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# Mechanical annealing in the flow of supercooled metallic liquid

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Flow induced structural evolution in a supercooled metallic liquid Vit106a ($Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$, at. %) was investigated via uni-axial compression combined with differential scanning calorimeter (DSC). Compression tests at strain rates covering the transition from Newtonian flow to non-Newtonian flow and at the same strain rate $2 \times 10^{-1}\ s^{-1}$ to different strains were performed at the end of glass transition ($T_{g\text{-}end} = 703$ K). The relaxation enthalpies measured by DSC indicate that the samples underwent non-Newtonian flow contain more free volume than the thermally annealed sample (703 K, 4 min), while the samples underwent Newtonian flow contain less, namely, the free volume of supercooled metallic liquids increases in non-Newtonian flow, while decreases in Newtonian flow. The oscillated variation of the relaxation enthalpies of the samples deformed at the same strain rate $2 \times 10^{-1}\ s^{-1}$ to different strains confirms that the decrease of free volume was caused by flow stress, i.e., "mechanical annealing." Micro-hardness tests were also performed to show a similar structural evolution tendency. Based on the obtained results, the stress-temperature scaling in the glass transition of metallic glasses are supported experimentally, as stress plays a role similar to temperature in the creation and annihilation of free volume. In addition, a widening perspective angle on the glass transition of metallic glasses by exploring the 3-dimensional *stress-temperature-enthalpy* phase diagram is presented. The implications of the observed mechanical annealing effect on the amorphous structure and the work-hardening mechanism of metallic glasses are elucidated based on atomic level stress model. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4892457]

## I. INTRODUCTION

Glass transition has been a long-standing issue in condensed matter physics, for the drastically slowdown of atomic dynamics approaching the glass transition temperature ($T_g$) and also for the diversity of the substances that can form a glass. Among the amorphous materials, metallic glasses are considered as a good research subject of glass transition because of their relatively simple atomistic character. Due to the fundamental issues related to glass transition,[1–7] mechanical properties of metallic glasses,[8–10] especially the flow and failure mechanisms,[11–14] have drawn great interests since the invention of this new species of glassy material. Stemming from their disordered structure, the flow and fracture behaviors of metallic glasses reveal an intimate dependence on temperature and strain rate near $T_g$.[15,16] Hence, to explore the essence of glass transition and the mechanical properties of metallic glasses, a profound understanding on the flow mechanism of supercooled metallic liquids would be of extraordinary importance.

Vast works, including theoretical modeling,[17–20] physical experiments,[21–23] and computer simulations,[24,25] have been carried out to uncover the elementary deformation events of metallic glasses and the origin of shear banding,[26–28] which is the dominant plastic deformation mode of metallic glasses at temperature below $T_g$. Incorporating the picture of structural relaxation processes on the potential energy landscape,[29] it was proposed that the flow of supercooled metallic liquids could be recognized as stress-driven structural α-relaxation and the elementary deformation event could be thought of as stress-driven $\beta$ relaxation,[3] where structural α-relaxation refers to a large scale irreversible atomic rearrangement process in supercooled metallic liquids, while $\beta$ relaxation is a local reversible atomic rearrangement process. The correlation between flow and structural relaxation of supercooled metallic liquids was underpinned by their equivalent activation energy.[2,7] Recent computer simulations reported the stress-temperature scaling in the glass transition of metallic glasses on a 2-dimensional phase diagram,[4] i.e., glass transition can be induced by either stress or temperature. It is proposed that the yielding behavior in a shear band could be taken as a stress-induced glass transition process. However, the newly recognized stress-temperature scaling requires that stress should play an equivalent role to temperature in the free volume dynamics of metallic glasses. The existence of a *"mechanical annealing"* effect of stress on metallic glasses similar to the well studied thermal annealing effect[30–32] of temperature, i.e., flow stress induced free volume decrease, is yet to be experimentally confirmed to solidify the basis of the stress-temperature scaling. On the other hand, the underlying mechanical annealing process would probably be the dominant work-hardening mechanism in metallic glasses[33–35] due to the lack of intersections between crystal defects (e.g., dislocations and grain

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boundaries). Proving the existence of the mechanical annealing effect would improve the current understanding on the ductility of metallic glasses. Furthermore, atomic level stress model[24,36] was developed in metallic glasses, which predicts a mechanical annealing effect based on two types of (i.e., tensile and compressive) atomic level stress state, or described as "positive" (*p* type) free volume and "negative"(*n* type) free volume, respectively. Mechanical annealing effect was also implied in the free volume model via numerical calculation.[37] From this aspect of view, verifying the mechanical effect of stress on the free volume in metallic glasses would also shed lights on their amorphous structure. In the past, experimental investigations on this issue were frustrated by the rapid structural relaxation process in supercooled metallic liquids, which prevents capturing their *in-situ* flow state. Recently, it is reported that the relaxation time of the annihilation of free volume is much longer than the Maxwell relaxation time,[38,39] providing an accessible time window to experimentally characterize the effect of flow stress on the free volume dynamics in metallic glasses.

