JOURNAL OF MATERIALS SCIENCE 22 (1987) 2185–2191

Correlation between electrical properties and thermal stability in Ni–Si–B metallic glasses

TAKAYUKI KOMATSU, YASUO TANAKA, RYOSUKE YOKOTA*
KAZUMASA MATUSITA
Department of Materials Science and Technology, Technological University of Nagaoka, Nagaoka, 940–21, Japan

The temperature coefficient of resistivity (TCR), specific resistivity $\varrho_{300\,K}$, crystallization temperature T_x and activation energy E_a for crystallization in various Ni–Si–B metallic glasses were measured and relationships among them were examined. It was found that the values of TCR decreased with increasing metalloid (Si, B) contents and by substituting silicon atoms for boron atoms, but conversely the values of $\varrho_{300\,K}$, T_x and E_a increased. A very close correlation was observed between TCR and T_x or E_a. The compositional dependences of TCR, $\varrho_{300\,K}$, T_x and E_a and good correlations among them can be explained qualitatively by considering the short-range structure and the directional chemical bonding between nickel and silicon or boron atoms.

1. Introduction

Metallic glasses prepared by rapid quenching techniques are thermodynamically unstable and relax toward more stable structure during thermal annealing and finally lead to crystallization. Since many excellent properties are generally lost by crystallization, the thermal stability which corresponds to resistance against crystallization is very important not only for technical applications but also for understanding the structure of metallic glasses. Donald and Davies [1] and Donald *et al.* [2] have examined the compositional dependence of crystallization temperature T_x in various iron- and nickel-based metallic glasses and have shown that the values of T_x are related to both the average outer-electron concentration of the transition elements in the alloy and the atomic size difference between solvent and solute metal species. It has been reported that the values of T_x in some metallic glasses increase as the temperature coefficient of electrical resistivity (TCR) becomes more negative [3–5]. Nagumo *et al.* [6] have indicated that the composition with a minimum in thermoelectric power in $Ni_{75}(Si, B)_{25}$ metallic glasses has a maximum in T_x. These results clearly indicate that the electrical properties of metallic glasses are closely related to their thermal stability. More extensive studies on the correlation between electrical properties and thermal stability in various metallic glasses are strongly desirable.

In the present study, the compositional dependences of TCR, specific resistivity $\varrho_{300\,K}$, T_x and activation energy E_a for crystallization in various Ni–Si–B metallic glasses were measured and correlations among them were examined in order to obtain more detailed information about the thermal stability of metallic glasses. Ni–Si–B metallic glasses are generally paramagnetic materials and thus magnetic effects on TCR, $\varrho_{300\,K}$, T_x and E_a can be negligible. Furthermore, the structure of nickel-based metallic glasses has been extensively studied and the short-range structure has been clarified [7–9]. It is considered therefore that Ni–Si–B metallic glasses are very suitable for the study of the correlation between electrical properties and thermal stability in metallic glasses.

2. Experimental procedure

Various Ni–Si–B metallic glasses, $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ ($24 \leqslant x \leqslant 34$), $Ni_{75}Si_xB_{25-x}$ ($3 \leqslant x \leqslant 16$), $Ni_{72}Si_xB_{28-x}$ ($2 \leqslant x \leqslant 14$) and $Ni_{70}Si_xB_{30-x}$ ($2 \leqslant x \leqslant 15$) were prepared in the form of a ribbon, about 20 μm thick and 1.5 mm wide, by rapid quenching using a single-roller casting apparatus. These compositions locate in the glass-forming region reported by Donald and Davies [10]. The amorphous state of samples was confirmed by X-ray diffraction.

The specific resistivity at room temperature $\varrho_{300\,K}$ and the TCR in Ni–Si–B metallic glasses were measured. The measurements of electrical resistivity were made using a four-point probe method. The samples were spot-welded carefully to small copper wires. The area of cross-section of ribbons for an estimation of specific resistivity was evaluated from the density, which was obtained using Archimedes' method. TCR was measured in the temperature range from 220 to 310 K. The values of $\varrho_{300\,K}$ and TCR in $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses have been reported in a previous paper by the present authors [11].

As a measure for the thermal stability of Ni–Si–B metallic glasses, the peak temperature of crystallization T_x and the activation energy for crystallization E_a were examined. The value of T_x was determined by differential scanning calorimetry (DSC) at a heating

Present address: Hoya Corporation, 572 Miyazawa-cho, Akishima, Tokyo, 196, Japan.

0022–2461/87 $03.00 + .12

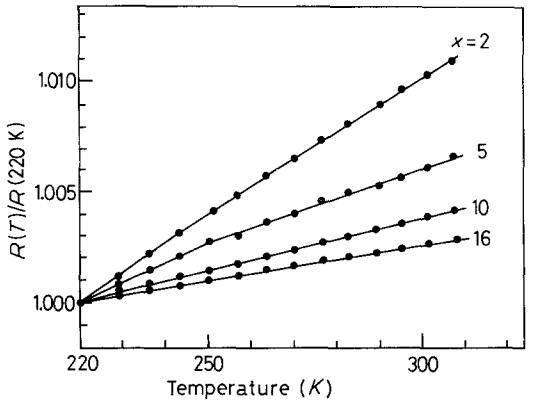

Figure 1 Temperature dependence of the relative resistivity changes $R(T)/R(220\,K)$ for $Ni_{70}Si_xB_{30-x}$ metallic glasses between 220 and 310 K.

