

High-temperature bulk metallic glasses developed by combinatorial methods

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Since their discovery in 1960¹, metallic glasses based on a wide range of elements have been developed². However, the theoretical prediction of glass-forming compositions is challenging and the discovery of alloys with specific properties has so far largely been the result of trial and error^{3–8}. Bulk metallic glasses can exhibit strength and elasticity surpassing those of conventional structural alloys^{9–11}, but the mechanical properties of these glasses are critically dependent on the glass transition temperature. At temperatures approaching the glass transition, bulk metallic glasses undergo plastic flow, resulting in a substantial decrease in quasi-static strength. Bulk metallic glasses with glass transition temperatures greater than 1,000 kelvin have been developed, but the supercooled liquid region (between the glass transition and the crystallization temperature) is narrow, resulting in very little thermoplastic formability, which limits their practical applicability. Here we report the design of iridium/nickel/tantalum metallic glasses (and others also containing boron) with a glass transition temperature of up to 1,162 kelvin and a supercooled liquid region of 136 kelvin that is wider than that of most existing metallic glasses¹². Our Ir–Ni–Ta–(B) glasses exhibit high strength at high temperatures compared to existing alloys: 3.7 gigapascals at 1,000 kelvin^{9,13}. Their glass-forming ability is characterized by a critical casting thickness of three millimetres, suggesting that small-scale components for applications at high temperatures or in harsh environments can readily be obtained by thermoplastic forming¹⁴. To identify alloys of interest, we used a simplified combinatorial approach^{6–8} harnessing a previously reported correlation between glass-forming ability and electrical resistivity^{15–17}. This method is non-destructive, allowing subsequent testing of a range of physical properties on the same library of samples. The practicality of our design and discovery approach, exemplified by the identification of high-strength, high-temperature bulk metallic glasses, bodes well for enabling the discovery of other glassy alloys with exciting properties.

The design of Ir–Ni–Ta–(B) high-temperature bulk metallic glasses (BMGs) starts with an Ir–Ta binary system, and is based on established correlations among physical properties and empirical criteria for enhancing their glass-forming ability (GFA). The glass transition temperature T_g of a BMG has been demonstrated to correlate with the elastic modulus E (refs^{18,19}) and the melting temperature T_m (ref.²⁰) of its constituent elements. Since Ir has a large E (the second-highest among metals, after osmium) and a very high T_m , incorporation of Ir into an alloy suggests a similarly high T_g . Among Ir binary alloys, Ir–Ta has been reported to form glasses at high cooling rates of 10^8 K s⁻¹ (ref.²¹); Ta has the fourth-highest T_m among the metallic elements. Ni was chosen because it differs in atomic size by more than 12% compared to Ir and Ta and has a large negative heat of mixing with both elements (Fig. 1a), obeying Inoue's empirical criteria for designing BMGs¹². Furthermore, binary Ni–Ta is a glass-forming system²², and Ni is completely soluble in Ir. Such characteristics have been recognized to

improve the GFA of ternary alloy systems^{12,23,24}. To further improve the GFA, we chose B because it has a high melting temperature (2,365 K) and exhibits characteristics associated with enhancing the GFA of Ir–Ni–Ta, such as its small size and large negative heat of mixing compared to the other three elements (Fig. 1a). The thermal stability ($\Delta T = T_x - T_g$)—the difference between the glass transition and crystallization temperatures—of a BMG is related to its GFA^{12,23}. Therefore, we begin our search for BMGs with high T_g and large ΔT in the Ir–Ni–Ta–(B) system by looking at specific alloys with a high GFA, especially alloys rich in Ir and Ta.

We first focus on ternary Ir–Ni–Ta alloys because the compositional space of a ternary system is two orders of magnitude smaller than a quaternary system³. In the past, a starting point for identifying BMG-forming alloys was to search for deep eutectic compositions where the liquid is stable and crystallization is possible only at lower temperatures^{12,23}. As other aspects also control glass formation, such as interfacial energy and compositional difference between liquid and solid, the alloy with the best GFA does not always have the same composition as the deep eutectics⁵. In the isothermal projection of the ternary Ir–Ni–Ta phase diagram²⁵, eutectics exist and cover a wide composition range (Fig. 1b). If one atomic per cent in one constituent is taken as the interval by which to distinguish two alloys³, the number of alloys covered by the eutectic points substantially exceeds those that can be considered with a traditional trial-and-error approach for BMG development. Furthermore, locating eutectics relies on phase diagrams. Although the diagrams can be easily found for simple binary alloy systems and few ternary systems, they are not usually available for multiple-component alloy systems. Hence, to discover alloys that exhibit high GFA, we performed massive parallel synthesis paired with high-throughput characterizations.

