RAPID PUBLICATION

Multicomponent Co-based Amorphous Alloys with Wide Supercooled Liquid Region

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A ferromagnetic Co-based amorphous phase with a wide supercooled liquid region before crystallization was found to be formed in rapidly solidified $\text{Co}_{70}\text{M}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ ($\text{M}=\text{Cr}$ or V) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloys. The glass transition temperature (T_g) and crystallization temperature (T_x) are in the ranges of 717 to 722 K and 766 to 768 K, respectively, and the temperature interval of the supercooled liquid region defined by the difference between T_g and T_x is 45 to 51 K. This is believed to be the first evidence on the appearance of Co-based amorphous alloys with the distinct glass transition and a wide supercooled liquid region. The crystallization takes place through a single stage resulting from the precipitation of four kinds of phases Co, Co_2P , Co_4B and Co_3C . The crystallization process implies the necessity of a long-range rearrangement of constituent elements in the supercooled liquid. The necessity seems to be closely related to the increase in the thermal stability of the supercooled liquid through the retardation of the precipitation of the four crystalline phases. These Co-based amorphous alloys exhibit soft ferromagnetism with Curie temperatures ranging from 365 to 420 K. The saturation magnetization, coercivity and permeability at 1 kHz are in the range of 0.27 to 0.34 T, 4.5 to 8.0 A/m and 4600 to 5800, respectively. From the combination of the soft magnetic properties and a wide supercooled liquid region, we can expect future development of Co-based amorphous alloys as a new soft magnetic material with large glass-forming ability and good viscous deformability.

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I. Introduction

Since an amorphous alloy in the Au-Si system was prepared by a rapid solidification technique in 1960⁽¹⁾, a great number of amorphous alloys have been synthesized in various kinds of alloy systems. Among these amorphous alloys, a part of amorphous alloys have been reported⁽²⁾ to exhibit the glass transition and supercooled liquid region before crystallization, though no glass transition phenomenon is observed for a majority of amorphous alloys. The amorphous alloys with a wide supercooled liquid region above 50 K had been limited to Pd- and Pt-based systems for long periods before 1988. In 1988, Mg-Ln-TM⁽³⁾ and Ln-Al-TM⁽⁴⁾ (Ln=lanthanide metal, TM=transition metal) amorphous alloys were found to exhibit a wide supercooled liquid region of 60 to 70 K. The amorphous alloys with ΔT_x larger than 60 K have attracted significant attention because of the easy formation of bulk glassy alloys with diameters above 1 mm⁽⁵⁾⁽⁶⁾. Subsequently, amorphous alloys with ΔT_x exceeding 60 K and large glass-forming ability leading to the formation of the bulk amorphous alloys have been found in Zr-Al-TM⁽⁷⁾⁽⁸⁾, Hf-Al-TM⁽⁹⁾, Ti-Zr-TM⁽¹⁰⁾, Ti-

Zr-Al-TM-Be⁽¹¹⁾, Zr-Ti-TM-Be⁽¹²⁾ and Pd-Cu-Ni-P⁽¹³⁾ systems. More recently, in addition to these nonferrous metal-based system without ferromagnetism, ferromagnetic Fe-based amorphous alloys with ΔT_x above 60 K have also been found in Fe-(Al, Ga)-(P, C, B, Si, Ge)⁽¹⁴⁾⁻⁽¹⁷⁾ systems. The maximum ΔT_x value for the Fe-based alloys reaches 65 K which is about three times as large as the largest value⁽¹⁸⁾ for previously reported Fe-based amorphous alloys. However, little is known about ferromagnetic Co-based amorphous alloys with glass transition and subsequent supercooled liquid region before crystallization. Based on the alloy compositions of the above-described bulk amorphous alloys, we have proposed three empirical rules⁽¹⁹⁾⁻⁽²⁴⁾ for the achievement of large glass-forming ability as well as for the appearance of a wide supercooled liquid region before crystallization, i.e., (1) multicomponent alloy systems consisting of more than three constituent elements, (2) large atomic size ratios above 12% among the constituent elements, and (3) large negative heats of mixing among the constituent elements. According to the three empirical rules, we have searched an amorphous Co-based alloy with a wide supercooled liquid region before crystallization. The appearance of a Co-based amorphous alloy with a wide supercooled liquid region is expected to cause the increase in the scientific and engineering importance of amorphous alloys. This paper is intended to present the

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compositions, thermal stability of supercooled liquid and magnetic properties of Co-based amorphous alloys with glass transition phenomenon before crystallization and to investigate the reason for the appearance of the glass transition for the multicomponent Co-based amorphous alloys.

