

Pressure effect on superconducting transition-temperature relaxation behavior of the $Zr_{70}Cu_{30}$ amorphous alloy on annealing at elevated pressures

Shen Zhongyi, Chen Guiyu, Zhang Yun, and Yin Xiujun
Institute of Physics, Chinese Academy of Sciences, Beijing, China
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The superconducting transition-temperature (T_c) relaxation behavior of $Zr_{70}Cu_{30}$ Metglas upon annealing at pressures up to 2.5 GPa is investigated. Our results show that although compression generally retards the relaxation process, it also oppositely influences atomic activation processes in T_c relaxation at the lower and higher sides of an appropriate pressure. A homogenization in amorphous structure induced by this pressure is suggested to be responsible for the above behavior.

I. INTRODUCTION

The structural relaxation of amorphous alloys upon annealing can have a marked effect on their physical properties. During this process, both topological and compositional short-range order (TSRO and CSRO) in the amorphous structure develop due to atomic rearrangements in the alloy. Thus, alteration in such properties may in turn reflect these rearrangements and identify the content of the structural relaxation. Since annealing would relax the quenched-in voids, thereby causing their collapse accompanied by volume contraction, one may think of exerting an external pressure on the amorphous alloy to promote the ordering process and enhance its relaxation. Little work has been done on pressure effects in the thermal relaxation of amorphous alloys. Yousuf *et al.*,¹ who examined two amorphous alloys in a diamond anvil cell using resistance and x-ray diffraction methods, and Slawska-Wanieska *et al.*,² who used electron-spin resonance, both showed some vague indications of pressure-promoted structural relaxation. On the other hand, our recent work on the effect of pressure on the magnetic Curie-temperature relaxation of two amorphous alloys showed explicit retardation.³ For comparison, we examine in this work the pressure annealing effect on the relaxation behavior of the superconducting transition temperature (T_c) of amorphous $Zr_{70}Cu_{30}$ alloy, and explore a possible change in mechanisms of the thermoactivated atomic rearrangement in its density fluctuating structure during annealing under elevated pressures.

II. EXPERIMENT

Samples of $Zr_{70}Cu_{30}$ were prepared by a single-roller quenching technique in the form of ribbon with an approximate thickness of 20 μm and a width of 2 mm. X-ray diffraction results showed that all of the prepared samples were in an amorphous state. The T_c value of as-quenched samples was 2.83 K, which is little higher than that reported in the literature.^{4,5} The corresponding superconducting transition width $T_c = 20$ mK is narrow enough to confirm its homogeneity as it is generally a criterion of a single amorphous phase.⁵ Ribbons were

preserved in liquid nitrogen for prevention of oxidation and unexpected deterioration in atmosphere at room temperature.

On annealing at room pressure, samples were sealed in quartz ampoules filled with argon. Pressure annealing was performed in a piston-cylinder-type apparatus. Samples were horizontally laid in the pressure chamber to avoid a large temperature gradient. Some oxidation of the samples, which is considered to be responsible for data spread, can be effectively prevented upon long annealing only at higher pressures when Teflon is chosen as the optimum pressure medium. Details of the experimental arrangement have been described elsewhere.⁶ T_c measurements were carried out at room pressure on quenched samples by the resistance method to an accuracy of 15 mK. Some broadening of the transition width was observed in annealed samples. Neither distinctive evidence of phase separation as had been reported for Zr-Cu alloy,⁷ nor indication of crystallization were observed by x-ray diffraction on tempered samples.

