JOURNAL OF MATERIALS SCIENCE 23 (1988) 3640–3647

Compositional range, thermal stability, hardness and electrical resistivity of amorphous alloys in Al–Si (or Ge)–transition metal systems

A. INOUE, Y. BIZEN*, H. M. KIMURA, T. MASUMOTO
*Institute for Materials Research, and *Graduate School, Tohoku University, Sendai 980, Japan*
M. SAKAMOTO
Miyagi Institute of Technology, Natori 981-12, Japan

An amorphous single phase was found to be formed in wide compositional ranges in rapidly solidified Al–Si–transition metal (M) and Al–Ge–M alloys. The compositional ranges are in the range from 12 to 53 at.% Si or Ge and 8 to 23% M and Al–Si–Co and Al–Ge–Fe alloys have the widest glass-formation ranges. Because the interaction between aluminium and silicon or germanium atoms is thought to be repulsive from the immiscible equilibrium phase diagrams, the glass formation is probably due to an attractive interaction of M–Si (or Ge) and Al–M pairs. Hardness, H_v, and crystallization temperature, T_x, increase with increasing M content and the highest values reach 1120 DPN and 715 K, while the change with silicon or germanium content is much smaller for H_v and is hardly seen for T_x. Additionally, the H_v and T_x have maximum values for Al–Si (or Ge)–M (M = Cr, Mn or Fe), decrease with the decrease and increase in the group number of M element and are the lowest for Al–Si (or Ge)–Ni alloys. The compositional dependence is interpreted under the assumption that T_x and H_v of the aluminium-based amorphous alloys are mainly dominated by the attractive interaction of M–(Si or Ge) and Al–M pairs. Room-temperature resistivity, ϱ_{RT}, increases in the range of 220 to 1940 $\mu\Omega$cm with increasing silicon or germanium and M contents. The change in ϱ_{RT} with the group number of M elements shows a maximum phenomenon for manganese. It has thus been clarified that the characteristics of the Al–Si–M and Al–Ge–M amorphous alloys have the different compositional dependence as compared with those for conventional metal–metalloid amorphous alloys, probably because of the unusual interaction among the constituent elements.

1. Introduction

Aluminium-based crystalline alloys have occupied an important position among a large number of engineering metallic materials, similar to iron- and titanium-based crystalline alloys. A large number of studies on the preparation and characterization of iron- and titanium-based amorphous alloys have been carried out over the last twenty years and these amorphous alloys have been used practically as magnetic, catalytic, soldering and high-strength reinforced materials, etc. Similarly, amorphization of aluminium-based alloys has actively been tried by the piston–anvil and gun-quenching techniques as well as the melt-spinning technique. However, achievement of amorphization has been limited to Al–Si [1], Al–Ge [2], Al–Cu [3], Al–Ni [4], Al–Cr [5] and Al–Pd [6] alloys for the coexisting amorphous and crystalline phases, and Al–Fe–B [7], Al–Co–B [7], Al–Fe– (Si or Ge) [8] and Al–Mn–Si [9] alloys for the mostly single amorphous phase. Most recently, it has been found [10] that a homogeneously amorphous phase is formed in wide composition ranges in rapidly solidified Al–Ge–M and Al–Si–M (M = V, Mn, Fe, Co or Ni) ternary systems and the Al–Si–Ni and Al–Ge–Ni amorphous alloys exhibit a good ductility which is shown by a 180° bending without fracture. This paper reports attempts to study the formation range, thermal stability, hardness and electrical resistivity of Al–Ge–M and Al–Si–M amorphous alloys and to investigate the features of the properties for the aluminium-based amorphous alloys in comparison with those for metal–metalloid type amorphous alloys.

2. Experimental procedure

The specimens used in the present work were Al–Si–M and Al–Ge–M (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni or Cu) ternary alloys ranging from 8 to 45 at.% Si, 8 to 60 at.% Ge and 5 to 30 at.% M. The subscripts represent nominal atomic percentages of the respective components. Mixtures of electrical aluminium, transition metal (M) and silicon or germanium were melted in an argon atmosphere using an arc furnace. Ribbon samples about 0.02 mm thick and 1 mm wide were prepared from these mixed alloys by a single-roller melt-

0022-2461/88 $03.00 + .12

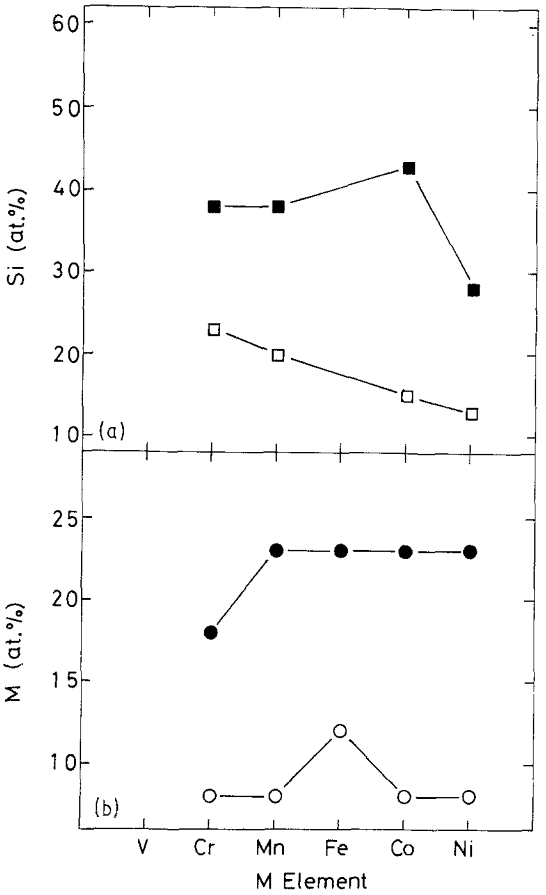

Figure 1 Compositional ranges for the formation of amorphous phase in rapidly quenched $Al_{90-x}Si_xM_{10}$ (a), and $Al_{75-x}Si_{25}M_x$ (b) (M = V, Cr, Mn, Fe, Co or Ni alloys).

