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Enhancement of the fracture strength and glass-forming ability of CoFeTaB bulk glassy alloy

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Abstract

$Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ bulk glassy alloy has the best glass-forming ability (GFA) among the Co-based glassy alloys, and the highest strength (the compressive true strength $\sigma_f = 5185$ MPa) among all known bulk crystalline and glassy alloys. With the aim of synthesizing new Co-based bulk glassy alloys with much higher strength and much larger GFA, we investigated the effect of Mo and Si additions on the enhancement of σ_f and GFA in the Co–(Fe, Mo, Ta)–(B, Si) system. The small amount of 2 at.% Mo added to the Co–Fe–Ta–B glassy alloy resulted in obtaining an ultrahigh true fracture strength of 5545 MPa and high Young's modulus (E) of 282 GPa. By further adding 1 and 2 at.% Si, Co–(Fe, Mo, Ta)–(B, Si) bulk glassy alloys were synthesized in the diameter range up to 3 mm, and they exhibited σ_f of over 4450 MPa and E of over 227 GPa. In addition, the ultrahigh-strength glassy alloys simultaneously exhibited excellent soft magnetic properties, i.e., saturation magnetization of 0.32–0.35 T, low coercive force of 0.7–1.1 A m^{-1}, and high effective permeability of 3.9–4.77×10^4 at 1 kHz. The improvement of GFA and σ_f is interpreted to result from the enhanced atomic bonding nature by adding Mo and Si.

From about 1988, systematic studies of glass formation in a variety of multi-component alloys have been carried out, and bulk glassy alloys in lanthanide (Ln)- and Mg-based systems were first synthesized by copper mould casting [1]. Subsequently, a large number of bulk glassy alloys have been developed and some glassy alloys have been used as practical materials [1, 2]. Now, bulk glassy alloys have been drawing increasing attention due to their scientific and engineering significance [3, 4]. For Fe- and Co-based bulk glassy alloys, since the first synthesis of the Fe–(Al, Ga)-metalloid bulk glassy alloy system in 1995 [5], a variety of bulk glassy alloy

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systems have been synthesized for the purpose of applications as soft magnetic materials [6, 7]. In addition to the good soft magnetic properties, it has recently been found that Fe- and Co-based bulk glassy alloy systems also exhibit ultrahigh strength of 4000 MPa, which gives great potential for applications as structural materials [8–12]. In particular, $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ bulk glassy alloy, in addition to its excellent soft magnetic properties, exhibits ultrahigh strength over 5000 MPa and high Young's modulus of 268 GPa [12]. With the aim of synthesizing a more useful Co-based bulk glassy alloy with much higher strength and glass-forming ability (GFA), we have examined the effects of the addition of Mo and Si in the Co–Fe–Ta–B bulk glassy alloy system, and have found that Co–(Fe, Mo, Ta)–B bulk glassy alloys exhibit ultrahigh true fracture strength as high as 5545 MPa, and Co–(Fe, Mo, Ta)–(B, Si) bulk glassy alloys can be synthesized with the diameters up to 3 mm by copper mould casting, in conjunction with high strength of 4450 MPa and excellent soft magnetic properties. This paper reports the synthesis, mechanical strength and magnetic properties of Co–(Fe, Mo, Ta)–B and Co–(Fe, Mo, Ta)–(B, Si) glassy alloy rods.

According to the Co–Ta–B ternary phase diagram [13], it is known that the composition of $Co_{63.5}Ta_{5.5}B_{31}$ alloy is one of the eutectic points in the Co–Ta–B ternary alloy system. So, in this study, to maintain the composition near this eutectic point, $Co_{53.5}Fe_{10}Ta_{5.5}B_{31}$ alloy was selected as a base composition alloy. One other reason to decrease the Fe content is to increase the fracture strength because Fe is not a refractory element. Multi-component Co-based alloy ingots with compositions of $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{100-x}Mo_x$ ($x = 0, 1, 2, 3$ and 4) and $[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0$, 1, 2 and 3) were prepared by arc melting mixtures of pure Co, Fe, Mo and Ta metals and pure B and Si crystals in an argon atmosphere. The alloy compositions represent nominal atomic percentages. Bulk glassy alloy rods with diameters of 1–4 mm were produced by the ejection copper mould casting method. Glassy alloy ribbons were also produced by the melt-spinning method. The glassy structure was identified by x-ray diffraction (XRD) with Cu Kα radiation, and the absence of micrometre scale crystalline phase was examined by optical microscopy. The thermal stability, associated with the glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x = T_x - T_g$), was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s^{-1}. The liquidus temperature (T_l) was measured with a differential thermal analyser (DTA). The mechanical properties, i.e., Young's modulus (E), true fracture strength (σ_f) and elastic strain (ε_e), were measured by a compression test with an Instron testing machine. The gauge dimension was 1.5–2 mm in diameter and 3–4 mm in length, and the strain rate was 6×10^{-4} s^{-1} for the 3 mm sample and 5×10^{-4} s^{-1} for the 4 mm sample. Vickers hardness (H_V) was measured with a Vickers hardness tester under a load of 100 g. The fracture behaviour was observed by scanning electron microscopy (SEM). The magnetic properties, i.e., saturation magnetization (I_s), coercive force (H_c) and effective permeability (μ_e) at 1 kHz, were measured with a vibrating sample magnetometer (VSM) under an applied field of 400 kA m^{-1}, a B–H loop tracer under a field of 800 A m^{-1} and an impedance analyser under a field of 1 A m^{-1}, respectively.

