

PII S0025-5408(99)00099-9

# THE INFLUENCE OF COOLING RATE ON THE FORMATION OF AN AMORPHOUS PHASE IN SI-BASED MULTICOMPONENT ALLOYS AND ITS THERMAL STABILITY

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(Refereed) (Received July 6, 1998; Accepted August 21, 1998)

## ABSTRACT

By adding Ni, Cr, and Zr to the Si–Al–Fe system and using a higher surface velocity of the copper wheel of 63 m/s, the composition range of an amorphous single phase was extended to 60 at% Si. An amorphous  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$  alloy was produced. The amorphous phase in the Si–Al–TM (TM = transition metals) alloys shows higher thermal stability than in the Al–Si–TM alloys. By the shift of differential scanning calorimetry (DSC) peaks with change of heating rate, the activation energy for the transformation was determined to be 343 kJ/mol for  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy and 374 kJ/mol for  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$  alloy. © 1999 Elsevier Science Ltd

KEYWORDS: A. amorphous materials, C. differential scanning calorimetry (DSC), C. electron microscopy

### **INTRODUCTION**

Positive influence of multicomponent alloying on the formation of the amorphous phase has been declared in some works (for example, ref. 1). It has also been shown that the addition of one component lowers the probability of the formation of any concentration fluctuations in liquid alloys, preventing formation of crystalline nuclei [2]. The presence of several types of atoms in the amorphous phase impedes diffusion and helps to prevent crystallization of the amorphous phase on heating. Mutual alloying of Al–Si–Fe by different transition metals

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causes an increase in the degree of the satisfaction of the empirical rules for achievement of high glass-forming ability, i.e., (1) multicomponent alloy system, (2) large atomic size ratios among the main constituent elements, and (3) negative heats of mixing among the constituent elements [1]. The Si–Al–TM (TM = transition metals) system satisfies these requirements. On the basis of these principles, Si-based amorphous alloys containing 50–55 at% Si have been produced [3] by adding several transition metals (namely, Ni, Cr, and Zr) to the ternary Al–Si–Fe alloys studied earlier [4–6]. The compositional ranges for the formation of the amorphous single phase at the surface velocity of the copper wheel of 42 m/s were found to be Si<sub>50</sub>Al<sub>22-28</sub>Fe<sub>10–18</sub>Ni<sub>3–7</sub>Cr<sub>3–7</sub> and Si<sub>55</sub>Al<sub>20-22</sub>Fe<sub>8–10</sub>Ni<sub>5–7</sub>Cr<sub>3–5</sub>Zr<sub>3–5</sub> [3]. The stability of the amorphous phase, however, has remained poorly studied. In the present paper, we describe the influence of cooling rate on the formation of the amorphous phase and thermal stability of multicomponent amorphous Si–Al–Fe–TM alloys.

#### EXPERIMENTAL

Ingots of Si–Al–Fe–Ni–Cr–Zr alloys were prepared by arc melting a mixture of pure Al (99.99%), Fe (99.9%), Cr (99.9%), Ni (99.9%), Zr (99.7%), and Si (99.9999%) in an argon atmosphere. From these alloys, ribbon samples of about 0.015–0.02 mm in thickness and 0.9–1.0 mm in width were prepared by rapid solidification of the melt on a single copper roller at different surface velocities of the copper wheel. The amorphous structure of ribbon samples was examined by X-ray diffraction with monochromatic Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) observation was carried out using a JEOL JEM 2010 electron microscope operating at 200 kV. Samples for TEM were polished electrolytically in a solution of 10 vol% perchloric acid and 90 vol% methanol at 208–213 K. Crystallization temperature and heat of crystallization were examined by differential scanning calorimetry (DSC) at different heating rates.

#### RESULTS

**Influence of the Cooling Rate on Amorphization.** In addition to  $Si_{50}Al_{26}Fe_{10}Ni_7Cr_7$  and  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  amorphous alloys, which were produced earlier [3], we observed the formation of an amorphous single phase in  $Si_{50}Al_{20-26}Fe_{8-12}Ni_{5-7}Cr_{3-5}Zr_{3-5}$  and  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$  alloys. Amorphization of the alloy containing 60% Si (Fig. 1) was achieved by using a surface velocity of the copper wheel of 63 m/s. Alloys with 50 and 55 at% Si were found to have a definite compositional area of homogeneity [3] of the amorphous phase, whereas a slight change in composition of the  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$  alloy led to precipitation of a crystalline phase. Conditions for the formation of the amorphous phase depending on the surface velocity of the copper wheel are summarized in Table 1.

