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Rejuvenation by enthalpy relaxation in metallic glasses

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Usually structural relaxation would lead to embrittlement in metallic glasses (MGs). Here, we show that rejuvenation of relaxed MGs is achieved simply by a thermal exposure at a temperature *higher* than the annealing temperature (but below glass transition temperature). The effect is driven by enthalpy relaxation (an endothermic reaction upon heating relaxed MGs). This rejuvenation lifts the energy state of the relaxed glass towards that of the as-cast glass. Importantly, we demonstrate that the plasticity and fracture toughness of the rejuvenated samples exceed those of the as-cast state. An analysis of the structural changes shows that the rearrangement of cluster connectivity at the medium-range length

scale is responsible for the rejuvenation. Our finding is significant for the tailoring of the mechanical properties of metallic glasses.

Relaxation¹⁻³, a structural ordering process, densifies atomic packing and reconfigures the atomic structure to a low-energy state that usually hardens and embrittles materials⁴. Generally annealing at a temperature below the glass transition temperature (T_g) leads to relaxation. Since there is a lack of volume-generating mechanisms at high temperatures, hardening and embrittlement are regarded as a definite consequence of relaxation induced by thermal annealing⁴.

As an opposite process, rejuvenation, a disordering process, generates excess defects (e.g., free volume) and elevates MGs to a high-energy state that improves their plasticity⁵⁻⁷. Rejuvenation can be achieved in several ways such as by irradiation⁸⁻¹⁰, elastostatic loading^{11,12}, plastic deformation^{6,13}, or thermal cycling⁵. Ion irradiation can induce void-free swelling and achieves high degrees of rejuvenation¹⁰. Loading of MGs within elastic regime leads to homogeneous flow and generates excess free volume¹¹. Plastic deformation such as heavy cold-working¹⁴ and shot peening¹⁵ is a commonly employed method to rejuvenate metallic glass. Its advantage is that the rejuvenated state can be obtained in samples with much larger cross-sections. Heating MGs above T_g into supercooled liquid region and then cooling it rapidly can achieve rejuvenation^{16,17}. Thermal cycling between room temperature and cryogenic temperature rejuvenates the glass, due to the nature of non-affine thermal expansion in metallic glasses⁵. This method is non-destructive, introduces no shape change, and can be applied to any sample geometry.

Despite many advantages, the above methods have their limitations. They either involve multiple steps, or are destructive or lead to possible shape change, or have difficulty in accessing to the radiation facilities. Furthermore, some of these methods would lead to the opposite relaxation effect^{6,18-22} or partial crystallization^{23,24}. The method of heating MGs above T_g and then quenching rapidly is not applicable to MGs (e.g., Fe based²⁵) without supercooled liquid region. *As such*, a simple yet effective and non-destructive method that can be applied to any shape of the relaxed MGs to revive the relaxation induced embrittlement so as to restore the lost ductility and toughness of the as-cast MGs still eludes us.

On the other hand, enthalpy relaxation^{26,27} is observed in many amorphous materials that are annealed after a wide variety of thermal and mechanical treatments. Upon heating of a relaxed sample, an endothermic event was recorded between the annealing temperature (T_a) and T_g , which indicated an increase in the enthalpy of the amorphous material²⁸. This effect provides an opportunity to rejuvenate MGs into a high-energy state²⁹. Here, we demonstrate that a simple thermal exposure in the temperature range for enthalpy relaxation rejuvenates the energy state of relaxed glasses towards that of as-cast glasses. This rejuvenation erases the effect of annealing-induced embrittlement and significantly enhances the plasticity and fracture toughness, even surpassing those of the as-cast state. Our findings here show that the structure and mechanical properties of MGs can be tailored by thermal treatment at a high temperature that is close to but still below T_g . Since enthalpy relaxation is observed in a wide range of amorphous structure materials, including polymers and

ceramics, our discovery provides a new perspective for the control of properties of amorphous materials.

