Formation Range, Mechanical Properties and Thermal Stability of Superconducting Zr-Si Amorphous Alloys

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Synopsis

New type of refractory metal-metalloid amorphous alloys containing less than 20 at% Si have been found in binary Zr-Si system by a modified melt-spinning technique for high melting point alloys. Specimens are in the form of continuous ribbons of 1-2 mm width and 0.02-0.03 mm thickness. The silicon content in the amorphous range is limited to the range 12 to 24 at%. The Vickers hardness increases from 395 to 495 DPN with increasing silicon content and the tensile strength is of the order of 1400 MPa. Crystallization temperature is the lowest(720 K) at $Zr_{83}Si_{17}$, increases with decreasing and increasing silicon content and reaches 804 K at $Zr_{88}Si_{12}$ and 768 K at $Zr_{76}Si_{24}$. The activation energy for crystallization is in the range 175 to 202 kJ/mol. These amorphous alloys are so ductile that no cracks are observed even after closely contacted bending test. The good ductility remains unchanged for 3.6 ks at temperatures below 650 K. Further, these amorphous alloys exhibit a superconducting transition which occurs very sharply. The superconducting transition temperature(T_c) increases with decreasing silicon content and reaches a maximum value of 3.2 K for $Zr_{88}Si_{12}$. Thus, the Zr-Si amorphous alloys are a superconductor which possesses the T_c values higher than zirconium metal in addition to high strength combined with good ductility.

I. Introduction

As an amorphous alloy containing a large amount of zirconium, metal-metal type amorphous alloys such as Zr-Be, Zr-Cu, Zr-Ni, Zr-Co and Zr-Fe and so forth have been found by a conventional melt-spinning

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technique[1]. However, the amorphous-phase formation of metal-metalloid type alloys containing zirconium as a major component has not been investigated in spite of the expectation that their amorphous alloys may exhibit a superconductivity better than the crystalline state[2] and active chemical characters such as hydrogen absorption[3]. This is probably because of the experimental difficulty due to the facts that the zirconium-based alloys have melting points much higher than Zr-M (M=Cu, Ni, Co or Fe) alloys and zirconium is a very active metal.

Recently, we have carried out systematic experiments of the amorphous-forming tendency of Zr-(B, C, Si, Ge, Al or Sn) binary and Zr-M-(B, C, Si, Ge, Al or Sn) (M=IV-VIII group transition metals) ternary and quaternary alloys using the modified melt-spinning apparatus constructed for refractory metal-based alloys, with a view to finding a good superconducting amorphous alloy combined with high strength as well as good ductility, and have found that the rapidly quenched Zr-Si binary and Zr-M-Si ternary alloys exhibit an amorphous single phase in a relatively wide composition range. The aim of this paper is to report the composition range for the formation of an amorphous phase for Zr-Si binary system and the mechanical properties, thermal stability and superconducting properties of the amorphous alloys.

II. Experimental Methods

Mixtures of 99.6 wt% zirconium and 99.999 wt% silicon were melted in an arc furnace in a water-cooled copper hearth with a non-consumable tungsten electrode. Melting was accomplished under a purified and gettered argon atmosphere at a pressure of about 8×10^4 Pa. The weight of the mixture melted in one run was about 30 g. The ingots were repeatedly turned over and remelted to insure homogeneity of composition. The compositions are determined by the weighed values in atomic percent since the difference between weighed and chemically analyzed compositions is less than 0.05 wt% for silicon.

Continuous ribbon specimens of about 1-2 mm width and 0.02-0.03 mm thickness were prepared from these master alloys under a protective argon atmosphere using a modified single-roller melt spinning apparatus adapted to a levitation furnace described in Ref. 4. Typically, the amount of alloys melted in one run was about 3 g and the rotation speed of the copper roller (20 cm in diameter) was about 4000 rpm.

Identification of the as-quenched phases was made by conventional x-ray diffraction method and transmission electron microscopy. The ribbons were classified to be amorphous when their x-ray intensities as a function of diffraction angle showed a typical liquid like structure.