In the present study, structural evolution in a supercooled metallic liquid Vit106a ($Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$, at. %) during uni-axial compression was investigated. The relaxation enthalpies of the deformed samples examined by differential scanning calorimeter (DSC) indicate that the thermally annealed sample contains more relaxation enthalpy than the samples underwent Newtonian flow, namely, Newtonian flow causes the decrease of free volume. The oscillated variation of the relaxation enthalpies of samples deformed at the same strain rate $2 \times 10^{-1}$ s$^{-1}$ to different strains confirms that the decrease of free volume was caused by the flow stress, i.e., mechanical annealing. Micro-hardness tests were also performed to show a similar structural evolution tendency of the deformed samples. Based on these observations, the stress-temperature scaling in the glass transition of metallic glasses is supported experimentally. Before concluding, the implications of the observed mechanical annealing effect on the mechanical properties and the structure of metallic glasses were elucidated based on atomic level stress model.

## II. EXPERIMENTAL PROCEDURE

$Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ (at. %, Vit106a) glassy alloy was selected for compression tests due to its outstanding glass forming ability and thermal stability.[40] Rods of 3 mm in diameter were prepared by suction casting the master alloy into a water-cooled copper mold. The thermal response of the as-cast sample was analyzed by Differential Scanning Calorimetry (DSC, Perkin-Elmer 7.0) under Ar atmosphere at a heating rate of 20 K/min. The prepared alloy revealed that the temperatures at the onset of the glass transition, at the end of glass transition, and at the onset of the crystallization are 684, 703, and 764 K, respectively. Cylindrical specimens of aspect ratio 1:1 (Ref. 41) were machined carefully to ensure the parallelism between the two ends. The high temperature compression test was carried out on a Zwick/roell mechanical testing system equipped with an air furnace. The temperature was selected to be 703 K ($T_{g\text{-}end}$) to assure the supercooled liquid state of the specimens. The fluctuation of the temperature in the furnace during testing was less than $\pm 2$ K. The furnace is preheated to 703 K for half an hour before test to reach a stable state. An extra thermocouple was added to monitor the temperature variation during the test to guarantee the stable state of the furnace and to confirm that the conditions for all the compression tests are consistent. In order to shorten the time for heating the sample, the load train was preheated to the test temperature. A sample was then rapidly placed into the load train and held for 3 min at 703 K to attain thermal equilibrium. The compression tests at strain rates $2 \times 10^{-3}$ s$^{-1}$, $5 \times 10^{-3}$ s$^{-1}$, $2 \times 10^{-2}$ s$^{-1}$, and $5 \times 10^{-2}$ s$^{-1}$ with a true strain of 0.5 and at the same strain rate $2 \times 10^{-1}$s$^{-1}$ to different true strains 0.1,0.2, 0.3, 0.5, and 0.7 were conducted. After the compression test, the sample was immediately taken out of the chamber and quenched in air (take the sample out in air then swiftly put it into water) to capture the *in-situ* structure. The time required for quenching the sample ($2 \sim 3$ s) is an order of magnitude less than the time required for complete structural relaxation of the supercooled metallic liquids ($20 \sim 50$ s) (Ref. 40) at 703 K estimated based on previous work. Relaxation enthalpy of the tested sample was measured by DSC at a heating rate of 20 K/min. The samples quenched after compression test is first heated above the crystallization temperature, then cooled down to room temperature. Without taking the sample out of the crucible, a second scanning of the crystallized sample is performed as the reference. By subtracting the reference trace from the trace of the first DSC scanning, the relaxation enthalpy can be obtained from the exothermal peak before glass transition.[32,42] Micro-Hardness test was carried out on an HV-1000 Micro-hardness tester, with a load of 300 gf and a dwelling time of 15 s. The average hardness was obtained from 7 to 10 indents on each sample. The as-cast sample and the thermally annealed sample (703 K, 4 min, the time for the compression test at strain rate $2 \times 10^{-3}$ s$^{-1}$) were taken as the references.

## III. RESULTS

Figure 1(a) shows the true stress-true strain curves of $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ bulk metallic glass (BMG) at strain rates $\dot{\varepsilon} = 2 \times 10^{-3}$ s$^{-1}$, $5 \times 10^{-3}$ s$^{-1}$, $2 \times 10^{-2}$ s$^{-1}$, and $5 \times 10^{-2}$ s$^{-1}$, respectively, with a final strain around 0.5 at 703 K. At strain rate $\dot{\varepsilon} = 2 \times 10^{-3}$ s$^{-1}$, the stress-strain curve shows monotonous increase in the flow stress $\sigma$ in the initial stage of deformation followed by a stress plateau indicating steady flow state. The final true strain of 0.5 was selected to guarantee the steady flow state of the sample in each test, i.e., reaching a flow stress plateau when the test was stopped. At strain rates above $5 \times 10^{-3}$ s$^{-1}$, a stress overshoot occurs before the flow stress reaches a stress plateau. The presence of stress overshoot indicates the transition of the flow behavior from Newtonian flow to non-Newtonian flow,[15,43] where the strain rate sensitivity value $m = \partial \lg \sigma / \partial \lg \dot{\varepsilon}$ decreases from near 1 to a smaller value of 0.4 as indicated in the inset of Fig. 1(a). The flow stress in the inset is determined from