DSC curves of  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$ ,  $Si_{55}Al_{20}Fe_8Ni_7Cr_5Zr_5$  and  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$ alloys are shown in Figure 2. The curves for the  $Si_{50}Al_{26}Fe_{10}Ni_7Cr_7$  and  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloys have been reported in ref. 3. The  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$ ,  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ , and  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ , and  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ , and  $Si_{55}Al_{20}Fe_8Ni_7Cr_5Zr_5$  amorphous alloys transform to a crystalline phase through a one-stage exothermic reaction leading to the formation of the multicomponent  $Si_{10}Al_4Fe_2NiCrZr$  [3] and a small amount of Fd3m Si phase.

**Transformation Diagrams.** Thermal stability of the amorphous phase in the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy was examined by isothermal annealing of as-solidified samples



FIG. 1

Bright-field electron micrograph (a) and selected-area electron diffraction pattern (b) of a rapidly solidified  $Si_{60}Al_{20}Fe_8Ni_4Cr_4Zr_4$  alloy.

at different temperatures. A transformation diagram is shown in Figure 3a. At higher temperatures, a diagram for ribbon samples, as plotted in Figure 3b, was constructed by using incubation time from isothermal calorimetry curves. The ribbon samples were annealed isothermally at temperatures of 667, 671, 675, and 679 K (Fig. 4a). Heating up to each annealing temperature was done at a heating rate of 3.3(3) K/s. Points on the curve correspond to less than 0.5% of the volume fraction transformed.

**Kinetics of Crystallization.** The study of the kinetics of crystallization of the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy was performed using the Johnson–Mehl–Avrami isothermal analysis for volume fraction x transformed as a function of time t on the basis of the following equation [7]:

$$x(t) = 1 - \exp[-(k(T)t)^{n}]$$
(1)

#### TABLE 1

Microstructure of Si-Based Alloys Depending on the Cooling Rate Controlled by the Copper Wheel Surface Velocity

Alloy composition	Copper wheel surface velocity, m/s				
	16	21	31.5	42	63
$Si_{50}Al_{26}Fe_{10}Ni_7Cr_7$ $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ $Si_{60}Al_{20}Fe_8Ni_4Cr_4Zr_4$	am. + cryst. <sup>a</sup> cryst. <sup>c</sup> cryst.	am. <sup>b</sup> am. + cryst. cryst.	am. am. + cryst. cryst.	am. am. am. + cryst.	am. am. am.

<sup>*a*</sup>Amorphous + crystalline.

<sup>b</sup>Fully amorphous.

<sup>c</sup>Crystalline.



DSC curves of the amorphous  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$ ,  $Si_{55}Al_{20}Fe_8Ni_7Cr_5Zr_5$ , and  $Si_{60}Al_{20}Fe_8Ni_4Cr_4Zr_4$  alloys.

The samples were annealed isothermally at several temperatures: 667, 671, 675, and 679 K (see Fig. 4a). The volume fraction transformed vs. the annealing time plot is shown in Figure 4b. The volume fraction transformed at the time t is assumed to scale with the fraction of the total heat released. Eq. (1) can be written as

$$\ln[\ln(1/(1-x))] = n(\ln(k) + n\ln(t))$$
(2)

where k is an effective rate constant and n is Avrami exponent. The Avrami plot of  $\ln[-\ln(1 - x) \text{ vs. } \ln(t) \text{ yields a straight line with slope n and intercept } n\ln(k)$ . Figure 4c shows this plot at different temperatures. The plots are reasonably linear. The average slope corresponds to n = 3.4.

**Energy Barrier Opposing Crystallization.** In differential scanning calorimetry, the temperature at which the maximum deflection is observed varies with heating rate. By making a number of differential calorimetry measurements at different heating rates, the kinetic constant can be obtained directly from the DSC data. The activation energy E (the energy barrier opposing the crystallization) and a frequency factor A (a measure of the probability that an atom having energy E will participate in the reaction) in the following equation for the fraction transformed x [8]:

$$dx/dt = A(1 - x)exp(-E/RT)$$
(3)

can be obtained directly from the temperature  $T_m$  (peak temperature) at which the ratio dx/dt attains the maximum [8]. The corresponding equation is:



FIG. 3

Transformation diagrams for the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy at different temperature ranges.  $T_x = crystallization$  temperature, measured by DSC at a heating rate of 0.042 K/s.

$$-E/R = d(\ln V_{\rm h}/T_{\rm m}^{2})/d(1/T_{\rm m})$$
(4)

where  $V_h$  is the heating rate and R is the gas constant. The data plotted as indicated by the relation  $(\ln V_h/T_m^2)$  vs.  $(1/T_m)$  for  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  are shown in Figure 5a. Heating rates used were 0.042, 0.083, 0.17, 0.67, and 1.33 K/s. From the slope, the activation energy was estimated to be 343 kJ/mol (or 3.55 eV). The same Kissinger plot  $(\ln V_h/T_m^2)$  vs.  $(1/T_m)$  for the  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$  alloy is shown in Figure 5b. The slope value is close to that for the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy (see Fig. 5a) and the activation energy is estimated to be 374 kJ/mol.