Hardness and tensile strength of the amorphous ribbons were measured by a Vickers microhardness tester with a 100 g load and an Instron-type tensile testing machine at a strain rate of 4.17×10^{-4} /s, respectively. The crystallization temperature, the activation energy for crystallization and the heat of crystallization were examined by a differential scanning calorimeter(DSC) at various heating rates of 0.083-1.33 K/s. The ductile-brittle transition behavior was tested for the specimens annealed for different periods at various temperatures in evacuated silica capsules. Ductility was evaluated by measuring the radius of curvature at fracture in a simple bend test. The deformation structure by bending and the fracture surface by tension were observed by a scanning electron microscope. Methods to evaluate the superconducting properties have been described in Ref. 5.

III. Results and Discussion

1. Formation range of the amorphous phase

The composition range in which the amorphous phase forms without any trace of crystallinity in the Zr-Si binary system is shown in Fig. 1, wherein the equilibrium phase diagram is also represented for comparison. The amorphous phase forms in the relatively wide range 12 to 24 at% Si. Also, one can notice that the alloys containing less than about 12 at% Si exhibit a nonequilibrium crystalline phase with a

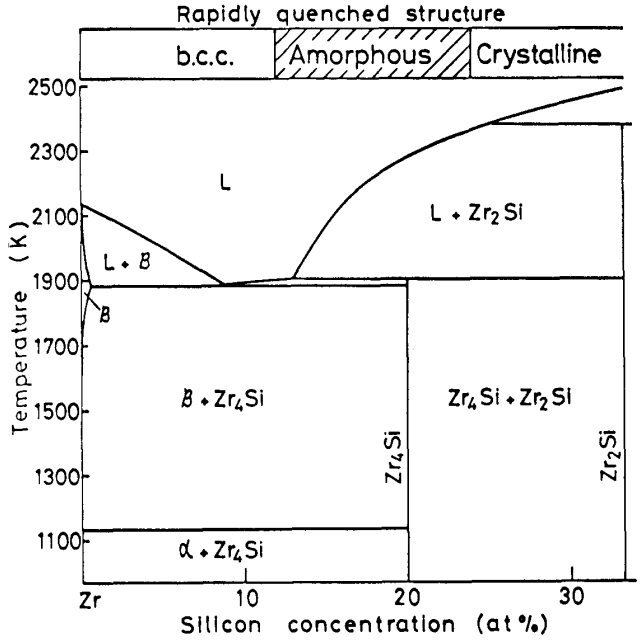

Fig. 1 Composition range for the formation of an amorphous phase in Zr-Si binary system. Binary phase diagram was adopted from Ref. 6.

b.c.c. structure. As examples, typical electron micrographs of the b.c.c. phase in $Zr_{91}Si_9$ alloy and the amorphous phase in $Zr_{85}Si_{15}$ alloy (all compositions are expressed in atomic percent as subscripts) are shown in Fig. 2, together with their selected area diffraction patterns. Lack of contrast in the bright field image for the latter alloy (Fig. 2 (c)) and the presence of diffuse haloes in the diffraction pattern (Fig. 2 (d)) clearly indicate that the $Zr_{85}Si_{15}$ alloy is amorphous. No evidence of crystalline inclusions was found by dark field electron microscopy for the alloys within the composition range described above. On the other hand, the b.c.c. phase in $Zr_{91}Si_9$ alloy contains numerous internal defects (Fig. 2 (a)) and the corresponding diffraction pattern taken by the aperture having the diameter $\simeq$ 0.2 μm shows many reflection spots which extend along the circumferential direction, indicating that the b.c.c. single phase consists of numerous subgrains with sizes less than about 100 nm.

