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INTRODUCTION

To date a large number of amorphous alloys have been produced by the melt quenching technique. Broadly speaking, these alloys can be classified into two categories. One is the metal-metalloid type consisting of a transition metal and a metalloid element such as P, Si, C or B. The other is the early transition metal(e.g., Ti, Zr etc.) alloyed with a late transition metal(e.g., Co, Ni, Cu etc.). Most amorphous alloys belong to the former type and they always contain about 15-30 at.% metalloid elements. On the other hand, the amorphous alloys belonging to the latter type usually contain solute metals more than about 30 at.% as exemplified for Cu-Ti, Cu-Zr and Ni-Nb.

Recently, we have found that an amorphous single phase is formed in a wide composition range of (Fe, Co, Ni)-IV or V group transition metal-B ternary alloys containing less than 10 at.%B. Further, these amorphous alloys contain less than about 20 at.% of the IV or V group transition metals and thus are interesting materials from industrial point of view because of high concentration of ferromagnetic elements such as Fe, Co and Ni. The aim of this paper is to present the composition range of Fe, Co or Ni-IV or V group transition metal-B ternary amorphous phase and the composition dependence of mechanical properties of these amorphous alloys.

EXPERIMENTAL

Alloys used in the present work are of the Fe, Co or Ni-IV or V group transition metal-B ternary systems such as (Fe, Co, Ni)-(Ti, Zr, Hf, V, Nb, Ta, Mo)-B. Mixtures of pure metals and boron were melted in argon atmosphere in an arc- or an induction furnace. Continuous ribbon specimens of 1 mm width and 0.02 mm thickness were prepared by melt spinning. Typically, the amount of alloys melted in one run was about 2 g and the rotation speed of the steel roller(20 cm in diameter) was about 6000 rpm. Identification of the as-quenched phases was made by conventional X-ray diffraction and transmission electron microscopy techniques. Hardness was measured by a Vickers microhardness tester with a 100 g load. Each hardness value was the average of seven to ten indentations. Crystallization temperature was examined by a differential thermal analyzer(DTA) at a heating rate of 8.33×10^{-2} K/s. Ductility was evaluated by measuring the radius of curvature at fracture in a simple bend test /1/. The deformed structure and the fracture surface were observed by a scanning electron microscope.

RESULTS

1. Formation range of the amorphous phase

The completely amorphous phase is obtained in wide composition ranges of Co-Ti-B, Fe-Zr-B, Co-Zr-B, Ni-Zr-B, Fe-Hf-B, Co-Hf-B, Ni-Hf-B, Fe-Nb-B, Co-Nb-B, Co-Ta-B, Ni-Ta-B and Co-Mo-B systems. As examples, Fig. 1 shows the formation ranges of the amorphous phase in Fe-Nb-B, Co-Nb-B, Co-Ta-B and Ni-Ta-B systems in which three elements are essential for the formation of amorphous phase. On the other hand, the formation ranges of the other amorphous alloys are omitted because amorphous single phase has been formed in Co-Ti /2/, (Fe, Co, Ni)-Zr /3,4/ and (Fe, Co, Ni)-Hf /5,6/ binary systems and the addition of B is not always necessary for the formation of amorphous phase. As seen in the figure, these amorphous alloys are limited to the range more than about 2 at.%B and the alloying elements are limited to the ranges of 10-14 at.%Nb for Fe-Nb-B, 7-22 at.%Nb for Co-Nb-B, 8-20 at.%Ta for Co-Ta-B and 10-23 at.%Ta for Ni-Ta-B. The formation range becomes narrower in the order of the Co-Zr-B > Co-Hf-B > Co-Ti-B > Co-Nb-B > Co-Ta-B > Fe-Zr-B > Fe-Hf-B > Ni-Zr-B > Ni-Hf-B > Ni-Ta-B > Fe-Nb-B systems and no amorphous phase was found in the alloy systems of (Fe, Ni)-Ti-B, (Fe, Co, Ni)-V-B, Ni-Nb-B and Fe-Ta-B.