III. RESULTS AND DISCUSSION

A. T_c degradation on high-pressure annealing

The obtained T_c isochronals at different pressures are shown in Fig. 1. As in other alloys, structural relaxation also causes a degradation of T_c in $Zr_{70}Cu_{30}$ glass, while pressure retards the T_c -degrading relaxation process. The higher the pressure, the less T_c reduces. The derivative of T_c to P is estimated to be 32 mK per GPa on samples annealed at 200°C for 1 h. Crystallization starts at 350°C at ambient pressure accompanied by a dramatic drop of T_c . On isothermal annealing at different pressures (Fig. 2), a general tendency is seen: T_c first drops steeply then gently tends towards saturation. The T_c 's of all samples degrade according to $\ln(t_a)$ for a length of annealing time t_a within a period of 20 h at 150°C. This means the relaxation kinetics still retains logarithmic character at higher pressures. This behavior is well known as a typical thermal relaxation process governed by a distribution in activation energy. Nevertheless, one can see that although the T_c relaxation is generally delayed by external

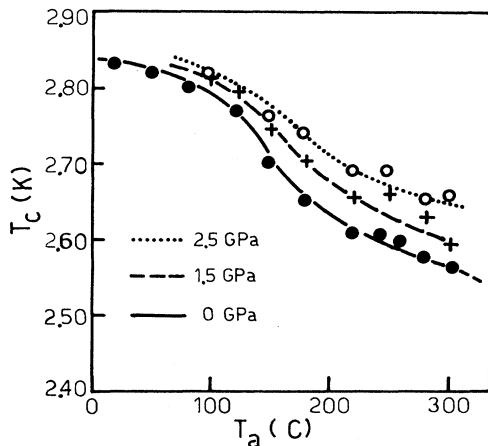


FIG. 1. Isochronals of the superconducting transition temperature T_c of amorphous $Zr_{70}Cu_{30}$ alloy on 1 h annealing at different pressures.

pressure, it shows quite dissimilar tendencies at identical stages of annealing at different pressures. We make out that T_c drops more speedily at the intermediate and late periods of annealing at 1.5 GPa in comparison with room-pressure annealing.

The correlation between the degradation of T_c and the alteration of structure during annealing in amorphous alloys has been studied by several authors on different superconducting alloys including $Zr_{70}Cu_{30}$ at room pressure. A descriptive scheme on local stress and strain fluctuation statistics and their relation to the structural defects were proposed by Egami.⁸ Suhl *et al.*⁹ suggested a close correlation between the local strain in structure and the superconducting transition temperature in alloys. They illustrated the T_c enhancing in Ir-Y eutectic alloys beyond their component metals and explained that strains induced by the lattice mismatch between the layerlike composite phases may weaken the interatomic effective elastic coefficient, soften the vibration mode of atoms in the alloy,

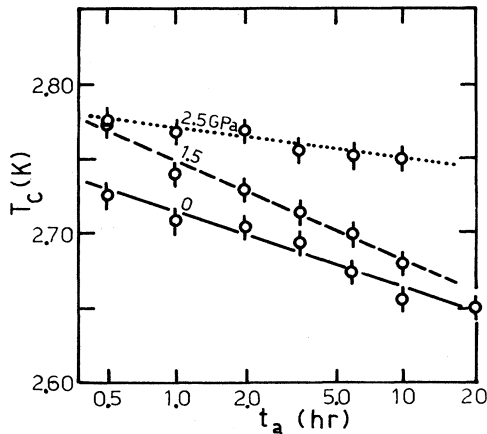


FIG. 2. Isothermal annealing of the superconducting transition temperature T_c of $Zr_{70}Cu_{30}$ amorphous alloy at 150°C at different pressures.

and lead to T_c enhancement. Poon¹⁰ spread this conclusion to amorphous alloys and pointed out that the major portion of T_c depression upon annealing can be attributed to the relaxation of quenched-in strains and the redistribution of voids in the amorphous structure. Inoue *et al.*¹¹ obtained the same conclusion on identical $Zr_{70}Cu_{30}$ alloy and reported that the degradation of T_c is irreversible. All authors inferred this change to originate from the decrease of the electron-phonon coupling constant λ due to the increase of the average ionic mass \bar{M} and the mean square of the phonon frequency $\langle \omega^2 \rangle$, and/or the decrease in the electronic dressed density of states at the Fermi level $N(E_F)$. All the above discussions, albeit qualitatively, demonstrate that the T_c degradation is closely related to annealing out of the excess volume in structure. These processes, in our opinion, can be expected to be anticipatorily affected by external pressure.