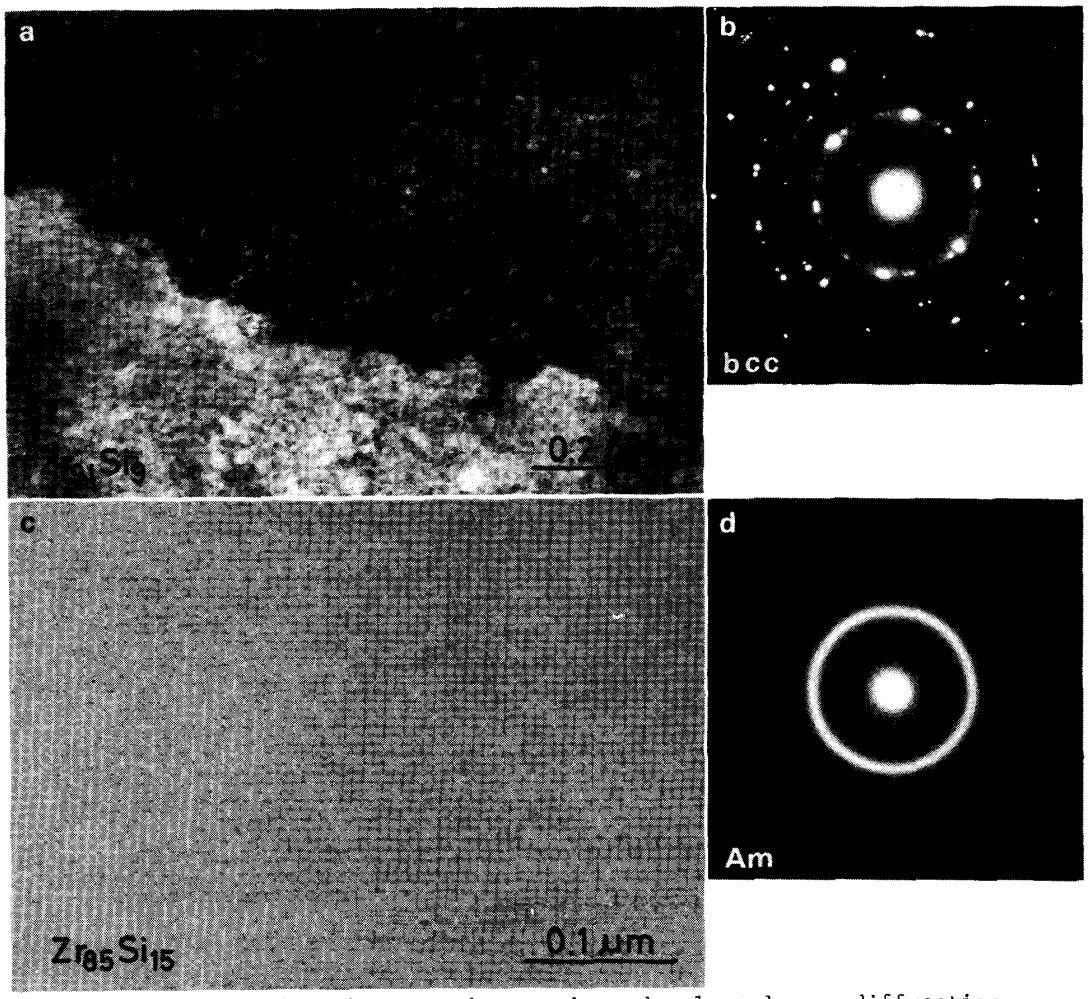

Fig. 2 Transmission electron micrographs and selected area diffraction patterns showing the as-quenched structure of $Zr_{91}Si_9$ (a and b) and $Zr_{85}Si_{15}$ (c and d) alloys.

