TOPICAL REVIEW — Amorphous physics and materials

Secondary relaxation and dynamic heterogeneity in metallic glasses: A brief review*

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Understanding mechanical relaxation, such as primary (α) and secondary (β) relaxation, is key to unravel the intertwined relation between the atomic dynamics and non-equilibrium thermodynamics in metallic glasses. At a fundamental level, relaxation, plastic deformation, glass transition, and crystallization of metallic glasses are intimately linked to each other, which can be related to atomic packing, inter-atomic diffusion, and cooperative atom movement. Conceptually, β relaxation is usually associated with structural heterogeneities intrinsic to metallic glasses. However, the details of such structural heterogeneities, being masked by the meta-stable disordered long-range structure, are yet to be understood. In this paper, we briefly review the recent experimental and simulation results that were attempted to elucidate structural heterogeneities in metallic glasses within the framework of β relaxation. In particular, we will discuss the correlation among β relaxation, structural heterogeneity, and mechanical properties of metallic glasses.

Keywords: metallic glass, structural heterogeneity, mechanical property, secondary relaxation

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1. Introduction

A glassy material is a matter with a disordered structure possessing no long-range translational periodicity. Metallic glasses, also known as amorphous alloys, are relatively newcomers to the family of glassy materials. Metallic glasses are usually obtained by quenching from the melts, which exhibit a unique combination of physical, chemical, and mechanical properties due to their intrinsic disordered atomic structure and (or) production route.[1–5] As prepared by rapid solidification, metallic glasses are in a non-equilibrium state below the glass transition temperature (T_g), which differs from that of their crystalline counterparts.

It is well documented that plastic deformation of conventional crystalline solids is closely connected to intrinsic structural defects (i.e., dislocations and grain boundaries), on the basis of which a theoretical framework of structure–property relations has been well constructed. In contrast to crystalline solids, it is quite difficult to characterize "defects", if any, in a glassy material, such as polymer glass, oxide glass, granular and chalcogenide glass, soft colloidal glass or metallic glass. Conceptually, this is partly because it is much easier to describe order than disorder. By definition, each construct of a disordered structure is different and the notion of a glass structure is simply an ensemble of many such different disordered structure constructs with equivalent macroscopic properties. In the metallic glass literature, one of the longstanding and central research topics is to establish the structure–property correlation. The relaxation modes in metallic glasses provide an important key to probe "defects" in their amorphous structure and to understand the corresponding structure–property correlation.[6–10]

However, the glass transition is consequence of a relaxation process, designated as primary or α. The primary relaxation process is a global, structural atomic reordering process, which eventually ends in the glass transition if temperature is increased. However, the intensity of α relaxation decreases as the glass is undercooled. Well below T_g, the most important relaxation mode for glassy materials is β relaxation, which is closely connected to localized motions of atoms or

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molecules. Contrary to other glasses, such as molecular glass, metallic glasses are an "atomic glass" simply made up of individual atoms via isotropic metallic bonding, which constitute a conceptually simpler glass structure. The lack of an intrinsic microstructure in metallic glasses implies that their properties mainly stem from structural disorder. As a consequence, metallic glasses provide a model system to study various intriguing phenomena in glass science, such as glass dynamics, structural relaxation, crystallization, and glass transition. Through the study of metallic glasses, one may not only gain insights into the phenomena of fundamental importance, such as glass transition, but also understand the physical origin of the unique mechanical properties that may drive future engineering applications, such as yield strength, fracture toughness, ductile-to-brittle transition temperature, and damping. Nevertheless, it is still challenging as of today to develop a structure–property correlation for metallic glasses.[6,10]

The thermal events of glassy materials always go hand-in-hand with their dynamic features. The typical dynamical features of glassy materials may be summarized as follows:

(i) **Non-Arrhenius temperature dependence of viscosity**[11] Since the steepness of α relaxation can be characterized by the fragility parameter m, which measures the deviation of a liquid viscosity from an Arrhenius relation,[12] fragile liquids (with large m values) usually exhibit pronounced β relaxations in the form of distinct peaks or broad humps, while strong liquids (with small m values) display β relaxations as "excess wings". Meanwhile, strong liquids often show an Arrhenius-like behavior whereas fragile ones do not, as shown in Fig. 1(a).

(ii) **The split of α and β relaxation** Although there is one relaxation behavior at a high temperature, α relaxation becomes "frozen" when the temperature is near T_g; however, β relaxation persists below T_g and is decoupled from α relaxation. It is important to note that α relaxation could be described by the Vogel–Fulcher–Tammann (VFT) equation while β relaxation obeys an Arrhenius law (see Fig. 1(b)).

(iii) **Complex relaxation processes** In general, there are two kinds of atomic cooperative rearrangements which correspond to two types of relaxation processes, i.e., the primary relaxation (α relaxation) and the secondary relaxation (β relaxation).[13–15] As illustrated in Fig. 1(c), α relaxation prevails within a lower frequency domain ($\sim 10^{-2}$ Hz), while slow β relaxation, as a fast process, prevails within the range from 10^2 to 10^9 Hz. A boson peak can be detected when the frequency further increases to around 10^{12} Hz. Physically, α relaxation stems from large scale rearrangements of atoms or molecules, being closely related to dynamic glass transition; while β relaxation constitutes the principal source of glass dynamics as α relaxation disappears below the glass transition temperature T_g.