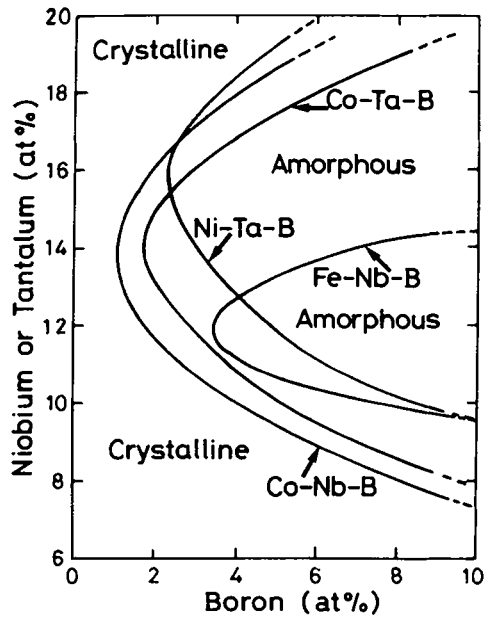

Fig. 1 Composition ranges for the formation of amorphous single phase in the Fe-Nb-B, Co-Nb-B, Co-Ta-B and Ni-Ta-B systems.

Melt-quenched eutectic (Fe, Co)-Nb and (Co, Ni) -Ta binary alloys show a crystalline structure without any trace of amorphous phase. On the other hand, the alloys with as low as about 2 at.%B show an amorphous structure. From these facts, it is concluded that the simultaneous dissolution of Nb or Ta and B enhances the amorphous-forming tendency of their alloys. That is, it is assumed that the bonding force between metal and metal as well as metal and metalloid plays an important role in the formation of an amorphous phase in the alloys investigated in the present work. This assumption also receives support from the fact that metal-metal type amorphous phase is formed in the binary alloy systems consisting of Fe, Co or Ni and Ti, Zr or Hf which are considered to possess stronger bonding force compared with that between Fe, Co or Ni and Nb or Ta.

2. Mechanical properties

The Vickers hardness values(Hv) of (Fe, Co, Ni) $_{94-x}M_xB_6$(M=Ti, Zr, Hf, Nb and Ta) ternary amorphous alloys are plotted as a function of the concentration of alloying elements M in Fig. 2. As seen in the figure (a), (b) and (c), the hardness values increase significantly with increasing amount of alloying elements, indicating that the bonding force between alloying element M and B is much stronger than that between Fe, Co or Ni and B. Further, one can notice that the hardness value is highest for