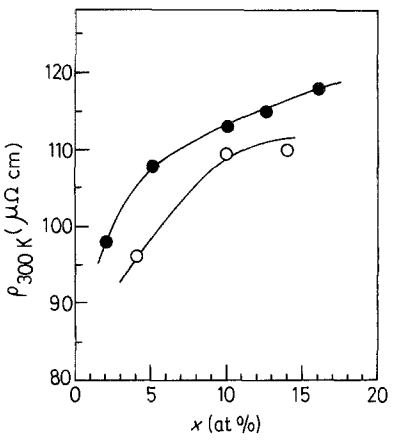

Figure 3 Specific resistivity $\varrho_{300\,K}$ at room temperature as a function of silicon content: (○) $Ni_{72}Si_xB_{28-x}$, (●) $Ni_{70}Si_xB_{30-x}$.

rate of $10\,K\,min^{-1}$. The crystals precipitated in Ni–Si–B metallic glasses were identified by the X-ray diffraction analysis. The value of E_a was determined from DSC curves at various heating rates. The kinetic equation for DSC data analysis used in the present study is the modified Ozawa-type plot proposed by Matusita *et al.* [12]. According to Matusita *et al.*, when crystal particles grow m-dimensionally, an equation expressing the relationship between the heating rate α and the volume fraction x of crystals precipitating in a glass is expresssed by

$$\ln \alpha = -1.052 \frac{mE_a}{nRT} - \frac{1}{n} \ln [-\ln(1 - x)] + \text{constant} \quad (1)$$

where n is a numerical factor depending on the nucleation process. The plot of $\ln\alpha$ against $1/T$, where T is the temperature at which the crystal volume fraction reaches a specific value, gives a straight line and the slope gives the value of $1.052\,(m/n)E_a$. Since it is known that the volume fraction of crystals at the peak temperature T_x in DSC curves is almost the same irrespective of heating rate [13], the above equation should apply for the peak temperature.

3. Results and discussion

3.1. Electrical properties

The temperature dependences of the relative resistivity changes $R(T)/R(220\,K)$ for $Ni_{70}Si_xB_{30-x}$ metallic glasses between 220 and 310 K are shown in Fig. 1. It is clear that the resistivity increases linearly with increasing temperature in this temperature range. The values of TCR were estimated using a least-squares fit of these data. A similar temperature dependence of resistivity was observed in other $Ni_{75}Si_xB_{25-x}$ and $Ni_{72}Si_xB_{28-x}$ metallic glasses. The values of TCR in these metallic glasses are shown in Fig. 2 as a function of silicon content. The values of $\varrho_{300\,K}$ are shown in Fig. 3. It can be seen from Figs 2 and 3 that the values of TCR decrease gradually with increasing metalloid contents and by substituting silicon atoms for boron atoms, but conversely the values of $\varrho_{300\,K}$ increase. The values of TCR in $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses decrease monotonically with increasing metalloid contents and the values of $\varrho_{300\,K}$ increase conversely, as reported in the previous paper [11]. The correlation between the values of TCR and $\varrho_{300\,K}$ in Ni–Si–B metallic glasses are shown in Fig. 4. It can be seen that the sign of TCR changes from a positive value to a negative value at around $\varrho_{300\,K} = 140\,\mu\Omega\,cm$. This indicates that the Mooij correlation [14] is retained in these Ni–Si–B metallic glasses.

3.2. Thermal stability

The DSC curves of $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses

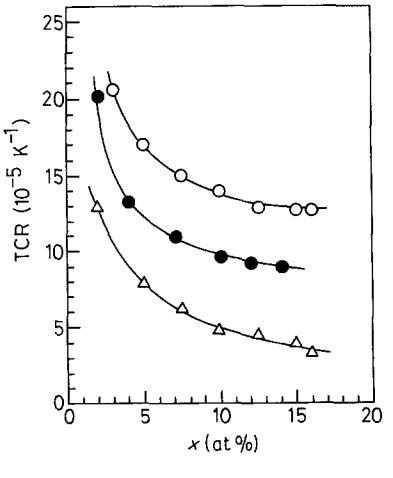

Figure 2 Temperature coefficient of resistivity (TCR) between 220 and 310 K as a function of silicon content: (○) $Ni_{75}Si_xB_{25-x}$, (●) $Ni_{72}Si_xB_{28-x}$, (△) $Ni_{70}Si_xB_{30-x}$.