B. Possible effect of pressure on activation processes during structural relaxation

A detailed mechanism or rigorous explanation of these processes may be difficult to approach at present, since we know very little as yet even about the mechanism of atomic movement at room pressure as well as the exact correlation between T_c and the structure. The observed T_c relaxation behavior is thought to be a combined result of thermal and compressive influences to the activation process. Athermal pressing to amorphous metal, as shown in our static computer simulative estimation,¹² is hardly going to promote their ordering processes. However, when a sample is subjected to combined tempering and pressing, the pressure would have a marked influence on the thermo-activated processes. Since the diversities in local structures, which may be a decisive controlling factor to the atomic mobility in amorphous alloys, are multifarious and the correlated activation energies would be spectrally distributed over a wide range,¹³ we can also expect the pressure effect would most likely be diversified.

In Fig. 3, the activation energies (E_a) corresponding to

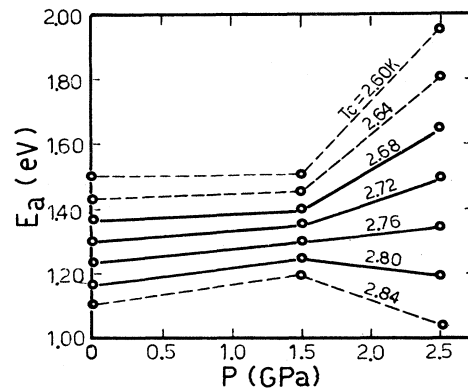


FIG. 3. Activation energy corresponding to $Zr_{70}Cu_{30}$ samples relaxed to every fixed step value of T_c in the AES model vs pressure.

samples relaxed to every step value of T_c calculated by the activation energy spectrum (AES) model¹³ are plotted against pressure. We assume that the hypotheses presumed in the AES model are good herein and that the pressure-induced frequency alteration $\Delta\nu_0$ is negligible. Some semiquantitative discussions might be done as follows.

As shown in Fig. 3, the activation spectra, which may be defined by equal changes of T_c is distributed in a more narrow energy range around 1.5 GPa in comparison with room-pressure annealing. This means the E_a spectrum is more sharply distributed and some homogenization in structure has been stimulated by definite external pressure. This result is likely consistent with our previous simulation¹⁴ on an amorphous iron model in which the first peak of the radial distribution function of the model sharpens up on raising the pressure to 1.8 GPa (and broadens on further increasing the pressure). This occurrence implies a homogenization of atomic spaces to the nearest neighbors in the model and therefore, a concentration in the activation energy spectrum. In fact, it is easy to realize that a density-fluctuated structure with random packing of soft spheres suffering from a definite uniform compression would bring about some homogenization in structure.

The anticipative broadening in distribution in activation events appears at about 2.5 GPa in Fig. 3; it mainly expands to the high-energy side. This fact seems to reflect a dehomogenization process induced by overpressing the amorphous structure. Although we cannot yet describe the exact changes in structure directly from the energy distribution of activation processes, by thinking of the intrinsic effect of pressure on the structure as volume shrinking or space compressing, it is reasonable to assume that the effect of pressure on the local loose or the quenched-in voids and the dense parts in the structure would be completely different and demonstrate opposite influences to their atomic activation processes. It implies that activation processes having lower E_a 's in the lower part of Fig. 3, which should be related to the atomic motions at voids or open structure, may be stimulated by external compression, while those processes proceeding in more dense local structures (higher E_a 's in the upper part

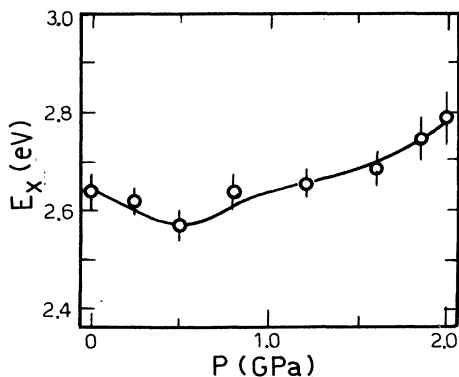


FIG. 4. The pressure dependence of the activation energy of crystallization of amorphous $Zr_{70}Cu_{30}$ alloy.