II. Experimental Procedure

Multicomponent $\text{Co}_{73-x}\text{M}_x\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ ($\text{M} = \text{Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe}$ or Ni) alloys with M contents below 10 at% were used in the present study. The ingots were prepared by induction melting a mixture of pure Co, Al, Ga and M metals, pre-alloyed Co-P and Co-C ingots and pure B crystal in a purified argon atmosphere. The composition is nominally expressed in atomic percentage. From the master alloy ingot, a ribbon with a cross section of about $0.02 \text{ mm} \times 1.5 \text{ mm}$ was prepared by a single roller melt-spinning technique in an argon atmosphere. The amorphicity of the melt-spun ribbon was examined by X-ray diffractometry with Cu-K α radiation and transmission electron microscopy (TEM). The TEM sample was prepared by thinning electrolytically the melt-spun ribbon at approximately 273 K in a solution of 10% perchloric acid and 90% methanol in volume ratio. The apparent specific heat (C_p) associated with glass transition and crystallization was measured at heating rates of 0.33 and 0.67 K/s with a differential scanning calorimeter (DSC). The elongation as a function of temperature was also measured under a constant load of $1.96 \times 10^{-3} \text{ N}$ and at a heating rate of 0.33 K/s by a thermal mechanical analyzer (TMA). The ductility was evaluated by the simple bend test in which the degree of ductility was determined by measuring the distance between parallel plates at fracture.

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of rapidly solidified $\text{Co}_{70}\text{M}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ ($\text{M} = \text{Cr}$ or V) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloys. Only a main broad peak is seen at a wave vector ($K_p = 4\pi \sin \theta / \lambda$) of 30.79 nm^{-1} for all the alloys and no appreciable peak corresponding to a crystalline phase is seen. Furthermore, we have confirmed that the bright-field electron micrographs taken from these alloys reveal the featureless contrast typical for an amorphous phase and the selected-area electron diffraction patterns consist of halo rings. These results indicate that the multicomponent Co-based alloys consist of an amorphous phase. Figure 2 shows the DSC curves of the amorphous Co-M-Al-Ga-P-B-C ($\text{M} = \text{Cr, V}$ or Fe) alloys. It is to be noticed that the three alloys exhibit an endothermic reaction due to the glass transition before crystallization, followed by an exothermic reaction due to crystallization (T_x). The temperature interval of the supercooled liquid region (ΔT_x) is defined by the difference between the glass transition temperature (T_g) and T_x and the $\Delta T_x (= T_x - T_g)$ value is above 45 K. Furthermore, these amorphous alloys crystallize through a

Fig. 1 X-ray diffraction patterns of rapidly solidified $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (a), $\text{Co}_{70}\text{V}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (b) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (c) alloys.

Fig. 2 DSC curves of rapidly solidified $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (a), $\text{Co}_{70}\text{V}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (b) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ (c) alloys.

single stage, indicating that the precipitation of crystalline phases in the narrow temperature range plays an important role in the appearance of the supercooled liquid region before crystallization. There have been no data on

Fig. 3 Change in the elongation under an initial stress of 0.46 MPa for the amorphous $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy. The data of the DSC curve are also shown for comparison.

the appearance of glass transition before crystallization for Co-based amorphous alloys and hence the above-described alloy systems are believed to be the first evidence on the appearance of the glass transition phenomenon for Co-based amorphous alloys. In order to confirm further that the endothermic reaction before crystallization is due to the glass transition, the thermomechanical result is shown for the amorphous $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy in Fig. 3. The elongation under a small initial stress of 0.46 MPa at a heating rate of 0.33 K/s begins to increase drastically around 716 K which agrees well with the glass transition temperature and the increase in elongation stops around 770 K corresponding to the crystallization temperature. The drastic increase in elongation in the temperature range between 716 and 770 K as well as the good correspondence of these temperatures to the T_g and T_x values on the DSC curve indicates that the amorphous solid changes to a supercooled liquid state in that temperature range.

Here, it is important to point out that the elimination of any constituent elements causes a significant decrease in ΔT_x and the simultaneous dissolution of the seven or eight elements is essential for the achievement of a large ΔT_x exceeding 45 K. These elements can be divided into three groups of (Co, M), (Al, Ga), (P, B, C). The three group elements satisfy the three empirical rules for the achievement of large glass-forming ability as well as for the appearance of a wide supercooled liquid region before crystallization. That is, the three group elements have significantly different atomic size ratios above about 12% and large negative heats of mixing with each other.

Fig. 4 X-ray diffraction pattern of the amorphous $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy annealed for 3.6 ks at 803 K.

The satisfaction of the three empirical rules is presumed to cause the formation of an amorphous alloy with a high degree of dense random disordered structure which enables the increase in the solid/liquid interface energy and the suppression of long-range diffusion for the simultaneous precipitation of the four kinds of crystalline phases. As a result, it is expected that the nucleation and growth reactions of crystalline phases in the supercooled liquid are significantly retarded, leading to the increase in the thermal stability of the supercooled liquid. Although the appearance of the supercooled liquid in the completely internal equilibrium state is limited to the very narrow temperature interval of about 10 K, the finding of the Co-based amorphous alloys with a wide supercooled liquid region before crystallization is important because of the high possibility of preparing a bulk Co-based amorphous alloy with soft ferromagnetism. The preparation and properties of bulk amorphous Co-based alloys will be presented elsewhere.