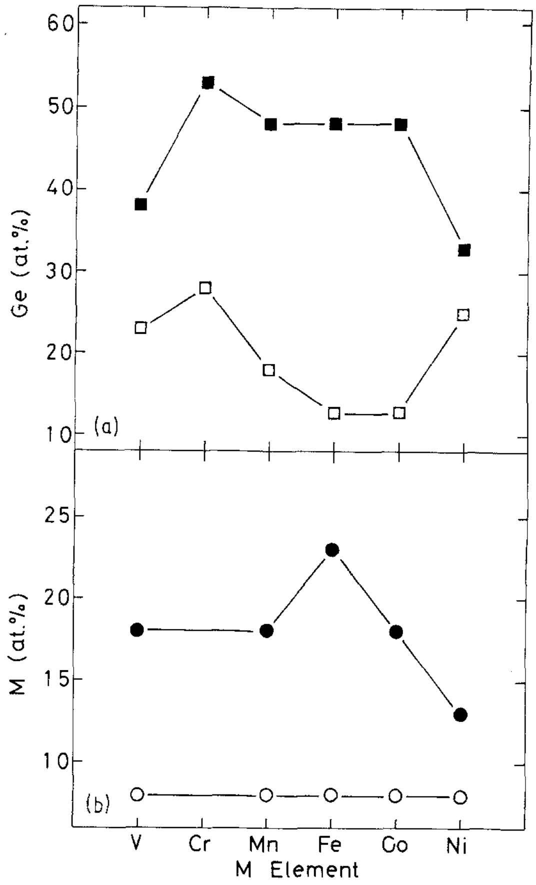

Figure 2 Compositional ranges for the formation of amorphous phase in rapidly quenched $Al_{90-x}Ge_xM_{10}$ (a), and $Al_{75-x}Ge_{25}M_x$ (b) (M = V, Cr, Mn, Fe, Co or Ni) alloys. Cu*K*α radiation.

spinning apparatus. The amorphous nature of the as-quenched samples was examined by X-ray diffraction analysis with monochromatic Cu*K*α radiation and transmission electron microscopy. Bending ductility was evaluated by the simple bend test; the methods have been described previously in detail [7]. The crystallization temperature and heat of crystallization were measured by differential scanning calorimetry (DSC) at a heating rate of 20 K min^{-1}. Hardness was measured by a Vickers microhardness tester with a 100 g load. Resistivity measurement was made by the four-point method over the temperature range 4.2 to 250 K. The temperature was measured using a calibrated germanium thermometer at temperatures below 90 K and a calibrated diode thermometer in the higher temperature range.

3. Results and discussion

3.1. Formation range of the amorphous alloys

A mostly single amorphous phase defined by no trace of crystallinity in the X-ray diffraction pattern was formed in Al–Si–M (M = Cr, Mo, Mn, Fe, Co or Ni) and Al–Ge–M (M = V, Cr, Mo, Mn, Fe, Co or Ni) systems. No amorphous phase was formed in Al–Si–M systems with M = Ti, Zr, Hf, V, Nb, Ta, W or Cu and Al–Ge–M systems with M = Ti, Zr, Hf, Nb, Ta, W or Cu. Figs 1 and 2 show the compositional range of Al–Si–M and Al–Ge–M amorphous alloys. Their amorphous phases are formed in the range 12 to 42% Si and 8 to 23% M for Al–Si–M alloys and 12 to 53% Ge and 8 to 23% M for Al–Ge–M alloys. The formation range of the Al–Si–M amorphous alloys is the widest for Al–Si–Co, followed by Al–Si–Fe, Al–Si–Mn, Al–Si–Ni and Al–Si–Cr, and that for the Al–Ge–M amorphous alloys is the widest for Al–Ge–Fe and becomes narrower in the order Al–Ge–Co, Al–Ge–Cr, Al–Ge–V and Al–Ge–Mn. The amorphous phase is also formed in the Al–Si–V system, but it is always coexistent with crystalline phase.

Although the compositional ranges of the amorphous phase are almost the same between Al–Si–M and Al–Ge–M systems, one can notice a difference, in that the metalloid concentration ranges are considerably wider for Al–Ge–M than for Al–Si–M and the M concentration range is wider for Al–Si–M. Fig. 3 shows the X-ray diffraction patterns of rapidly quenched $Al_{90-x}Ge_xMn_{10}$ alloys with different germanium concentrations. It is notable that the amorphous alloys have two broad diffraction peaks at about k_p = 23.71 and 31.74 nm^{-1}. The split of the broad halo peaks is also observed in the electron diffraction pattern, as exemplified for $Al_{60}Ge_{30}Mn_{10}$ in Fig. 4, even though no appreciable change in contrast corresponding to the split of the first broad peak is seen in the bright-field electron micrograph. Fig. 3 also shows that the decrease and increase of germanium content from the glass-formation range result in precipitation of fcc aluminium and cubic germanium phases, respectively.

It is generally known that the formation of an amorphous alloy is easier in the vicinity of eutectic