Specifically, we simultaneously fabricated a large compositional library through magnetron co-sputtering, a technique which has been used in many different fields, including the fabrication of metallic glasses^{6–8} (Fig. 1c). The desired alloy range of the compositional libraries is achieved by altering the orientation angles of the sputtering targets relative to the substrate, and by tuning the sputtering power applied to the targets⁷ (Fig. 1c). As shown in Fig. 1c and d, the libraries were deposited on silicon substrates 100 mm in diameter from targets made of single elements. We fabricated libraries of different compositional gradients, covering nearly the entire ternary phase diagram, such as 0–90% Ir, 0–90% Ni and 10–100% Ta (Fig. 2a). X-ray diffraction (XRD) mapping revealed that approximately 50% of the considered alloys in the Ir–Ni–Ta system form a glass phase (Fig. 2a) owing to the high cooling rate of sputtering²⁶, which cover 10–50% Ir, 0–70% Ni, and 30–85% Ta. Such a broad glass-forming composition range suggests that potential glass-forming alloys may be overlooked because only a few discrete compositions are typically attempted when using the conventional trial-and-error alloy development method.

For high-throughput characterization, we consider electrical resistivity measurements. It has been suggested that the electronic structure of

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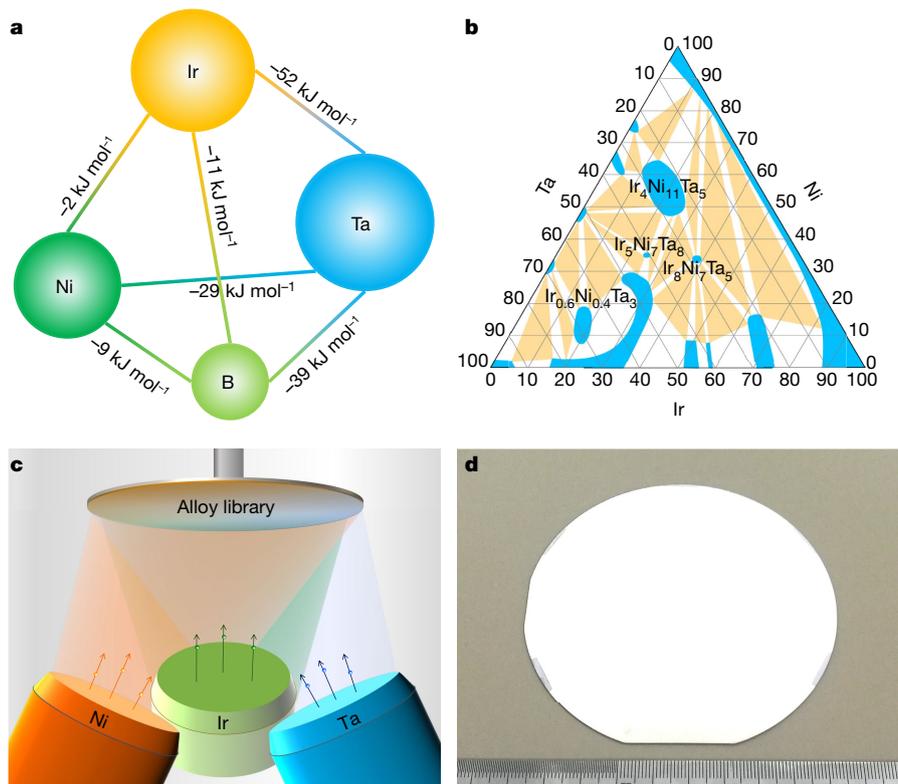


Fig. 1 | Design and combinatorial fabrication of Ir-Ni-Ta-(B) bulk metallic glass forming alloy system. a, The heat of mixing between the selected elements is shown and their relative size difference is indicated by spheres. **b**, Isothermal projection of the Ir-Ni-Ta ternary phase diagram.