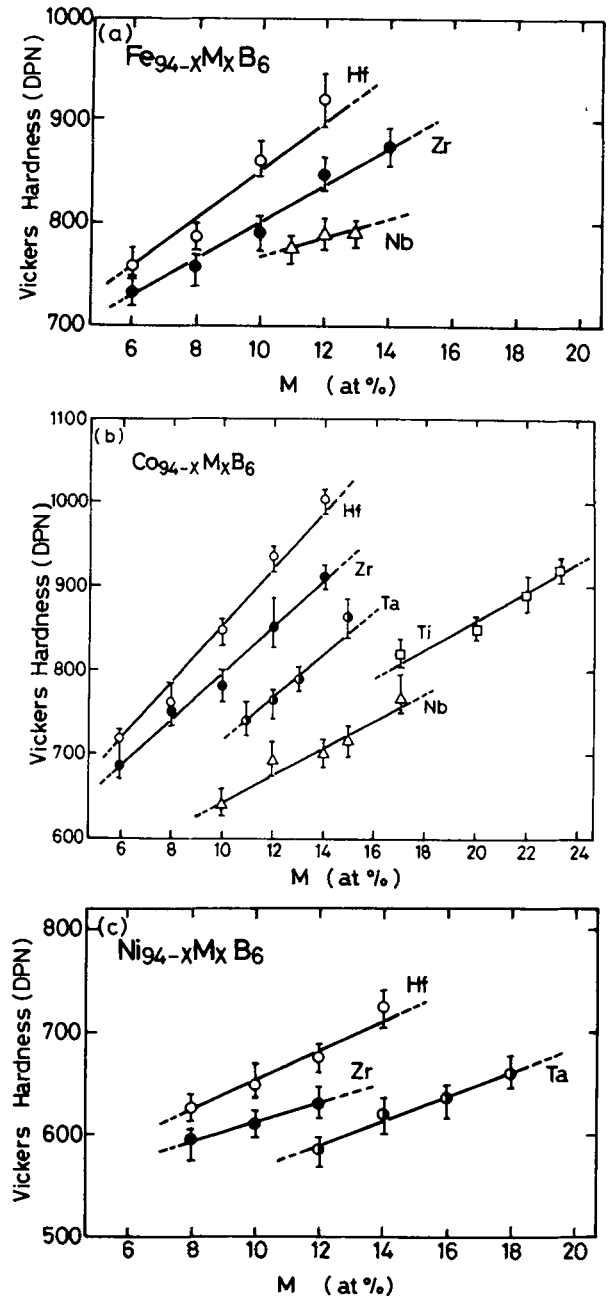

Fig. 2 Change in Vickers hardness(Hv) for $Fe_{94-x}M_xB_6$, $Co_{94-x}M_xB_6$ and $Ni_{94-x}M_xB_6$(M=Ti, Zr, Hf, Nb and Ta) amorphous alloys with the amount of alloying elements M.

the alloys containing Hf and decreases in the order of Zr > Ta > Ti > Nb. This tendency is the same in the three alloy systems of Fe, Co and Ni, indicating that the bonding force between M and Fe, Co or Ni or M and B decreases in the order of Hf > Zr > Ta > Ti > Nb. The highest hardness value obtained is about 1000 DPN for $Co_{80}Hf_{14}B_6$ alloy.

Figure 3 shows the change in the Vickers hardness of (Fe, Co, Ni)$_{88-x}M_{12}B_x$ amorphous alloys with

the B concentration. The hardness value increases with increasing B content and the increasing rate is largest for the Co-base alloys. Further, similar to that for (Fe, Co, Ni)$_{94-x}M_xB_6$ alloys, the hardness value decreases in the order of Hf > Zr > Ta > Nb systems. The highest hardness value in these alloy systems is about 1000 DPN for $Co_{80}Hf_{12}B_8$ alloys.

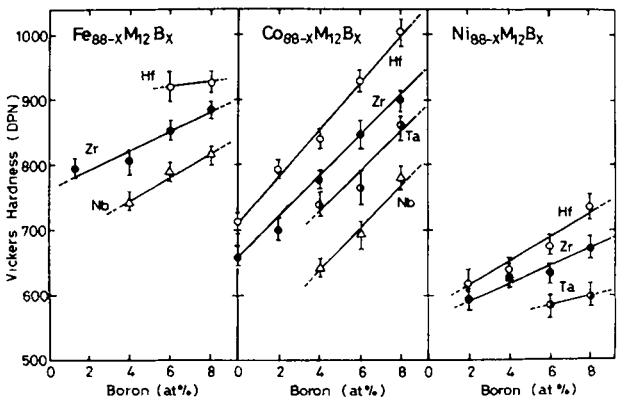

Fig. 3 Change in Vickers hardness(H_V) for $Fe_{88-x}M_{12}B_x$, $Co_{88-x}M_{12}B_x$ and $Ni_{88-x}M_{12}B_x$(M=Ti, Zr, Hf, Nb and Ta) amorphous alloys with B content.

All the amorphous alloys of the present systems possess good bend ductility, as in the case of typical metal-metalloid or metal-metal amorphous alloys. Ductile-brittle transition behavior of $Fe_{82}M_{12}B_6$, $Co_{82}M_{12}B_6$ and $Ni_{82}M_{12}B_6$(M=Ti, Zr, Hf, Nb and Ta)

Table I Crystallization temperature(T_x), critical fracture temperature(T_f), T_f/T_x and Vickers hardness(H_V) for Fe_{82}(Zr, Hf, Nb)$_{12}B_6$, Co_{82}(Ti, Zr, Hf, Nb, Ta)$_{12}B_6$ and Ni_{82}(Zr, Hf, Ta)$_{12}B_6$ ternary amorphous alloys.