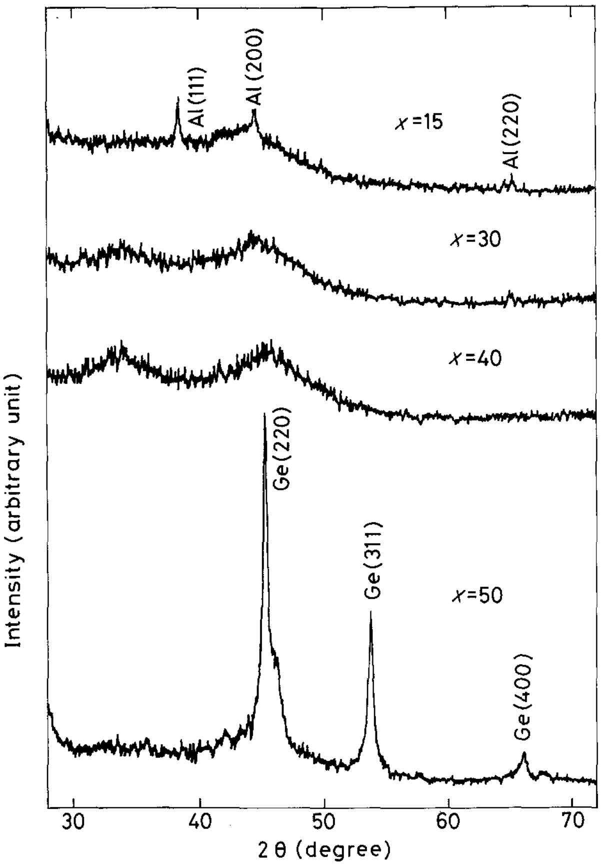

Figure 3 X-ray diffraction patterns of rapidly quenched $Al_{90-x}Ge_xMn_{10}$ (x = 15, 30, 40 and 50 at. %) alloys.

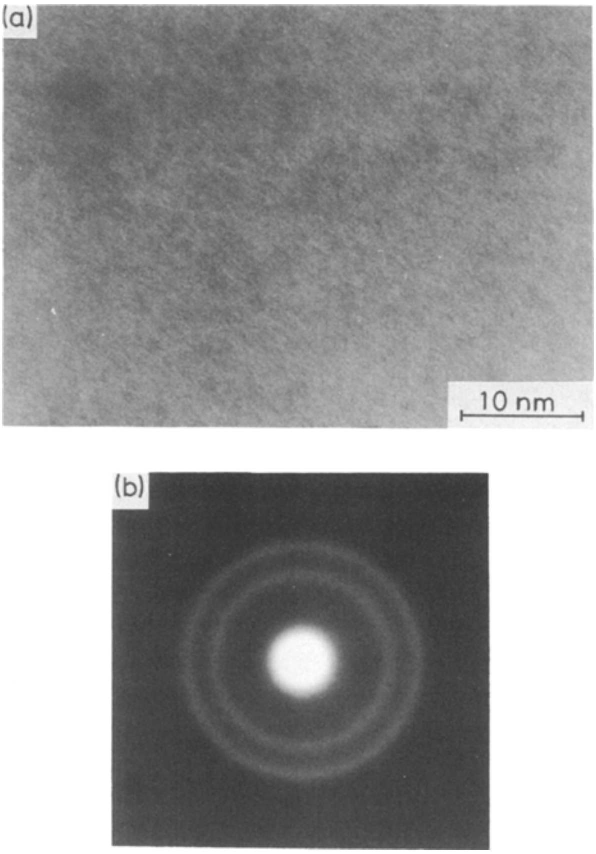

Figure 4 Bright-field electron micrograph and selected-area electron diffraction pattern of a rapidly quenched $Al_{60}Ge_{30}Mn_{10}$ alloy.

composition with lower melting temperature. No equilibrium phase diagrams of Al–Si–M and Al–Ge–M alloys are available over the present wide composition ranges. The eutectic composition of Al–Si and Al–Ge binary alloys is 11.3 at. % Si and 30.3 at. % Ge [11], being significantly different between both the alloys. The metalloid concentration where the amorphous phase is formed is in the range 12 to 53 at. % Ge and 12 to 42 at. % Si. This indicates that the formation range extends over both sides of the eutectic composition of Al–Ge for the Al–Ge–M system and only on the hypereutectic side of Al–Si for the Al–Si–M system. Thus the lowering of melting temperature (T_m) at a eutectic point is not thought to be a dominant factor for the amorphization of Al–Si–M and Al–Ge–M alloys. On the other hand, the M content for the glass formation is in the range 8 to 23 at. %, where various kinds of intermetallic compounds are formed in Al–M binary alloys, and T_m is in the range 1533 to 1921 K [12]. The limitation of the M content is probably due to the increase of T_m on the upper side and the decrease of the attractive bonding nature of aluminium and M atoms for the glass formation on the lower side. The reason for the limitation of the compositional range for the metalloids (germanium and silicon) without the formation tendency of intermetallic compounds against aluminium remains unknown, even though a further increase and decrease of silicon and germanium contents results in precipitation of silicon or germanium and aluminium phases, respectively, in an amorphous matrix. In any case, the new information that an amorphous single phase is formed over wide composition ranges in Al–Si–M and Al–Ge–M alloys containing a large amount of silicon or germanium without an attractive interaction with aluminium is different from the general concept [13] for the glass formation of metal–metalloid type alloys. The abnormality is expected to result in the appearance of significantly different structure and properties. This has already been confirmed by the split of the first halo peak in the X-ray and electron diffraction patterns and extremely high electrical resistivities [10].

3.2. Hardness

Figs 5 and 6 show the change of hardness, H_v, as a function of M content for Al–Si–M (M = Cr, Mn, Fe, Co or Ni) and Al–Ge–M (M = Cr, Fe or Co) amorphous alloys with 25% Si and 30% Ge. H_v has a distinct M concentration dependence and increases with increasing M content from 365 to 600 DPN at 10% M to 730 to 1120 DPN at 20% M. The compositional dependence of H_v is very similar in Al–Si–M and Al–Ge–M alloys. Figs 5 and 6 also show that the H_v values of Al–Si–M and Al–Ge–M alloys are higher for the alloys with M = Cr, Mn or Fe than for the alloys with M = Ni or V and there is no appreciable difference in H_v between the alloys with M = Cr, Mn or Fe. It is notable that the H_v values at 20% M may be as high as 700 to 1100 DPN even for aluminium-based alloys, comparable to the high H_v values [14] for transition metal–metalloid type amorphous alloys. Fig. 7 shows the change of H_v as a function of silicon or germanium content for Al–Si–M and Al–Ge–M amorphous alloys with constant M contents of 10 and 15 at. %. The H_v values are higher