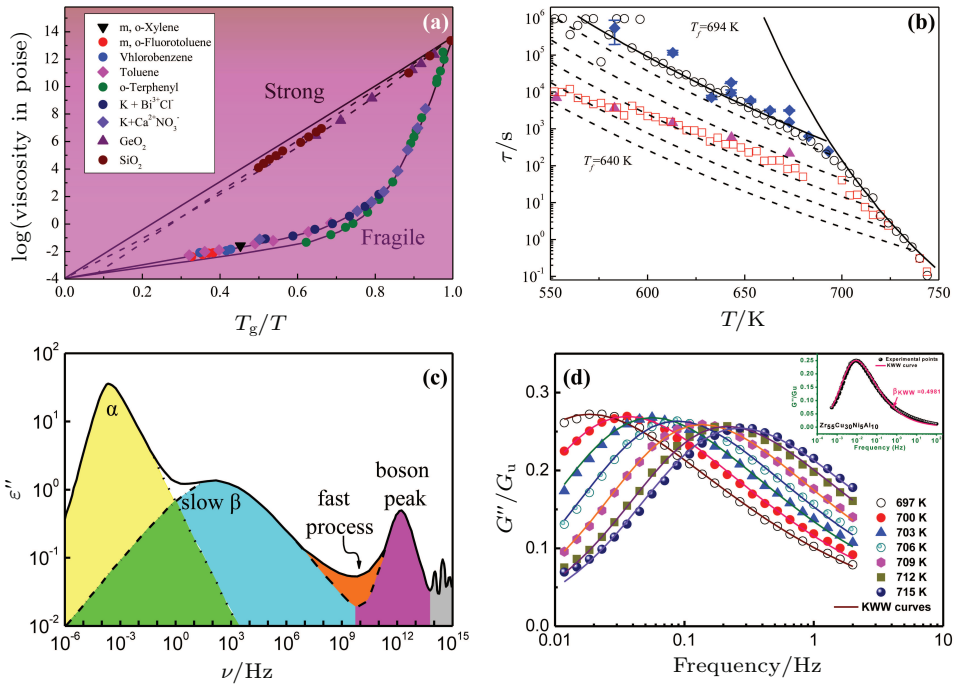


Fig. 1. (color online) Typical dynamical characters in glassy materials. (a) Non-Arrhenius temperature dependence of viscosity in various glassy materials.[1] Reprinted by permission from Macmillan Publishers Ltd: Nature. Copyright (2001). (b) The split of α and β relaxation in Zr-based metallic glass.[16] Reprinted from Ref. [16]. Copyright (2015), with permission from Elsevier. (c) Schematic illustration of dielectric loss as a function of the frequency in glassy materials. There are distinct dynamic relaxation modes from the left to the right (from low frequency domain to high frequency domain): primary (α) relaxation, slow β relaxation, fast process and boson peak;[13] (Courtesy of P. Lunkenheimer, University of Augsburg, Germany). (d) Non-exponential relaxation dynamics of Zr-based metallic glass.[17] Reprinted from Ref. [17], with the permission of AIP publishing.

(iv) **Non-exponential relaxation dynamics** It is widely accepted that the relaxation dynamics in amorphous materials displays a typical non-exponential behavior, which could be described by Kohlrausch–Williams–Watts (KWW) equation (as shown in Fig. 1(d)).

Many recent investigations have revealed that structural or dynamical heterogeneities are intrinsic to metallic glasses.[4] The correlation between the β relaxation and structural heterogeneities is one of the challenging issues in glassy physics. In this paper, we briefly review the recent advances in the research on secondary relaxation in metallic glasses. In Sections 2 and 3, we discuss the state-of-art research on the relaxation behaviors (i.e., the slow and fast β relaxations) of metallic glasses. In Section 4, we review the various connections among mechanical properties, physical properties and relaxations in metallic glasses. Finally, we give general conclusions and an outlook for the research of mechanical relaxations in metallic glasses.

2. Slow β relaxation of metallic glasses

When a glass forming liquid is cooled fast enough below its melting point, crystallization is inhibited and the liquid undergoes supercooling. The relaxation time of the supercooled liquid increases dramatically in the supercooled temperature region until it becomes so large that the liquid fails to flow on an experimental timescale, thereby leading to glass transition. From a kinetic viewpoint, one may argue that glass transition is purely of a kinetic origin, involving no actual phase transition. Therefore, the atomic structure remains unaltered with only the timescale for atomic movements increasing with supercooling. In such a case, relaxation phenomena can be regarded as a manifestation of the kinetic behavior in a frozen liquid. The atomic movement is global in the liquid state while constrained or local in the glass state.

Dynamical mechanical analysis, also called mechanical spectroscopy, is a powerful tool to investigate the mechanical relaxation behavior of metallic glasses. The complex shear modulus ($G = G' + \mathrm{i}G''$) is usually obtained with the storage (G') and loss (G'') shear modulus. The loss factor (also named as internal friction) $\tan\delta = G''/G'$ can be also extracted. Early studies on the dynamic characteristics of Pd-,[18,19] Fe-, and Co-based metallic glasses[20,21] varied with physical aging or crystallization. Because those prior measurements were carried out over a wide temperature range, from low temperatures to the glass transition temperature, the activation energy of internal friction can be estimated, falling in the range of 0.5–1.5 eV. The observed internal friction was then considered to result from the diffusion of constituent atoms. Morito *et al.* examined the effect of heat treatment on internal friction and the Curie point of the Fe–Ni–Cr–P–B amorphous alloys, which showed that these alloys underwent a reversible change among various metastable states. In addition, they proposed that the change in internal friction during an isochronal heating process stemmed from an activation-energy distribution of the relaxation process in a glass structure.[22]