Fig. 1a shows the differential scanning calorimetry (DSC) curves of an as-cast MG and the relaxed sample annealed at T_a of 570 K for 9 hours. Although there seems to be little change between these two curves, a close comparison of the curves just below the T_g (the inset in Fig. 1a) shows a noticeable difference. For the as-cast sample, the curve (dashed line) shows an exotherm before T_g , like that of many as-cast glasses reported previously³⁰. The exothermic heat of relaxation ΔH_{rel} (Supplementary Fig. 1a) upon heating to T_g (690 K) for the as-cast sample is 0.58 kJ mol⁻¹. For the relaxed sample (solid line), this exotherm is replaced by an endothermic peak at the same temperature range, also known as enthalpy relaxation/recovery, a typical outcome of annealing for most glassy materials. The changes in the enthalpy relaxation ΔH_{endo} ³¹, quantified as the area between the relaxed DSC curve and the standard curve (Supplementary Fig. 1b), is approximately -0.26 kJ mol⁻¹ (the minus sign differentiates this heat with the exothermic heat).

The endothermic event shown on the DSC curve of the relaxed sample indicates an increase in the enthalpy of the system²⁸. This hints that if the relaxed sample is placed in this temperature range and then quenched quickly, rejuvenation can be expected. The magnified inset of the DSC curves (Fig. 1b) shows a comparison of the relaxed sample and the relaxed sample treated at 660 K for 90 s (a temperature between T_a and T_g) and quenched in iced-water. The endothermic peak shown in the curve (dashed line) for the relaxed sample almost disappears in the curve (solid line)

for the treated sample. Instead, an exothermic peak reappears on the curve after thermal exposure, confirming that rejuvenation of the relaxed MGs indeed took place at the expense of enthalpy relaxation.

To illustrate the dependence of rejuvenation on the exposure temperature, the samples relaxed at 570 K for 9 hours were exposed to a series of temperatures from 640 to 680 K, all of which are below T_g . As the rejuvenation temperature increases, the DSC scans show that the intensity of the endothermic peak after rejuvenation gradually decreases and vanishes eventually at 670 K, while the intensity of the exothermic peak increases (Supplementary Fig. 2 and inset of Fig. 2a). Fig. 2a shows that the ΔH_{rel} generally increases as the rejuvenation temperature increases, but there is a maximum in ΔH_{rel} value: 0.129 kJ mol⁻¹ at 660 K. Overall, the ΔH_{rel} values of the rejuvenated relaxed samples do not revert to the value of the as-cast sample even though the maximum restoration of the enthalpy is 22.1% compared with that of the as-cast sample. Moreover, the endothermic enthalpy relaxation ΔH_{endo} of rejuvenated samples changes from -0.26 kJ mol⁻¹ to 0 kJ mol⁻¹ at 670 K (Fig. 2b).

Relaxation hardens and embrittles glasses, while rejuvenation softens and toughens them. Here, we investigated the effect of relaxation and subsequent rejuvenation on the mechanical properties of MGs. The hardness (Hv, kgf mm⁻²) of the as-cast sample is 511. In the relaxed sample, the hardness is 526, an increase of 2.93% compared to that of the as-cast sample, which is consistent with that of many previous reports³². Upon rejuvenation of the relaxed samples, the hardness of rejuvenated samples generally decreases towards that of the as-cast sample. As shown

in Fig. 2c, there is a minimum hardness; however, the hardness is 517.7 Hv after rejuvenation at 660 K, which is close to but still higher than that of the as-cast sample. The hardness minimum matches the maximum in the ΔH_{rel} shown in Fig. 2a. Furthermore, we systemically evaluated the effect of rejuvenation on the compressive plastic strain over a wide range of rejuvenation temperatures (Supplementary Fig. 3). The plastic strain decreases from 5.1% for the as-cast sample to 3.4% after relaxation at 570 K for 9 h, confirming that embrittlement is induced by the annealing process. Exposing the pre-relaxed samples at a temperature between 640 K and 680 K results in an increase in the plastic strain when compared with that of the as-cast sample (Fig. 2d); surprisingly, most of the strains are even *higher* than that of the as-cast sample. The maximum plastic strain obtained at 660 K is 8.5%, which is 2.5 times that of the relaxed sample and 65% higher than that of the as-cast state. This maximum plastic strain again matches the maximum enthalpy (Fig. 2a) and minimum hardness (Fig. 2c).