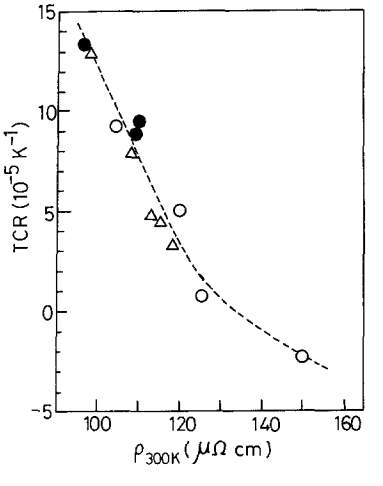

Figure 4 Correlation between the temperature coefficient of resistivity (TCR) and the specific resistivity $\varrho_{300\,K}$: (○) $Ni_{100-x}(Si_{0.25}B_{0.75})_x$, (●) $Ni_{72}Si_xB_{28-x}$, (△) $Ni_{70}Si_xB_{30-x}$.

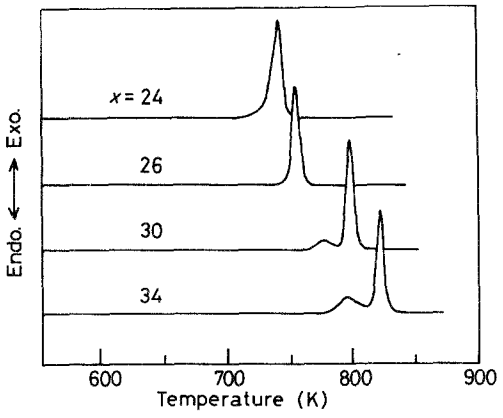

Figure 5 DSC curves of $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses at a heating rate of 10 K min^{-1}.

at a heating rate of 10 K min^{-1} are shown in Fig. 5. In metallic glasses (x = 24, 26 and 28) with around $Ni_{75}(Si, B)_{25}$ composition, only one peak was observed. It was found from X-ray diffraction that this peak is due to the crystallization of an Ni_3B-type phase. In metallic glasses (x = 30, 32 and 34) with high metalloid contents, two peaks were observed. The crystalline phase of the first small peak in these metallic glasses could not be identified at the present study. The second large peak is due to the crystallization of an Ni_3B-type phase. In the DSC curves of other metallic glasses, $Ni_{75}Si_xB_{25-x}$, $Ni_{72}Si_xB_{28-x}$ and $Ni_{70}Si_xB_{30-x}$, one or two crystallization peaks were observed depending on the ratio of silicon and boron contents, and it was found that the crystallization of Ni_3B-type phase occurs mainly in these metallic glasses. That is, the results of DSC measurements and X-ray diffraction analysis indicate that the main and common product in the crystallization in all Ni–Si–B metallic glasses which were used in the present study is the Ni_3B-type phase. The peak temperatures T_x of crystallization of Ni_3B-type phase in these Ni–Si–B metallic glasses are shown in Figs 6 to 8. In $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses, the values of T_x increase with increasing metalloid contents. In

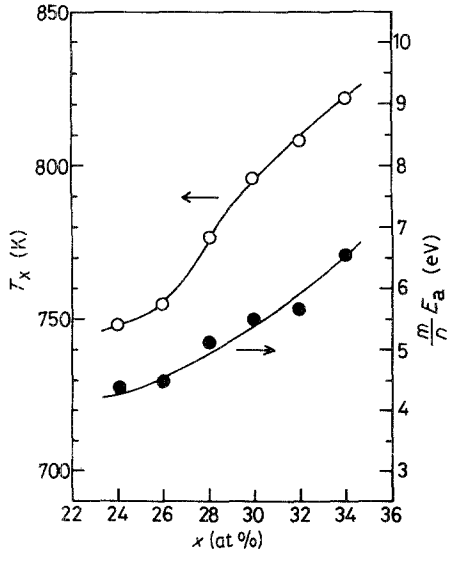

Figure 6 Peak temperature T_x and activation energy $(m/n)E_a$ of crystallization of Ni_3B-type phase as a function of metalloid content in $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses.

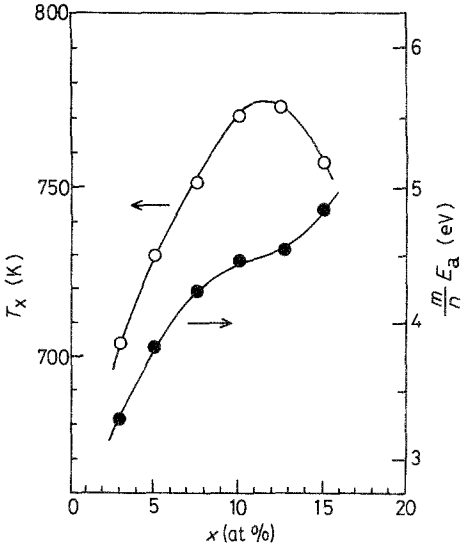

Figure 7 Peak temperature T_x and activation energy $(m/n)E_a$ of crystallization of Ni_3B-type phase as a function of silicon content in $Ni_{75}Si_xB_{25-x}$ metallic glasses.