In the 1990s, a series of metallic glasses, such as La-based and Zr-based systems, were developed following Inoue *et al.* and Johnson *et al.*, which exhibited high thermal stability in the supercooled liquid state.[23–25] Okumura *et al.* were the first to identify a dynamic glass transition phenomenon in these metallic glasses and also reported sub-T_g relaxation.[26–28] Subsequently, Perera *et al.* measured the activation energy and/or relaxation time distribution for the Pt–Ni–P, Pd–Ni–P, and Zr–Ti–Cu–Ni–Be metallic glasses.[29,30] Pelletier *et al.* showed that the dynamic glass transition and sub-T_g relaxation observed in the Pd–Ni–Cu–P alloys were equivalent to the α and β relaxations, respectively, as observed in other glasses.[31]

Figure 2(a) shows the storage modulus G' and the loss modulus G'' as a function of temperature in a typical $La_{60}Ni_{15}Al_{25}$ metallic glass.[32] The features of the dynamic mechanical behaviors of the $La_{60}Ni_{15}Al_{25}$ metallic glass can be described as follows. (i) At temperatures below 450 K, the material stays in the amorphous state and the storage modulus G' remains nearly constant and high whereas G'' is negligibly low. This is a temperature range that corresponds to a typical elastic behavior of the metallic glass. Interestingly, a secondary peak is observed in the loss modulus G'', around 360 K, being accompanied by a slight decrease in the storage modulus G'. These slight variations are typical of a secondary β relaxation for amorphous materials. (ii) At intermediate temperatures, G' decreases strongly while G'' reaches a maximum value. This corresponds to the so-called main or α relaxation. The α relaxation is connected to a dynamic glass transition process in amorphous materials. (iii) At higher temperature (above about 500 K), crystallization occurs, which causes a large increase in the storage modulus G' and a maximum in the loss modulus G''.

Fundamentally, the α and β relaxations of glassy materials are temperature and frequency (or time) dependent. As mentioned above, the α relaxation time shows a non-Arrhenius temperature dependence, while the β relaxation time shows an Arrhenius behavior over a wide range of temperatures. They approach to each other with increasing temperature and frequency. The mode coupling theory predicts that these two relaxations merge into a single relaxation termed "α-process" in a crossover region. In polymer glasses, the merging phenomenon can be well observed, e.g., by dielectric spectroscopy.[33] In metallic glasses, the merging of α and β relaxation is always impeded by crystallization at a high temperature. For this reason, no direct experimental observation of the merging between them is reported for metallic

glasses.

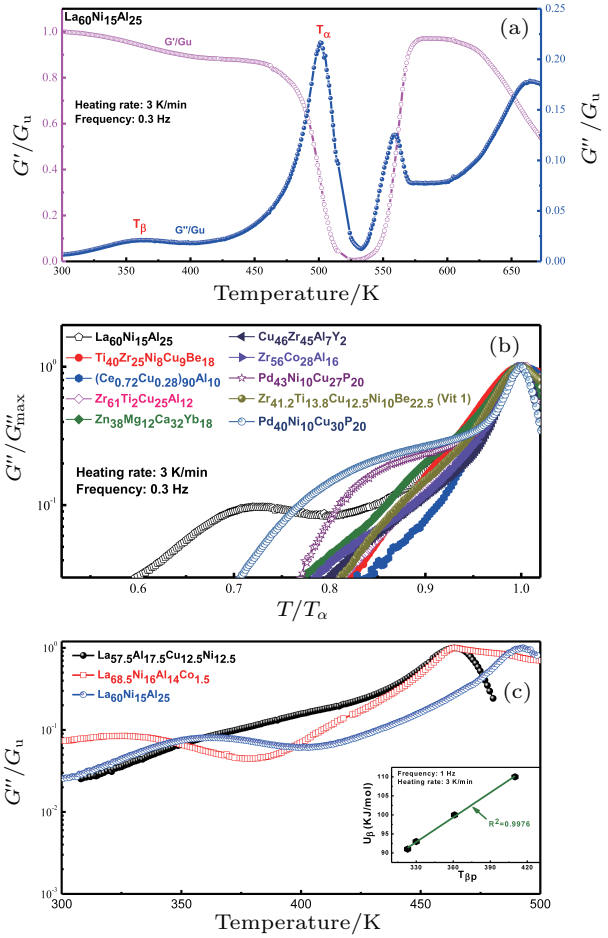


Fig. 2. (color online) (a) Normalized storage modulus G' and loss modulus G'' versus temperature in $La_{60}Ni_{15}Al_{25}$ bulk metallic glass, G_u is the unrelaxed modulus, assumed to be equal to G' at room temperature.[32] Reprinted from Ref. [32], with the permission of AIP publishing. (b) Temperature dependence of the normalized loss modulus G''/G''_{max} (G''_{max} is the peak value of α relaxation in the loss modulus) in various amorphous alloys. Reprinted with permission from Ref. [11]. Copyright (2013) American Chemical Society. (c) Temperature dependence of the normalized loss modulus G''/G''_u in typical La-based amorphous alloys. Reprinted with permission from Ref. [11]. Copyright (2013) American Chemical Society.

