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Dmitri V. Louzguine, Larissa V. Louzguina, and Akihisa Inoue

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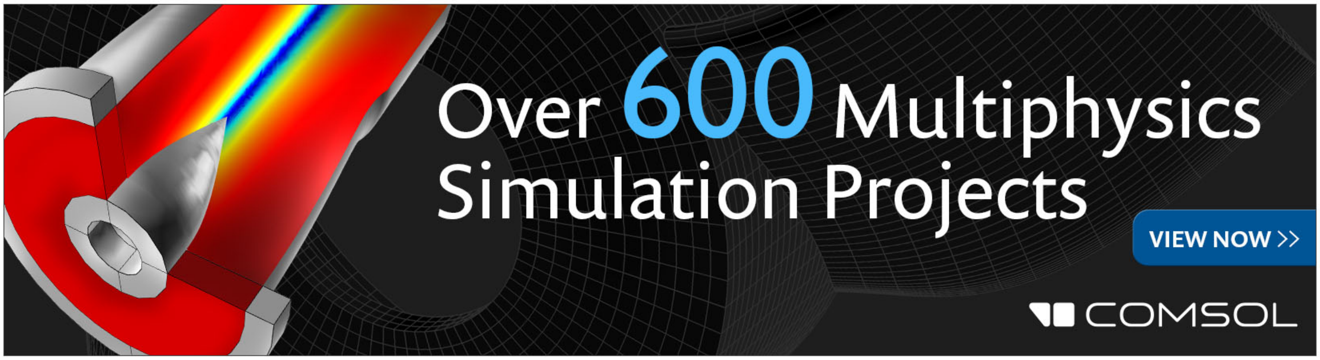

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Factors influencing glass formation in rapidly solidified Si,Ge–Ni and Si,Ge–Ni–Nd alloys

Dmitri V. Louzguine,[a] Larissa V. Louzguina, and Akihisa Inoue
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-Ku, Sendai 980-8577, Japan

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In this letter we compare the glass-forming capabilities of binary Si,Ge–Ni and ternary Si,Ge–Ni–Nd alloys. The addition of Nd caused the formation of an amorphous single phase in the Ge–Ni–Nd alloy. The structure and crystallization behavior of the amorphous alloy were studied by differential scanning calorimetry and x-ray diffractometry. No amorphous phase formed in any of the Nd-free alloys or in the Si–Ni–Nd alloy. The higher glass-forming capability of the Ge–Ni–Nd alloy compared to Si–Ni–Nd cannot be explained on the basis of the widely used geometrical and chemical factors, viscosity, or diffusion data. The importance of the electronic structure characteristics is suggested to be a reason. © *2002 American Institute of Physics.*

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A number of Si- and Ge-based amorphous alloys were produced by rapid solidification of the melt in Si–Al–transition metals (TMs),[1] Ge–Al–Cr,[2] and Ge–Al–Cr–rare earth (RE)[3,4] systems. It has also been shown that Si–Al–TM alloys can be produced in bulk form by hot pressing.[5] The maximum possible Ge content in an amorphous single phase after rapid solidification was restricted to 70 at. %,[6] and the Si content to 60 at. %.[7] These alloys showed splitting of the first diffraction maximum in an x-ray diffraction (XRD) pattern.[8] This phenomenon is a result of the formation of a framework like amorphous Ge and Si by Ge–Ge and Si–Si atomic pairs which is completely different from the metallic bonding between other atoms and metalloids (Ge or Si) with other metals. As has been shown in the $Ge_{50}Al_{40}Cr_{10}$ alloy Ge forms a covalent network with a partial coordination number close to 4 with other Ge atoms.[9] Splitting of the first diffraction maximum was observed in pure amorphous Ge as well.[10,11] The structure of amorphous Si was also studied.[12] However, in some other alloys splitting of the first diffraction maximum was explained by phase separation of the amorphous phase into two phases over a short range.[2] At the same time no splitting of the diffraction peak was observed in Ge–Al–La alloys.[13] One should note, however, that, in Ge–Al–RE alloys the amorphous phase always formed together with the crystalline one(s).