It is known that the values of T_g and T_l of glassy alloys reflect the degree of the bonding force among the constituent elements [14], and there have been reports that the strength of a glassy alloy can be improved by adding a high melting-point element [15]. Therefore, we investigated the adding effect of adding the high melting-point element Mo on the GFA and σ_f in $Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31}$ glassy alloy because Mo was effective in increasing both the GFA and σ_f in Fe-based bulk glassy alloys [16]. Figure 1 shows DSC curves of the $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{100-x}Mo_x$ glassy alloys produced by melt-spinning. It is seen that T_g and T_x increase gradually from 900 to 915 K and 956 to 992 K, respectively, with an increase of Mo content to 3 at.%, leading to the increase of ΔT_x from 56 to 77 K. The further

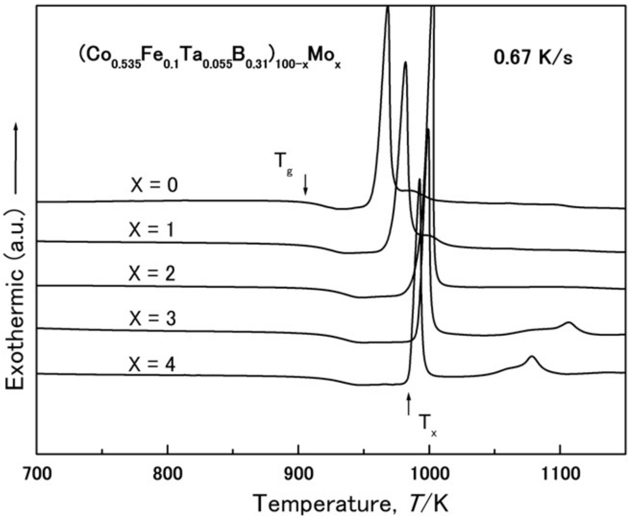

Figure 1. DSC curves of melt-spun $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{100-x}Mo_x$ (x = 0, 1, 2, 3, and 4) glassy alloy ribbons.

increase of Mo content results in the decrease of T_g, T_x and ΔT_x. For the crystallization mode, just the $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy with ΔT_x of 75 K exhibits a single exothermic stage, which means that the precipitation of the crystalline phases is more difficult, and therefore the supercooled liquid of this glassy alloy is more stable than the other glassy alloys. Consequently, we tried to form a cylindrical glassy rod of this glassy alloy, and bulk glassy rods with a diameter of 1.5 mm were formed.

Using the 1.5 mm diameter rods, we measured the mechanical properties by hardness and compressive tests. It is found that $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy rod exhibits a high H_V of 1693, high E of 282 GPa and ultrahigh σ_f of 5545 MPa; these values are higher than those (1478, 268 GPa and 5185 MPa) of $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ bulk glassy alloy [12]. Figure 2 shows the fracture surface morphology of the $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy rod. It is seen that the fracture occurs in a shear band mode at room temperature. The compressive fracture surface has an angle of 44° with the stress axis as marked in the figure, in agreement with previous results obtained from a number of bulk glassy alloys including high-strength Fe-based bulk glassy alloys [11]. It is noted that this fracture behaviour was obtained even for the ultrahigh-strength alloy exceeding 5500 MPa. Thus, the strongest and hardest bulk metallic alloy is formed in the Co–(Fe, Mo, Ta)–B glassy alloy system. Here, it is also worth pointing out that a $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy ribbon with a thickness of about 20 μm produced by the melt-spinning method has good bending ductility, and can be bent through 180° without fracture, in conjunction with high tensile fracture strength of about 4900 MPa, though the tensile fracture strength of the ribbon sample is slightly lower than the compressive fracture strength of the corresponding bulk glassy alloy. Figure 3 shows the surface morphology of the melt-spun $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy ribbon subjected to 180° bending observed by SEM. A number of shear deformation bands can be seen in a wide region (shown in figure 3(a)), but no cracks are observed even at the tip of the bent region in the enlarged SEM photograph (shown in figure 3(b)), which gives evidence for the good ductility in conjunction with high fracture strength.

