Cobalt-based bulk glassy alloy with ultrahigh strength and soft magnetic properties

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Bulk metallic glasses—formed by supercooling the liquid state of certain metallic alloys—have potentially superior mechanical properties to crystalline materials. Here, we report a $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ glassy alloy exhibiting ultrahigh fracture strength of 5,185 MPa, high Young's modulus of 268 GPa, high specific strength of 6.0 × 10^5 Nm kg^{-1} and high specific Young's modulus of 31 × 10^6 Nm kg^{-1}. The strength, specific strength and specific Young's modulus are higher than previous values reported for any bulk crystalline or glassy alloys[1–3]. Excellent formability is manifested by large tensile elongation of 1,400% and large reduction ratio in thickness above 90% in the supercooled liquid region. The ultrahigh-strength alloy also exhibited soft magnetic properties with extremely high permeability of 550,000. This alloy is promising as a new ultrahigh-strength material with good deformability and soft magnetic properties.

The synthesis of new alloys has accompanied and supported the development of civilization. Alloys in bulk form have historically been cast from the liquid state. Because of the extreme instability of supercooled liquid[4,5], such bulk alloys usually consisted of crystalline structures. This structural limitation was broken towards the end of the last century by the discovery of stabilization of supercooled liquid[6–8]. Bulk glassy alloys consisting only of metallic components in Mg-, lanthanide- and Zr-based systems have been formed by casting[9–11] and their diameter reached 30 mm. Subsequently, various engineering properties were obtained for a number of bulk glassy alloys including Fe-, Co-, Ni- and Cu-based systems[10,11]. Regarding mechanical properties reported for bulk alloys, the highest strength found is 2,800 MPa for glassy alloys[1] and 3,300 MPa for crystalline alloys[2]. It is important to search for an ultimate strength limit in bulk metallic materials and to clarify its origin. This paper reports the synthesis of a $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ bulk glassy alloy with record ultrahigh strength of over 5,000 MPa and good deformability.

A glassy $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy rod with a diameter of 2 mm and a length of 70 mm was prepared (see Methods). The glass-transition temperature (T_g) and crystallization temperature (T_x) were 910 K and 982 K, respectively, and the supercooled-liquid region defined by the difference between T_g and T_x was 72 K.

Figure 1 shows the temperature dependence of compressive true stress–strain curves for the Co-based glassy alloy rods. Young's modulus (E) and compressive fracture strength ($\sigma_{c,f}$) are as high as 268 GPa and 5,185 MPa, respectively, at room temperature. The yield strength (σ_y) remains almost unchanged in the temperature range up to 658 K, increases slightly to 5,334 MPa at 698 K, and then decreases gradually accompanied by distinct plastic deformation through a homogeneous deformation mode. With further increase of the testing temperature, σ_y decreases rapidly on the transition from the glass to supercooled liquid region in the higher temperature range above 818 K. The alloy rods have nearly constant elastic strain ($\varepsilon_{c,f}$) of about 0.02 in a wide temperature range up to 0.8T_g, although no distinct plastic strain is seen in the temperature range up to 698 K where the deformation occurs through an inhomogeneous deformation mode[12]. We further examined tensile

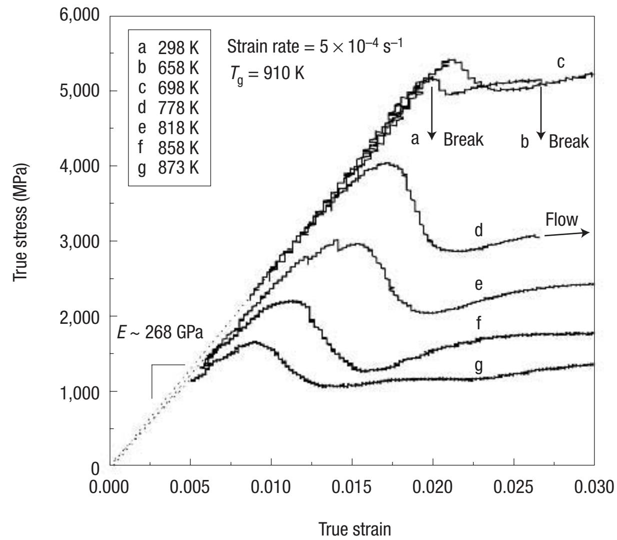

Figure 1 True stress–strain curves of bulk glassy $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy rods with a diameter of 2 mm tested under a compressive applied load at various temperatures between room temperature and 873 K. Young's modulus (E) and compressive fracture strength were 268 GPa and 5,185 MPa, respectively, at room temperature. The yield strength of the samples were (in MPa): b 5,147; c 5,334; d 3,810; e 2,762; f 2,048; and g 1,382.