The fracture toughness is a sensitive macroscopic measure of the glass state and is of great practical importance for structural materials³³. Here, we measured the fracture toughness of the as-cast, relaxed and rejuvenated samples. Fig. 3a shows that the MGs exhibit embrittlement after annealing, and the fracture toughness (K_Q) decreases to 24 MPa m^{1/2} from 87 MPa m^{1/2} of the as-cast glass. On the other hand, the K_Q (97 MPa m^{1/2}) of the sample rejuvenated at 667 K is 3.48 times and 11.5% *higher* than that of the relaxed and the as-cast samples, respectively. To show the effect of rejuvenation, the sample surfaces after fracture toughness testing were

examined for the as-cast, relaxed and rejuvenated samples (Fig. 3b-d). A representative micrograph (Fig. 3b) of the near-notch region of the as-cast sample, just before fracture initiation, shows multiple curved shear bands. The crack propagation path is deflected and bifurcated (inset of Fig. 3b), which is commonly observed in MGs with a high toughness³³. No visible shear bands are observed (Fig. 3c) for the relaxed sample, and the crack propagates in a straightforward manner (inset of Fig. 3c), showing brittle fracture behaviour. After rejuvenation, however, extensive curved shear bands are formed again at the crack tip (Fig. 3d), and the deflected and bifurcated crack propagation shown in the inset of Fig. 3d results in an additional barrier for crack extension. The plastic zone size measured is ~ 0.64 mm, which is 1.1 times higher than that (~ 0.58 mm) of the as-cast sample. The observation of the compressed samples (Supplementary Fig. 4) shows a similar trend: multiple shear bands are observed in the as-cast and rejuvenated samples, while few shear bands are observed in the relaxed sample. All these are consistent with the values of the fracture toughness measured for these samples.

X-ray diffraction patterns (Supplementary Fig. 5) and high-resolution transmission electron microscopy (Supplementary Fig. 6) of the relaxed and rejuvenated samples confirm that they are still fully amorphous after relaxation and subsequent rejuvenation. To study the effect of rejuvenation on the atomic structure, we also employed synchrotron radiation to investigate the structural changes. Fig. 4a shows the position of the first sharp diffraction peak (FSDP, i.e., Q_1) for the as-cast sample, the sample after relaxation and the sample after rejuvenation at different

temperatures. The value of Q_1 is in the right proportion to the mass density³⁴. It shows that after relaxation at 570 K, the value of Q_1 shifts higher, indicating that the packing density increases, which is consistent with many previous reports. However, after rejuvenation at 660 K, the Q_1 values decrease, indicating a decreased packing density and an increased atomic volume compared to those of the relaxed samples. Interestingly, the peak value of Q_1 at approximately 660 K is even smaller than that of the as-cast sample. These structural changes correlate well with the changes in ΔH_{rel} , Hv, and plastic strain.

The second coordination peak of the pair distribution function (PDF) profile (Supplementary Fig. 7) is related to the connection of short-range clusters at the medium-range order (MRO) length scale³⁵. It has been suggested that the connection modes of clusters at the MRO length scale in metallic glasses may affect the macroscopic plasticity^{35,36}. Generally, there are four kinds of cluster connection modes, i.e., vertex-shared (1-atom), edge-shared (2-atom), face-shared (3-atom), and intercross-shared modes (4-atom)³⁷. The proportion for these four modes (Fig. 4b-e) shows that there are decreasing 3-atom and 4-atom connection modes and increasing 1-atom and 2-atom connection modes in the rejuvenated sample (e.g., the 660-K sample) compared to those in relaxed samples. Therefore, the average distances of connected clusters at MRO length scales for the rejuvenated samples are larger than those in the relaxed samples, resulting in a decreased packing density. The cluster connectivity of 1- to 4-atoms shown in Figs 4b-e may well explain the exceptionally high ductility and fracture toughness of the rejuvenated samples.

Our results show that the enthalpy relaxation, i.e., the endotherm in the relaxed sample, can be employed to rejuvenate the relaxed glass effectively. Although the energy state does not reach that of the as-cast sample, the plasticity and toughness can be enhanced even *better* than that of the as-cast sample. This could be attributed to the rearrangement of cluster connectivity at the MRO length scale induced by enthalpy relaxation. We are not aware that such a great improvement in the plasticity and toughness by high-temperature annealing has been reported previously in monolithic glasses, especially at a temperature so close to T_g , where the common consequences of annealing are hardening and embrittlement. This method of restoration of ductility is expected to apply for a wide range of metallic glasses as enthalpy relaxation is observed in many MGs^{26,31}. Similar rejuvenation induced ductilization is confirmed in an Fe-based MG (see Supplementary Fig. 8).