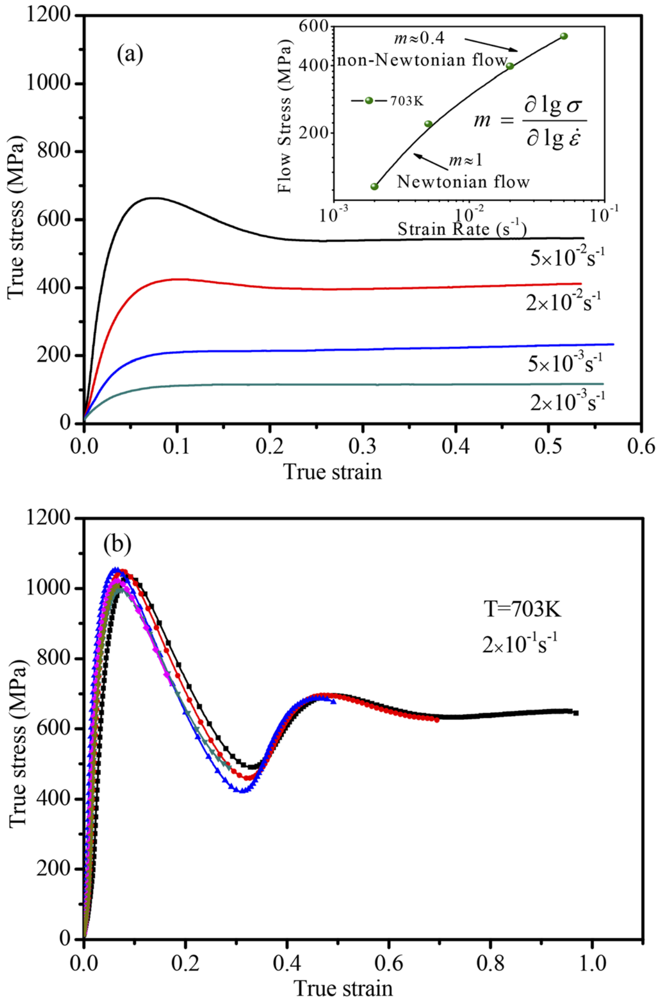


FIG. 1. Stress-strain curves of Vit106a alloy for compression tests at 703 K. (a) At different strain rates: $2\times10^{-3}$ $s^{-1}$, $5\times10^{-3}$ $s^{-1}$, $2\times10^{-2}$ $s^{-1}$, and $5\times10^{-2}$ $s^{-1}$. Inset: the steady state flow stress-strain rate relationship. (b) To different strains: 0.1, 0.2, 0.3, 0.5, and 0.7, at $2\times10^{-1}$ $s^{-1}$. The stress-strain curve with a final strain 1.0 was also presented for comparison.

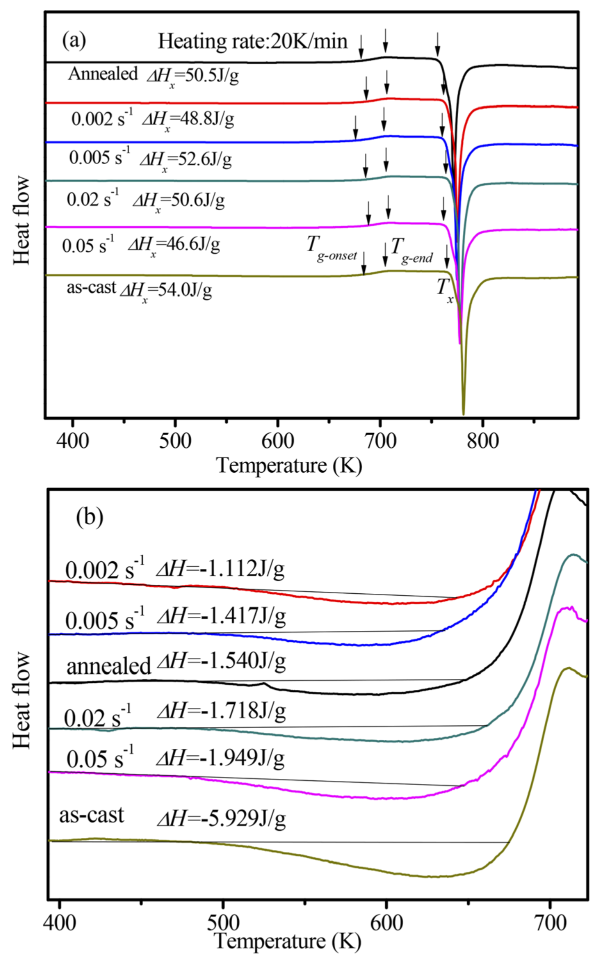


FIG. 2. DSC curves of Vit106a alloys deformed at 703 K. (a) At different strain rates: $2\times10^{-3}$ $s^{-1}$, $5\times10^{-3}$ $s^{-1}$, $2\times10^{-2}$ $s^{-1}$, and $5\times10^{-2}$ $s^{-1}$. (b) The calculated relaxation enthalpy. The results for the as-cast sample and the thermally annealed sample are also shown.

the plateau part of the true stress-true strain curve. Fig. 1(b) shows the true stress-true strain curves of $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ BMG at a strain rate $\dot{\varepsilon}=2\times10^{-1}$ with different true strains: 0.1, 0.2, 0.3, 0.5, and 0.7, at 703 K. The stress-strain curve with a final strain of 1.0 is also given for comparison. It can be seen that the stress-strain curves of different tests are almost overlapped, indicating the good repetition of the tests.