In this letter we compare the glass-forming capabilities of metalloid-based binary Si,Ge–Ni and ternary Si,Ge–Ni–Nd alloys. Binary phase diagrams of Si–Ni (Ref. 14) of Ge–Ni (Ref. 15) systems reveal eutectics in the metalloid-rich area, i.e., at 56 at. % Si and at 67 at. % Ge. The compositions of the alloys studied were chosen to be close to those of eutectic points.

Ingots of $Si_{56}Ni_{44}$, $Si_{60}Ni_{40}$, $Ge_{60}Ni_{40}$, $Ge_{67}Ni_{33}$, $Si_{55}Ni_{40}Nd_5$, $Si_{60}Ni_{35}Nd_5$, and $Ge_{60}Ni_{35}Nd_5$ alloys (all alloy compositions are given in nominal at. %) were prepared by arc melting mixtures of Si 99.999 mass % purity, Ge 99.999 mass % purity, Ni 99.9 mass % purity, and Nd 99.9 mass % purity in argon atmosphere. From these alloys, ribbon samples 0.01 mm in thickness and 0.9 mm in width were prepared by rapid solidification of the melt on a single copper roller (the so-called melt spinning technique) at a wheel surface velocity of 42 m/s. The structure of the ribbon samples was examined by x-ray diffractometry with monochromatic Cu $K\alpha$ radiation. Differential scanning calorimetry (DSC) was carried out at a heating rate of 0.67 K/s. Isothermal annealing of the ribbon samples encapsulated in quartz tubes was conducted in a vacuum of 1×10^{-3} Pa.

Amorphous single phase was obtained only in the $Ge_{60}Ni_{35}Nd_5$ alloy [Fig. 1(a)]. $Fd3m$ Ge, orthorhombic *Pbnm* GeNi, and a small fraction of unidentified phase were obtained in the $Ge_{60}Ni_{40}$ and $Ge_{67}Ni_{33}$ alloys after rapid solidification while rapidly solidified ribbons of the $Si_{56}Ni_{44}$ and $Si_{60}Ni_{40}$ alloys consisted of *Pbnm* NiSi and $Fm3m$ $NiSi_2$ phases, in accordance with the corresponding equilibrium phase diagrams. The $Si_{55}Ni_{40}Nd_5$ and $Si_{60}Ni_{35}Nd_5$ alloys also crystallized during solidification.

A DSC scan of the $Ge_{60}Ni_{35}Nd_5$ alloy is shown in Fig. 2.

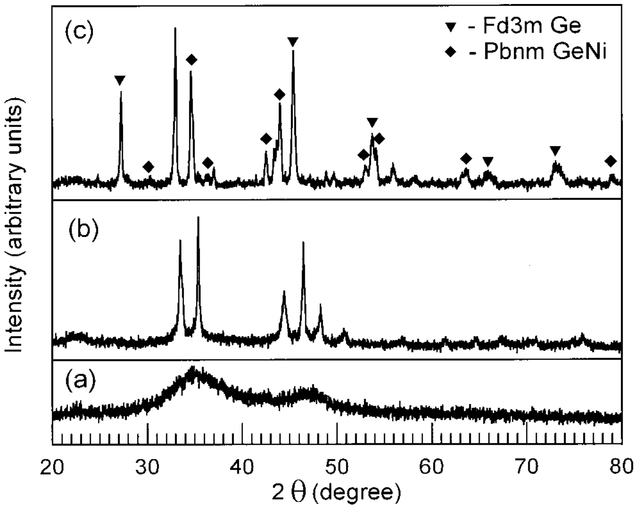

FIG. 1. X-ray diffraction patterns of the $Ge_{60}Ni_{35}Nd_5$ alloy in (a) the rapidly solidified state, (b) annealed for 1.2 ks at 600 K, and (c) after DSC up to 800 K.