Rejuvenation of relaxed samples by thermal exposure at temperatures above T_g has been reported previously^{16,17}. Our present study confirms that thermal exposure at 720 K above T_g (690 K) also rejuvenates the relaxed glass. The ΔH_{rel} and hardness after rejuvenation are 0.535 kJ mol⁻¹ and 511, respectively (Supplementary Table 1), very close to 0.582 kJ mol⁻¹ and 511 of the as-cast sample, respectively. Nevertheless, the plasticity of 3.7% (Supplementary Table 1) is smaller than the value of 5.15% for the as-cast sample and is much smaller than the value of 8.53% for the rejuvenated sample (660 K) after enthalpy relaxation. These results indicate that rejuvenation at a temperature above T_g is ineffective for recovering the plasticity of MGs after relaxation. This could show that the underlying rejuvenation mechanisms for enthalpy

relaxation (below T_g) and for rejuvenation at temperatures well above T_g may be quite different. Although both processes increase the enthalpy, treatment at above T_g leads MGs into a supercooled liquid region where the prior ageing effects are erased³, whereas enthalpy relaxation occurs in the relaxed glasses in the solid glassy state.

Our study indicates that both temperature and cooling rate play important role in the rejuvenation process. Fig. 2d shows that precise control in the rejuvenation temperature is required to maximize the ductility. Any rejuvenated glass would tend to relax. Since the enthalpy relaxation can occur at a heating rate of 0.33 K s^{-1} , the cooling rate required to retain the rejuvenation effect is low, that the cooling rate of water quenching is sufficient, as shown in our study.

The energy state has a strong influence on the mechanical properties of MGs. It has been reported that the ΔH_{rel} and hardness are directly correlated⁶. The trend that the hardness decreases with increasing ΔH_{rel} , shown in our present study (Supplementary Fig. 9), follows this expected correlation, while the peak in the plastic strain with ΔH_{rel} is unexpected. This demonstrates that a slight change in the energy state, induced by enthalpy relaxation, does have a great effect on mechanical properties, such as the plastic strain and fracture toughness. This has a significant influence on approaches to enhance the plasticity and toughness in metallic glasses. Since enthalpy relaxation is widespread in amorphous materials, an improvement in the plasticity is expected in many other amorphous materials, such as polymers and ceramics; our results therefore have broad implications and impacts.

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Methods

Preparation of metallic glass specimen. Master alloys with a nominal composition of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (at.%) were prepared by arc-melting mixtures of high-purity (at least wt.99.9%) metals in a high-purity argon atmosphere. Melted alloys were drop-cast into a copper mold with dimensions of 2.2 mm $\times$ 22 mm $\times$ 60 mm. Cylindrical specimens with a diameter of 2 mm and a length of 30 mm were fabricated by copper mold casting under a Ti-gettered argon atmosphere. The Fe-based amorphous ribbons, $Fe_{78}Si_{13}B_7$, are provided by Advanced Technology & Materials Co.

Thermal exposure. The relaxed $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ specimens were prepared by sealing the as-cast cylindrical rods and plates in an evacuated quartz capsule and annealing at 570 K for 9 h. The rejuvenated specimens were prepared by putting the relaxed specimens into a tube furnace with specific temperature (640-730 K) and holding 90 s, subsequently quenching into iced-water. The schematic diagram of heating history is shown in Supplementary Fig. 10. The temperature of the specimens was monitored by a thermocouple. The estimated heating and cooling rates are ~ 200 K min^{-1} and ~ 300 K s^{-1} respectively. The relaxed $Fe_{78}Si_{13}B_7$ samples were prepared by annealing at 600 K (onset temperature of crystallization $T_x = 800$ K) for 1 h, the rejuvenated samples were prepared by exposed the relaxed samples at 688 K for 10 s and then quenching into iced-water.

Thermal analysis. The thermal behavior of as-cast, annealed and rejuvenated specimens was investigated by differential scanning calorimetry (DSC, TA Q2000) with a heating rate of 20 K min^{-1} . Specimens were heated from room temperature up

to 710 K (into the supercooled liquid state) and cooled to room temperature. A second run, heated up to 873 K, using the same heating rate to obtain specific heat, $C_{p,s}$, of “reference” sample. A third run under the same condition was used to determine the baseline for each measurement. The heat of relaxation ΔH_{rel} is calculated from the area between the two curves of first and third run, from the onset of relaxation to the glass transition as reported in Ref.³⁰, as shown in Supplementary Fig. 1. The change of enthalpy relaxation ΔH_{endo} is calculated from equation (1)³¹:

$$\Delta H_{endo} = \int \Delta C_p (= C_p - C_{p,s}) dT, \Delta C_p \geq 0 \quad (1)$$

where C_p is heat capacity of each specimen, $C_{p,s}$ is heat capacity of the reference sample.