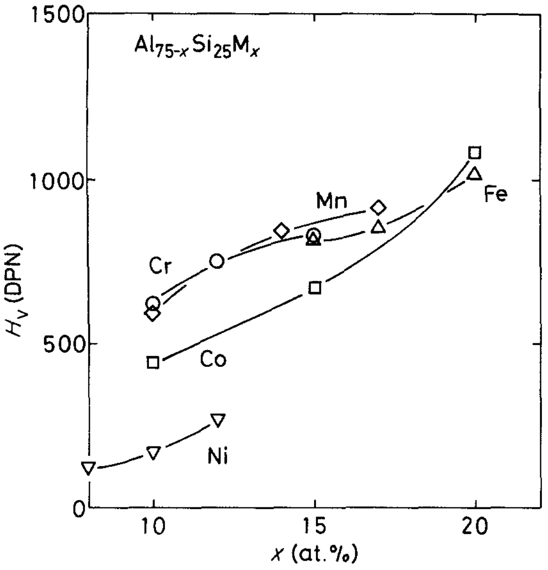

Figure 5 Change in Vickers microhardness (H_v) of Al–Si–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with M content. Load = 25 g.

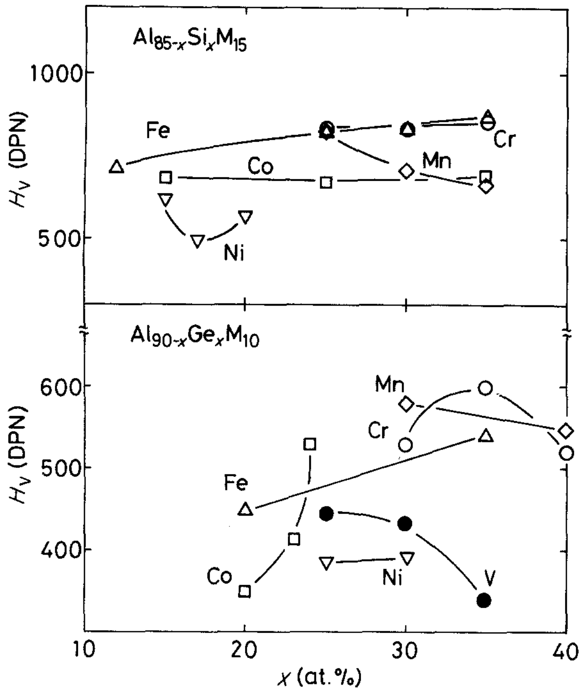

Figure 7 Change in Vickers microhardness (H_v) of Al–Si–M and Al–Ge–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with silicon or germanium content. Load = 25 g.

for the alloys with higher silicon or germanium concentration and the compositional dependence is more significant for Al–Ge–M alloys. Thus, the replacement of aluminium by M gives rise to significant increase in H_v for all the alloy systems, whereas the increase in H_v by the replacement of aluminium by silicon or germanium is less significant and the degree is much smaller for Al–Si–M alloys. The bonding nature of the constituent atoms in Al–Si (or Ge)–M alloys increases in the order M–(Si or Ge) > Al–M > Al–(Si or Ge) from the data that T_m [12] and H_v [15] are larger for M–(Si or Ge) compounds than for Al–M compounds and no compound is formed in Al–(Si or Ge) alloys [11]. Accordingly, increases in M and silicon or germanium contents are presumed to bring about increase in hardness of the amorphous alloys, consistent with the results shown in Figs 5 to 7.

3.3. Crystallization temperature (T_x)

T_x was also found to show a similar compositional dependence as that for H_v. As shown in Figs 8 and 9, as the M content increases from 8 to 20 at. %, T_x increases from 498 to 715 K for Al–Si–(Cr, Mn, Fe or

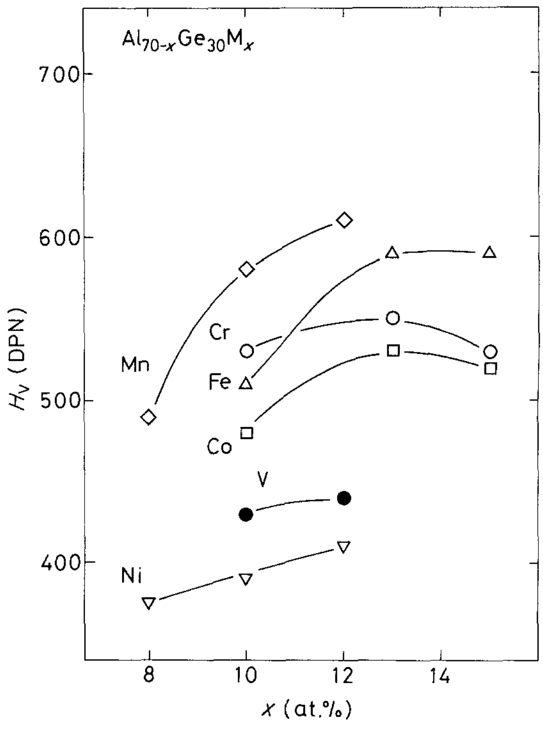

Figure 6 Change in Vickers microhardness (H_v) of Al–Ge–M (M = Cr, Fe or Co) amorphous alloys with M content. Load = 25 g.