an alloy can affect the stability of a glassy structure and that increased stability of the amorphous structure is realized when the Fermi surface touches the quasi-Brillouin boundary^{15,16}. Energy gaps are predicted to occur at the boundaries of Brillouin zones, where energy levels are forbidden and the density of energy states is suppressed, leading to the reduced electronic conductivity that is often associated with enhanced GFA^{15–17} (see also Methods). To rapidly unveil the composition range in which alloys of high GFA may exist, we take this correlation as a guideline. Figure 2b shows the variation of sheet resistance with composition for as-deposited libraries without any post-deposition processing. As can be seen, in the ternary plot (Fig. 2b), there exists a region of higher electrical resistance, suggesting that alloys within this region may have higher GFA. This argument is supported by the fact that the curved band-like region extends towards the known glass-forming compositions in the binary Ir-Ta and Ni-Ta systems^{21,22}, as indicated by the two black dots in Figure 2b. Since our aim is to identify BMGs with high T_g , we consider alloys that are rich in Ir and Ta within the high-resistance region (see the thin solid line in Fig. 2b), because they have higher T_m and E , indicating higher T_g (refs^{18–20}). This region is small enough that it can be evaluated by samples prepared through conventional copper-mould suction casting with cooling rates that are orders of magnitude lower than those during sputtering. We found that within the composition range of 20–35% Ir, 35–40% Ta, and 25–40% Ni (see the purple dots in Fig. 2b), 2-mm-diameter fully glassy rods are readily achievable (Fig. 2c), which was confirmed by XRD (Fig. 2d). In the considered composition range, Ir₃₃Ni₂₈Ta₃₉ exhibits the highest GFA, as reflected by fully glassy rods of 3 mm diameter (Fig. 2c and d). The critical cooling rate for Ir₃₃Ni₂₈Ta₃₉ is estimated to be about 100 K s⁻¹, comparable to that for the majority of known BMG-forming alloys¹². Addition of B further improves GFA. For example, by substituting Ni with 5% B, the critical rod diameter can be increased from 2 mm for Ir₃₅Ni₂₅Ta₄₀ to 3 mm for Ir₃₅Ni₂₀Ta₄₀B₅ (see Fig. 2c and the XRD spectra of Fig. 2d). Since few impurities in BMG rods and raw

materials are detected (Extended Data Table 1), the increased GFA can be attributed to the addition of a minor amount of B. The formation of bulk glasses confirms that mapping electrical resistance is an effective high-throughput approach, and so combinatorial synthesis can be substantially simplified because complicated pre-/post-sputtering procedures^{7,8} can be avoided. The approach is translatable to a broad range of alloy systems so that compositions of high GFA can be identified.

The large thermal stability and the extraordinarily high T_g of the Ir-Ni-Ta-(B) alloys can be seen in Fig. 2e. For Ir₃₅Ni₂₅Ta₄₀, T_g reaches 1,162 K. To our knowledge, this is the highest T_g reported for a BMG (Fig. 3a). Addition of B slightly reduces T_g to 1,147 K, probably owing to the lower T_m of B, but the increase in T_x to 1,283 K leads to a broadened supercooled liquid region (Figs. 2e and 3a). For Ir₃₅Ni₂₀Ta₄₀B₅, ΔT reaches 136 K, which is among the widest reported supercooled liquid regions for BMGs (Fig. 3a). Except for Ir₂₅Ni₃₅Ta₄₀, most of the ternary BMG-forming alloys have compositions that are different from eutectics, exhibiting two melting peaks (Fig. 2f). According to the measured T_g , T_x and the liquidus temperature T_l , the GFA indexes $T_{rg} = T_g/T_l$ (ref. 27) and $\gamma = T_x/(T_g + T_l)$ (ref. 28) are estimated to be 0.65–0.69 and 0.424–0.454 for the Ir-Ni-Ta-(B) alloys. Such T_{rg} and γ values are comparable to BMGs of high thermoplastic formability, such as Zr-, Pt- and Au-based glass-forming alloys¹⁴.