Fig. 2(a) shows the DSC traces of the samples in Fig. 1(a), the as-cast sample and the thermally annealed sample (703 K, 4 min). The crystallization enthalpies for all the tested samples are also shown, where hardly any appreciable changes compared to the reference samples can be detected, suggesting the maintenance of the amorphous state after compression. Fig. 2(b) shows the enlargement of the enthalpy relaxation part in the DSC traces, indicating the change in the relaxation enthalpy of the samples deformed at different strain rates.[44,45] The relaxation enthalpy values calculated from the heat release before glass transition on the DSC traces are shown in Table I. It can be seen that in contrast to the as-cast sample, all the deformed samples and the thermally annealed sample show smaller relaxation enthalpy values. This result is reasonable, because that the amorphous structure in the as-cast sample corresponds to a much higher fictive temperature due to the rapid cooling process during the suction cast. As reported previously,[42,46,47] the relaxation enthalpy of the deformed sample increases with increasing strain rate. However, compared to the thermally annealed sample, the samples underwent non-Newtonian flow contain more relaxation enthalpy but the samples underwent Newtonian flow contain less relaxation enthalpy. It is noted that less relaxation enthalpy in the samples underwent Newtonian flow was not caused by thermal annealing, as the thermally annealed sample was subjected to exactly the same thermal treatment, i.e., 703 K, 4 min. Based on the relationship between relaxation enthalpy and free volume concentration,[32,42] the results in Fig. 2 indicate that the free volume of supercooled metallic liquids increases in non-Newtonian flow, while decreases in Newtonian flow.

The DSC traces of the samples in Fig. 1(b) and the reference samples are shown in Fig. 3(a) and the corresponding enthalpy relaxation part is shown in Fig. 3(b), respectively. The relaxation enthalpy values in Fig. 3(b) are summarized in Table II. It can be seen that, in good accordance with the true stress-true strain curves, the relaxation enthalpy shows a similar oscillated variation trend. With increasing strain,

TABLE I. Relaxation enthalpy of Vit106a alloys (from Fig. 2(b)) deformed at different strain rates: $2 \times 10^{-3}$ $s^{-1}$, $5 \times 10^{-3}$ $s^{-1}$, $2 \times 10^{-2}$ $s^{-1}$, and $5 \times 10^{-2}$ $s^{-1}$, at 703 K.

| Strain rate ($s^{-1}$) | $2 \times 10^{-3}$ | $5 \times 10^{-3}$ | $2 \times 10^{-2}$ | $5 \times 10^{-2}$ | Thermally annealed | As-cast |
|---|---|---|---|---|---|---|
| $\Delta H(J/g)$ | −1.112 | −1.417 | −1.718 | −1.949 | −1.540 | −5.929 |

TABLE II. Relaxation enthalpy of Vit106a alloys (from Fig. 3(b)) deformed at strain rate $2 \times 10^{-1}$ $s^{-1}$ to different strains: 0.1, 0.2, 0.3, 0.5, and 0.7, at 703 K.

| Strain | 0.1 | 0.2 | 0.3 | 0.5 | 0.7 | Thermally annealed | As-cast |
|---|---|---|---|---|---|---|---|
| $\Delta H(J/g)$ | −2.199 | −1.754 | −0.976 | −1.732 | −1.530 | −1.540 | −5.929 |

increasing and decreasing of the relaxation enthalpy occurs alternatively indicating the oscillated variation of free volume during flow. For instance, as the strain increases from 0 to 0.1, the relaxation enthalpy increases from 1.540 J/g to 2.199 J/g. It is noted that the thermally annealed sample is assumed to be at a meta-stable equilibrium state and can be chosen as a "zero" strain state. When the strain increases from 0.1 to 0.3, the relaxation enthalpy decreases from 2.199 J/g to 0.976 J/g showing a flow induced free volume decrease. However, as the strain further increases to 0.5, the relaxation enthalpy increases again, and nearly reaches a plateau value from a strain of 0.5 to a strain of 0.7, corresponding to the steady flow state in the true stress-true strain curve in Fig. 1(b). Hence, although the relaxation enthalpy is increased at the final steady flow state (from a strain of 0.5 to a strain of 0.7) at $\dot{\varepsilon} = 2 \times 10^{-1}$ $s^{-1}$ in the non-Newtonian regime, during the transient process of the flow, i.e., from a stain of 0.1 to a strain of 0.5, the relaxation enthalpy exhibits an oscillated variation mode similar to that of the flow stress on the true stress-true strain curve.

Figs. 4(a) and 4(b) show the micro-hardness values of the deformed samples, the as-cast sample, and the thermally annealed sample. It has been shown that hardness can be also taken as a measure of the free volume concentration in metallic glasses.[45] Higher hardness value implies lower free volume concentration, and *vice versa*. In Fig. 4(a), the hardness value of the as-cast sample is smaller than that of the deformed samples and the thermally annealed sample, indicating more free volume in the as-cast sample. The hardness value of the deformed sample decreases with increasing strain rate. Compared to the thermally annealed sample, the samples underwent Newtonian flow (at strain rate $5 \times 10^{-3}$ $s^{-1}$ and below) exhibit higher hardness values, while the samples