$Ni_{75}Si_xB_{25-x}$, $Ni_{72}Si_xB_{28-x}$ and $Ni_{70}Si_xB_{30-x}$ metallic glasses, the values of T_x increase by substituting silicon atoms for boron atoms up to around 10 at % Si, but decrease by further substitution.

The activation energy E_a for the crystal growth of Ni_3B-type phase in Ni–Si–B metallic glasses was examined by using Equation 1. The relationship between the natural logarithm of heating rate, ln α, and the reciprocal of peak temperature, $1/T_x$, in DSC curves of $Ni_{75}Si_xB_{25-x}$ metallic glasses is shown in Fig. 9. From the slopes, the values of $(m/n)E_a$ were determined. To determine the value of n, the variation of ln [− ln (1 − x)] with ln α was examined. The results in $Ni_{75}Si_3B_{22}$ metallic glass are shown in Fig. 10, where x is the volume fraction of Ni_3B-type crystals precipitating at 693 K. The value of n = 2.94 was obtained and this value is very close to n = 3. The variation of ln [− ln (1 − x)] at 767 K with ln α in $Ni_{75}Si_{12.5}B_{12.5}$ metallic glass is shown in Fig. 11 and the large value of n = 7.18 was obtained. Similar large

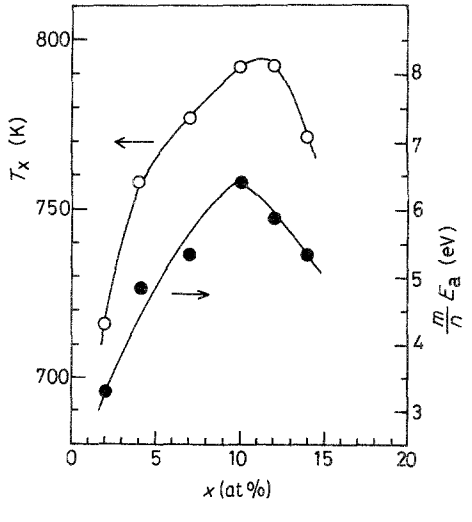

Figure 8 Peak temperature T_x and activation energy $(m/n)E_a$ of crystallization of Ni_3B-type phase as a function of silicon content in $Ni_{72}Si_xB_{28-x}$ metallic glasses.

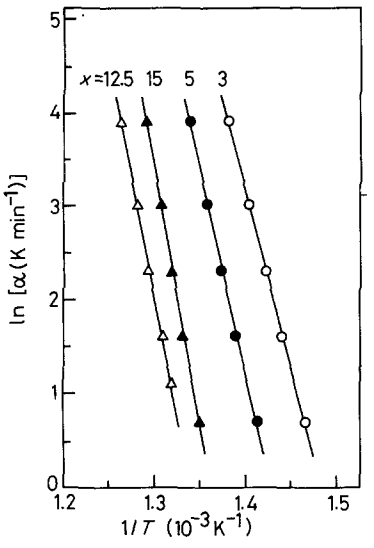

Figure 9 Relationship between natural logarithm of heating rate, ln α, and reciprocal of peak temperature of crystallization, $1/T_x$, in DSC curves of $Ni_{75}Si_xB_{25-x}$ metallic glasses.

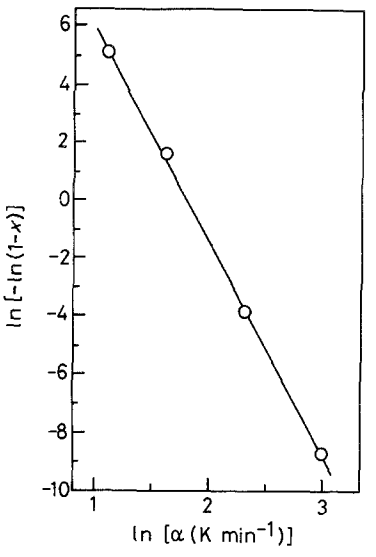

Figure 11 Variation of ln [−ln (1 − x)] at 767 K with natural logarithm of heating rate, ln α, in $Ni_{75}Si_{12.5}B_{12.5}$ metallic glass; $n = 7.18$.

values were obtained in other metallic glasses such as $Ni_{66}(Si_{0.25}B_{0.75})_{34}$ ($n = 5.90$).

It is well known that the value of n must be below 4 theoretically, and thus the large values of n beyond 4 obtained in some metallic glasses are not fully understood. These large values of n might arise from the feature of crystallization in metallic glasses that the nucleation and growth occur almost simultaneously. The crystallization mechanism in Ni–Si–B metallic glasses has been studied by some authors [15–17], but the kinetics of nucleation and growth have not been clarified. We are now in the course of more extensive study on the crystallization mechanism in Ni–Si–B metallic glasses.