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[a] Author to whom correspondence should be addressed; electronic mail: dmluz@imr.tohoku.ac.jp

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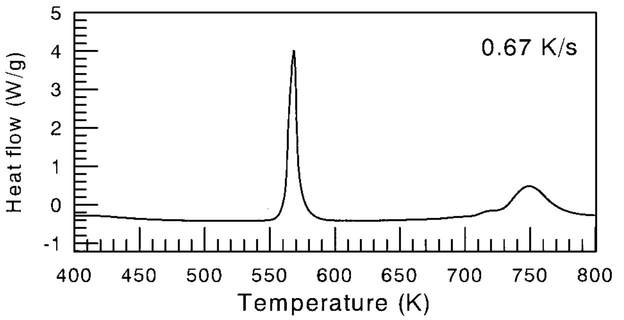

FIG. 2. DSC trace of the $Ge_{60}Ni_{35}Nd_5$ alloy taken at 0.67 K/s.

It exhibits two exothermic heat effects with onset temperatures of 560 and 712 K. The high-temperature exothermic peak consists of two shoulders. The value of the heat released during the first peak of −50 J/g is close to that of the second one (−44 J/g). Melting of the sample began at 1015 K. Melting of the $Si_{60}Ni_{35}Nd_5$ alloy started at 1227 K. An unknown metastable phase precipitated primarily in the $Ge_{60}Ni_{35}Nd_5$ alloy at the first phase transformation [Fig. 1(b)]. After completion of all phase transformations the structure consisted of $Fd3m$ Ge, *Pbnm* GeNi, and an unidentified phase [Fig. 1(c)].

From the general concept of glass formation in binary alloys, compositions which are close to "deep" eutectics in phase diagrams are suitable for glass formation, provided that the constituent elements have large negative heats of mixing with each other. Binary metal-metalloid (Si, Ge, B) (Ref. 16) amorphous alloys of nearly eutectic composition in the metal-rich range are a classical example of glass formation by rapid solidification of the melt using melt spinning. However, in Si,Ge–Ni alloys "deep" eutectics at Si- and Ge-rich areas do not favor glass formation. The eutectic temperature for $L \rightarrow NiSi + NiSi_2$ is 1239 K, which is 0.73 of the melting temperature of pure $Fd3m$ Si of 1687 K. The eutectic temperature for $L \rightarrow NiGe + Ge$ is 1035 K. It is equivalent to 0.85 of the melting temperature of pure $Fd3m$ Ge of 1211 K. The melting temperatures measured for the $(Si, Ge)_{60}Ni_{35}Nd_5$ alloys are slightly lower than the corresponding binary eutectic temperatures, which indicates lowering of the temperature of the solidus by addition of Nd.

It is known that, in order to obtain a high glass forming capability for an alloy and to promote the formation of bulk metallic glass, three empirical rules should be followed, i.e., there should be (1) multicomponent systems consisting of at least three elements, (2) significant atomic size ratios above about 1.12 among the three main constituent elements (here the geometrical factor), and (3) negative heats of mixing among the three main constituent elements (here the chemical factor).[17,18] Si,Ge–Ni–Nd alloys satisfy the above-mentioned requirements. The Goldschmidt atomic radii of Si, Ge, Ni, and Nd are 0.117, 0.123, 0.125, and 0.182 nm,[19] respectively. Thus, although the atomic size mismatch ratios for the Ni–Si (1.07) and Ni–Ge (1.02) pairs are less than 1.12, the values for Nd–Si (1.56) and Nd–Ge (1.48) atomic pairs significantly exceed 1.12. In any case the Si-bearing pairs have higher atomic size mismatch ratios than the Ge-bearing pairs. The heats of mixing for liquid binary alloys are −23 kJ/mol for Si–Ni, −11 kJ/mol for Ge–Ni, −56 kJ/mol for Si–Nd, and −61 kJ/mol for Ge–Nd atomic pairs.[20] At nearly the same values of heat of mixing in Si–Nd and Ge–Nd atomic pairs Si has double the absolute value of heat of mixing with Ni than Ge does. Taking into consideration geometrical and chemical factors, Si–Ni–Nd alloys show better adherence to the above requirements. However, the amorphous single phase was obtained only in the Ge–Ni–Nd system. One should draw attention to the fact that the same ribbon thickness of about 0.01 mm was obtained for all alloys, which allows direct comparison of the data.