The reason for the high thermal stability of the supercooled liquid against crystallization was investigated through the crystallized structure of the $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ amorphous alloy. As indexed in the X-ray diffraction pattern of the sample annealed for 3.6 ks at 803 K shown in Fig. 4, the crystallized structure consists of multiple phases of fcc-Co and orthorhombic Co_2P , Co_4B and Co_3C compounds. Consequently, it is presumed that the necessity of long-range rearrangement of the constituent elements to form these compounds from the homogeneously mixed supercooled liquid retards the precipitation of these crystalline phases, leading to the appearance of the wide supercooled liquid region in the temperature range before crystallization.

The present Co-based amorphous alloys also exhibit ferromagnetism with Curie temperatures ranging from 365 to 420 K, as exemplified for the $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy in Fig. 5. The Curie temperature determined from the relation of the square of magnetization versus temperature is 370 K for the Cr-containing alloy,

Fig. 5 Thermomagnetic curves of the amorphous $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy.

Fig. 6 Hysteresis B-H loops of the amorphous $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy.

365 K for the V-containing alloy and 420 K for the Cr- and Fe-containing alloy. We also examined the hysteresis B-H loops of the Co-based amorphous alloys with the wide supercooled liquid region before crystallization, as exemplified for the $\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloy in Fig. 6. The saturation magnetization (B_s) and coercivity (H_c) are about 0.27 to 0.34 T and about 4.5 to 8.0 A/m, respectively, at room temperature and there is a tendency for the Fe-containing alloy with higher T_c to have higher B_s and B_r . The permeability (μ_e) at 1 kHz is measured to be 5800 for the Cr-containing alloy, 4600 for the V-containing alloy and 5000 for the Cr- and Fe-containing alloy. Table 1 summarizes the thermal stability and mag-

netic properties for the Co-based amorphous alloys, together with the data⁽¹⁴⁾⁽¹⁶⁾ of Fe-(Al, Ga)-(P, C, B) amorphous alloys with wide supercooled liquid region before crystallization. In comparison with the data of the Fe-based amorphous alloys, one can notice that the μ_e value is considerably higher, though the B_s , B_r and T_c values are lower. Consequently, the Co-based amorphous alloys are attractive as soft ferromagnetic alloys with high μ_e values and large viscous deformability in the supercooled liquid region.

IV. Summary

Based on the three empirical rules for the achievement of large glass-forming ability and for the appearance of a wide supercooled liquid region before crystallization, we have searched a new ferromagnetic Co-based amorphous alloy with a wide supercooled liquid region. The results obtained are summarized as follows;

(1) The multicomponent Co-based alloys with composition $\text{Co}_{70}\text{M}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ ($\text{M}=\text{Cr}$ or V) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ were found to have a wide supercooled liquid region exceeding 45 K before crystallization. The T_g and T_x are in the range of 717 to 722 K and 766 to 769 K, respectively. The Co-based alloys consist of three group elements of (Co, M), (Al, Ga) and (P, B, C) which satisfy the three empirical rules for the achievement of large glass-forming ability.

(2) The crystallization of these amorphous alloys takes place through a single stage, accompanying the precipitation of Co, Co_2P , Co_4B and Co_3C phases. The crystallization mode implies the necessity of atomic rearrangements on a long-range scale which is favorable for the retardation of precipitation reaction of crystalline phases.

(3) The Co-based amorphous alloys exhibit soft ferromagnetism with Curie temperatures of 365 to 420 K and their saturation magnetization and coercivity are in the range of 0.27 to 0.34 T and 4.5 to 8.0 A/m, respectively, at room temperature. The permeability at 1 kHz is in the range of 4600 to 5800. The rather good soft magnetic properties and the appearance of the wide supercooled liquid region before crystallization allow to expect the future development of the Co-based amorphous alloys as a new soft magnetic material with large glass-forming ability and good viscous workability.

Table 1 Thermal stability and magnetic properties of the amorphous $\text{Co}_{70}\text{M}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ ($\text{M}=\text{Cr}$ or V) and $\text{Co}_{67}\text{Cr}_3\text{Fe}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$ alloys. The data of the amorphous $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ alloy with a wide supercooled liquid region in a cylindrical form of 1.5 mm in diameter are also shown for comparison.

Alloy (at%)	T_g (K)	T_x (K)	ΔT_x (K)	B_s (T)	H_c (A/m)	B_r (T)	μ_e	T_c (K)
$\text{Co}_{70}\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$	717	768	51	0.27	4.5	0.08	5800	370
$\text{Co}_{70}\text{V}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$	722	769	47	0.29	5.8	0.12	4600	365
$\text{Co}_{67}\text{Fe}_3\text{Cr}_3\text{Al}_5\text{Ga}_2\text{P}_{15}\text{B}_4\text{C}_1$	721	766	45	0.34	8.0	0.13	5000	420
$\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$	732	793	51	1.07	12.7	0.39	3600	596

B_s , T_c : $H_m=800$ kA/m, H_c , B_r : $H_m=80$ A/m, μ_e : $f=1$ kHz, $H_m=0.8$ A/m.

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