Although the values of $(m/n)E_a$ are apparent activation energies for the crystallization of Ni_3B-type phase in Ni–Si–B metallic glasses, it seems meaningful to examine the compositional dependence of the values of $(m/n)E_a$, because the Ni_3B-type phase is a common and main product in the crystallization and it is considered that the crystallization mechanism of Ni_3B-type phase will not be very different within the same Ni–Si–B metallic glass system. The values of $(m/n)E_a$ obtained in the present study are shown in Figs 6 to 8. In $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses, the values of $(m/n)E_a$ increase with increasing metalloid contents. In $Ni_{75}Si_xB_{25-x}$ metallic glasses, the values of $(m/n)E_a$ increase by substituting silicon atoms for boron atoms, and this compositional dependence is different from that of T_x. In $Ni_{72}Si_xB_{28-x}$ metallic glasses, the compositional dependence of $(m/n)E_a$ is almost the same as that of T_x. The correlation between the values of $(m/n)E_a$ and T_x is shown in Fig. 12. It can be seen that the values of $(m/n)E_a$ increase with increasing values of T_x.

3.3. Correlation between electrical properties and thermal stability

The relationship between the TCR and T_x in $Ni_{100-x}(Si_{0.25}B_{0.75})_x$, $Ni_{75}Si_xB_{25-x}$, $Ni_{72}Si_xB_{28-x}$ and $Ni_{70}Si_xB_{30-x}$ metallic glasses is shown in Fig. 13. It can be seen that a good correlation is observed between them and the values of T_x increase with decreasing values of TCR. A similar good correlation was observed between TCR and the activation energy $(m/n)E_a$, as shown in Fig. 14. That is, the activation energy of

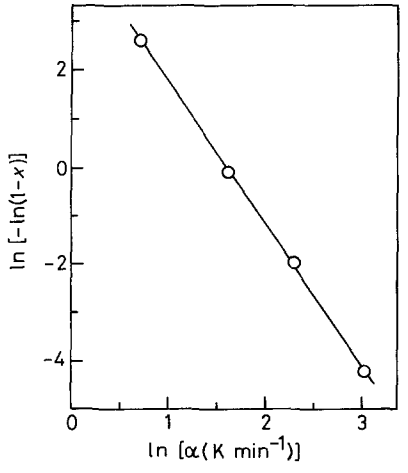

Figure 10 Variation of ln [−ln (1 − x)] at 693 K with natural logarithm of heating rate, ln α, in $Ni_{75}Si_3B_{22}$ metallic glass; $n = 2.94$.

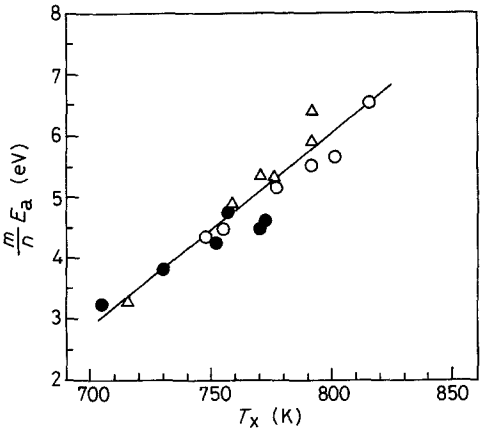

Figure 12 Correlation between peak temperature T_x and activation energy $(m/n)E_a$ of crystallization of Ni_3B-type phase in various Ni–Si–B metallic glasses: (○) $Ni_{100-x}(Si_{0.25}B_{0.75})_x$, (●) $Ni_{75}Si_xB_{25-x}$, (△) $Ni_{72}Si_xB_{28-x}$.

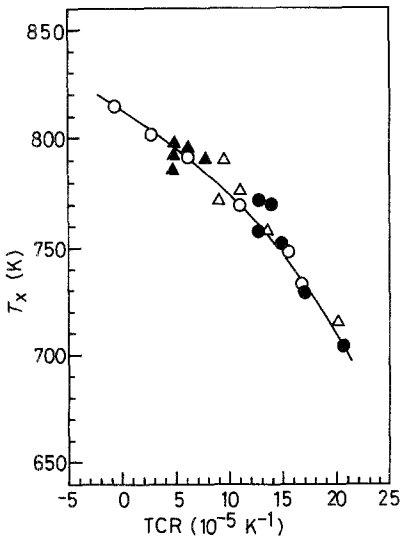

Figure 13 Correlation between temperature coefficient of resistivity (TCR) and crystallization peak temperature T_x in various Ni–Si–B metallic glasses: (○) $Ni_{100-x}(Si_{0.25}B_{0.75})_x$, (●) $Ni_{75}Si_xB_{25-x}$, (△) $Ni_{72}Si_xB_{28-x}$, (▲) $Ni_{70}Si_xB_{30-x}$.