The high T_g of the high-temperature BMGs suggests that their strength can be maintained at high temperatures, potentially even beyond 1,000 K. As can be seen in Fig. 3b, the strength of Ir₃₅Ni₂₅Ta₄₀ high-temperature BMG is 5.1 GPa at room temperature (approximately 21 °C) and remains as high as 3.7 GPa, even at 1,040 K. Such strength is up to an order of magnitude higher than that of high-temperature alloys and high-entropy alloys at similar temperature^{9,13}. The large ΔT of the high-temperature BMGs (Fig. 3a) implies that they are highly processable in their supercooled liquid region, which can be quantified by $S = (T_x - T_g)/(T_l - T_g)$ (ref. 14). For Ir₃₅Ni₂₀Ta₄₀B₅, the S parameter is estimated to be around 0.255, similar to BMGs with high

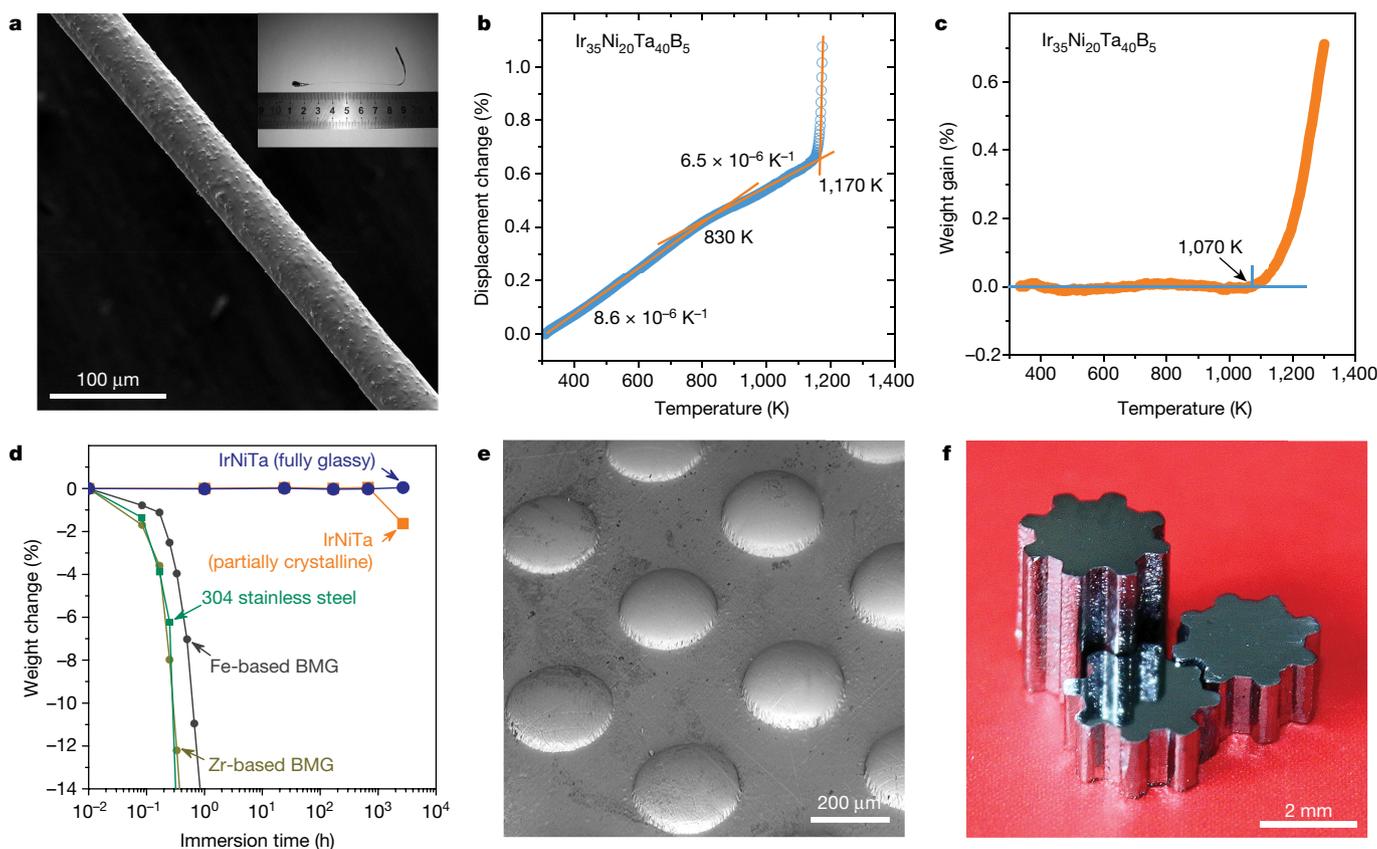


Fig. 4 | Properties of our Ir–Ni–Ta–(B) BMGs. **a**, An $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ micro-wire with diameter around $45\ \mu\text{m}$ processed via thermoplastic forming. **b**, The thermal expansion of $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ BMG in its glass state. **c**, The strong oxidation resistance of $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ BMG up to $1,070\ \text{K}$ in air. **d**, In aqua regia, 304 stainless steel and Zr- and Fe-based BMGs are

