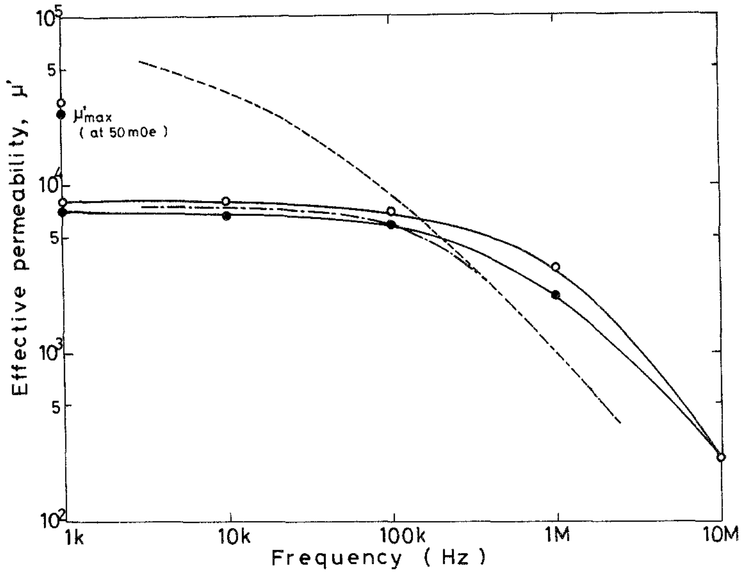

Figure 7 Effective permeability μ' at a driving field of 10 mOe as a function of frequency for $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ amorphous alloy. ●, As-prepared; ○, 493 K annealed, water quenched. The data of $Co_{67}Fe_4Si_{19}B_{10}$ amorphous alloy at 4 mOe are also shown for comparison. —·—·—, As-prepared; - - - 723 K annealed, water quenched.

by the dissolution of carbon is thought to originate from a strongly attractive interaction between silicon and carbon metalloids, as pointed out previously for Ni–B–C amorphous alloys by the present authors [3]. From the large values of melting temperature (T_m), Vickers hardness (H_v), formation energy (ΔH) of the SiC compound [4], the bonding between silicon and carbon atoms is thought to be very strong. The strong bonding nature between carbon and silicon is thought to cause a decrease of atomic mobility in Co–C–Si supercooled liquid with high concentrations of silicon and carbon and a rapid increase of viscosity with lowering temperature, leading to an enhancement of the formation ability of Co–C–Si amorphous phase in the high carbon and silicon concentration range. It has previously been reported [3] that an amorphous phase in Ni–B–C system is formed in the boron-rich composition range of 11 to 54 at % B and 0 to 20 at % C and the formation is due to a strongly attractive interaction between boron and carbon. The previous result allows us to expect that the amorphous phase in Co–C–Si alloys is formed in a more carbon and silicon-rich composition range as compared with the glass-formation range shown in Fig. 1. However, the further increase in carbon and silicon contents makes the preparation of a rapidly quenched ribbon through a rise of T_m difficult, and hence the glass-formation range of Co–C–Si alloys at the carbon- and silicon-rich side could not be determined. Even though the interaction between metal and metalloid atoms has generally been known [16] to be a dominant factor to form an amorphous phase, it is concluded that the attractive interaction between metalloids can also play an important role on the glass formation. By extending this concept, the glass formation in Fe–C–Si [17] and Co–C–B [18] systems has newly been found in the high metalloid composition range and hence this concept is proposed as a guiding principle to look for a new amorphous phase in metal–metalloid alloys with high metalloid concentrations.

5. Summary

Compositional dependence of phases in rapidly quenched Co–C–Si and Ni–C–Si alloys was examined by X-ray diffractometry, TEM and DTA. The results obtained are summarized as follows.

1. Amorphous and fcc β phases in the Co–C–Si system and an ordered bcc β' phase in the Ni–C–Si system were formed as nonequilibrium phases. The formation ranges of their phases are above 10 at % C and 12 to 23 at % Si for the amorphous phase, 4 to 9 at % C and 0 to 16 at % Si for the β phase, and above 4 at % C and 15 to 21 at % Si for the β' phase. Additionally, an fcc supersaturated solid solution (α) in the Ni–C–Si system was formed in the range below about 11 at % C and 14 at % Si.
2. The glass formation in the high metalloid concentration range for Co–C–Si alloys is thought to be attributed to a strongly attractive interaction between silicon and carbon atoms, because the dissolution of carbon into Co–Si alloys results in a decrease of attractive bonding nature between metal and metalloids through the increase of the number in Co–C bonding with repulsive interaction.
3. T_x and H_v of the Co–C–Si amorphous phase are 671 to 708 K and 833 to 942 DPN, respectively. Furthermore, the amorphous alloys exhibit a soft ferromagnetism and the values of T_c, B_{100}, H_c and μ'_{max} are 395 to 432 K, 4.33 to 5.50 kG, 0.031 to 0.210 Oe and 31 000, respectively, in the as-quenched state.
4. The effective permeability (μ') of the $(Co_{0.94}Fe_{0.06})_{67.5}C_{12.5}Si_{20}$ amorphous alloy at frequencies higher than about 200 kHz is considerably better than that of the $Co_{67}Fe_4Si_{19}B_{10}$ amorphous alloy with zero magnetostrain, indicating the possibility that the Co–Fe–C–Si amorphous alloy exhibits an excellent high-frequency characteristic.
5. A continuous wire with about 120 μm diameter was prepared for $Co_{75}C_{15}Si_{10}$ with the β phase and $Ni_{80}C_{10}Si_{10}$ with the α phase. The $\sigma_{0.2}$, σ_f and ε_p of the wires are 1190 MPa, 1340 MPa and 2.3% respectively, for β phase and 790 MPa, 1000 MPa and 2.9%, respectively, for α phase. The high strengths are presumably because of a great solid solution strengthening by carbon and silicon and the refinement of grain size.

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