The prominent peak of β relaxation in La-based metallic glasses allows one to obtain the activation energy based on the Arrhenius equation. The information one can obtain in this manner the apparent activation energy of the β relaxation in amorphous materials can be calculated from the Arrhenius equation: $f = f_\infty \exp(-U_\beta/RT)$, where R is the gas constant, and f_∞ is a pre-factor equal to the high temperature limit of the frequency. With the Arrhenius equation, one can extract the activation energy of the β relaxation of metallic glasses using the Kissinger method.[34] The activation energy of β relaxation (or excess wing) determined this way for metallic glasses generally obeys $U_\beta \sim 26RT_g$, as for organic glass liquid formers and other glassy materials.[35–38] This result is important, which supports the proposal from the cooperative shear model that the shape of the potential landscape associated with β relaxation should be similar to that with α relaxation. As this scaling relation holds for non-metallic glasses, Ngai *et al.* provided an alternative explanation from the perspective of coupling model.[32] Aside from humps, β relaxation of glassy materials also manifests as an excess wing on the mechanical spectroscopy. Many previous publications demonstrated that β relaxation and α relaxation are the universal characteristics of glassy materials.[4,6,7,10]

Contrary to La-based and Pd-based metallic glasses, the Zr-based metallic glass exhibits another form of secondary relaxation according to Rösner *et al.*,[39] the so-called excess wing at the high-frequency side (low-temperature side) of the dynamic α relaxation peak, as shown in Fig. 2(b).[11] Thereafter, Ngai theoretically demonstrated that the β relaxation of the Zr–Al–Cu alloy can occur at the temperature and/or frequency region where an excess wing is observed, which supported the idea of Rösner *et al.*[40] Subsequently, Zhao *et al.* reported that, depending on the coupling strength (difference in activation energy) of Johari–Goldstein (JG) relaxation and α relaxation, the JG relaxation of glassy materials is either distinctly isolated and observed as slow β relaxation, or partially covered by α relaxation and observed as an excess wing. These behaviors are strongly dependent on the fragility of the supercooled liquid.[41]

Generally, a higher activation energy is required to activate local atomic motions with a higher peak temperatures $T_{\beta p}$ in metallic glasses, which follows the empirical relationship, $U_\beta \approx 33(\pm 1)RT_{\beta p}$. It was found that the peak temperatures $T_{\beta p}$ of the β relaxation increases almost linearly with its activation energy U_β (inset of Fig. 2 (c)).[11] Interestingly, this scaling behavior of metallic glasses is in good agreement with that of amorphous polymers, i.e., $U_\beta \approx 31.5RT_{\beta p}$ (at the driving frequency of 1 Hz). This correlation between U_β and $T_{\beta p}$ suggests that the high T limit, f_{max}, might be approximately the same ($\approx 2 \times 10^{14}$ Hz) for all metallic glasses. Moreover, many previous investigations indicated that β relaxation acts as a precursor to the α relaxation.[4,14] Based on the activation energy of α relaxation U_α and β relaxation U_β obtained for typical metallic glasses, the ratio of U_α/U_β ranges from 3 to 8.[16,42,43] In general, β relaxation is strongly compositional dependent,[44] sometimes manifesting a pronounced peak, sometimes an "excess wing" or even a "shoulder".

Next, let us discuss the micro-alloying effect on the β relaxation in metallic glasses. The temperature dependence of the loss modulus G''/G''_{max} (G''_{max} is the loss modulus at the peak of α relaxation) of the $Cu_{46}Zr_{47-x}Al_7Dy_x$ ($x = 0$, 0.5, 1, 2, and 4) bulk metallic glasses is shown in Fig. 3(a).[45] Clearly, the β relaxation of $Cu_{46}Zr_{47-x}Al_7Dy_x$ is decreased by increasing the content of Dy. From a mixing enthalpy point of view, large and similar negative values of the mixing enthalpy between the constituent atom pairs favour pronounced β relax-

ation in metallic glasses [44,46,47] while positive or significant mismatch in the enthalpy of mixing suppresses β relaxation. On the basis of the empirical rules for determination $\Delta H_{\rm mix}$, the mixing enthalpy of $Cu_{46}Zr_{47-x}Al_7Dy_x$ metallic glasses can be estimated, as shown in Fig. 3(b).[45] A similar behaviour was verified for the Pd-based and La-based metallic glass systems in which β relaxation tends to be suppressed with the increasing concentration of Ni, the element causing a large mixing enthalpy mismatch.[44,46,47]

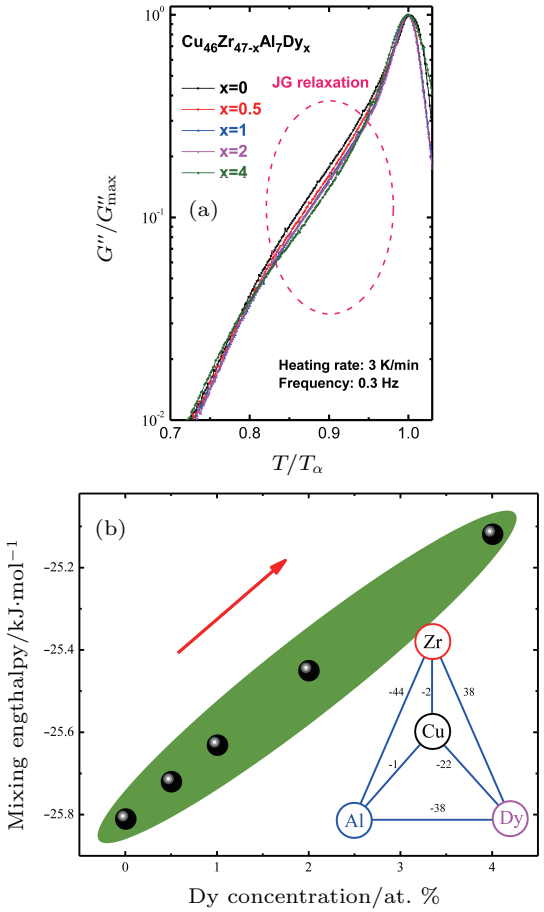


Fig. 3. (color online) (a) Temperature dependence of the loss modulus $G''/G''_{\rm max}$ in $Cu_{46}Zr_{47-x}Al_7Dy_x$ ($x = 0$, 0.5, 1, 2 and 4) metallic glass-forming liquids. (b) Mixing enthalpy of $Cu_{46}Zr_{47-x}Al_7Dy_x$ ($x = 0$, 0.5, 1, 2, and 4) metallic glasses. The inset exhibits the mixing enthalpy of the constituent atoms.[45] Reprinted from Ref. [45]. Copyright (2016), with permission from Elsevier.