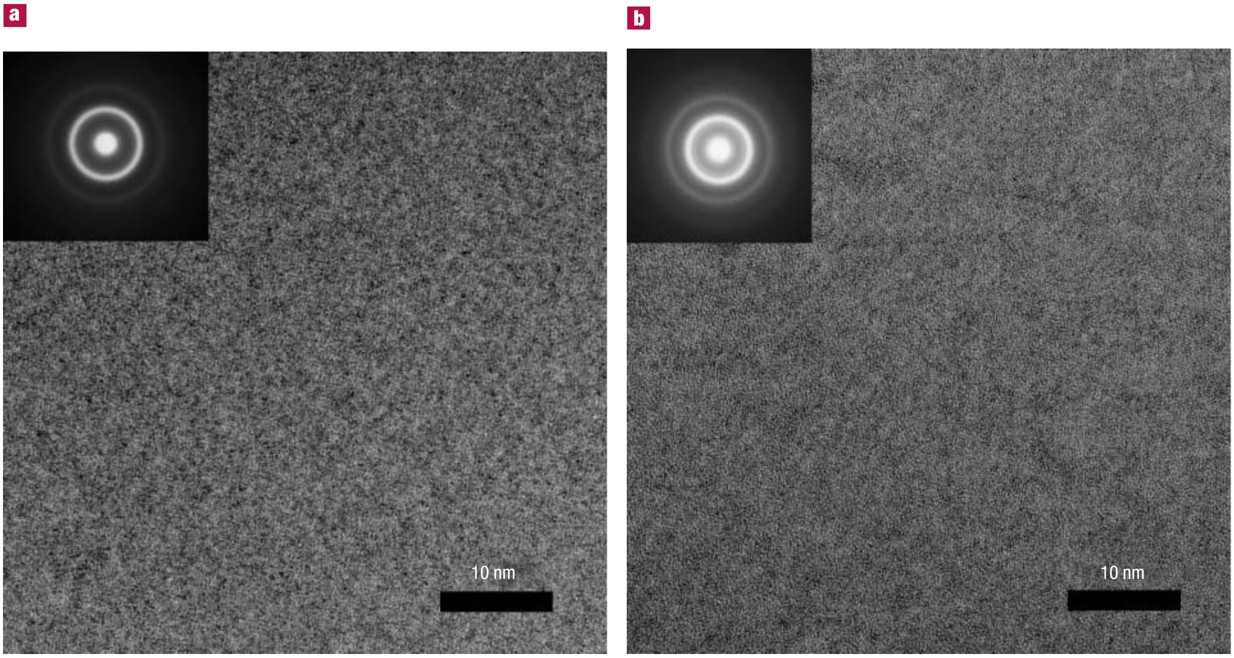

Figure 2 HRTEM images of bulk glassy $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy rods with a diameter of 2 mm. a, The as-cast state. The inset displays the selected-area electron diffraction pattern taken from the circular region of 350 nm in diameter. **b**, The annealed state for 240 s at 698 K. This annealing corresponds to the heating condition just before compressive deformation test for sample c in Fig. 1. The inset displays the selected-area electron diffraction pattern taken from the circular region of 350 nm in diameter.

fracture strength and elongation using melt-spun ribbon specimens. The strength and elongation at room temperature were measured as 5,210 MPa and 0.019, respectively, which were nearly the same as $\sigma_{c,f}$ and $\varepsilon_{c,f}$ for the Co-based glassy alloy rod. Such high-strength characteristics have not been obtained for any kind of bulk metallic materials in the crystalline or glassy state[13]. Figure 2 shows high-resolution transmission electron microscope images (HRTEM) and selected-area electron diffraction patterns (insets) of the $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy rods in the as-cast (Fig. 2a) and annealed (at 698 K for 240 s) states (Fig. 2b). The annealing condition is the same as that for the sample subjected to the mechanical test at 698 K. Only modulated contrast typical to a glassy single structure is observed for the as-cast sample. No distinct contrast due to a crystalline phase is seen even for the annealed sample, although slight development of fringe contrast is recognized in very fine regions of less than about 0.5 nm. The diffraction patterns taken from the region of 350 nm in diameter consist of halo rings for both the samples. These data reveal that the alloy rods in the as-cast and annealed states consist of a glassy single phase. It is therefore concluded that the ultrahigh strength for the as-cast alloy rod originates from the glassy structure, and the further increase in σ_y at 698 K is due to the progress of structural relaxation in the glassy phase.