Alloy System (at%)	Crystallization Temp T_x (K)	Critical Fracture Temp. T_f (K, x3.6ks)	T_f/T_x	Vickers Hardness Hv (DPN)
$Fe_{82}Zr_{12}B_6$	868	563	0.64	845
$Fe_{82}Hf_{12}B_6$	885	598	0.68	920
$Fe_{82}Nb_{12}B_6$	820	623	0.76	790
$Co_{72}Ti_{22}B_6$	833	613	0.74	890
$Co_{82}Zr_{12}B_6$	782	648	0.83	850
$Co_{82}Hf_{12}B_6$	820	698	0.85	935
$Co_{82}Nb_{12}B_6$	705	743	1.05	690
$Co_{82}Ta_{12}B_6$	723	753	1.04	765
$Ni_{82}Zr_{12}B_6$	703	683	0.97	675
$Ni_{82}Hf_{12}B_6$	725	693	0.96	630
$Ni_{82}Ta_{12}B_6$	653	693	1.06	585

T_f/T_x : (Co, Ni)-(Nb, Ta) > Ni-(Zr, Hf) > Co-(Ti, Zr, Hf), Fe-Nb > Fe-(Zr, Hf)

T_x, H_V: Fe-(Zr, Hf) > Co-(Ti, Zr, Hf), Fe-Nb > Ni-(Zr, Hf) > (Co, Ni)-(Nb, Ta)

amorphous alloys was examined as a function of aging temperature for 3600 s and the data are shown in Table I together with the crystallization temperature(T_x), T_f/T_x and hardness. T_x is the temperature determined as being the beginning point of the first exothermic peak on the DTA curves. As summarized beneath the table, T_f/T_x decreases in the order of (Co, Ni)-(Nb, Ta) > Ni-(Zr, Hf) > Co-(Ti, Zr, Hf), Fe-Nb > Fe-(Zr, Hf), in contrast to the order of hardness. That is, the embrittlement tendency increases with increasing bonding force among the constituent elements in the alloys.

DISCUSSION

The effect of alloy addition on the T_x and H_V of amorphous alloys has been examined by some investigators /7-11/ for the transition metals(Ti, V, Cr, Mo, W, Mn, Fe, Co, Ni, Cu) belonging to the fourth period or the VI group in the periodic table. However, there is hardly any systematic information on such an effect for amorphous alloys containing the IV and V group metals(Ti, Zr, Hf, Nb, Ta) with high reactivity and high melting point. The present investigations provide some insight into the role of these refractory metals on the strength of amorphous alloys.

The hardness values of (Fe, Co, Ni)$_{82}M_{12}B_6$(M=Ti, Zr, Hf, Nb and Ta) ternary amorphous alloys are plotted against the group number of alloying elements M in Fig. 4. As shown in the previous section, the hardness value decreases in the order of

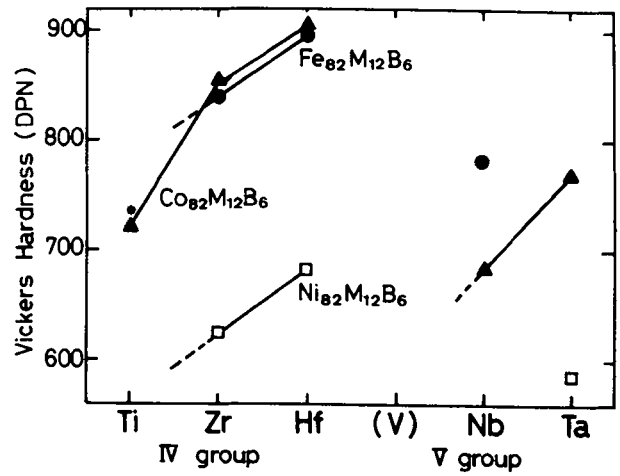

Fig. 4 Change in Vickers hardness(H_V) for $Fe_{82}M_{12}B_6$, $Co_{82}M_{12}B_6$ and $Ni_{82}M_{12}B_6$(M=Ti, Zr, Hf, Nb and Ta) amorphous alloys with group number in the periodic table. The value marked with asterisk is an extrapolated one from the data of $Co_{71-77}Ti_{17-23}B_6$ amorphous alloys.