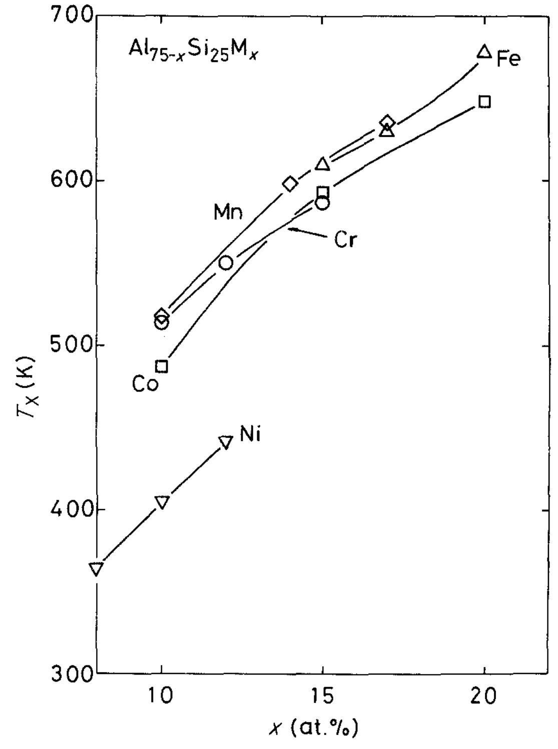

Figure 8 Change in crystallization temperature (T_x) of Al–Si–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with M content. Heating rate = 40 K min^{-1}.

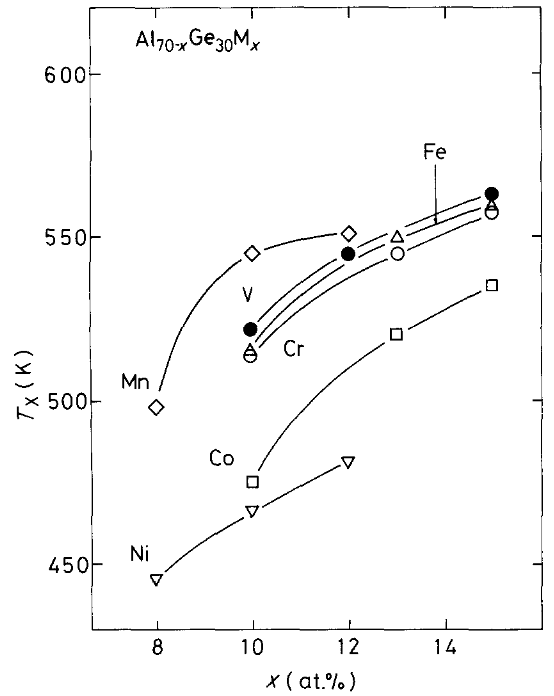

Figure 9 Change in crystallization temperature (T_x) of Al–Ge–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with M content. Heating rate = 40 K min^{-1}.

Co) alloys and from 370 to 575 K for Al-Si-Ni alloys. On the other hand, increase in T_x of Al–Ge–M alloys with increase in M content is considerably smaller than that of Al–Si–M alloys and the increase of T_x with increasing M content from 8 to 15 at. % is as small as about 50 K. Furthermore, T_x is higher by 50 to 150 K for Al–Si–M alloys than for Al–Ge–M alloys. This difference is probably because the eutectic temperature of Al–Si alloy is higher by 153 K than that of Al–Ge alloy [11]. The T_x values of Al–Si–M alloys are considerably higher for Al–Si–(Cr, Mn, Fe or Co) alloys than for Al–Si–Ni alloy and the Al–Si–M (M = Cr, Mn, Fe or Co) alloys have nearly the same T_x values. No distinct change in T_x with silicon and germanium contents is observed as shown in Fig. 10. Thus, the H_v and T_x of Al–Si–M and Al–Ge–M amorphous alloys increase significantly with increase in the amount of Al replaced by M, while those as a function of silicon or germanium content do not show a significant change. Such compositional dependences probably occur because increasing M content results in an increase in the number of M–Si (or Ge) bondings with strongly attractive interaction and a decrease in the number of Al–Si (or Ge) bondings with repulsive interaction. On the other hand, an increase in silicon or germanium content does not cause a change in the number of M–Si (or Ge) bondings. Such a change as a function of metalloid content is significantly different from the general tendency that H_v and T_x of transition metal–metalloid amorphous alloys increase with increasing metalloid content. The significant difference is interpreted as due to the difference of bonding nature between transition metal–Si (or Ge) atoms with strongly attractive interaction and Al–(Si or Ge) with repulsive interaction. Thus, it is said that the interaction of the constituent atoms for aluminium-based amorphous alloys is significantly different from that for transition metal–metalloid type amorphous alloys reported previously, even though the alloy compositions belong to the same category of metal–metalloid type.

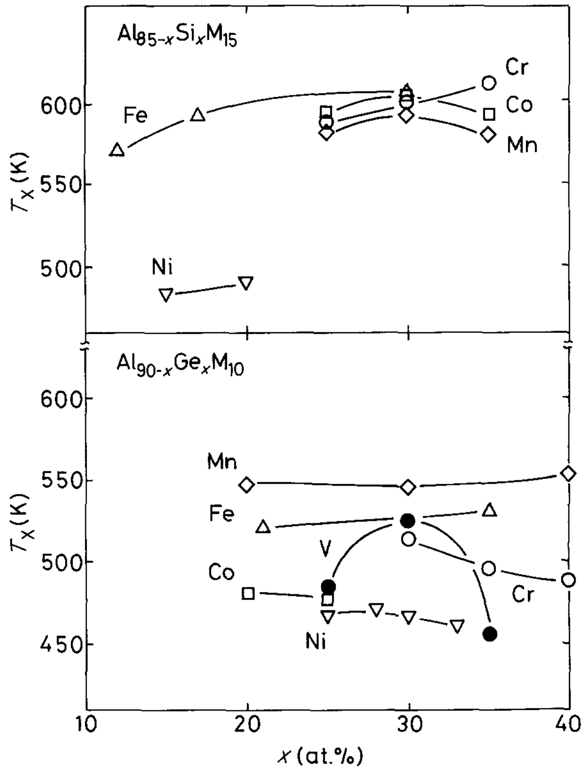

Figure 10 Change in crystallization temperature (T_x) of Al–Si–M and Al–Ge–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with silicon or germanium content. Heating rate = 40 K min^{-1}.