Turnbull[7] has noted that a deep eutectic in an alloy system is connected with a comparatively large negative heat of formation. This view suggests that the formation of an amorphous phase may be the easiest for a eutectic alloy which has a deep trough in melting temperature. In fact, many amorphous phases have been detected in alloys corresponding to the eutectic compositions[8]. However, the eutectic alloy $Zr_{91}Si_9$ in Zr-Si system[6] exhibits only the b.c.c. phase shown in Fig. 2 (a) and (b) as a quenched structure. It is to be noticed that the formation range of the amorphous phase in binary Zr-Si system deviates largely from the eutectic point which is located at 8.8 at% Si[6], and lies in the vicinity of the Zr_4Si compound. This result suggests that a strong chemical interaction between metal and metalloid atoms plays an important role in forming an amorphous phase, in addition to the deep trough of melting temperature. Another reason for such a deviation of the amorphous-forming region from the eutectic point appears to be due to the lean metalloid content. Considering the previous results[8] that the formation of an amorphous phase in binary alloys is commonly limited to the metalloid range about 13 to 30 at%, it may be said that the silicon content (≃9 at%) at the eutectic composition is too low to form the amorphous phase of Zr-Si alloys.

2. Mechanical properties and crystallization temperature

Vickers hardness(H_V) of Zr-Si amorphous alloys is shown in Fig. 3. Their hardness values are the average over seven measurements. The H_V

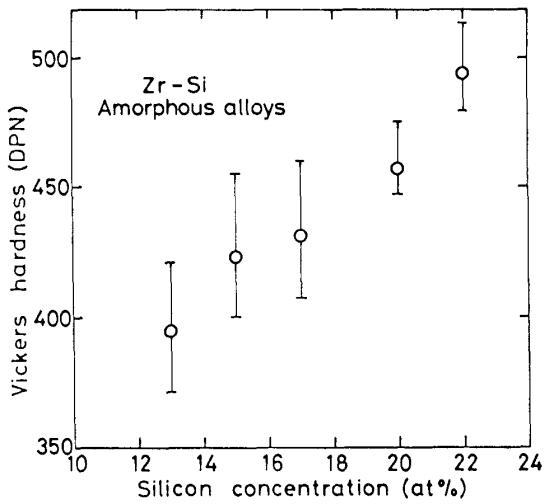

Fig. 3 Change in Vickers hardness(H_V) for Zr-Si amorphous alloys with silicon content.

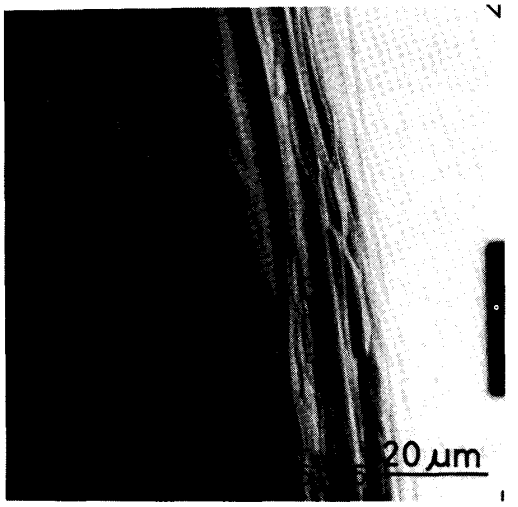

Fig. 4 Scanning electron micrograph showing the deformation marking at the tip of $Zr_{85}Si_{15}$ amorphous alloy bent through 180° around the edge of a thin razor blade.

gradually increases with the amount of silicon and reaches about 495 DPN for $Zr_{78}Si_{22}$ alloy. The fracture strength is about 1390 MPa for $Zr_{85}Si_{15}$ alloy. Further, the alloys possess very good bend ductility. Figure 4 shows the deformation structure of $Zr_{85}Si_{15}$ amorphous alloy bent completely around the edge of a thin razor blade. While numerous deformation markings can be seen near the bent edge, no cracks are observed. Even when $Zr_{85}Si_{15}$ amorphous alloy is annealed for 3.6 ks at various temperatures up to about 670 K, its good ductility remained unchanged. The activation energy for embrittlement for $Zr_{85}Si_{15}$ alloy was estimated to be about 93 kJ/mol by Arrhenius-plotting the time where the specimens annealed at each temperature of 623, 648, 673, 698 and 723 K begin to occur fracture.