Structural characterization. The structure of the as-cast, annealed and rejuvenated specimens were confirmed to be fully glassy by X-ray diffraction (XRD, Bruker D2 phaser) with Cu-K α radiation ($\lambda = 0.154$ nm). The lateral and surface morphologies of specimens after deformation were characterized by scanning electron microscopy (Zeiss Supra 55) operated at an acceleration voltage of 20 kV. Microstructure of as-cast, annealed and rejuvenated specimens was characterized by transmission electron microscopy (FEI Tecnai F20) operated at 200 kV. TEM specimens were first mechanically ground to a thickness of 20 ~ 30 μm using SiC paper, then finalized using ion milling.

Synchrotron radiation. The high-energy synchrotron X-ray diffraction was carried out at the beamline 11-ID-C at the Advanced Photon Source (APS), Argonne National Laboratory. High energy X-ray with a beam size of 500 $\times$ 500 μm^2 and wavelength of

0.1173 Å. Two-dimensional diffraction patterns were obtained for rejuvenated samples using a Perkin-Elmer amorphous silicon detector. The static structure factor, $S(Q)$ with $Q_{\max} \sim 30 \text{ Å}^{-1}$ was derived from the two-dimensional diffraction ring patterns by integrating images, subtracting the appropriate background, and correcting for oblique incidence, absorption, multiple scattering, Compton scattering and Laue correction using software Fit2D and PDFgetX2.

The average cluster radius R is estimated by the weighted bond length of coordination atoms. The center distance of the four cluster connection modes can be calculated as $2R$ (1-atom), $\sqrt{3}R$ (2-atom), $\sqrt{8/3}R$ (3-atom), $\sqrt{2}R$ (4-atom), respectively³⁵. Therefore, the second-nearest-neighbor coordination shell of $g(r)$ could be fitted by four Gaussian functions, and the area of each Gaussian peak could be regarded as its proportion in the MRO. Four center distances are input as initial values of Gaussian fitting, and a slight adjustment is allowed during the fitting process.

Mechanical testing. Compression tests of the as-cast, annealed and rejuvenated specimens with a diameter of 2 mm and a length of 4 mm were performed on a Shimadzu AG-I at room temperature at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Prior to the compressive testing, the ends of specimens were polished carefully to ensure parallelism. Microhardness testing of as-cast, annealed and rejuvenated specimens were conducted on a Qness Q10 A+ microhardness tester with a Vickers indenter. The indentation peak load with a load of 500 g and dwell time of 15 s.

Single-edge bend (SE(B)) specimens for fracture toughness tests, with a

thickness (B) of 2 mm, with (W) of 4 mm and total length (L) of 22 mm, were fabricated by electro-discharge machining from the as-cast MGs plates. Notches with a root radius of $\sim 200 \mu\text{m}$ and a length of 1.3 mm were cut in all SE(B) specimens using a diamond wire saw. The fatigue pre-cracking of SE(B) specimens was conducted on a 3 kN Electropuls E3000 fatigue test machine at 25 Hz frequency under load control at a constant ratio (minimum and maximum applied load) of $R = 0.1$ with the stress-intensity range ΔK of $\sim 10\text{-}12 \text{ MPa}\cdot\text{m}^{1/2}$. The crack length, a (the length of notch plus the fatigue pre-crack), was $\sim 0.45\text{-}0.6W$, confirming to the ASTM standards³⁸. Pre-cracked specimens were tested in three-point bending, with a loading span of $S = 16 \text{ mm}$, at a constant displacement rate of 0.1 mm min^{-1} . Physical crack extension in the unloaded and fractured specimens was also measured by SEM (Zeiss Supra55). The fracture toughness K_Q can be calculated using equation (2) and (3)

$$K = \frac{P_Q S}{BW^{\frac{3}{2}}} \cdot f\left(\frac{a}{W}\right) \quad (2)$$

$$f\left(\frac{a}{W}\right) = 3\sqrt{\frac{a}{W}} \cdot \frac{1.99 - \left(\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)\left[2.15 - 3.93\frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right]}{2\left(1 + 2\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)^{\frac{3}{2}}} \quad (3)$$

where P_Q is the conditional value of force according to the ASTM standard E399³⁸, S is the loading span ($S = 16 \text{ mm}$), B is the specimen thickness, W is the specimen width, and a is the crack length.

