Relating structural heterogeneity to $\beta$ relaxation processes in metallic glasses

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ABSTRACT
The $\beta$ relaxation is a crucial feature in metallic glasses (MGs). However, its structural origin is not fully elucidated. Using a contact resonance atomic force microscope, we investigated the local structural heterogeneity of MGs and its correlation with $\beta$ relaxations. It was found that MGs have various degrees of the heterogeneity, resulting in different intensities of $\beta$ relaxations. Local zones with a prominent heterogeneity lead to a broad energy state distribution and more pronounced $\beta$ relaxation. Our results provide a direct experimental evidence to clarify the mechanism of the $\beta$ relaxations, suggesting a guideline for controlling $\beta$ relaxations of MGs.

1. Introduction
The $\beta$ relaxation is an intrinsic and fundamental characteristic in metallic glasses (MGs), which is important to understand many crucial issues in material sciences and glassy physics, such as mechanical properties, diffusion behavior, crystallization process and glass transition [1–8]. Consequently, an in-depth understanding of the structural origin of the $\beta$ relaxation is deemed necessary for both scientific researches and practical applications of MGs. Generally, some MGs exhibit $\beta$ relaxations as a peak or pronounced hump, which are separated from the $\alpha$ relaxation, whereas some others exhibit $\beta$ relaxations as an unobvious excess wing, which is merged with the $\alpha$ relaxation [1–3].

During the past decades, the underlying mechanism of the $\beta$ relaxations has been actively discussed and several models are constructed, such as ‘islands of mobility’, ‘flow units’, ‘local bonding switching’ and ‘string-like atomic rearrangements’ [6,9–14]. These models have significantly promoted the understanding of the origin of the $\beta$ relaxation in MGs. However, it should note that there is still no agreement on this key issue, mainly because of the lack of direct experimental characterization on the intrinsic structural feature of the disordered MGs.

Recently, abundant experimental and simulation results have revealed that the microstructure of MGs is heterogeneous at the nanoscale, which is an important...
structural characteristic and has an important impact on the properties of MGs [8,15–19]. Although the structural heterogeneity has been observed, a direct experimental evidence on the correlation between the structural heterogeneity and β relaxation is still missing. Therefore, it is necessary to further investigate this unsolved topic.

In the current study, from the perspective of the structural heterogeneity of MGs, we explored the structural origin of the β relaxation in MGs. A state-of-the-art method of contact resonance atomic force microscope (CR-AFM) was employed to probe the local elastic heterogeneity of MGs at the nanoscale [15,20]. A set of samples of La60Ni15Al25, La60Cu15Al25 and Zr52.5Cu17.9Ni14.6Al10Ti5 (Vit105) were selected as model alloys, because they possess representative types of β relaxation behaviors. The correlation between the structural heterogeneity and β relaxations was established and interpreted using the theory of the potential energy landscape (PEL). Our experimental results could shed light on the understanding and controlling of the β relaxations in MGs by tuning the structural heterogeneity.

2. Experimental procedures

Four kinds of MGs with representative β relaxation behaviors, as well as the outstanding glass forming ability, were selected with the nominal composition of La60Ni15Al25, La60Cu15Al25, Vit 105 and Pd40Ni10Cu30P20 (at.%). Ribbons with a cross-section of ∼2.0 mm × 0.05 mm were prepared by a melt spinning method. The samples of Pd40Ni10Cu30P20 were annealed at 533 K for 6 h. The microstructure of the ribbons was investigated by X-ray diffraction (XRD, MXP21VAHF, Cu Kα) and differential scanning calorimetry (DSC, Perkin-Elmer 8000).

The surface profile and local structural heterogeneity of the samples were measured using CR-AFM (Bruker, Dimension Icon and Asylum Research 3D). A Tap300Al-G probe with a force constant of ∼40 N/m and a tip radius of ∼10 nm was adopted. The surface profile and resonance frequency were recorded simultaneously during the same scanning. Details of the experiment and calculation processes have been reported in previous work [15,20].