Crystallization temperature(T_x) and the activation energy for crystallization (ΔE) determined using the Kissinger method from the temperatures at exothermic peaks on the DSC curve are plotted as a function of silicon content in Figs. 5 and 6. The T_x shows a minimum value(720 K) at $Zr_{83}Si_{17}$, rises with decreasing and increasing silicon content and reaches 804 K at $Zr_{88}Si_{12}$ and 768 K at $Zr_{76}Si_{24}$. On the other hand, the ΔE shows a maximum value (about 202 kJ/mol) in the vicinity of 15 at% Zr and decreases with decreasing and increasing silicon content. Thus, the compositional dependence of ΔE is in contrast with that of T_x, indicating that there is no close correlation between T_x and ΔE. The reason for such a difference of the compositional dependences between T_x and ΔE for Zr-Si amorphous alloys is unknown at present. Since it is expected that the detailed investigation of crystallization behavior will shed some light upon this problem, a systematic investigation on this line is in progress at present.

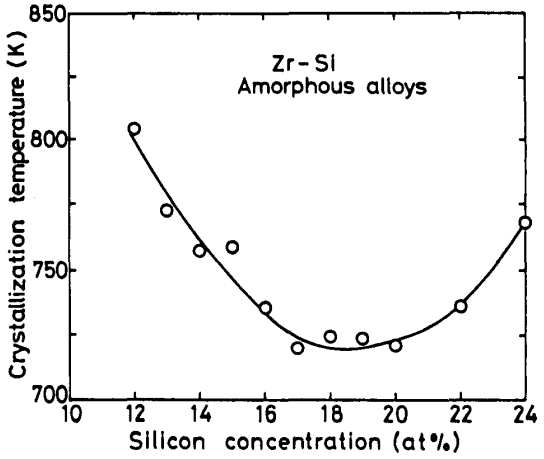

Fig. 5 Change in crystallization temperature(T_x) for Zr-Si amorphous alloys with silicon content.

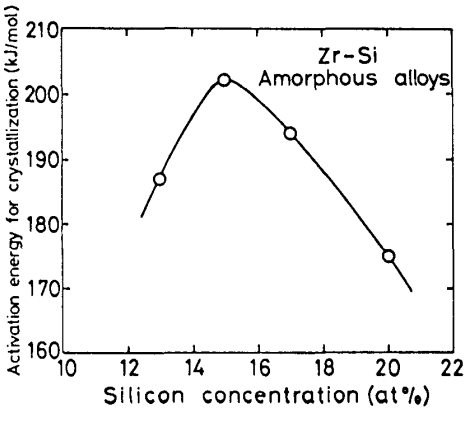

Fig. 6 Change in the activation energy for crystallization(ΔE) for Zr-Si amorphous alloys with silicon content.

4. Superconducting properties

Electrical resistance of several Zr-Si amorphous alloys at low temperatures was measured under no applied magnetic field. The result is shown in Fig. 7. One can notice that the transition occurs very sharply within a temperature width less than 0.1 K, in spite of their electrical resistivities (about 270 μΩcm) much larger than the crystalline alloys. Such a sharp transition indicates that these alloys possess very homogeneous structure on the scale of coherence length as pointed out in Ref. 9. The values of T_c and ΔT_c are plotted in Fig. 8 as a function of silicon content. The values of T_c is taken as the temperature corresponding to R/Rn = 0.5, where Rn is the resistance in the normal state. The transition width ΔT_c is the temperature difference between 0.1 and 0.9 of R/Rn. T_c increases from 2.1 to 3.2 K with decreasing silicon content. It is to be noticed that these T_c values are much higher than that (0.55 K)[10] of zirconium metal. Further, it may be important to note that the T_c value (3.2 K) for the $Zr_{88}Si_{12}$ amorphous alloy is the same level as the highest value of amorphous zirconium metal obtained by vapor-deposition onto a cryogenic substrate, in spite of the dissolution of a relatively large amount of metalloid. Furthermore, from the experimental data of the upper critical magnetic field H_{c2}, the critical current density J_c, $(dH_{c2}/dT)_{T_c}$, the hypothetical upper critical magnetic field determined only by the orbital effect $H^*_{c2}(0)$ and electrical resistivity ρ for Zr-Si amorphous alloys,