corroded within one hour. However, our fully glassy $\text{Ir}_{35}\text{Ni}_{25}\text{Ta}_{40}$ BMG rod showed no weight loss for up to 112 days. The partially crystalline $\text{Ir}_{35}\text{Ni}_{25}\text{Ta}_{40}$ rod exhibited measurable weight loss after 28 days. **e**, An $\text{Ir}_{33}\text{Ni}_{28}\text{Ta}_{39}$ microscale mould fabricated by thermoplastic forming. **f**, $\text{Ir}_{33}\text{Ni}_{28}\text{Ta}_{39}$ micro-gears fabricated by copper mould casting.

are values unprecedented for BMGs. The bending strain to failure rate of about 2.9% for the as-cast $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ BMG suggests that it has moderate ductility²⁹ despite high hardness and modulus. The linear thermal expansion coefficient of $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ high-temperature BMG was measured to be $8.6 \times 10^{-6}\ \text{K}^{-1}$ at temperatures lower than $830\ \text{K}$, and $6.5 \times 10^{-6}\ \text{K}^{-1}$ for temperatures above $830\ \text{K}$ (Fig. 4b). Compared to published data on BMGs³⁰, such thermal expansion coefficients are among the smallest values.

Figure 4c shows the oxidation behaviour of $\text{Ir}_{35}\text{Ni}_{20}\text{Ta}_{40}\text{B}_5$ high-temperature BMG as a function of temperature measured in air. No substantial weight change can be observed up to $1,070\ \text{K}$, a temperature close to its T_g . Annealing tests further confirm that the high-temperature BMGs can be exposed to high temperatures in air without substantial oxidation (Extended Data Figs. 1, 2). Oxidation resistance is often associated with general resistance to corrosion. As shown in Fig. 4d, corrosion takes place within an hour in 304 stainless steel, and in Zr- and Fe-based BMGs when they are immersed in aqua regia. However, no weight loss in the fully glassy IrNiTa high-temperature BMG can be seen even after 112 days, while the partially crystalline IrNiTa sample exhibits obvious weight loss after 28 days. This finding reveals that the high-temperature BMGs can withstand extremely corrosive conditions. It also highlights the importance of both chemistry and microstructure for the corrosion resistance as the partially crystalline alloy reacts much faster.

The combination of superb properties and plastic-like processability—wide ΔT and high GFA, high-temperature strength, excellent thermoplastic formability, low thermal expansion, superior oxidation and corrosion resistance—make the Ir–Ni–Ta–(B) high-temperature BMGs promising for a range of technological applications at low and ambient temperatures but also at temperatures beyond $1,000\ \text{K}$ and

even in extreme environments. For example, taking advantage of their thermoplastic formability, mechanical properties, and low thermal expansion, the glasses are excellent candidates for fabrication of micro- and nano-devices and high-precision moulds (Fig. 4e). With their remarkable mechanical properties and corrosion and oxidation resistance, they can be used as micro-components such as gears for applications in harsh environments (Fig. 4f). With their high T_g , oxidation resistance and mechanical properties, combined with inexpensive and versatile processability by thermoplastic forming, they are in many ways superior to currently used Ir alloys, which have broad applications but suffer from poor processability owing to their intrinsic brittleness³¹.

The development of high-temperature BMGs has taken nearly three decades so far^{32,33}. However, previous trial-and-error approaches focusing on eutectic compositions (in particular, in tungsten-based alloys) have identified only glass formers that require very high cooling rates to avoid crystallization^{32,33}. The discovery process described here for the Ir–Ni–Ta–(B) alloys represents a paradigm shift in the development of practical BMGs because it allows for the simultaneous optimization of many of the properties required for a BMG to be of commercial use.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/10.1038/s41586-019-1145-z>.

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METHODS

Sample preparation. The combinatorial thin-film libraries were fabricated by magnetron co-sputtering deposition from elemental sputtering targets, and 100-mm-diameter Si wafers were used as substrates⁶. Alloy ingots were prepared by arc melting in Ar atmosphere. Copper-mould suction casting was used to fabricate rod samples. Micro-wires were fabricated by rapidly heating 1-mm-diameter glassy rods into the supercooled liquid region, followed by rapid drawing out (by attaching a weight to one end of the rod).