The dynamic mechanical behavior of the samples was obtained by a film tensile mode in a nitrogen-flushed atmosphere with a strain of 0.4%, using a dynamic mechanical analyzer (DMA, TA Q800). The storage (E′) and loss (E″) modulus were recorded with a driving frequency of 1 Hz and at a heating rate of 3 K/min.

3. Results and discussion

3.1. Structural characterization of the samples

The fully glassy nature of the samples was verified by XRD and DSC in Figure 1(a,b). Figure 1(c) depicts a topographic image of the Vit 105 model alloy. The surface roughness of the ribbons is less than 1 nm, indicating an ideal model for the subsequent AFM work due to the negligible influence from effects of the surface fluctuations [15,20–22].

3.2. Dynamic mechanical relaxation behaviors

Figure 2 demonstrates the normalized loss modulus E″ of the MGs as a function of the scaled temperature. Here, the loss modulus has been scaled by the maximum loss modulus E″ max of the α relaxation peak. It can be seen that three typical β relaxation processes can be obtained: a pronounced peak for La60Ni15Al25, a shoulder for La60Cu15Al25 and an excessive wing for Vit 105 MG.

It is well known that: crystalline defects, such as the grain boundaries, are critical in determining the internal friction behavior of crystalline metals, named as the grain...
Figure 2. Temperature dependence of the loss modulus $E''$ for the La$_{60}$Ni$_{15}$Al$_{25}$, La$_{60}$Cu$_{15}$Al$_{25}$ and Vit 105 MGs.

boundary relaxation [23]. In MGs, the microstructure is also heterogeneous at the nanoscale. The actual structure of MGs can be regarded as viscous weak-bond regions embodied in the elastic strong-bond matrix, as described in the model of flow units and soft spots [8,24–27]. Here, the viscous weak-bond regions (generally referred to as the liquid-like regions, loose-packing regions, flow units or soft spots) were treated as ‘defects’ in MGs. In the next section, we will explore the relationship between the structural ‘defects’ and $\beta$ relaxations in MGs, using the method of CR-AFM.

3.3. Correlation between the structural heterogeneity and $\beta$ relaxations in MGs

First of all, we detected the resonance frequency map of the Vit 105 MG, as shown in Figure 3(a). In theory, the resonance frequency is proportional to the elastic modulus [15,20]. As one can see that the distribution of the resonance frequency is heterogeneous. The fluctuation of the frequency over the region is $\sim 0.3$ kHz. The characteristic length of the heterogeneity is 5–10 nm, in agreement with the previously reported Zr-based MGs [20–22].

In the case of La$_{60}$Cu$_{15}$Al$_{25}$ specimen, the resonance frequency fluctuates within a broader range of $\sim 0.7$ kHz, as shown in Figure 3(b). This result indicates that the La$_{60}$Cu$_{15}$Al$_{25}$ MG has a more heterogeneous structure compared with the Vit 105. Additionally, the characteristic length of the heterogeneous zones with lower elastic modulus is at a scale of 30–50 nm. Those evidences clearly demonstrate that the La$_{60}$Cu$_{15}$Al$_{25}$ MG has a higher degree of structural heterogeneity.

Next, we detected the resonance frequency map of La$_{60}$Ni$_{15}$Al$_{25}$ MG. Interestingly, it can be noted that the scale of the frequency fluctuation is $\sim 1.2$ kHz. Furthermore, the characteristic length is increased to 80–250 nm, reflecting a much more heterogeneous structure. It is worthy to mention that our AFM result for the La$_{60}$Ni$_{15}$Al$_{25}$ MG ribbon is in good agreement with the transmission electron microscope analysis reported by Yu et al., where the structural heterogeneity with a range of 50–200 nm was observed in another MG with a close composition of La$_{68.5}$Ni$_{16}$Al$_{14}$Co$_{1.5}$ [5]. All those combined results confirmed that the La$_{60}$Ni$_{15}$Al$_{25}$ has the most heterogeneous microstructure among the three MGs.