To further increase the GFA of the Co–(Fe, Mo, Ta)–B glassy alloy system, Si was added to this glassy alloy system. Figure 4 shows the DSC curves of the

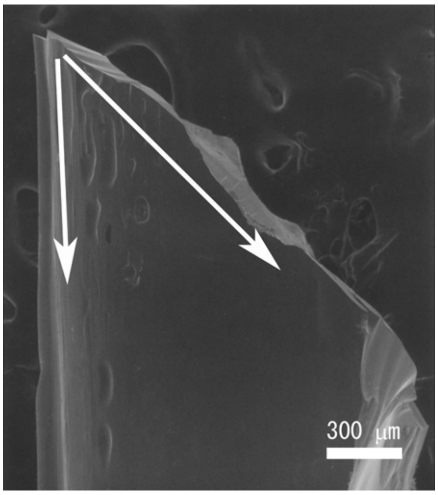

Figure 2. Fracture surface morphology of the cast $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy rod subjected to a compressive deformation test.

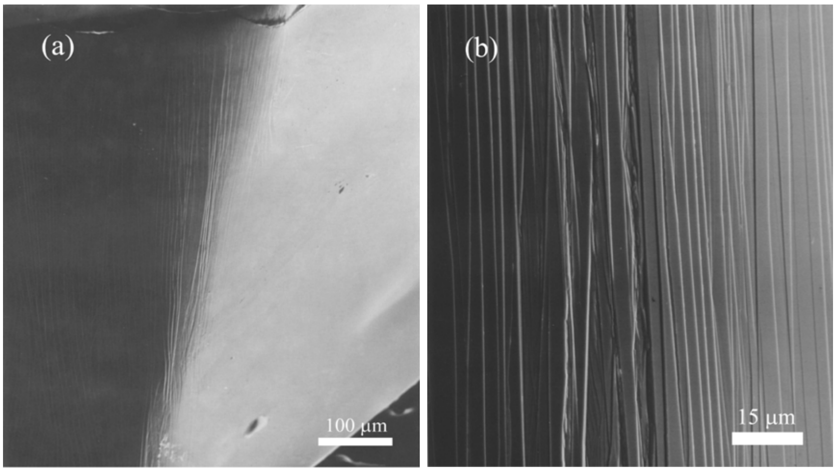

Figure 3. Surface morphology of the melt-spun $(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$ glassy alloy ribbon subjected to 180° bending.

$[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0, 1, 2$ and 3) glassy alloys produced by melt-spinning. It is seen that T_g and T_x decrease gradually from 915 to 890 K and 990 to 963 K, respectively, with increasing Si content to 3 at.%, which results from the addition of low melting-point Si. However, ΔT_x increases from 75 to 82 K as the Si content increases to 1–2 at.%, and the crystallization mode maintains a single exothermic stage. This therefore means that the stability of the supercooled liquid increases by the addition of 1 or 2 at.% Si. We also measured the T_l of the $[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0, 1$ and 2) glassy alloys with DTA, and noticed that the T_l decreases gradually from 1565 to 1500 K, and the reduced glass transition temperature (T_g/T_l) increases from 0.586 to 0.597, indicating that higher GFA may be obtained in this glassy alloy system. Therefore, we tried to form a cylindrical glassy rod with the 1 and 2 at.% Si-containing alloys, and succeeded in producing

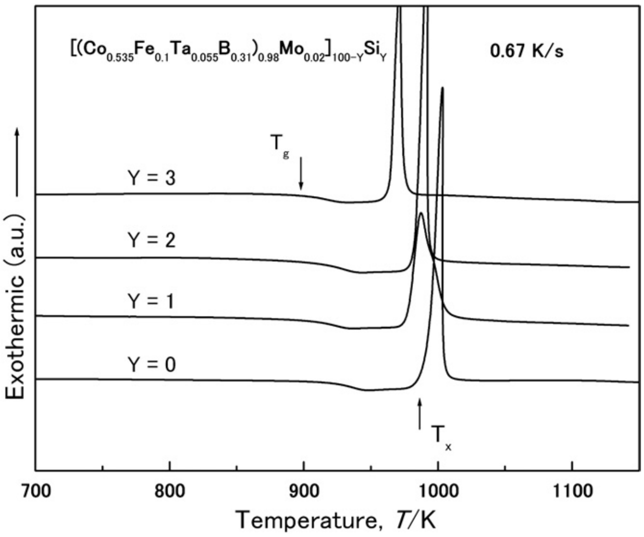

Figure 4. DSC curves of melt-spun $[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0, 1, 2,$ and 3) glassy alloy ribbons.

bulk glassy alloy rods with diameters up to 2.5 mm for the 1 at.% Si alloy, and 3 mm for the 2 at.% Si glassy alloy.