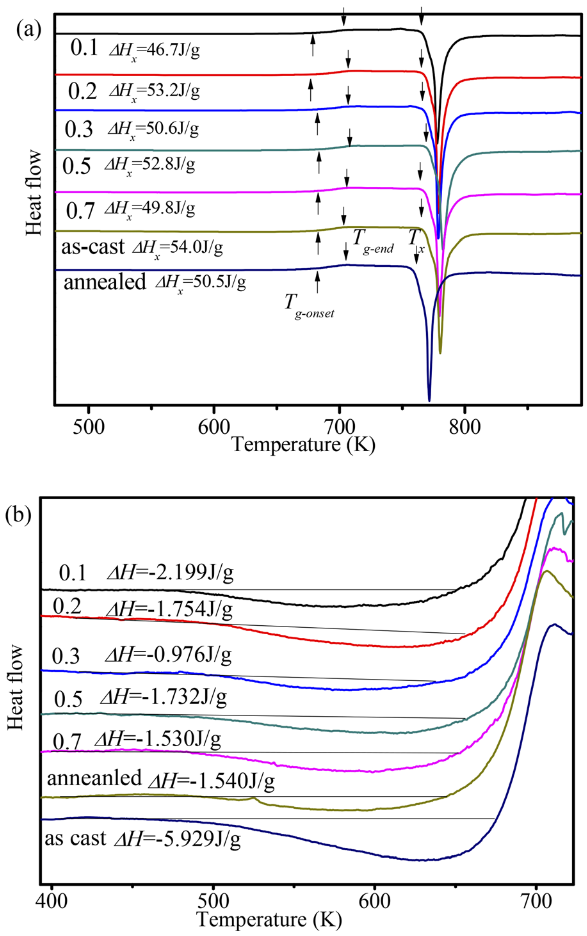


FIG. 3. DSC curves of Vit106a alloys deformed at 703 K. (a) To different strains: 0.1, 0.2, 0.3, 0.5, and 0.7, at $2 \times 10^{-1}$ $s^{-1}$. (b) The calculated relaxation enthalpy. The results for the as-cast sample and the thermally annealed sample are also shown.

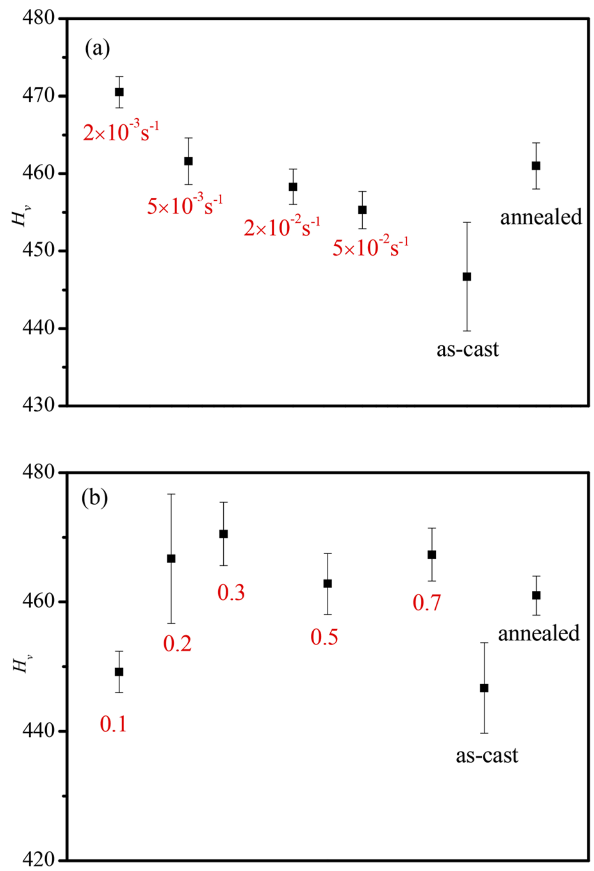


FIG. 4. Micro-hardness values of Vit106a alloys after compression test at 703 K. (a) At different strain rates: $2 \times 10^{-3}$ $s^{-1}$, $5 \times 10^{-3}$ $s^{-1}$, $2 \times 10^{-2}$ $s^{-1}$, and $5 \times 10^{-2}$ $s^{-1}$. (b) To different strains: 0.1, 0.2, 0.3, 0.5, and 0.7. The results for the as-cast sample and the thermally annealed sample are also shown.

underwent non-Newtonian flow (at strain rate $2 \times 10^{-2}$ s$^{-1}$ and above) exhibit lower hardness values. In Fig. 4(b), in consistent with the DSC results, the hardness values also show a similar oscillated variation trend. With increasing strain, decreasing and increasing of the hardness value occurs alternatively before the sample reaching steady flow state. Based on the above results, the variation of the micro-hardness and the relaxation enthalpy demonstrates the same structural evolution tendency of supercooled metallic liquids in flow.

## IV. DISCUSSION

### A. Mechanical annealing

The flow mechanism of supercooled metallic liquids is assumed to be the free volume facilitated local shear transformations,[18] which is a local cooperative atomic rearrangement process consisting of several tens or hundreds of atoms. The macroscopic flow of supercooled metallic liquids is recognized as the percolation of these local shear transformations.[3] A key feature of the shear transformation event is that excess free volume will be created locally after its operation,[17,18] i.e., shear dilation. On the other hand, the supercooled metallic liquids will try to recover its meta-equilibrium state and reduce the newly created free volume. Considering the competition between the annihilation and the creation of free volume, the condition for the steady state flow is the dynamic balance between the two competing processes. The time dependent free volume content $c_f$ (the concentration of free volume sites or flow defects) at a strain rate $\dot{\varepsilon}$ can be formulated as[42]

$$dc_f/dt = \alpha_x \dot{\varepsilon} c_f \ln^2 c_f - k_r c_f (c_f - c_{f,eq}), \tag{1}$$

where $c_f^+ = \alpha_x \dot{\varepsilon} c_f \ln^2 c_f$ is the creation rate of flow defects created by shear dilatation, while $c_f^- = k_r c_f (c_f - c_{f,eq})$ is the annihilation rate of the flow defects. Here, $t$ is time; $\alpha_x$ is a proportionality factor in association with temperature; $k_r = \upsilon_r \exp(-Q_r/kT)$ is a rate constant; $v_r$ is a prefactor; $Q_r$ is the activation energy for the annihilation of a flow defects; $k$ is Boltzmann constant; $c_{f,eq}$ is the equilibrium concentration of flow defects at a given temperature $T$.