#### DISCUSSION

Changing the surface velocity of the copper wheel is a widely used procedure to influence the cooling rate during rapid solidification. It is seen from Table 1 that an increase of surface



(a) Isothermal differential calorimetry curves, (b) the fraction transformed vs. the annealing time, and (c) the Avrami plot for the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy.

velocity, which means an increase of cooling rate, enables the formation of amorphous alloys with higher Si content. Compositional ranges for the formation of the amorphous phase are  $Si_{50}Al_{22-28}Fe_{10-18}Ni_{3-7}Cr_{3-7}$  [3],  $Si_{50}Al_{20-26}Fe_{8-12}Ni_{5-7}Cr_{3-5}Zr_{3-5}$ ,  $Si_{55}Al_{20-22}Fe_{8-10}Ni_{5-7}Cr_{3-5}Zr_{3-5}$  [3], and  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$ . From the data obtained and the narrowing of the composition range for the formation of the amorphous phase with an increase in Si content, we can conclude that 60 at% is the highest Si content at which an amorphous single phase can be obtained in Si-Al-Fe-Cr-Ni-Zr and some other Si-Al-TM systems by the melt spinning technique. To the reasons enumerated in our previous work [3], for the formation of the amorphous phase in the Si-rich alloys, we can add a large difference in the atomic radii among the Si, Al, and TM elements. Al, Zr, and other TM atomic radii are 1.22, 1.62, and about 1.07 times, respectively, larger than Si atomic radius.

The amorphous phase in the Si–Al–TM alloys exhibits a relatively high thermal stability in comparison with that in Al–Si–TM alloys [9]. Figure 3a shows that at temperatures lower -12.0

-14.0

-15.0

-16.0 -17.0 -18.0

-11.0 -12.0 -13.0

In(RC/Tm)



Kissinger plot for (a)  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  and (b)  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$  alloys.

than 600 K, the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy was stable for more than 100 h. At lower temperatures, the C curve becomes practically parallel to the axis of time.

 $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$ ,  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ , and  $Si_{55}Al_{20}Fe_8Ni_7Cr_5Zr_5$  amorphous alloys transformed into a crystalline state through a one-stage exothermic reaction, leading to the formation of the multicomponent  $Si_{10}Al_4Fe_2NiCrZr$  and a small amount of *Fd3m* Si phase. Crystalline particles formed during crystallization are shown in Figure 6. This figure shows that the transformation was not completed and the amorphous phase still remained. The homogeneous distribution of the particles observed in different parts of the ribbon sample leads us to believe that each crystallite grew from its own nuclei. We consider that the crystallization of the amorphous phase in  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  is close to polymorphous transformation into a multicomponent  $Si_{10}Al_4Fe_2NiCrZr$  phase. The value of Avrami exponent 3.4 is usual for a transformation involving an overlap three-dimensional linear growth on quenched-in nuclei and on new nuclei. The activation energy as the energy barrier opposing the crystallization of  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy of 343 kJ/mol is close to the value of 345 kJ/mol for the polymorphic crystallization of  $Ti_2Ni$  alloy [10].



FIG. 6

Microstructure of the Si<sub>55</sub>Al<sub>20</sub>Fe<sub>10</sub>Ni<sub>5</sub>Cr<sub>5</sub>Zr<sub>5</sub> alloy after annealing for 6000 sec at 667 K.

### CONCLUSIONS

In conclusion, it can be said that by adding Ni, Cr, and Zr to the Si–Al–Fe system and using a higher speed of the copper wheel, an amorphous  $Si_{60}Al_{18}Fe_{12}Ni_4Cr_3Zr_3$  alloy was produced.  $Si_{50}Al_{25}Fe_{10}Ni_5Cr_5Zr_5$ ,  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$ , and  $Si_{55}Al_{20}Fe_8Ni_7Cr_5Zr_5$  amorphous alloys transform into a crystalline state through a one-stage exothermic reaction. At temperatures lower than 600 K, the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy was stable for more than 100 h. The crystallization kinetics of the  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy was analyzed on the basis of the Johnson–Mehl–Avrami relation. The Avrami exponent n was found to be 3.4. The activation energy for the transformation determined by the shift of DSC peaks with change of heating rate to be 343 kJ/mol for  $Si_{55}Al_{20}Fe_{10}Ni_5Cr_5Zr_5$  alloy is close to the value of 345 kJ/mol for the polymorphic crystallization of  $Ti_2Ni$  alloy.

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