Fig. 11 shows the change in the heat of crystallization (ΔH_x) for Al–Si–M and Al–Ge–M amorphous alloys with M content. As the M content increases, ΔH_x tends to decrease, in good contrast to the significant rise of T_x. The decrease of ΔH_x probably occurs because the short-range atomic configuration in the amorphous alloys approaches that of crystalline compounds consisting mainly of M–(Si or Ge) and Al–M bondings with increasing M content. This presumption is consistent with the interpretation described above that the increases of such atomic bondings result in increases in H_v and T_x.

3.4. Electrical resistivity

Figs 12 and 13 show the change of electrical resistivity at room temperature (RT), ϱ_{RT}, for Al–Si–M amorphous alloys with M and silicon contents. The ϱ_{RT} increases significantly with increasing M and silicon contents and the increase is more remarkable for the increase in M content. The ϱ_{RT} values lie in the range 220 to 1760 $\mu\Omega$cm which are two to six times higher than those (100 to 300 $\mu\Omega$cm) for transition metal-based amorphous alloys. A similar metalloid composition dependence of ϱ_{RT} is also recognized in Al–Ge–M amorphous alloys, as shown in Fig. 14. The ϱ_{RT} value increases significantly from 500 to 850 $\mu\Omega$cm at 20% Ge to 860 to 1940 $\mu\Omega$cm at 40% Ge. Although the increase in ϱ_{RT} with increasing silicon or germanium content can be interpreted by taking the semiconducting nature of silicon and germanium into consideration, the increase in ϱ_{RT} with

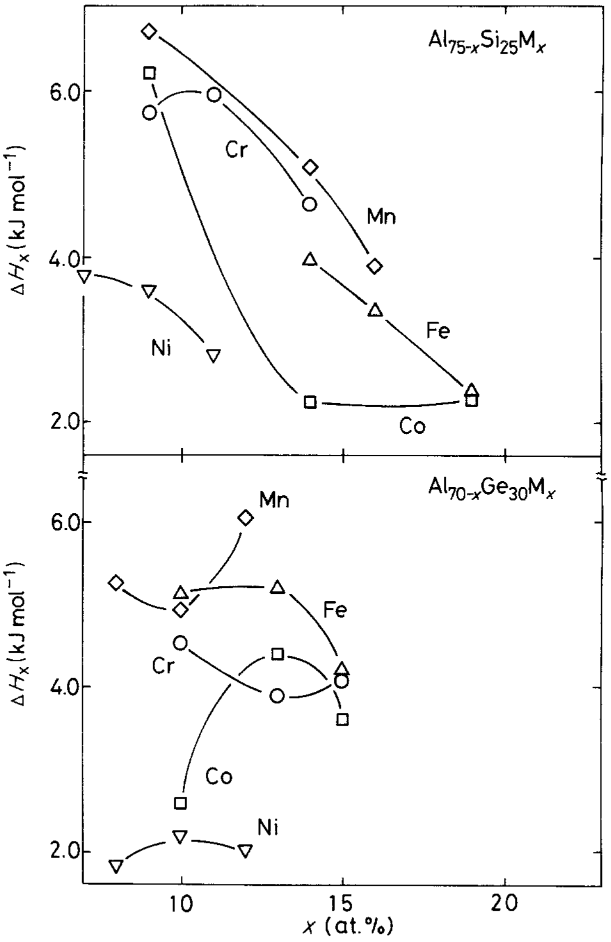

Figure 11 Change in the heat of crystallization (ΔH_x) of Al–Si–M and Al–Ge–M (M = V, Cr, Mn, Fe, Co or Ni) amorphous alloys with M content.

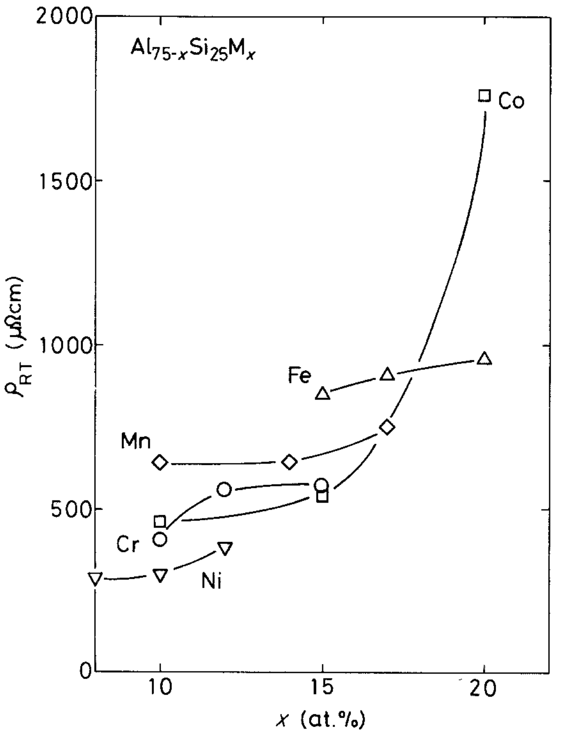

Figure 12 Change in electrical resistivity at room temperature (ϱ_{RT}) of Al–Si–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with M content.

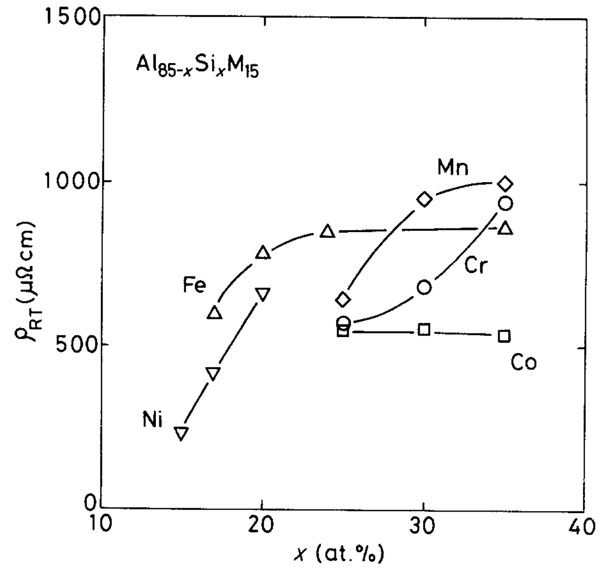

Figure 13 Change in electrical resistivity at room temperature (ϱ_{RT}) of Al–Si–M (M = Cr, Mn, Fe or Ni) amorphous alloys with silicon content.