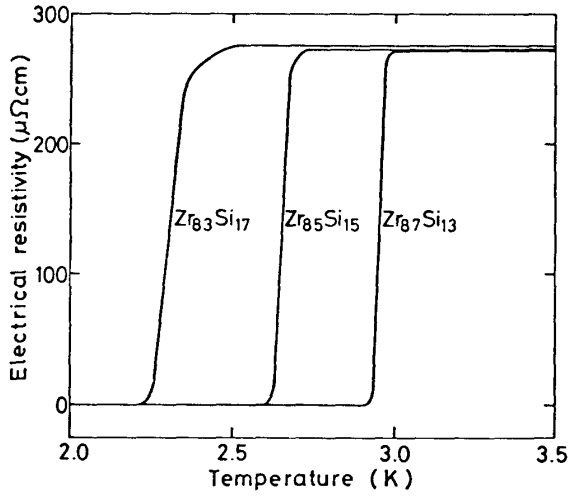

Fig. 7 Electrical resistivity as a function of temperature for several Zr-Si amorphous alloys.

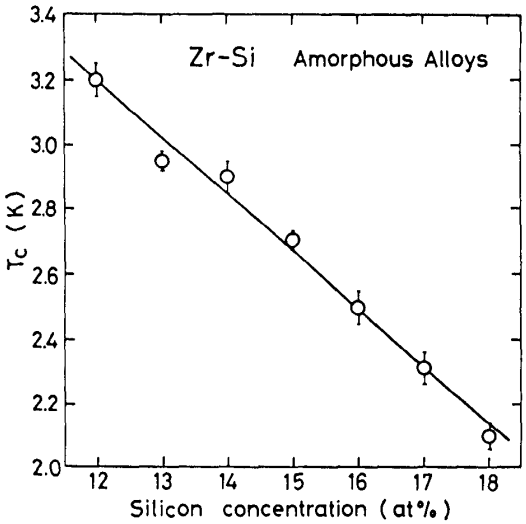

Fig. 8 Changes in the superconducting transition temperature(T_c) and the transition width(ΔT_c) for Zr-Si amorphous alloys with silicon content. Vertical bars represent the transition width.

the Ginzburg-Landau parameter κ and the Ginzburg-Landau coherence length $\xi^*(0)$ are estimated by using the Gorkov-Goodmann relation[11] and the Zr-Si amorphous alloys have been demonstrated to be a typical "soft" type II superconductor with high "dirty limit". The detailed data of these superconducting properties will be presented in the subsequent papers[9,12].

IV. Summary

A new type of amorphous alloys exhibiting superconductivity and high strength combined with highly ductile nature was found in the Zr-Si binary system. Specimens were produced in the form of a continuous ribbon about 1-2 mm wide and about 0.02-0.03 mm thick using a rapid quenching apparatus designed for high melting point alloys. The amorphous single phase was obtained in the composition range of between about 12 and 24 at%. The Vickers hardness and the tensile strength were in the range 395-495 DPN and about 1400 MPa respectively. Crystallization temperature and the activation energy for crystallization were in the ranges of 720 to 804 K and 175 to 202 kJ/mol respectively. Further, these amorphous alloys were so ductile that no crack was found at the tip of a specimen bent through 180° around the edge of a thin razor blade. The ductility remained unchanged for 3.6 ks at temperatures below 670 K for $Zr_{85}Si_{15}$. In addition, the Zr-Si alloys showed a sharp superconducting transition at temperatures below 3.2 K. The transition temperature T_c increased from 2.1 to 3.2 K with decreasing silicon content, being much higher than that of zirconium metal.

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