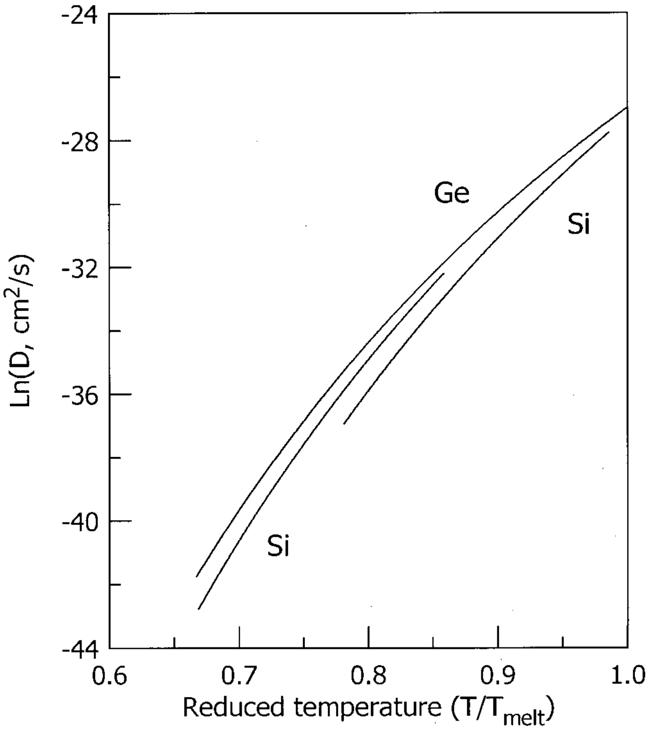

FIG. 3. Temperature dependence of the self-diffusion coefficients of Si and Ge. T_{melt} is the melting temperature.

Another important characteristic is the viscosity of the liquids at the melting temperature. According to Ref. 21 liquid Si has a higher viscosity ($0.94\ mN\,s\,m^{-2}$) than Ge ($0.73\ mN\,s\,m^{-2}$). There are no data for the temperature dependence of the viscosity for Si and Ge but the higher viscosity of Si should favor glass formation.

The diffusivity of Si and Ge can be considered as another important factor that influences the glass-forming capability because faster diffusion promotes crystallization. The coefficients (D) for self-diffusion of Si and Ge have been calculated in definite temperature intervals according to the Arrhenius equation:

$$D = A \exp(-Q/RT), \tag{1}$$

where R is the gas constant and T is the absolute temperature. The frequency factor (A) and activation energy (Q) values were taken from Ref. 22. Because D greatly varies according to the temperature the natural logarithm of D data versus reduced temperature are plotted in Fig. 3. Two pairs of A and Q values for Ge from Ref. 19 gave identical results, while two curves are plotted for Si. It is seen that the diffusion coefficient of Ge is higher than that of Si at the same reduced temperature. Moreover, D^{Si} and D^{Ge} at eutectic tem-

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peratures of 1239 and 1035 K are 1.6×10^{-17} and 1.2×10^{-14} cm^2/s, respectively, thereby validating the higher diffusion rate of Ge. The activation energy for self-diffusion of Si is also about 1.5 times higher than that of Ge.

Thus, according to all the above factors Si-based alloys should not have lower glass-forming capability than Ge-based ones. According to recent data obtained for Al–Re–Ni–Co alloys[23] the electronegativity of the constituent RE element was found to affect the formation of the supercooled liquid although all of the constituent elements were metals. Ge has a higher electronegativity compared to Si, i.e., 2.01 and 1.90 (in Pauling units),[24] respectively. The above-mentioned values may indicate the influence of the electronic structure of the alloy on its glass-forming capability. It has been proposed[25] that an alloy for which the Fermi level lies in the minimum in the electronic density of states (i.e., it shows a pseudogap) is stabilized against crystallization. However, the presence of the *f*-element Nd hampers any possible calculation of the electronic density of states.

In conclusion, the addition of 5 at. % Nd to the Ge–Ni alloy caused the formation of an amorphous single phase. The higher glass-forming capability of the Ge–Ni–Nd alloy compared to that of Si–Ni–Nd cannot be described on the basis of the widely used geometrical and chemical factors, viscosity and diffusion data. The authors suggest the importance of the electronic structure characteristics to be a reason.

One of the authors (L.V.L.) is a volunteer at the Institute for Materials Research at Tohoku University.

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