Table 1 summarizes the maximum diameter, thermal stability, and mechanical and magnetic properties of the $[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0, 1$ and 2) glassy alloy rods. The mechanical properties H_V, E, and σ_f are in the range of 1314–1693, 227–282 GPa, and 4454–5545 MPa, respectively. Except for the ultrahigh σ_f, this bulk glassy alloy system also exhibits excellent soft magnetic properties in an annealed state (830 K, 600 s), i.e., I_s of 0.32–0.35 T, low H_c of 0.7–1.1 A m^{-1}, and high μ_e of 39 000–47 700. It is therefore concluded that the Co–(Fe, Mo, Ta)–(B, Si) bulk glassy alloys simultaneously possess ultrahigh strength and excellent soft magnetic properties, in addition to the rather high glass-forming ability.

Finally, we discuss the reason why the Co–(Fe, Mo, Ta)–(B, Si) bulk glassy alloys simultaneously possess high GFA, ultrahigh σ_f, and excellent soft magnetic properties. One of the reasons for the ultrahigh strength is thought to result from the strong bonding achieved between the transition metals and metalloids. It has been pointed out by Chen *et al* that electrons transfer from the metalloids, fill the d shells of the transition metals, and then s–d hybrid bonding is formed [17, 18]. In this study, it is presumed that except for the strong s–d hybrid bonding of Co–B and Fe–B atomic pairs, s–d hybrid bonding of Mo–B atomic pairs would also be formed because of the 4d band supplied by the Mo. Accordingly, the s–d hybrid bonding would become much stronger by adding Mo transition metal and this would hinder the interparticle displacements much more effectively, and therefore raise the elastic modulus. One of the other reasons for the ultrahigh strength is attributed to the mixing enthalpies, which have large negative values. The enthalpy of mixing is -19 kJ mol^{-1} for the Mo–B atomic pair, larger than that (-11 kJ mol^{-1}) of the Fe–B pair [19]. As a result, a highly dense random packed structure with strong bonding nature is obtained in the Co–(Fe, Mo, Ta)–B glassy alloy system. The formation of such a structure state causes the increase in T_g from 900 to 915 K, and ΔT_x from 56 to 75 K, respectively, as well as the ultrahigh σ_f of 5545 MPa, in addition to the increase in GFA to 1.5 mm in diameter. By further adding Si, with large negative mixing

Table 1. Maximum diameter, thermal stability, and mechanical and magnetic properties of cast $[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{100-y}Si_y$ ($y = 0$, 1, and 2) glassy alloy rods.

	Diameter	Thermal stability			Mechanical properties			Magnetic properties		
Alloy	ϕ (mm)	T_g (K)	ΔT_x (K)	T_g/T_l	H_V	E (GPa)	σ_f (MPa)	I_s (T)	H_c (Am^{-1})	μ_e (1 kHz)
$(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{98}Mo_2$	1.5	915	75	0.586	1693	282	5545	0.35	1.1	39 000
$[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{99}Si_1$	2.5	895	82	0.593	1450	238	4915	0.33	0.85	46 000
$[(Co_{0.535}Fe_{0.1}Ta_{0.055}B_{0.31})_{0.98}Mo_{0.02}]_{98}Si_2$	3	890	82	0.597	1314	227	4454	0.32	0.7	47 700

enthalpies to Fe, Co, Mo and Ta, that is, -18 kJ mol^{-1} for the Si–Fe pair, -21 kJ mol^{-1} for the Si–Co pair, -18 kJ mol^{-1} for the Si–Mo pair, and -39 kJ mol^{-1} for the Si–Mo pair [19], ΔT_x increases from 75 to 82 K, while the melting temperature, T_l, decreases and T_g/T_l increases from 0.586 to 0.597, implying that the GFA is increased. Indeed, the critical diameter of the Co–(Fe, Mo, Ta)–(B, Si) glassy alloy rod increases from 1.5 to 3 mm, though σ_f decreases to 4454 MPa. It has further been reported that the Co–Fe–Ta–B bulk glassy alloy exhibits excellent soft magnetic properties [12]. In this study, just small amounts of Mo and Si were added to the Co–Fe–Ta–B glassy alloy, resulting in the increase of the GFA. Therefore, hardly any harmful effect of the alloying on the soft magnetic properties can be thought to result from the high GFA of this glassy alloy system, which causes the formation of a glassy structure with a high level of homogeneity in the absence of any crystalline nuclei [20].

In conclusion, the addition of a small amount of Mo can improve the strength of the ultrahigh-strength $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ bulk glassy alloy, and a small amount of Si can improve the GFA without deteriorating the good soft magnetic properties. The improvement is due to the enhancement of the atomic bonding achieved by adding Mo and Si. This new Co–(Fe, Mo, Ta)–(B, Si) bulk glassy alloy system with those novel characteristics is promising for future applications in new engineering and functional materials.

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