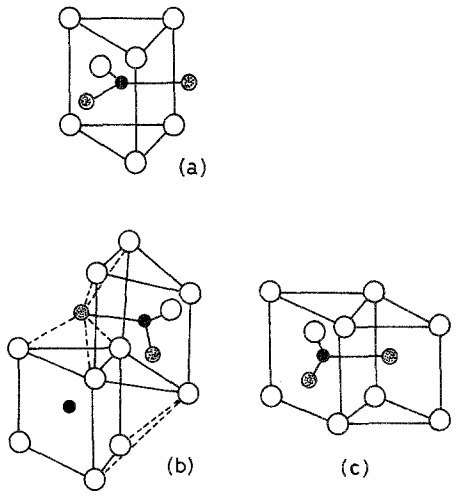

Figure 15 (a) Trigonal prismatic coordination polyhedron observed in Ni–B metallic glasses. (b) Arrangement of trigonal prismatic polyhedra to share edges. (c) Arrangement of trigonal prismatic polyhedra to share rectangular faces allowing B–B contact. This arrangement might be possible in Ni–B metallic glasses with high boron contents. (○) nickel, (●) boron, (⊜) nickel for high nickel contents or boron for high boron contents.

crystallization in Ni–Si–B metallic glasses with small values of TCR is larger than that in metallic glasses with large positive values of TCR. A similar close relationship between TCR and T_x has been reported in Fe–Ni–B metallic glasses by Hilmann and Hilzinger [3], in $Fe_{80}TM_3B_{17}$ (TM; 3d, 4d and 5d transition metals) metallic glasses by Lovas *et al.* [4] and in $Pd_{83-x}TM_xSi_{17}$ (TM; Fe, Co and Ni) metallic glasses by Xinming *et al.* [5].

Some authors [3, 5] explained successfully the correlation between TCR and T_x using the Nagel and Tauc's model [18], which indicates that metallic glasses with a composition of $2k_F = K_P$ are the most stable against crystallization, where k_F is the Fermi wave vector and K_P is the wave vector of the first peak in the structure factor. However, the Nagel and Tauc model has been criticized [19, 20] and it does not appear to be universally applicable [21]. Furthermore, since accurate values of $2k_F$ in Ni–Si–B metallic glasses have not been determined experimentally, we will discuss the correlation between TCR and T_x or $(m/n)E_a$ obtained in the present study by using information about the short-range structure and the nature of bonding between constituent atoms.

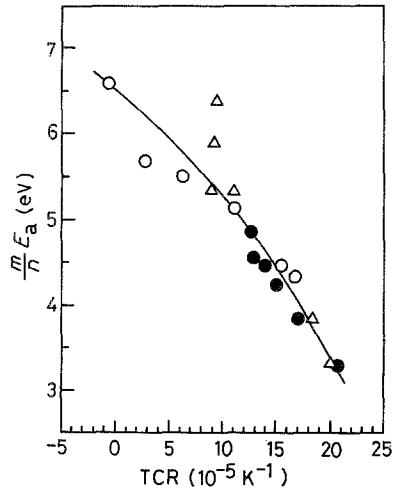

Figure 14 Correlation between temperature coefficient of resistivity (TCR) and activation energy of crystallization $(m/n)E_a$ in various Ni–Si–B metallic glasses: (○) $Ni_{100-x}(Si_{0.25}B_{0.75})_x$, (●) $Ni_{75}Si_xB_{25-x}$, (△) $Ni_{72}Si_xB_{28-x}$.

It has been reported that the basic structure unit in Ni–B metallic glasses is a trigonal prism Ni_3B and this trigonal prism is retained in a wide composition range ($Ni_{100-x}B_x$; $18 \leqq x \leqq 40$) [7–9]. In particular, Panissod *et al.* [8] have suggested that, when the boron concentration increases, more trigonal prisms share rectangular faces allowing boron–boron contact. Donald and Davies [10] have reported that Ni–Si–B metallic glasses with high metalloid (Si, B) concentrations are less ductile in the as-quenched state, probably due to the increasing proportion of directional metalloid–metalloid covalent bonds. The structure of the trigonal prism Ni_3B and two possible arrangements of trigonal prisms in Ni–B metallic glasses are shown in Fig. 15. The structure of Ni–Si–B metallic glasses has not been clarified and thus the structural positions of silicon atoms are not known at the present time. However, since the main metalloid atom in Ni–Si–B metallic glasses used in the present study is boron, it might be reasonable to assume that a trigonal prism of Ni_3B-type is a basic structure unit in these Ni–Si–B metallic glasses, and that as-quenched metallic glasses are composed of a random packing of trigonal prisms of Ni_3B-type.

The values of T_x and $(m/n)E_a$ estimated in the present study correspond to a degree of resistance against the crystallization of Ni_3B-type phase in Ni–Si–B metallic glasses. In other words, these values correspond to the degree of resistance against rearrangements of trigonal prisms of Ni_3B-type from a random packing to a long-range ordered state. In $Ni_{100-x}(Si_{0.25}B_{0.75})_x$ metallic glasses, the thermal stability (T_x and $(m/n)E_a$) increases with increasing metalloid contents as shown in Fig. 6, and this might be interpreted as follows.