Hf > Zr > Ta > Ti > Nb for the Fe-, Co- and Ni-base alloys, indicating the tendency that the hardness of the amorphous alloys increases with increasing difference of the group number and/or the periodic number between the base metal(Fe, Co or Ni) and the alloying element. We tried to explain the reason for such a tendency by various factors such as average outer electron concentration, atomic size, electronegativity and the hardness and melting point of intermetallic compounds in (Fe, Co, Ni)-M binary alloys which have been considered to be important for understanding the effect of alloying elements /7-11/. As a result, we have found for $(Fe, Co, Ni)_{82}M_{12}B_6$ ternary amorphous alloys that there exists an apparent linear relationship between the hardness values and the difference of electronegativity between the base metal(Fe, Co, Ni) and M or the metalloid(B) and M. The result is shown in Figs. 5 and 6 and one can notice that the larger the difference in electronegativity, the higher is the hardness. Such an apparent linear relationship was not established between the hardness values and the other factors. Judging from the fact that the hardness values are significantly influenced by the difference of the electronegativity among the constituent elements, it is concluded that a strong chemical bonding between the base metal(Fe, Co, Ni) and M(Ti, Zr, Hf, Nb, Ta) or B and M plays an important role in the hardness of the amorphous alloys found in the present work.

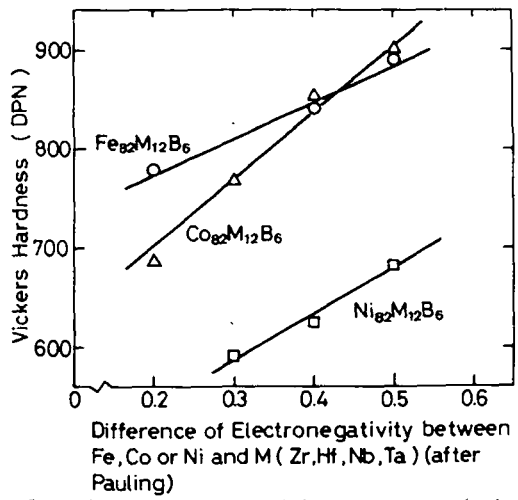

Fig. 5 Relation between Vickers hardness(H_V) and the difference in electronegativity between Fe, Co or Ni and M(Zr, Hf, Nb, Ta) for $Fe_{82}M_{12}B_6$, $Co_{82}M_{12}B_6$ and $Ni_{82}M_{12}B_6$ amorphous alloys.

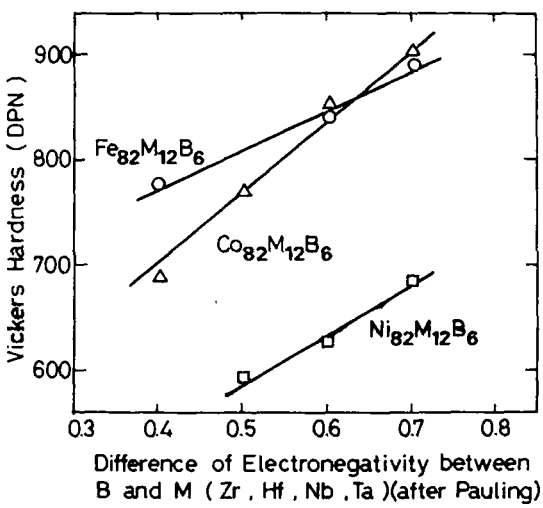

Fig. 6 Relation between Vickers hardness(H_V) and the difference in electronegativity between B and M(Zr, Hf, Nb, Ta) for $Fe_{82}M_{12}B_6$, $Co_{82}M_{12}B_6$ and $Ni_{82}M_{12}B_6$ amorphous alloys.

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