Structural relaxation like physical aging and rejuvenation is an intrinsic feature of glassy materials, which originates from local processes that causes the whole system migrating into a more energetically stable state.[49–51] In practice, glasses with enhanced thermodynamic and kinetic stability are attractive for both scientific research and engineering applications. Figure 4 shows the evolution of the loss factor $\tan\delta$ with temperature during a continuous heating of cold-rolled samples.[48] It is important to note that the higher is the cold-rolling ratio the higher is the loss factor. In comparison with physical aging, cold rolling introduces heterogeneities and leads to the rejuvenation of metallic glasses. In this scenario, one can anticipate that atomic mobility is increased by plastic deformation; in other words, local dynamic heterogeneities are enhanced during cold rolling.

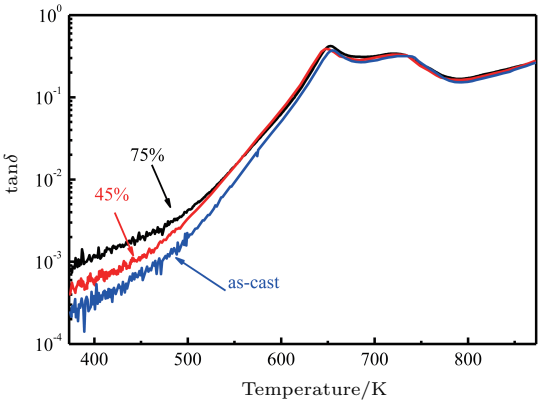


Fig. 4. (color online) Influence of the cold-rolling ratio ($\varepsilon = 45\%$ and $\varepsilon = 75\%$) on the loss factor $\tan\delta$ in $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ bulk metallic glass during continuous heating. In comparison with as-cast state.[51] Reprinted from Ref. [51]. Copyright (2012), with permission from Elsevier.

Regarding the structural origin of β relaxation and its relationship with the α relaxation, Stevenson *et al.* suggested that α relaxation takes place through the activated events involving compact regions, while β relaxation is governed by more ramified, string-like or percolation-like clusters of particles.[52] Indeed β relaxation and α relaxation are usually correlated. As discussed previously, α and β relaxation seen in various glass materials are closely correlated, and the origin of this correlation is of fundamental importance, which, once understood, could help elucidate the complicated glass dynamics in glassy materials. Two important theories emerged in the past to explain the origin of β relaxation. On the one hand, Williams and Watts proposed that β relaxation is caused by the slight re-orientational motion of all atoms.[53] On the other hand, Johari and Goldstein proposed that it is caused by the re-orientational motion of atoms or a group of atoms in a loosely packed region.[54,55] The internal friction of metallic glass associated with β relaxation was observed even by the mechanical methods that usually do not cause the re-orientational motion of atoms. Moreover, this relaxation does not result in the distinct creep of an entire sample. From these facts, Johari claimed that β relaxation is essentially due to the translational motion of atoms and is equivalent to the JG relaxation generated in an "island of mobility."[56] In light of this, Ichitsubo *et al.*[57] demonstrated that, by activating β relaxation through an ultrasonic heat treatment, a Pd–Ni–Cu–P metallic glass can be transformed into a nano-scale composite structure, which consisted of a network of metastable crystalline phases. As this phenomenon could not be observed in a simple heat treatment, the formation of the crystalline network is thus suggestive of nanoscale heterogeneities, which were intrinsically frozen-in in the quenched Pd–Ni–Cu–P metallic glass. β relaxation thereby takes place in the weakly bonded

regions, which behave like islands of mobility. Additionally, partial crystallization proceeds owing to the atomic translational motion in β relaxation. General speaking, these experimental findings support the description of Johari.

The dynamics of supercooled liquids is thought to be spatially heterogeneous, characterized by a dynamic correlation length.[58] Many investigations[59–61] suggested that such a length scale would increase with decreasing temperature (or increasing density), causing the dynamic slow-down and eventually the glass transition. Nevertheless, Wei *et al.* reported an interesting observation that the correlation length of the $Fe_{50}Co_{50}$ metallic glass decreases around the glass transition temperature T_g, which is seemingly contradictory to the previous findings and worth further investigation.[62] To determine experimentally the number of units within a correlating region, different metrics have been proposed. In the previous investigations, the number of correlating units N_c (i.e., atoms in a metallic glass, segments in a polymer, molecules in a simple liquid) in metallic glass-forming liquids was found significantly larger than that in other glass-forming materials.[63,64]

A causal link between dynamical slow-down and structural heterogeneity was recently suggested on the basis of simulations. For instance, by extensive computer simulations, Tanaka *et al.* found that the drastic slow-down and the heterogeneous dynamics are the results of critical-like fluctuations of static structural orders.[65] Their results link the structural heterogeneity and the heterogeneous dynamics, which strongly suggests that the α relaxation has a structural origin. The structural order in their work can be interpreted as the medium-range bond-orientational order, which can be linked to the geometry of an equilibrium crystal. However, this kind of structural order depends on the specific atomic interactions of a system and is not completely different from that in crystalline nuclei. In short, the possible connections between the dynamical slow-down and static structure have been actively discussed on the basis of various theories, such as the Adam–Gibbs theory,[66] the elastic model,[67] the mode-coupling theory,[68] cooperative shear model (CSM),[69] the random first-order transition theory,[70] quasi-point defects theory,[71] coupling model, [72,73] flow units model,[8,74–77] and so on.