Figure 3 shows a scanning electron microscope (SEM) image revealing the deformation marking of the alloy rod with the highest σ_y of 5,334 MPa subjected to the strain of 0.021 at 698 K. A number of shear bands as well as the crack for final rupture localized on one major shear band are observed on the rod surface. The fracture surface consisted of vein and smooth patterns typical for glassy alloys with ductility. The compressive fracture angle between the stress axis and the main fracture plane was measured to be 44°, which slightly deviated from the maximum shear stress plane declined by 45° to the stress axis. The deviation indicates that the deformation and fracture behaviour of the bulk glassy alloy rod do not completely follow the von Mises criterion, in agreement with the previous data[14] obtained for other bulk glassy alloys. However, the present fracture angle is slightly larger than the previous value (43°)[14], which can be expected from a combined effect of the normal and shear stresses on the compressive fracture plane. The difference can be interpreted by the increase in the contribution of shear stress on the fracture surface resulting from the higher testing temperature of 698 K. We also observed a number of slip markings without cracks around the indentation traces obtained by a Vickers hardness indenter with a load of 9.8 N in the temperature range from 298 to 698 K. In the supercooled-liquid region at 930 K, the glassy alloy rod exhibited extremely large tensile elongation reaching 1,400% at a strain rate of about 0.1 s^{-1}, as well as good deformability leading to 90% reduction in thickness in one cycle of the pressing treatment.

We further examined the relation between σ_y and E for typical metallic alloys in crystalline and glassy states. There was a clear tendency for σ_y to increase with increasing E, but the slope of the linear relation corresponding to elastic strain was significantly different between the bulk glassy and crystalline alloys. The elastic strain limits of the bulk glassy alloys were about 2.5 times larger than those for the crystalline alloys. The glassy alloys also exhibited high σ_y, which was about 2.5 times higher than those for crystalline alloys, when the comparison was made at the same E level. It is concluded that the new Co-Fe-Ta-B glassy alloy has the highest strength for all metallic bulk materials reported to date. These high values are interpreted to result from the strong bonding nature among the constituent elements as is expected from the mixed enthalpies with large negative values from 9 to 39 kJ mol^{-1} for Co-Ta, Fe-Ta, Ta-B, Co-B, and Fe-B pairs[15]. We also examined[16] a primary crystallization phase from the supercooled liquid phase and confirmed that the primary phase was a metastable complex face-centered cubic $(Co,Fe)_{21}Ta_2B_6$ with a large lattice parameter of 1.055 nm. This phase agrees with $(Fe,M)_{23}B_6$ (M = Nb, Ta), which has been identified as the primary crystallization phase of bulk glassy Fe-Nb-B and Fe-Nb-Ta-B alloys[17,18]. Based on the previous experimental data on the coordination numbers and atomic distances of glassy $Fe_{60-70}Nb_{10}B_{20-30}$ alloys obtained

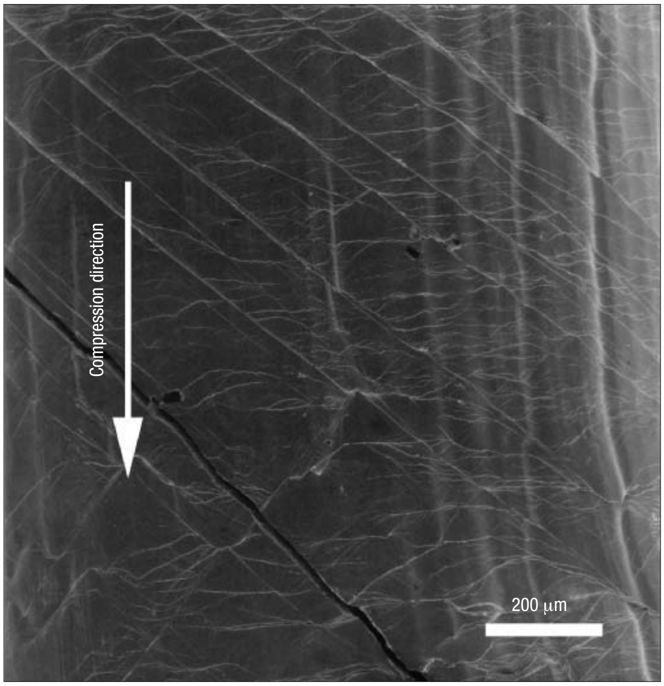

Figure 3 SEM image revealing the deformation and fracture behaviour of the bulk glassy $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ alloy rod with a diameter of 2 mm deformed up to a true strain of 0.021 at 698 K. Shear bands and shear deformation-induced fracture are observed on the specimen surface. The compressive fracture angle between the stress axis and the fracture plane is 44°, which slightly deviates from the maximum shear stress plane (45°).