It is well known that the directional chemical

bonding between transition metal and metalloid atoms has a very significant role for the glass-forming ability or the thermal stability in transition metal–metalloid metallic glasses [22, 23]. Tanaka *et al.* [23] studied the valence electronic structures of Ni–B and Ni–Si metallic glasses using soft X-ray spectroscopy and have reported that chemical bondings between nickel and silicon or boron atoms are very important for glass formation. Messmer [24] has suggested theoretically that there are considerable bonding nickel and boron atoms in $Fe_{40}Ni_{40}B_{20}$ metallic glass. Thus, it seems reasonable to consider that in Ni–Si–B metallic glasses the portion of directional chemical bonding between nickel and silicon or boron atoms increases with increasing metalloid content, and conversely that the portion of isotropic metallic bonding between nickel atoms decreases. Furthermore, it is expected that local arrangements of trigonal prisms such as those shown in Fig. 15 will be connected more tightly in Ni–Si–B metallic glasses with high metalloid contents, and rearrangements of trigonal prisms to the long-range ordered state by thermal annealing will be harder.

In $Ni_{75}Si_xB_{25-x}$, $Ni_{72}Si_xB_{28-x}$ and $Ni_{70}Si_xB_{30-x}$ metallic glasses, the thermal stability (T_x, $(m/n)E_a$) increases by substituting silicon atoms for boron atoms up to around 10 at % Si. The dependence of thermal stability on the Si/B ratio might arise from both the difference in the strengths of Ni–Si and Ni–B chemical bondings and the large difference in atomic sizes of silicon and boron atoms. The atomic sizes of silicon and boron are 0.102 and 0.078 nm, respectively [25]. It should be mentioned here that the melting temperatures of Ni_3Si and Ni_3B compositions are 1523 and 1428 K, respectively [26]. It is considered that in Ni–Si–B metallic glasses with high contents of silicon atoms of larger atomic size the diffusion of constituent atoms by thermal annealing is harder than that in metallic glasses with high contents of boron atoms of smaller atomic size, and consequently the crystallization temperature or the activation energy for crystallization would increase with increasing silicon content. Furthermore, if the directional chemical bonding between nickel and silicon atoms in Ni–Si–B metallic glasses is stronger than that between nickel and boron atoms, the substitution of silicon atoms for boron atoms would also increase the thermal stability as observed in the present study.

As can be seen in Figs 7 and 8, the values of T_x increase by substituting silicon atoms for boron atoms up to around 10 at % Si, but decrease by further substitution. The reasons for the decrease of T_x are not clear at the present moment. However, it should be emphasized that metallic glasses with high silicon contents beyond 15 at % cannot be formed easily. Recently, Komatsu *et al.* [27, 28] measured the compositional dependences of the thermal expansion coefficient α, the difference ($\Delta T = T_x - T_g$) between the glass transition T_g and crystallization T_x temperatures, and the volume changes ΔV_R due to the structural relaxation in $Ni_{75}Si_xB_{25-x}$ metallic glasses, and found that the values of α, ΔT and ΔV_R reach a maximum around Si/B = 1. That is, the compositional dependences of these quantities are very similar to that of T_x in $Ni_{75}Si_xB_{25-x}$ metallic glasses. As discussed by Komatsu *et al.* [27, 28], the distribution of bond lengths, angles and coordination numbers in the short-range structure and the packing of basic structural units in Ni–Si–B metallic glasses might vary considerably with the composition, depending on the Si/B ratio. These results may indicate that the short-range structure, e.g. distortion or packing of basic structural units, is one of the important factors for the thermal stability of Ni–Si–B metallic glasses.

The close correlation between electrical properties and thermal stability observed in the present study would indicate that the electron transport phenomena in Ni–Si–B metallic glasses are strongly affected by the directional chemical bondings between nickel and silicon or boron atoms or the short-range structure. When the directional chemical bonding increases and thus the isotropic metallic bonding decreases, conduction electrons will be more scattered, and it is expected that $\varrho_{300\,K}$ increases and the TCR decreases with increasing silicon or boron contents. On the other hand, the electrical properties in nickel-based metallic glasses such as Ni–P, Ni–B and Ni–Si–B have been explained qualitatively using the Ziman theory by several authors [11, 28–32]. If it is assumed that the value of the Fermi wave vector k_F of nickel atoms in Ni–Si–B metallic glasses increases with increasing silicon or boron content, it is expected that the value of TCR decreases with increasing silicon or boron content using the Ziman theory. One of the most severe problems for an application of the Ziman theory to the electrical properties of transition metal–metalloid metallic glasses is to estimate accurately the value of k_F, and therefore it is strongly desirable to determine the value of k_F experimentally as a function of metalloid content.

4. Conclusion

The temperature coefficient of resistivity (TCR), specific resistivity $\varrho_{300\,K}$, crystallization peak temperature T_x and activation energy $(m/n)E_a$ for crystallization in various Ni–Si–B metallic glasses were measured and relationships among them were examined. Good correlations were obtained between TCR and $\varrho_{300\,K}$, between T_x and $(m/n)E_a$, between TCR and T_x, and between TCR and $(m/n)E_a$. The present results strongly suggest that the thermal stability in Ni–Si–B metallic glasses is closely related to the electrical properties. The compositional dependences of TCR, $\varrho_{300\,K}$, T_x and $(m/n)E_a$ and good correlations among them can be well explained qualitatively by considering the short-range structure and the directional chemical bonding between nickel and silicon or boron atoms.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education in Japan.