Here, it is worth mentioning that, according to the CSM model, β relaxation is associated with the activation of isolated shear transformation zones (STZs) confined within an elastic glass matrix. Nanoscale STZs have a lower activation energy than in surrounding regions inside metallic glasses; therefore, glass visco-elasticity can be ascribed to the local plastic deformation in these domains. This contrasts the relatively high activation energy of a steady state viscous flow, which is equal to the activation energy of α relaxation.[9] It is generally perceived that soft regions in metallic glasses may trigger the formation of STZs under stress or behave like "islands of mobility" for β relaxation under thermal activation. Following this line of reasoning, one can envision that α relaxation may be associated with the collapse of the confining glass matrix caused by the percolation of these local relaxations. Aside from dynamic mechanical analysis, differential scanning calorimetry (DSC) is another technique to study the β relaxation of metallic glasses.[78–80] With the hyperquenching-annealing-calorimetric scan (HAC) approach, Hu *et al.* investigated the JG relaxation behavior of the $La_{55}Al_{25}Ni_{20}$ metallic glass and found that the activation energy of the β relaxation is correlated with the glass transition temperature, i.e., $U_\beta \sim 26RT_g$. Interestingly, through DSC, fragile-to-strong transition and relaxation processes (α and β relaxations) were also found to be correlated for metallic glasses.[81]

3. Fast β relaxation of metallic glasses

According to the prior work,[14] there may be two types of β relaxations in amorphous materials. The first type of β relaxation is tied to the above-mentioned α relaxation; while the second may be loosely connected with the α relaxation, which comes with a rather low activation energy. Based on the magnitude of the relaxation frequency, one may call the one with a slower relaxation frequency as "slow β relaxation" and the one with a faster frequency as "fast β' relaxation". Fast β' relaxation is caused by the rattling motion of loosely bonded atoms caged by relatively tightly bonded atoms.[82] Because the rattling motion is activated with a low activation energy, which only shows small temperature dependence, fast β relaxation is often treated as nearly a constant loss in a low-temperature region. Reports related to fast β relaxation of metallic glass are still scarce compared to those for slow β relaxation; however, the activation energy of the former is on the same order of magnitude with internal friction. Barmats *et al.* found a low activation energy of 0.03–0.05 eV for internal friction in the Ni–P–B–Al, Fe–P–Si–Al and Fe–P–C–Al–Si metallic glasses,[83] and Mayer *et al.*[84] detected activation energy in the Zr–Ti–Cu–Ni–Be equilibrium liquid by quasi-elastic neutron scattering.

In the case of Pd–Ni–Cu–P metallic glass, Pelletier [31] and Zhao[41,85] reported only slow β and α relaxations, based on the data from room temperature up to glass transition temperature T_g. The fast β relaxation in metallic glasses, however, could be also detected. Strikingly, compelling experimental evidence was provided more recently that there exists a pronounced faster β' relaxation in rare earth based amorphous alloys.[86,87] Figure 5(a) shows the DMA results of the $La_{56.16}Ce_{14.04}Ni_{19.8}Al_{10}$ bulk metallic glass.[86] At the low temperature around 226 K, another notable relaxation peak

is seen from the loss modulus, indicative of a broad distribution of relaxation times similar to the β relaxation. We should stress that the intensity of the secondary relaxation or slow β relaxation is usually around 10% of that of α relaxation. However, the amplitude or strength of β' relaxation peak is rather low, only around 1% of the α relaxation.