Importantly, the various degrees of the structural heterogeneities in our three MGs with different $\beta$ relaxations are also consistent with the literature [15,20–22]. For example, Samwer et al. have demonstrated the

Figure 3. (a–c) Contact resonance frequency maps of the three samples. The length of the scale bars is 200 nm. (d–f) The profiles of the cross-section of the resonance frequency, corresponding to the dotted lines in (a–c).
local heterogeneity in PdCuSi MGs with a scale of tens nanometers, which exhibit a pronounced $\beta$ relaxation [1,2,15]. However, other studies have revealed that several Zr- and Fe-based MGs have a structural heterogeneity at a scale below 5 nm, which only have their $\beta$ relaxations as an excessive wing [20–22].

To further study the correlation between the structural heterogeneity and $\beta$ relaxations, the annealing treatment below the glass transition temperature was performed for a Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ MG with a high oxidation resistance and pronounced $\beta$ relaxation. As shown in Figure 4, compared with the annealed sample, the as-cast one shows a broad distribution of the contact resonance frequency and larger characteristic length, indicating a higher degree of the structural heterogeneity. A similar work on a reduced $\beta$ relaxation after the annealing process was also reported [1]. Therefore, it is reasonable to conclude that a higher degree of the structural heterogeneity leads to a more pronounced $\beta$ relaxation in MGs.

3.4. Structural origin of the $\beta$ relaxation in MGs

It is well documented that the elastic modulus is an intrinsic structural parameter in MGs, which can be correlated with many properties in MGs, such as mechanical properties, diffusion behaviors and glass transition [17,24]. It has also been proved that the elastic modulus is tightly correlated with the relative content of the structural ‘defects’ in MGs [8,17,28,29]. As demonstrated in the flow unit model, interstitialcy model and the three-parameter viscoelastic model: a higher concentration of the ‘defects’ leads to a lower elastic modulus [8,17,28,29]. On the basis of our AFM results of the elastic modulus mapping, it is reasonable to conclude that the $\beta$ relaxation can be correlated well with the structural heterogeneity of MGs. Furthermore, it is believed that these zones with lower elastic modulus and more structural ‘defects’ are favorite to pronounced $\beta$ relaxations. Accordingly, these ‘defects’ in MGs have a similar effect of the grain boundaries in the relaxations of crystalline metals.

From the viewpoint of the PEL [30–32], as manifested in Figure 4(c), two distinct relaxation processes are identified in MGs: the $\alpha$ relaxation corresponds to the jumps between the basins that are sparse and widely separated in the low energy region; however, the $\beta$ relaxation corresponds to the hoppings between the neighboring local minima or sub-basins that are very dense in the high energy region. In the following text, two aspects of the distribution and organization of the local minima will be considered with the $\beta$ relaxation.

The structural evolutions of the PEL have been investigated in a MG system with different cooling histories and the number density of local minima in the PEL has been quantified by the method of molecular dynamics simulation [33]. It is found that the density of the sub-basins in the PEL is strongly related to the stability of the system. In particular, the distributions of sub-basins are very dense in an unstable system with a higher degree of the heterogeneity (Figure 4(c)), whereas the sub-basins are rarer in a stable system (Figure 4(g)). Which is consistent with our results of the contact resonance frequency distribution in Figure 4(b,f).

Except the difference of the individual $\beta$ processes for the two samples, the organizations between different sub-basins are significantly dependent on the overall stability of the system. For an unstable system with a higher structural heterogeneity, the average distances between sub-basins are smaller; whereas for a stable system, the distributions of the sub-basins are sparse and have large average separations. The smaller separations of the sub-basins make the $\beta$ activation barriers lower in a more unstable system [34,35].

In our results, the zones with lower elastic modulus corresponding to a high concentration of structural ‘defect’ located at high energy states in the energy landscape. The high degree and broad distribution of the structural heterogeneity means a large fluctuation of the PEL, suggesting more unstable energy states and more $\beta$ jumping events, such as in the as-cast Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ MG ribbons. However, the degree of the heterogeneity is lower for the annealed MGs as reflected in the flatten energy landscape, indicating weak $\beta$ relaxations. Therefore, it is reasonable to believe that the local zones with a higher degree of the heterogeneity correspond to more unstable energy states, and the distribution of the energy landscape is more fluctuant, which are preferred to pronounced $\beta$ relaxations.