Applying the above flow mechanism, which is based on the competition between the annihilation and the creation of free volume to the present study, contradiction arises in the experimentally observed free volume decrease in Newtonian flow in Fig. 2. Based on Eq. (1), the free volume concentration $c_f$ cannot decrease, when the supercooled metallic liquid at meta-equilibrium (i.e., the initial value of $c_f$ is $c_{f,eq}$) is deformed at any none zero strain rates. At most, it remains unchanged, namely, the annihilation of free volume is rapid enough to cancel the effect of shear dilation. This is in conflict with our results in Figs. 2(b) and 4(a), where the free volume decreases in Newtonian flow. Note that the annihilation of free volume in the isothermal crystallization process during the compression of supercooled metallic liquids is not considered here, because of its far longer time scales ($30 \sim 40$ min) at 703 K (Ref. 40) than the enduring time of the compression test ($1 \sim 4$ min) for the outstanding thermal stability of the selected glassy system. As indicated in Fig. 2(b), compared to the thermally annealed sample, less relaxation enthalpy in the sample deformed at a strain rate of $5 \times 10^{-3}$ s$^{-1}$ of which the enduring time of the compression (2 min) is shorter than the annealing time (4 min) of the thermally annealed sample supports the assumption made above. Besides, with respect to the structural evolution at different deformation stages, as shown in Figs. 3(b) and 4(b), the oscillated variation behaviors of the relaxation enthalpy or micro-hardness and the underlying free volume concentration $c_f$ cannot be explained merely based on Eq. (1) either. Because that since the competition between the creation and the annihilation of free volume implies a 1-dimensional nonlinear dynamic system,[48] i.e., only 1 time-dependent parameter (the free volume concentration $c_f$) in the system, this dynamic system will assume its steady state monotonously with $c_f$ reaching a constant value. This can be understood in the following non-stringent but comprehensive way:[48] if the creation rate $c_f^+$ at certain strain rate is larger than the annihilation rate $c_f^-$, the free volume will increase; the increased free volume will promote the annihilation process and reduce the gap between the creation rate and the annihilation rate continuously and monotonously; once the gap between the creation rate and the annihilation rate vanishes, steady state is reached; and *vice versa*. Hence, the oscillated variation behavior of the free volume concentration $c_f$ cannot take place. Based on the above illustration, the current understanding on the free volume dynamics might not be enough to address all the flow properties of supercooled metallic liquids.

To interpret the observed experimental results, the questions confronted are as follows. (i) How did the free volume decrease in Newtonian flow? (ii) How did the oscillation behavior come into being? The first question seems to be subtle and will be discussed later, but the second one is rather clear. As stated above, in nonlinear dynamics, oscillation does not exist in 1-dimensional systems,[48] while does exist in 2 or higher dimensional systems. Therefore, it is concluded that there should be another parameter involved in the free volume dynamics during flow, besides the free volume concentration $c_f$. Since the test strategy is strain rate control, i.e., the strain rate is taken as a constant in $c_f^+$, the effect of flow stress on the free volume dynamics has to be taken into consideration. This can be realized by considering the transient process before the flow reaches steady state. Examples of numerical calculations on the mechanical effect of flow stress on the free volume dynamics can be found in many works.[37,49–51] Both the stress-induced free volume decrease and the oscillated variation of $c_f$ during flow are shown.[49] The detailed numerical calculation process is trivial and not our main concern here. The following content will concentrate on the mechanical effect of the steady state flow stress on the supercooled metallic liquids, which can be summarized as: in Newtonian flow, flow stress will cause the decrease of free volume; in non-Newtonian flow, flow stress will cause the increase of free volume, as shown in Figs. 2(b) and 4(a). Accordingly, the present study provides experimental evidences for the flow stress induced free volume decrease, i.e., "*mechanical annealing*." Pressure induced similar annealing effect[52] was also reported to support the mechanical effect of stress on metallic glasses. These results would provide important information on the stress-temperature scaling in the free volume dynamics and also the glass transition of metallic glasses.

### B. Stress-temperature scaling in glass transition

Based on scaling analysis,[4] it is reported that the yielding behavior of metallic glasses in shear bands could be a stress-induced glass transition process and that the effects of temperature and stress on glass transition could be scaled onto a 2-dimensional elliptical phase diagram. This conclusion is directly supported by the experimental results in Sec. III. As observed in the present study, the mechanical effect of steady state flow stress (The flow stress in the inset of Fig. 1(a)) on supercooled metallic liquids can be described similarly to the thermal effect of temperature as shown in Figs. 2(b) and 4(a). The flow of supercooled metallic liquid at lower flow stress level (i.e., in Newtonian flow regime in the inset of Fig. 1(a)) will induce an annealing effect similar to that of thermal annealing at temperature below $T_g$, where the free volume decreases compared to the initial state. While, the flow of supercooled metallic liquids at higher flow stress level (i.e., in non-Newtonian flow regime, in the inset of Fig. 1(a)) will induce an effect similar to that of heating the supercooled liquid to a higher temperature (more free volume will be introduced into the supercooled liquid), where the free volume increases compared to the initial state.