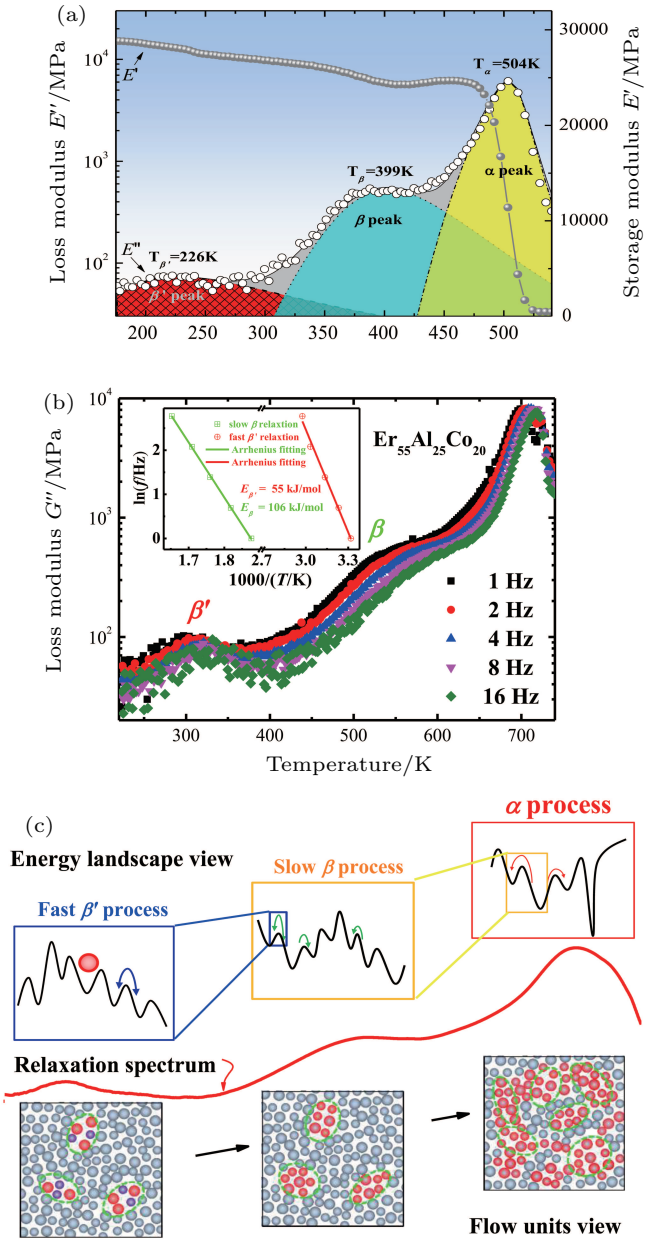


Fig. 5. (color online) (a) The emergence of two secondary relaxations in $La_{56.16}Ce_{14.04}Ni_{19.8}Al_{10}$ metallic glass on the isochronal spectrum of mechancial spectrosopy;[86] (b) Temperature dependence of the slow β-relaxation and the fast β'-relaxation measured at frequencies of 1, 2, 4, 8 and 16 Hz for $Er_{55}Co_{20}Al_{25}$ metallic glass;[87] (c) The schematic illustration of mechanisms of mechanical relaxations in amorphous alloy. The red atoms represent the active atoms, and atoms surrounded by green dash line represent flow units.[87] Reprinted from Ref. [87], with the permission of AIP publishing.

More recently, Zhao *et al.* provided a further evidence on this point.[87] Figure 5(b) presents the temperature dependence of the loss modulus E'' of the $Er_{55}Al_{25}Co_{20}$ metallic glass obtained at different frequencies.[87] Both T_β and $T_{\beta'}$ shift to higher temperatures with the increase of frequency. The activation energy of slow β relaxation, U_β, and fast β' relaxation, $U_{\beta'}$, are determined from the Arrhenius plot. The inset of Fig. 5(b) shows the Arrhenius fit of the measured data of $Er_{55}Al_{25}Co_{20}$ metallic glass. Its U_β is determined to be about 106 kJ/mol, and $U_{\beta'}$ is determined to be around 55 kJ/mol, which is only about half of the slow β relaxation U_β.

Another example is from the recent research by Kato *et al.*, with the help of time-temperature superposition (TTS) principle, a fast β' relaxation in the high frequency domain ($\sim 10^{12}$–10^{14} Hz) in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glass was reported.[88] From the profile of the activation energy, the three discrete relaxation modes with various activation energies, i.e., α relaxation (7.98 eV) is linked to the cooperative motion of ~ 5 atoms, slow β relaxation (1.39 eV) is associated with single atomic diffusion, and fast β' relaxation (0.25 eV) is mainly connected to rattling motion of atoms. It was demonstrated that the mechanical deformation behavior of metallic glasses depends on various relaxation processes (i.e., α and β relaxation).

The above analysis implies that the secondary relaxations (i.e., slow β and fast β relaxation) might be a universal feature of metallic glasses. To further understand the fast β' relaxation of the metallic glasses, these secondary relaxation modes are correlated with a dynamic heterogeneity in the framework of the flow unit theory,[76,77] as schematically illustrated in Fig. 5(c).[87] More specifically, the fast β' relaxation is associated with most mobile atoms that produce the individual localized inelasticity events, while the slow β relaxation with the local but collective atomic rearrangements that generates a typical local plastic flow event. The α relaxation then arises from the percolation of the local flow events through the elastic glass matrix.

Another important recent research worthy of discussion is the discovery of ultra-stable organic and metallic glassy films, which possess an elevated glass transition temperature, striking dynamic properties, high densities and moduli compared to regular glasses.[89–94] With a carefully controlled deposition rate and substrate temperature in physical vapor deposition, ultra-stable glasses can be made to sustain temperatures higher than the conventional glass transition temperature. In the recent study, Yu *et al.* reported that around 70% of the β relaxation intensity is suppressed in ultra-stable toluene (as shown in Fig. 6). This finding implies that it is possible to tailor the mechanical properties of metallic glasses or polymers by controlling the β relaxation.[95]

Boson peak is also a hot topic of fundamental research pertaining to the dynamic relaxation behavior of amorphous materials. However, its structural origin in metallic glasses is under intense debate.[92,96] It has been shown that the position and height of the boson peak in metallic glasses can be

tuned by annealing or severe plasticity induced rejuvenation. A connection between the boson peak and β relaxation was recently suggested for metallic glasses.[97] Huang *et al.* found that the boson heat capacity anomaly in metallic glasses is always coupled with the slow β relaxation. The structural origin of slow β relaxation is thus ascribed to the loose packed domain, where boson arises in metallic glasses.[97] However, the intrinsic nature of Boson peak and its influence on the mechanical and physical properties of metallic glasses is still not clear, which warrants further research.

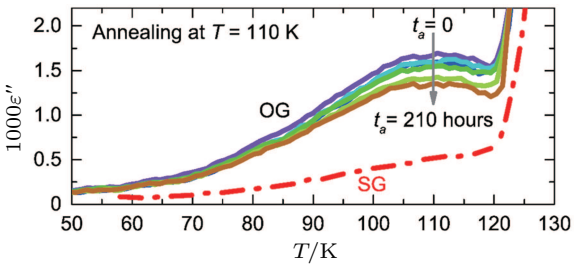


Fig. 6. (color online) The intensity of β relaxation during annealing for the ordinary glass. The solid lines are dielectric loss spectra of ordinary glasses annealed at $T = 110$ K, and the annealing time is 0, 1, 4, 15, 63, and 210 h from top to bottom. The dashed line is for the ultrastable glass.[95] Reprinted figure with permission from Ref. [95]. Copyright (2015) by the American Physical Society.