Based on the above results and discussions, the process of the $\beta$ relaxation in MGs can be described as follows: the structural and density fluctuations always exist in the actual metal liquids for the energy fluctuation [36]. During the fast cooling process, the heterogeneity will be frozen in the state of non-crystalline solids. Therefore, the energy state of the MGs will be different from one part to another, being demonstrated as the structural heterogeneity [8,15–17,19]. Furthermore and importantly, we should note that the degree and characteristic length of the structural heterogeneity can be variable for different MGs. This intrinsic feature could bring a significant influence on the properties of MGs, as well as the $\beta$ relaxation. If we heat the MGs to a high temperature again, the local zones with lower elastic modulus and high energy state, where a high concentration of structural ‘defects’ exist, will firstly transform into the supercooled liquid state. The increasing of the loss modulus from the supercooled
Figure 4. Schematic diagrams of the correlation between the structural heterogeneity and $\beta$ relaxations in MGs. (a) The elastic modulus map of the as-cast Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ MG with a high degree of the heterogeneity and larger characteristic length. (b) The distribution of the contact resonance frequency in (a). (c) The PEL of the as-cast sample: there are more sub-basins corresponding to various local structure in (a), resulting more $\beta$ jumping events. (d) More $\beta$ jumping events accumulate a broad shoulder in the relaxation spectrum. (e) The elastic modulus map of the annealed Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ MG with a lower degree of the structural heterogeneity. (f) The distribution of the contact resonance frequency in (e). (g) The PEL of the annealed sample. The relatively homogeneous structure leads to a narrow distribution of the energy states and a flatten PEL. (h) Less $\beta$ jumping events cause a reduced $\beta$ relaxation. The length of the scale bars is 200 nm.

liquid manifests as $\beta$ relaxations. Consequently, more prominent heterogeneities are favorable for pronounced $\beta$ relaxations.

The above-mentioned processes of the structural evolution during the $\beta$ relaxations can also be confirmed by previous experiments. As an example, crystallization of a Pd-based MG by utilizing ultrasonic annealing below the glass transition temperature was found by Ichitsubo et al., due to the accumulation of atomic jumps associated with $\beta$ relaxations being stochastically resonant with the supersonic vibrations [8]. In addition, our results can also explain the enhancement of the $\beta$ relaxation after
thermal cycling [37], because the structural rejuvenation can bring a higher degree of structural heterogeneity into the MGs.

The β relaxation is an intrinsic and universal feature of MGs [1–8]. Knowledge of the structural origin of the β relaxation in MGs can promote the understanding of the fundamental aspects of the disordered materials. Our results also provide a novel guideline for further developing MGs with optimized properties by controlling their structural heterogeneities and β relaxations. For instance, we can tune the microstructure and relaxations behavior of MGs through the thermal cycling [37], micro-alloying [38] and contact resonance vibration [20], by manipulating the degree of the structural heterogeneity.

### 4. Conclusion

The relationship between the β relaxation and structural heterogeneity in various MGs was investigated using the CR-AFM. The structural heterogeneity at a nanoscale was directly captured. The microstructural heterogeneity varies with the degree and characteristic length for different MGs, all of them can be well correlated with the β relaxation. The contribution of each part of the MGs to the β relaxations is different for the local structural variation. This correlation was explained using the theory of the PEL. The local zones with a higher degree of the heterogeneity correspond to more unstable energy states, and the distribution of the energy landscape is more fluctuant, which are favorable to pronounced β relaxations. Our direct CR-AFM experimental results serve as the stepping stones for the understanding of the structural origin of the β relaxation in MGs, and shed light on the manipulation of the β relaxation behaviors and properties of MGs through the control of the microstructural heterogeneity.

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### Disclosure statement

No potential conflict of interest was reported by the authors.

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