increasing M and silicon or germanium contents is also thought to be related to the anomalous structure of the aluminium-based amorphous alloys. That is, as shown in Figs 3 and 4, the X-ray and electron diffraction patterns of the Al–Si–M and Al–Ge–M amorphous alloys show split first halo peaks, the split being thought due to the phase separation into aluminium-rich and silicon- or germanium-rich phases over a short range [10, 14], i.e. the sites of aluminium and silicon or germanium atoms in the amorphous structure are not random and are distributed in a distinguishable site on the scale of about 1 nm. It has been clarified [10] that the splitting phenomenon becomes significant with increasing M content. The split structure on a scale of about 1 nm is presumed to result in

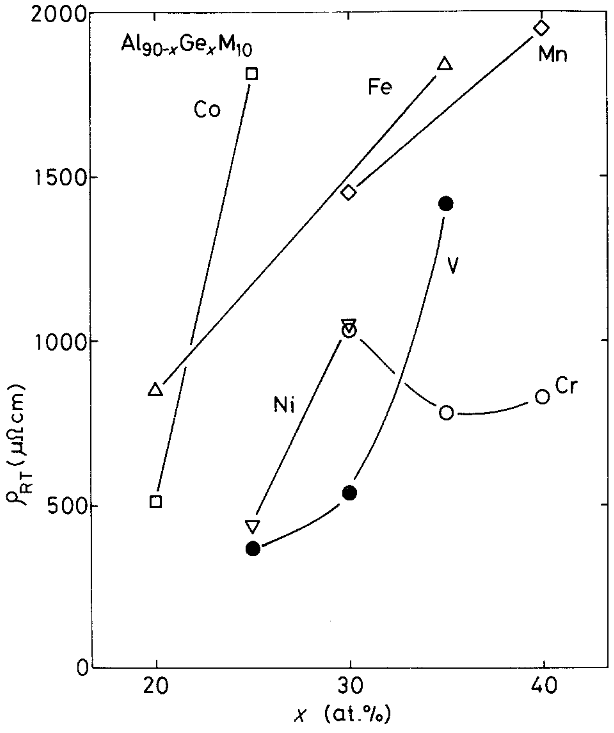

Figure 14 Change in electrical resistivity at room temperature (ϱ_{RT}) of Al–Ge–M (M = Cr, Mn, Fe, Co or Ni) amorphous alloys with germanium content.

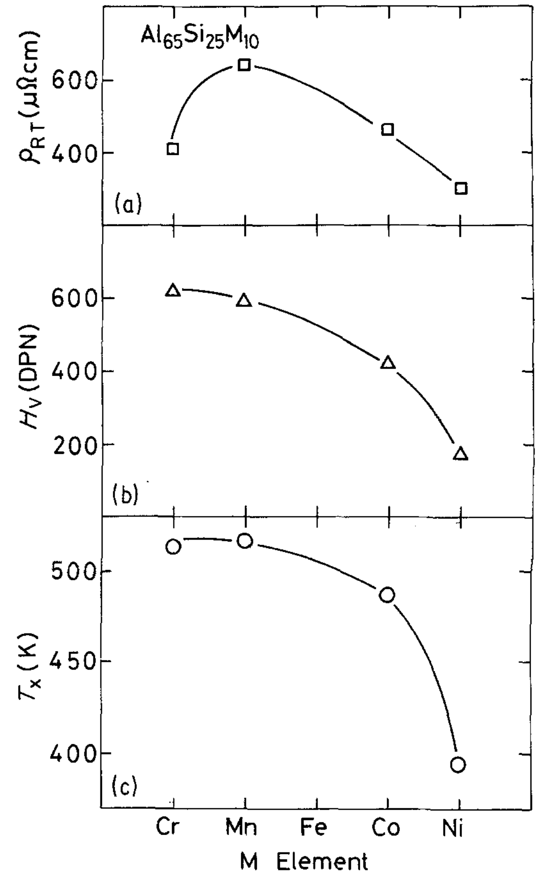

Figure 15 Changes in (a) ϱ_{RT}, (b) H_v, load 25 g, and (c) T_x, heating rate = 40 K min^{-1}, of Al–Si–M amorphous alloys with the group number of M metals.

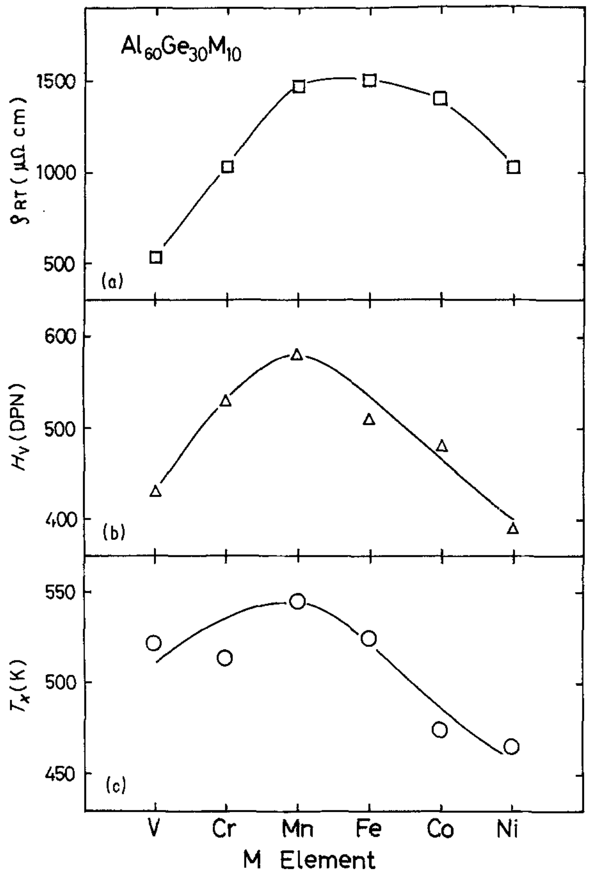

Figure 16 Changes in (a) ϱ_{RT}, (b) H_v, load 25 g, and (c) T_x, heating rate = 40 K min^{-1}, of Al–Ge–M amorphous alloys with the group number of M metals.

electrical resistivities much higher than those of amorphous alloys with a homogeneously single structure.