References

1. I. W. DONALD and H. A. DAVIES, *Phil. Mag.* **A42**

(1980) 277.
2. I. W. DONALD, H. A. DAVIES and T. KEMENY, *J. Non-Cryst. Solids* **50** (1982) 351.
3. H. HILMANN and H. R. HILZINGER, in Proceedings of 3rd International Conference on Rapidly Quenched Metals, Brighton, 1978, edited by B. Cantor (The Metals Society, London, 1978) p. 371.
4. A. LOVAS, L. GRANASG, K. ZAMBO-BALLA and J. KIRALY, in Proceedings of Conferences on Metallic Glasses Science and Technology, Budapest, 1980, Vol. 2, edited by C. Hargitai, I. Bakonyi and T. Kemeny, (Kultura, Budapest, 1981) p. 291.
5. Z. XINMING, H. R. KHAN and C. J. RAAB, *Appl. Phys.* **A34** (1984) 167.
6. M. NAGUMO, T. TAKAHASHI, T. ARAI and T. HASEGAWA, in Proceedings of 3rd International Conference on Rapidly Quenched Metals, Brighton, 1978, edited by B. Cantor (The Metals Society, London, 1978) p. 383.
7. F. MACHZAUD, F. A. KUHNAST and J. FLECHON, *J. Non-Cryst. Solids* **68** (1984) 271.
8. P. PANISSOD, I. BAKONYI and R. HASEGAWA, *Phys. Rev. B* **28** (1983) 2374.
9. K. SUZUKI, T. FUKUNAGA, F. ITOH and N. WATANABE, in Proceedings of the 5th International Conference on Rapidly Quenched Metals, Würzburg, 1984, Vol. 1, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1985) p. 479.
10. I. W. DONALD and H. A. DAVIES, *J. Mater. Sci.* **15** (1980) 2754.
11. R. YOKOTA, Y. TANAKA, T. KOMATSU and K. MATUSITA, *J. Non-Cryst. Solids* **76** (1985) 313.
12. K. MATUSITA, T. KOMATSU and R. YOKOTA, *J. Mater. Sci.* **19** (1984) 291.
13. K. MATUSITA and S. SAKKA, *Bull. Inst. Chem. Res. Kyoto Univ.* **59** (1981) 159.
14. J. H. MOOIJ, *Phys. Status Solidi (a)* **17** (1973) 521.
15. A. INOUE, T. MASUMOTO, M. KIKUCHI and T. MINEMURA, *J. Jpn Inst. Metals* **42** (1978) 294.
16. D. G. MORRIS, *Acta Metall.* **32** (1984) 837.
17. O. PILZ and P. L. RYDER, in Proceedings of the 5th International Conference on Rapidly Quenched Metals, Würzburg, 1984, Vol. 1, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1985) p. 377.
18. S. R. NAGEL and J. TAUC, *Phys. Rev. Lett.* **35** (1975) 380.
19. U. MIZUTANI, K. T. HARTWIG, T. B. MASSALSKI and R. W. HOPPER, *ibid.* **28** (1978) 661.
20. J. D. RILEY, L. LEY, J. AZOULAY and T. TERAKURA, *Phys. Rev. B* **20** (1979) 776.
21. M. G. SCOTT, in "Amorphous Metallic Alloys", edited by F. E. Luborsky (Butterworths, London, 1983) p. 149.
22. H. S. CHEN and B. K. PARK, *Acta Metall.* **21** (1973) 395.
23. K. TANAKA, T. SAITO, K. SUZUKI and R. HASEGAWA, *Phys. Rev. B* **32** (1985) 6853.
24. R. P. MESSMER, *ibid.* **23** (1981) 1616.
25. T. EGAMI and Y. WASEDA, *J. Non-Cryst. Solids* **64** (1984) 113.
26. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) pp. 256, 1040.
27. T. KOMATSU, K. MATUSITA and R. YOKOTA, *J. Non-Cryst. Solids* **72** (1985) 279.
28. *Idem, ibid.* **85** (1986) 358.
29. T. KOMATSU, M. TAKEUCHI, K. MATUSITA and R. YOKOTA, *ibid.* **57** (1983) 129.
30. J. P. CARINI, S. R. NAGEL, L. K. VARGA and T. SCHMIDT, *Phys. Rev. B* **27** (1983) 7589.
31. L. K. VARGA, A. LOVAS, J. TOTH and S. ARAJS, *J. Non-Cryst. Solids* **65** (1984) 417.
32. K. F. KELTON and F. SPAEPEN, *Phys. Rev. B* **20** (1984) 5516.

Received 5 August
and accepted 22 September 1986