For a clear view of the above discussion, Figs. 5(a) and 5(b) show the 2-dimensional *stress-temperature* phase diagram and 3-dimensional *stress-temperature-enthalpy* phase diagram of the scaling of temperature and stress, respectively. In Fig. 5(a), the glass transition is represented by a dotted line for its ambiguous transition nature. In our compression tests, the phase point ($T_f$, 0) of the supercooled metallic liquid is dragged to ($T_f$, $\sigma_0$) by flow stress. The relaxation enthalpy variation caused by flow is depicted in Fig. 5(b). The thin green arrow line indicates the compression test on the 3-dimensional phase diagram. The solid blue line shows the experimentally observed enthalpy variation at different flow stress levels. It can be seen that at lower stress levels the enthalpy decreases, while increases at higher stress levels. Similar relaxation enthalpy increase at room temperature caused by high stress near yielding in metallic glasses was also reported.[53,54] It is important to note that the low flow stress limit approaching point ($T_f$, 0, 0) indicated by a dashed circle, where the *enthalpy-stress* relation shows distinct singularity reflects the peculiar property of glass transition from a different angle. By extrapolating the solid blue line towards the *stress-enthalpy* plane at $T = 0\,$K, the mechanical annealing process (dotted blue line: L1 and L2) can be observed as a resemblance to the thermal annealing process (dotted black line: L3 and L4). Approaching the glass transition, the glassy state of supercooled metallic liquids is captured by the "frozen" of structural α-relaxation. At stress or temperature inside the dotted line of glass transition (L5), the annealing effect of stress or temperature will eliminate the free volume concentration of the "frozen" glass, while at

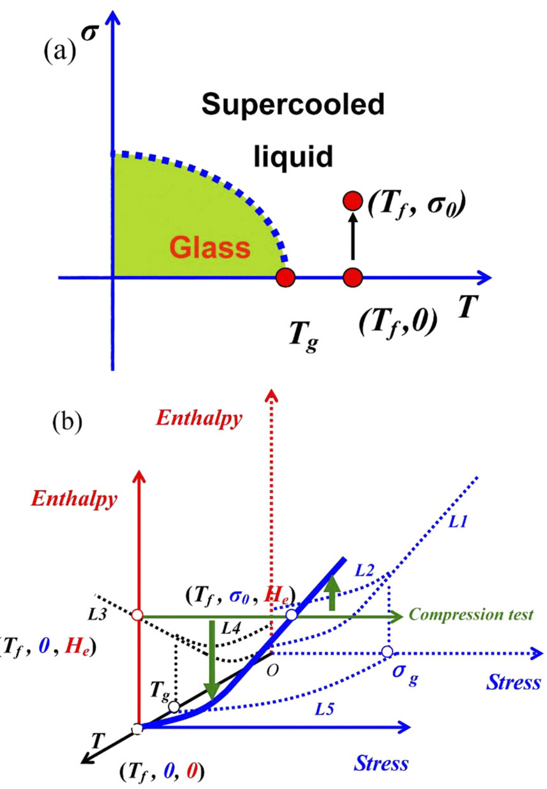


FIG. 5. (a) Scaling of temperature and stress in glass transition on a schematic 2-dimensional diagram. The compression test is indicated by the black arrow. (b) Schematic illustration of *stress-temperature-enthalpy* 3-dimensional phase diagram. The thin green arrow indicates the compression test. The solid blue line shows the experimentally observed relaxation enthalpy variation at different flow stress levels. It can be seen that at lower stress, the free volume decreases, while increases at higher stress level. By extrapolating the solid blue line towards the *stress-enthalpy* plane, the mechanical annealing process (dotted blue line: L1 and L2) can be predicted as a resemblance to the thermal annealing process (dotted black line: L3 and L4). L5 corresponding to the dotted line in (a).

temperature or stress outside the dotted line, the "frozen" glass will evolve into the supercooled liquid state, i.e., glass transition. Thereafter, the present study experimentally supports the stress-temperature scaling in the glass transition of metallic glasses.

In experimental investigations, the activation of structural α-relaxation process is usually considered as the beginning of glass transition.[40,55] Based on the stress-temperature scaling in the glass transition, it is inferred that the flow of supercooled metallic liquids indicated by the arrow lines in Figs. 5(a) (thin black) and 5(b) (thin green) could probably be considered as a stress-driven generalized "glass transition," since the increasing flow stress will enhance the movements of the atoms and shorten the nominal structural α-relaxation time as atomistic simulations predicted.[56] Via exploring the 3-dimensional *stress-temperature-enthalpy* phase diagram, the present study might provide a widening perspective angle on the glass transition of metallic glasses.

### C. Negative and positive free volume

Although the flow behaviors of supercooled metallic liquids can be well interpreted based on the free volume facilitated shear transformations, many essential details, for instance, the specific structural features of a potential shear transformation region and the annihilation or creation of free volume, are left open due to the barren understanding on the amorphous structure. Consensus has been achieved that the local shear transformation is "event oriented."[57] That is to say, the shear transformation zone is not a structural motif of metallic glasses, but a local region where the atomic configuration rearranged under the effect of stress to afford plastic deformation. In spite of the "event" nature of local shear transformation, the observed mechanical annealing effect may serve as an important clue to track some detectable characteristics of the amorphous structure.