Compositional and structural characterizations. The compositions of the combinatorial libraries, calibrated with bulk alloys of known compositions, were measured by energy-dispersive X-ray spectroscopy attached to a Phenom scanning electron microscope. X-ray diffraction was used to characterize phase formation of the combinatorial libraries by using Rigaku SmartLab X-ray diffractometer with a Cu-K α radiation source⁶. The amorphous nature of rod samples was confirmed by XRD using a Bruker D8 X-ray diffractometer with a Cu-K α radiation source.

Electrical resistance measurement and its correlation with glass forming ability. Sheet resistance mapping over the as-deposited films was done using the automatic four-point probes method (Cresbox, Napson). For each wafer, 225 uniformly distributed points were measured. The argument of Nagel and Tauc¹⁵ assumed a spherical Fermi surface and a spherically symmetric structural factor in an amorphous structure. Because glass, considered as a liquid metal, is in a metastable state and any perturbation due to a decreased degree of disorder will destroy the spherical symmetry of $S(q)$, the total energy of the system increases as more electron states are moved up to the Fermi energy E_F , where they have higher energy. According to Nagel and Tauc¹⁵, the increased stability of an amorphous structure is realized when the Fermi surface touches the quasi-Brillouin boundary, or $q_p = 2K_F$ (where K_F is the Fermi wave vector, and q_p is the first maximum of the structural factor $S(q)$). Energy gaps are predicted to occur at the boundaries of Brillouin zones, at which energy levels are forbidden and the density of energy states is suppressed, leading to reduced electronic conductivity¹⁶. In the Nagel–Tauc model¹⁵, transition metals as well as the noble metals are treated as if they had only one free electron per atom in the liquid, and the effect of alloying is treated as a rigid shift of E_F and K_F . These two assumptions were verified by Nagel and Tauc with experimental data¹⁵. Recent reports on various transition-metal systems further indicate a positive correlation between glass-forming ability and electronic resistivity^{15,16}. Here we took this correlation as a guideline and carried out resistivity mapping to narrow down the composition range in which alloys of high glass-forming ability may exist.

Thermal analysis. The differential scanning calorimetry experiments were performed using a DSC 404F3 (Netzsch) under a constant flow of high-purity argon gas. The heating rate was 0.33 K s⁻¹. Thermal mechanical analysis at a heating rate of 0.083 K s⁻¹ under a constant flow of high-purity argon gas was conducted by using a TMA 402F3 (Netzsch). The load applied on the specimen was 3 gram force.