4. Correlation between mechanical/physical properties and mechanical relaxations

Many researchers proposed that the mechanical properties of conventional metallic glasses should be connected to structural heterogeneities. However, such connections remain elusive. Compared to conventional alloys, it is very important to define what a structural "defect" means in an amorphous structure in order to understand its possible effects on the overall mechanical properties of metallic glasses. A number of conceptual models,[4] such as liquid- and solid-like region, flow units and etc, were therefore proposed for metallic glasses. In general, it is perceived that the flow defects in metallic glasses may come from liquid-like regions, which possess a high potential energy and loosely packed cluster conformation.[74]

As stated in the previous section, the β relaxation of metallic glasses is associated with dynamic heterogeneity, which can be further linked to mechanical/physical properties. By examining the slow β relaxation of over 40 individual metallic glasses, Yu *et al.* found that the activation energy U_β of the slow β relaxation in those metallic glasses is equivalent to the potential energy barriers of STZs, $W_{\rm STZ}$, that is $W_{\rm STZ} = U_\beta$.[36] This result suggests an intrinsic correlation among activation of potential STZs, the β relaxation, and the inhomogeneous atomic structure of metallic glasses. Furthermore, it was proposed that the slow β relaxation is related to the diffusion motion of the smallest constituent atom in metallic glasses (i.e., Zr- and Pd-based metallic glasses).[98] Liu *et al.* proposed that the slow β relaxation in a metallic glass stems from the short range collective rearrangement of large solvent atoms.[99] More recently, with the help of the amplitude-modulation dynamic atomic force microscopy, Zhu *et al.* demonstrated that the evolution of nanoscale structural heterogeneity in a metallic glass during β-relaxation, which provides direct evidence that β relaxation in the metallic glass might be ascribed to spatial heterogeneity.[100]

According to the prior works,[4,7,10,14,49,101–103] β relaxation is an intrinsic and universal feature of all kinds of glassy materials. Since β relaxation persists in both a super-cooled liquid and glassy state, it affects the mechanical properties of glassy materials. In many polymer glasses the transition from ductile to brittle deformation occurs at the characteristic temperature of the β relaxations. Consequently, impact toughness, yield strength, and failure modes can be also correlated with β relaxations. It should be noted that amorphous polymers with the notable β relaxations always have excellent ductility, and vice versa.[104,105] However, exceptional cases were also reported, which may be attributed to the complicated structures (consisting primarily of chains units) and dynamics in glassy polymers that could yield different β relaxation mechanisms. However, β relaxation in metallic glasses is expected to share the same mechanism. Today, whether there is a similar connection between mechanical properties and β relaxation in metallic glasses is still a topic of ongoing research.

Compared to secondary relaxation in "soft" regions, relaxation through "hard" or less defective regions leads to α relaxation or overall yielding. Following this reasoning, a correlation between α relaxation and yielding in metallic glasses can be constructed. As the internal energy required for α relaxation is equivalent to the work done by an external shear stress at the yield point, the following equation relating the glass transition temperature $T_{\rm g}$ to the yield shear stress ($\tau_{\rm y}$) can be derived as[106]

$$\tau_{\rm y} = 3R(T_{\rm g} - T_{\rm ambient})/V, \tag{1}$$

where $T_{\rm ambient}$ is the room temperature (300 K) and V is the molar volume. Similarly, the internal energy required for β relaxation is considered to be equivalent to the work done to activate the individual STZ. Thus, the shear stress for the STZ activation $\tau_{\rm STZ}$ can be expressed as a function of T_β, the β relaxation temperature

$$\tau_{\rm STZ} = 3R(T_\beta - T_{\rm ambient})/V. \tag{2}$$

5. Concluding remarks and outlook

Secondary relaxation is widely observed not only in metallic glasses but also in other glassy materials such as polymer glasses and oxide glasses. In spite of the different bonding natures in these amorphous materials, they seem to exhibit

a similar mechanical relaxation behavior at the macroscopic scale. The microscopic origin of secondary relaxations and its dependence on the glass structure remain unclear. Since the particular mechanical relaxation modes (α and β relaxation) are theoretically linked with local shear flows and structural heterogeneity, unveiling the physical origin of the secondary mechanical relaxation mode (i.e., secondary relaxations) becomes important for one to understand the fundamental deformation mechanisms in these amorphous materials. The outcome of the research may ultimately enable us to find recipes or clues that could lead to the enhanced mechanical properties of, or deciphering the mythological glass transition in metallic glasses.

Finally, we would like to discuss a few issues that are related to secondary relaxations in metallic glasses and may deserve further research, being listed as below.

(i) The fast β relaxation was found previously in rare-earth metal based metallic glasses. It is not clear whether the same relaxation behavior could be observed in other metallic glasses.

(ii) As many previous studies[45,107–110] demonstrated that metallic glasses show an excellent plasticity behavior at a cryogenic temperature, it is not known yet whether such temperature dependence of plasticity could be correlated with the secondary relaxation of metallic glasses, particularly the fast β relaxation.

(iii) While the slow β and α relaxations are correlated, it is unclear whether a correlation is valid between the fast and slow β relaxations.

(iv) It is known that plasticity and physical aging can tune the slow β relaxation in metallic glasses. How they could possibly affect the fast β relaxation remains unclear.

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