Finally, the effect of M element on T_x, H_v and ϱ_{RT} values of Al–Si–M and Al–Ge–M amorphous alloys is summarized in Figs 15 and 16. T_x and H_v show a similar change; both values are the highest for alloys containing chromium, manganese and iron and tend to decrease with decreasing group number in the periodic table. The systematic change as a function of the group number is interpreted as due to the bonding nature of M–Al, M–Si and M–Ge atomic pairs being stronger for the VI and VII group number elements. Additionally, the compositional effect of ϱ_{RT} is thought to reflect the result that the number of conductive free electrons in the outer d-shell which do not contribute to the covalent bonding of M–Al, M–Si and M–Ge pairs is smaller for M = Cr and Mn and the hybridization between the d-band of the transition M metal and s and p bands of aluminium is stronger for M = Cr and Mn [15].

4. Conclusions

1. An amorphous single phase was obtained over a wide compositional range in rapidly quenched Al–Si–M and Al–Ge–M (M = V, Cr, Mo, Mn, Fe, Co or Ni) alloys. The compositional ranges are the widest for M = Co or Fe and extend from 14 to 42% Si and 8 to 23% Co for the Al–Si–Co system and from 12 to 48% Ge and 8 to 18% Co for the Al–Ge–Co system. The compositional range becomes narrower in the order Co > Fe > Mn > Ni > Cr for the Al–Si–M system and Fe > Co > Mn > Cr > V > Ni for the Al–Ge–M system. The glass formation was interpreted as due to attractive interaction of M–Si (or Ge) and Al–M atomic pairs because of repulsive interaction of Al–(Si or Co) pairs.

2. H_v increases significantly with increasing M content and the highest value reached is about 1120 DPN for $Al_{50}Si_{30}Fe_{20}$. Similarly, H_v also increases with increasing silicon or germanium content, but the increase is much smaller compared to the case for M content. The compositional dependence probably occurs because the hardness is mainly dominated by the bonding nature of M–Si (or Ge) and Al–M atoms with attractive interaction rather than the Al–Si (or Ge) bonding with repulsive interaction.

3. The change in T_x with M content has a similar compositional dependence as that for H_v. The increase in M content results in an increase in T_x and the highest value reached is 715 K for $Al_{50}Si_{30}Fe_{20}$, while no distinct change in T_x with silicon or germanium content is seen.

4. The ϱ_{RT} has a similar compositional dependence as H_v and increases from 220 to 1940 μΩcm with increasing metallic, M, and semiconducting, silicon or germanium, contents. The change in ϱ_{RT} is closely related to the degree of phase separation in a short-range scale in the amorphous phase and there is a tendency that the clearer the split of the first halo peaks on the X-ray and electron diffraction patterns, the higher is ϱ_{RT}.

Thus, the compositional dependences of H_v, T_x and

ϱ_{RT} for the present aluminium-based amorphous alloys are significantly different from those for previous metal–metalloid amorphous alloys and the difference probably occurs because the aluminium-based amorphous alloys dissolve a large amount of silicon or germanium with a repulsive interaction with aluminium.

Acknowledgements

The authors thank Mr A. P. Tsai and Miss M. Kumagaya for carrying out some of the determinations of the glass-formation range.

References

1. P. PREDECKI, B. C. GIESSEN and N. J. GRANT, *Trans. Met. Soc. AIME* **233** (1965) 1438.
2. P. RAMACHANDRARAO, M. LARIDJANI and R. W. CAHN, *Z. Metalkde* **63** (1972) 43.
3. H. A. DAVIES and J. B. HULL, *Scripta Metall.* **6** (1972) 241.
4. K. CHATTOPADYAY, R. RAMACHANDRARAO, S. LELE and T. R. ANANTHARAMAN, Proceedings 2nd International Conference on Rapidly Quenched Metals, edited by N. J. Grant and B. C. Giessen (Massachusetts Institute of Technology, Massachusetts, 1976) Section I, p. 157.
5. P. FURRER and H. WALIMONT, *Mater. Sci. Engng* **28** (1977) 127.
6. G. V. S. SASTRY, C. SURYANARAYANA, O. N. SRIVASTAVA and H. A. DAVIES, *Trans. Indian Inst. Metals* **31** (1978) 292.
7. A. INOUE, A. KITAMURA and T. MASUMOTO, *J. Mater. Sci.* **16** (1981) 1895.
8. R. O. SUZUKI, Y. KOMATSU, K. E. KOBAYASHI and P. H. SHIGU, *ibid.* **18** (1983) 1195.
9. H. S. CHEN and C. G. CHEN, *Phys. Rev.* **B33** (1986) 668.
10. A. INOUE, M. YAMAMOTO, H. M. KIMURA and T. MASUMOTO, *J. Mater. Sci. Lett.* **6** (1987) 194.
11. M. HANSEN (ed.), "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) pp. 96, 132.
12. F. E. LUBORSKY (ed.), "Amorphous Metallic Alloys" (Butterworths, London, 1983).
13. H. S. CHEN, *Rep. Prog. Phys.* **43** (1980) 353.
14. J. M. DUBOIS, G. Le CAER and K. DEHGHAN, "Rapidly Quenched Metals", edited by S. Steeb and H. Warlimont (Elsevier, Amsterdam, 1985) p. 197.
15. E. VOISIN and A. PASTUREL, *Phil. Mag. Lett.* **55** (1987) 123.

Received 29 June
and accepted 9 October 1987