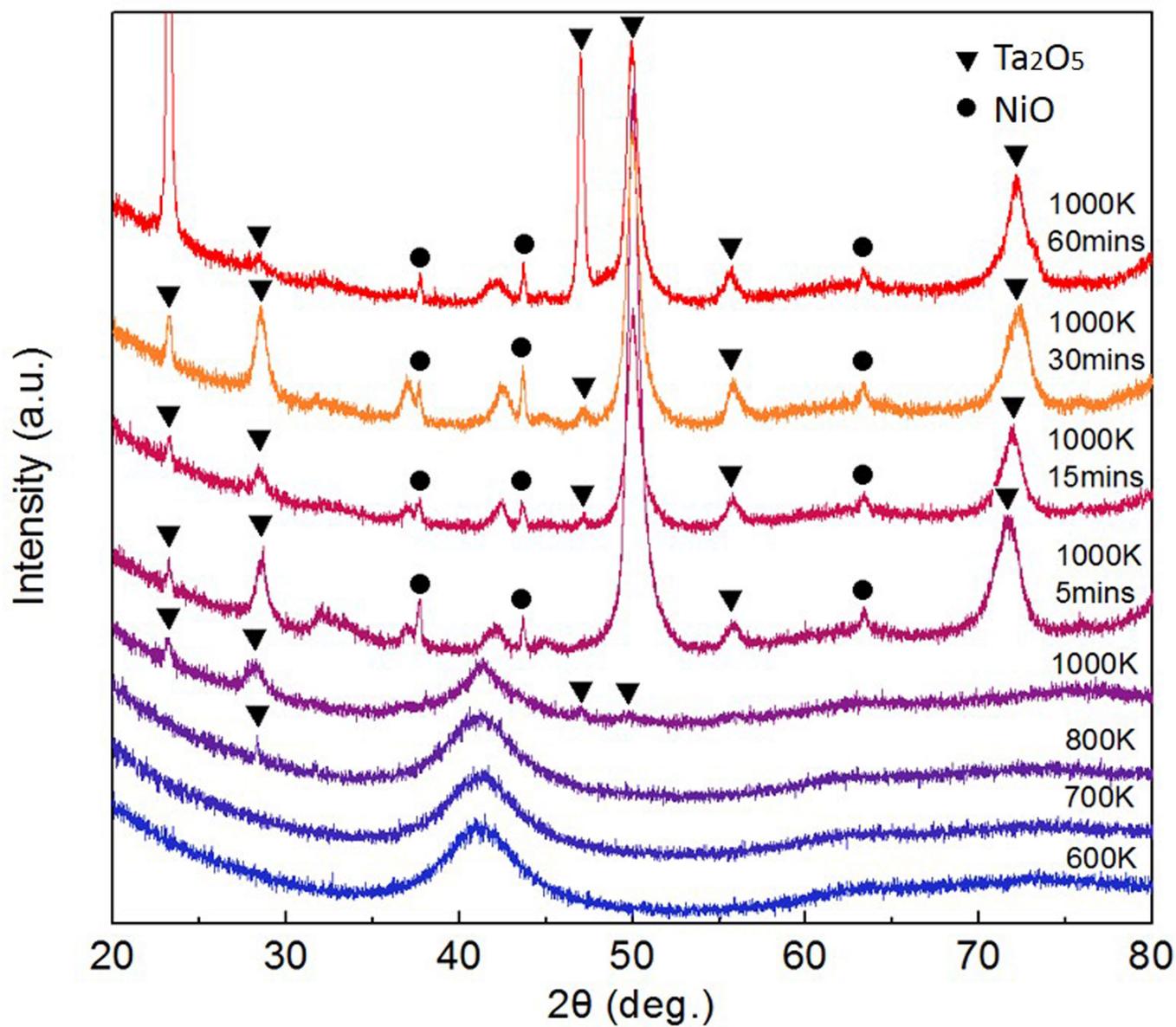
Mechanical characterization. Compressive tests were conducted on 1 mm diameter \times 2 mm long rod samples by using a custom-made high-temperature mechanical tester at a strain rate of 0.012 s⁻¹. The bending strain to failure rate was measured by bending beams (10 mm \times 2 mm \times 0.85 mm) around mandrels of differing radii at room temperature. Hardness and elastic modulus were measured using nanoindentation equipped with a standard Berkovich indenter.

Oxidation behaviour. Weight loss measurements were performed in air in a Mettler TGA/SDTA851e Instrument. Cylinder specimens 2 mm in diameter and 1 mm in length were scanned from 323 K to 1,473 K at a constant heating rate of 0.33 K s⁻¹. Furthermore, we annealed Ir₃₃Ni₂₈Ta₃₉ BMG disks in air at different temperatures (600 K, 700 K, 800 K and 1,000 K). XRD characterizations on the surface of the annealed disks indicated that the oxide layer is mainly composed of Ta₂O₅ and NiO. Ta₂O₅ starts to form at 800 K, while NiO starts to form at 1,000 K (Extended Data Fig. 1). We also conducted characterizations on the cross-section of the annealed disk by scanning electron microscopy, as shown in Extended Data Fig. 2. Composition mapping by energy-dispersive X-ray spectroscopy indicates that the thickness of the oxide layer is about 4 μ m after the disks were annealed at 1,000 K for 1 min, because beyond the 4- μ m-thick oxide layer, the concentrations of Ir, Ta, and Ni change back to their nominal ratio and that of O decays to zero. After being annealed for 60 min at 1,000 K, the thickness of the oxide layer increased from 4 μ m only to 8 μ m. A clear boundary of oxide layer can be seen (Extended Data Fig. 2). For the sample annealed for 1 min at 1,000 K, Ir and Ta decreased a little. After annealing for 60 min, Ir and Ta remained nearly constant, but Ni decreased substantially. This is probably owing to the formation of NiO, which is denser than Ta₂O₅ and can prevent further oxidation. Extended Data Fig. 2 also shows the microstructure of the oxide layer at different annealing times. With prolonged annealing time, no obvious change could be seen in the oxide layer, suggesting that the dense and uniform layer composed of Ta₂O₅ and NiO limited the oxide reaction to the surface.