Bending tests for $\text{Fe}_{78}\text{Si}_{13}\text{B}_7$ ribbon samples were performed using two parallel plates at room temperature³⁹. The ribbons were clamped between two plates and then the distance between the two plates was reduced slowly. It is determined that $\varepsilon_f = 1$ when the ribbon can be bent completely. Each test was repeated more than 40 times.

Data availability

All data generated or analysed during this study are included in the published article and Supplementary Information, and are available from the corresponding authors upon reasonable request.

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Author Contributions

Y.L. led the project and the writing of the paper. All authors contributed to the interpretation and presentation of the results. Casting, relaxation and rejuvenation of the metallic-glass samples, their characterization by microhardness testing, compression testing and fracture toughness measurement, differential scanning calorimetry, and surface observation by scanning electron microscopy was by Y.H.M and S.Y.Z. Synchrotron radiation measurement including calculation of radial distribution functions was by S.L.

Competing interests

The authors declare no competing interests.

Additional Information

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Fig. 1 | Relaxation and rejuvenation induced changes in the MG state. a, Differential scanning calorimetry (DSC) upscans (heating rate 20 K min^{-1}) of the as-cast and relaxed MG. The two samples show the same crystalline behaviour. The inset shows a close-up comparison of the two samples. The as-cast sample (dashed line) exhibits an exotherm before the glass transition temperature, while an endotherm is clearly observed on the relaxed sample (solid line) annealed at 570 K for 9 h. **b,** After rejuvenation, an exothermic peak reappears on the curve (solid line), while the endothermic peak observed on the pre-annealed sample (dashed line) almost disappears.

Fig. 2 | Consistent change between enthalpy and properties. **a**, Heat of relaxation ΔH_{rel} , **b**, endothermic enthalpy relaxation ΔH_{endo} , **c**, microhardness Hv, and **d**, compressive plastic strain as a function of the rejuvenated temperature. The maximum of the ΔH_{rel} makes the minimum hardness and optimized plasticity much higher than that of the as-cast sample. The different specific heat C_p between the first upscanned DSC curves and baseline is shown in the inset of **a**, and the different specific heat C_p between relaxed and rejuvenated samples and reference is shown in the inset of **b**, where the detailed calculation of ΔH_{rel} and ΔH_{endo} can be seen in the Methods. The inset of **d** shows the compressive stress-strain curves of the as-cast, relaxed and typical rejuvenated samples.

Fig. 3 | Fracture toughness measurements and SEM micrographs of the as-cast, relaxed and rejuvenated samples. **a**, Annealing embrittles the MG; the fracture toughness (K_Q) decreases from 87 MPa m^{1/2} (as cast) to 24 MPa m^{1/2} (relaxed), while rejuvenation toughens the pre-annealed MG, and its K_Q (97 MPa m^{1/2}) is even higher than that of the as-cast MG. **b-d**, SEM side-surface morphology of the as-cast, relaxed and rejuvenated MG subjected to unloading before fracture. Multiple shear bands are observed at the tip of fatigue pre-crack for the as-cast (**b**), while no shear band is observed on the relaxed MG (**c**); however, after thermal exposure at 667 K, multiple shear bands formed again for the rejuvenated MG. The inset of **b-d** shows the fracture side surface; the relaxed MG exhibits a straight crack propagation path (brittle manner), while the as-cast and rejuvenated MG shows a bifurcated crack propagation path (high toughness).

Fig. 4 | Structure evolution after rejuvenation. **a**, The position Q_1 of the first sharp diffraction peak at different rejuvenation temperatures. **b-e**, The proportion of the 1- to 4-atom connection modes decomposed from the Gaussian fitting results of the second coordination shells in pair distribution functions, $g(r)$ (see Supplementary Fig. 7). The schemes of four types of sheared atoms of two coordination polyhedrons, including 1~4 atom sheared modes, are shown in the inset of **b-e**.

Figures

Figure 1

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