by anomalous X-ray scattering, it has been reported that the Fe-Nb-B glassy alloys have a unique network-like structure, in which distorted trigonal prisms consisting of Fe and B are connected with each other through glue atoms of Nb, and its network-like structure leads to the precipitation of the metastable $(Fe,Nb)_{23}B_6$ phase, in addition to the high stability of the supercooled liquid against crystallization resulting from the necessity of long-range atomic rearrangements for crystallization[19,20]. Although no data on local atomic configurations have been obtained for the Co-Fe-Ta-B glassy alloy, the similarities of the primary crystallization phase and the alloy components allow us to presume the formation of the similar network-like atomic configurations that can act as the origins for high resistance against plastic yielding and crystallization. The elastic strain of about 0.02 at room temperature agrees with the value (0.0195) derived from the slope of linear relation between σ_y and E, implying that the glassy alloy keeps an elastic–plastic deformation mode[21]. The Co-Fe-Ta-B alloy rod had the mass density of 8.65 Mg m^{-3}, and hence exhibited the highest specific σ_y of 6.0×10^5 Nm kg^{-1} and the highest specific E of 31×10^6 Nm kg^{-1} in comparison with those for all bulk metallic materials[3].

In addition, the ring-shaped sample with a thickness of 1 mm, an outer diameter of 7 mm and an inner diameter of 3 mm exhibited excellent soft magnetic properties. The coercive force was as low as 0.25 A m^{-1} and the maximum permeability was as high as 550,000, though the saturation magnetization had a relatively low value of 0.49 T. The extremely soft magnetic properties can be interpreted to result from the formation of a glassy structure with a high level of homogeneity in the absence of any crystalline nuclei[22]. Thus, the present bulk glassy alloy is also regarded as a new soft magnetic material with ultrahigh mechanical strength.

METHODS

The pure metals of Co (99.9 mass%), Fe (99.9%) and Ta (99.8%), and pure crystalline B (99.5%) were purchased from Sendai Wako Pure Chemical Industries (Sendai, Japan).

A $Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$ ingot was prepared by arc-melting the mixture of pure metals and pure B crystal in an argon atmosphere. The alloy compositions represent nominal atomic percentages. Glassy alloys were produced in rod and ring forms by the copper-mould-casting method and in a ribbon form by the melt-spinning method. Bulk glassy alloys in a rod form with diameters up to 3 mm and a length of 70 mm, and in a ring form with an outer diameter of 7 mm, an inner diameter of 3 mm and a thickness of 1 mm were produced by an ejection copper-mould-casting method. The as-cast and annealed structures were examined by X-ray diffraction using a RINT 2000 diffractometer with Cu K_α radiation at 40 kV (Rigaku International Corporation, Japan) and HRTEM (JEM 2010, 200 kV, JEOL, Japan).

T_g and T_x were determined by differential scanning calorimetry at a heating rate of 0.67 K s^{-1} (SII DSC 6300, Seiko Instruments, Japan). Density was measured by the archemedian method using a chemical solution of toluene at 298 K.

Mechanical properties including Young's modulus, yield strength, fracture strength, elastic strain and fracture strain were measured in the temperature range from 298 to 930 K by a mechanical testing machine with a vacuum chamber (Shimadzu EHF-EA25, Shimadzu Corporation, Japan). The gauge dimension was 2 mm in diameter and 4 mm in length for compressive tests, and 10 mm in length and 0.02×1.0 mm^2 in cross-section for tensile tests. The strain was measured by a strain-gauge meter (Kyowa Electronic Instruments, Japan). The strain rate was 5.0×10^{-4} s^{-1} and 8.3×10^{-4} s^{-1}, respectively. The yield strength was defined by the stress at the elastic strain of 0.02 for the sample that did not show plastic deformation. For the sample showing plastic deformation, the yield strength was defined by the stress at the plastic strain of 0.002.

Vickers hardness was measured with a Vickers hardness tester under a load of 1.96 N (Akashi MVK-VL, Japan). The generation of slip marking was made in the temperature range from 298 to 873 K under a load of 9.8 N. Deformation and fracture behaviour were examined by SEM (HITACHI S-800, 20 kV, Hitachi, Japan).

Saturation magnetization was measured under an applied field of 1,500 A m^{-1} with a vibrating sample magnetometer (VSM-5, Toei Industries, Japan). Coercive force and maximum permeability were measured under a field of 3 A m^{-1} with a B-H curve tracer (BHH-50, Riken Denshi, Japan).

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Competing financial interests

The authors declare that they have no competing financial interests.