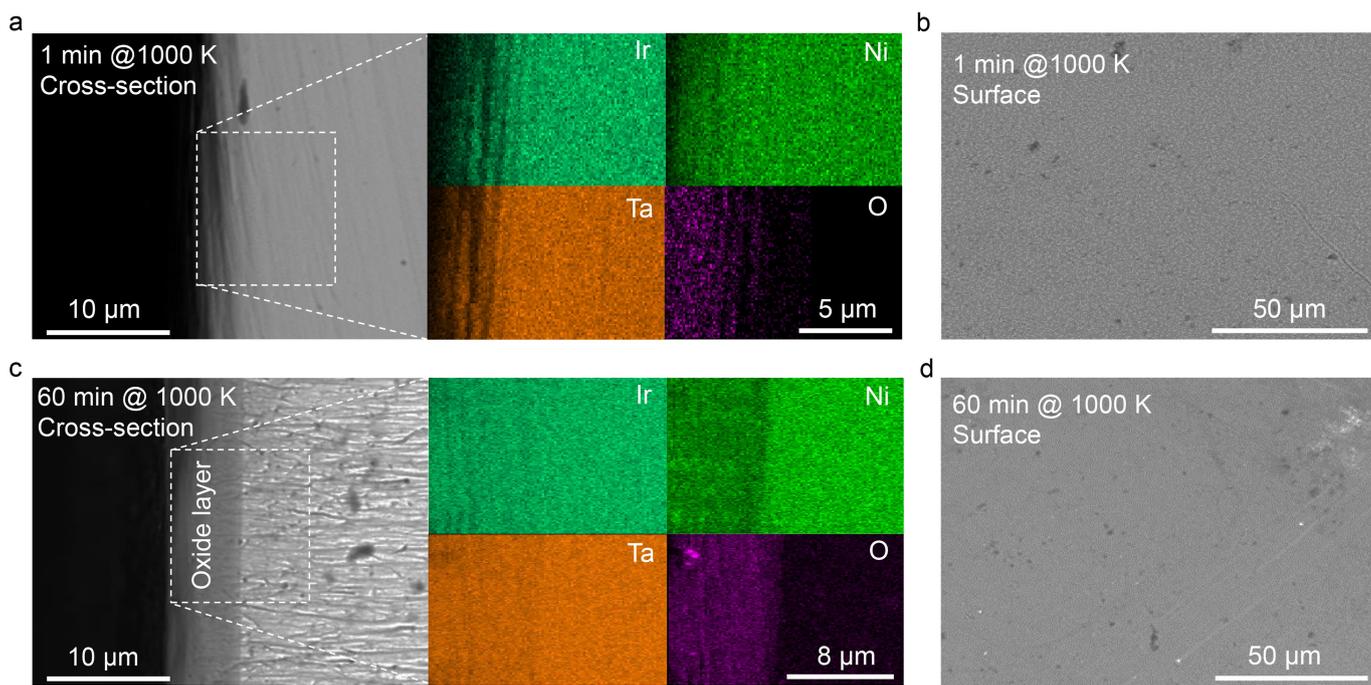
Impurity of the developed BMGs. We analysed the impurities of Ir₃₃Ni₂₈Ta₃₉ BMG by using a LECO TC-600 nitrogen/oxygen analyser and an infrared absorption carbon–sulphur analyser. As shown in Extended Data Table 1, the contents of impurities, including oxygen, carbon and nitrogen, were all beyond the resolution of the analyser (0.01 at.%), indicating the low concentration of these impurities. We also analysed the impurities of the raw Ir, Ni, Ta materials. Again, the contents are all below 0.01 at.%.

Data availability

The authors declare that the data supporting the findings of this study are included within the paper and available from the corresponding author on reasonable request.



Extended Data Fig. 1 | Oxide formation with temperature and time. XRD characterizations on the surfaces of annealed BMG disks indicate that the oxide layer is mainly composed of Ta_2O_5 and NiO.



Extended Data Fig. 2 | Morphologies of oxide layer. a, b, Cross-section and surface morphology along with corresponding element distribution on disk sample annealed at 1,000 K for 1 min. **c, d,** Cross-section and

surface morphology along with corresponding element distribution on disk sample annealed at 1,000 K for 60 min.

Extended Data Table 1 | Concentration of impurities in the Ir₃₃Ni₂₈Ta₃₉ BMG

Element	O	C	N	Pb	Si	Ca	Se	Ag
Concentration	<0.01 %	<0.01 %	<0.01 %	15 PPM	10 PPM	3 PPM	3 PPM	2 PPM

PPM, parts per million.