The picture of the atomic structure of metallic glasses is envisioned as the coexistence of liquid-like regions and solid-like regions. The liquid-like regions are recognized as loosely packed regions and act as shear transformation regions. The solid-like regions are assumed to be densely packed regions and act as the elastic matrix.[3] However, based on this picture of metallic glasses, the annihilation of the free volume may not be reasonable. As the free volume disappears locally, it will move to surrounding areas and not annihilate. This dilemma is exactly the question (i) put forward in Sec. IV A. Now, an attempt to give an answer for this question based on the mechanical annealing effect is made as follows. Among the structure models of metallic glasses, the atomic level stress model[24] predicts the observed mechanical annealing effect and matches our results well. More interestingly, based on the *p* (*positive*) type and *n* (*negative*) type free volume proposed in the atomic level stress model, the annihilation of free volume in Newtonian flow and in the transient process of non-Newtonian flow (before the steady flow state is reached) can be interpreted as the coalescence of the *p* type and the *n* type of free volume under the mechanical effect of flow stress. As shown in Fig. 6, the yellow circles represent the elastic matrix. Free volume moving to regions of purple circles (loosely packed, i.e., positive free volume region) corresponds to diffusion (i.e., percolation of the local shear transformations); free volume moving to regions of green circles (densely packed, i.e., negative free volume region) corresponds to annihilation. Hence, by incorporating the concept of negative and positive free volumes, the difficulty in the annihilation mechanism of free volume in flow can be resolved. Here, it is noted that the positive free volume regions and negative free volume regions are not static but exhibit temporal and spatial fluctuations. On the other hand, it is reasonable to assume that shear dilatation will always induce the positive free volume, as shear induces volume expanding. With increasing strain rate, the effect of shear dilatation will exceed the annealing effect caused by flow stress and temperature, so that the free volume in the supercooled metallic liquid will increase. The flow behavior of supercooled metallic liquids will change from Newtonian flow to non-Newtonian flow as observed in Fig. 1(a). The mechanism of free volume creation remains a subject for future study. It is also noted that the densely packed regions are closely surrounded by the elastic matrix, namely, the negative free volume region remains acting as the elastic matrix during flow. Consequently, the physical picture of flow provided by free volume model keeps intact and so do the constitutive equations to give a pretty good description on the flow behavior of supercooled metallic liquids due to their phenomenological nature, even if the detailed annihilation mechanism of free volume discussed above is considered.

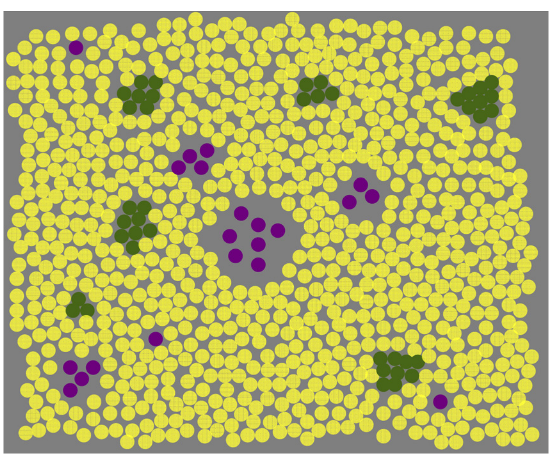

FIG. 6. Schematic illustration for the diffusion process and the annihilation process of free volume. The yellow circles represent the elastic matrix. Free volume moving to regions of purple circles (loosely packed, i.e., positive free volume region) corresponds to diffusion; free volume moving to regions of green circles (densely packed, i.e., negative free volume region) corresponds to annihilation.

Based on the idea of negative and positive free volumes, the structure of metallic glasses may consist of correlated fluctuations[58,59] rather than random heterogeneity. This can be reflected by the self assembled corrugations, dimples or even vein patterns on the fracture surface of metallic glasses.[60,61] On the other hand, the lack of work-hardening mechanism in the plastic deformation of metallic glasses has been deemed as the central issue in the limited ductility of metallic glasses. However, it is reported that the densification of metallic glasses under the effect of applied stress, which is exactly the very mechanical annealing effect discussed in our work could probably be the dominant work-hardening mechanism for metallic glasses and plays a key role in the ductility of metallic glasses.[33,62] Consequently, our work might provide important clues for uncovering the underlying work-hardening mechanism stemming from the coalescence of the negative type and the positive type of free volume in metallic glasses and will enhance the current understanding on the ductility of metallic glasses. More works on these issues will impart us more thorough understanding on both the structure and the properties of metallic glasses.

## V. CONCLUSION

Structural evolution of $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ supercooled metallic liquid during flow was examined via compression tests, micro-hardness tests, and thermal analysis. It was found that in non-Newtonian mode flow, the concentration of free volume increased due to shear dilatation as usually observed, while in Newtonian mode flow, the concentration of free volume decreased. The decrease of free volume was proved to be caused by the flow stress, i.e., mechanical annealing, by the oscillated variation of the relaxation enthalpies of the samples deformed to different strains at the same strain rate $2 \times 10^{-1}\ s^{-1}$. Similar results on the structural evolution of supercooled metallic liquids in flow were also detected in micro-hardness tests. Our observations support the stress-temperature scaling in the glass transition of metallic glasses, because that stress works in the same way to temperature on free volume, as lower stress causes the annihilation of free volume, while higher stress induces the creation of free volume. Via exploring the 3-dimensional *stress-temperature-enthalpy* phase diagram, a widening perspective angle on the glass transition of metallic glasses is presented. Previous works and the present study probably imply a stress-induced generalized glass transition process and provide useful information on the nature of supercooled liquid state. Finally, our results also support the atomic level stress model of metallic glasses, which predicts the mechanical annealing effect, and provide a probable work-hardening mechanism in metallic glasses.

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