of Fig. 3) should be obstructed. If we substitute the slopes of the lines in two pressure regions (0–1.5 GPa and 1.5–2.5 GPa) in Fig. 3 for the average values of the activation volume \bar{V}_p , some distinct activation behaviors in different pressure and energy regions may be described as follows:

(a) *Pressure effects on low-energy activation processes.* In the low-pressure range (0–1.5 GPa), E_a increases slightly with pressure, $V_p < 10 \text{ \AA}^3$ (0.06 eV/GPa), while in the higher region (1.5–2.5 GPa), pressure promotes the low-energy activation processes (for processes having $E_a < 1.27$ eV at room pressure) and V_p become negative. This characteristic feature appears on the initial stage of relaxation corresponding to T_c degradation from 2.83 to 2.80 K. The above response calls to mind a collapsing process of the structural voids under the action of external pressure, which is resisted in the earlier stage of loading and progressively given way to when a pressure threshold is exceeded.

(b) *Pressure effect on higher E_a processes.* In the low-pressure range, the repression effect of external pressure on T_c degradation is much weaker and gradually reverses to a promoting action when E_a exceeds 1.5 eV. On the other hand, at higher pressures (1.5–2.5 GPa), high- E_a processes are strongly restrained by external pressing, $\bar{V}_p < 80 \text{ \AA}^3$ (0.5 eV/GPa), this behavior is expected and could be explained by the overcompaction of the structure. As high- E_a processes are generally related to the atomic motions in denser local structure, the interatomic repulsions therein would progressively increase by excessive space reduction, thus a speeding up in the increasing of E_a is displayed. If the focusing tendency on broken lines around 1.5 GPa in Fig. 3 is extrapolated to the high-energy side, approaching an activation energy of crystallization, there should be a depression on each $E_a - p$ curve. This trend is identified in our determination of the pressure dependence of the activation energy of crystallization on the same alloy (Fig. 4, accomplished on the same pressure assembly using resistance measurements and by the Kissinger method) and also had been observed in our previous work on another alloy.¹⁴

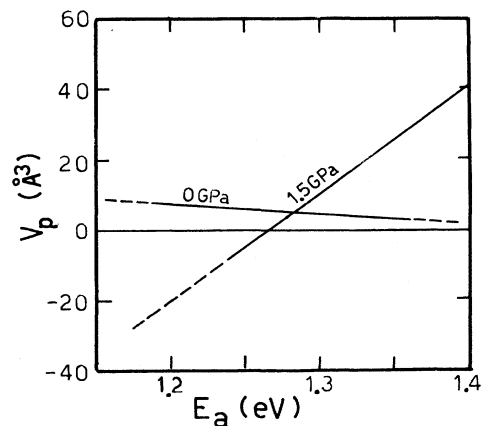


FIG. 5. The activation volume of the superconducting transition-temperature relaxation of $Zr_{70}Cu_{30}$ alloy vs the corresponding activation energy at pressures of 0 and 1.5 GPa.

(c) If we regard the slopes of both sides of each broken line in Fig. 3 as the value of \bar{V}_p at pressures of 0 and 1.5 GPa, respectively, we could draw a relation between \bar{V}_p and E_a as shown in Fig. 5. One can see that processes with $E_a < 1.27$ eV will possess negative \bar{V}_p at 1.5 GPa, displaying a pressure-induced promotive effect. Thus we can estimate a value of E_a at which the pressure stimulation would be equivalent to what the activation process itself demanded. This value is 0.62 eV, corresponding to a V_p of -204 \AA^3 . In fact, such an activation energy is a tiny value. A rough estimation could be made from the simplified relation $E_a = K_B T_a \ln(v_0 t_a)$ proposed by Gibbs

and Evetts,¹³ which says that processes with such a low E_a should be complete in 20 msec at room temperature. It seems that for this reason we were unable to observe the pressure-induced relaxation process in our experiments.

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