Giant changes in atomic dynamics on microalloying metallic melt

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We report unexpectedly strong variations in the relaxational dynamics in a glass-forming metallic melt while microalloying. Analysis of quasielastic neutron scattering data revealed that changes in the values of stretching of the self-correlation function and the temperature dependence of self-diffusivity showed an Arrhenius to non-Arrhenius transition. The intermediate structure of the melts did not show any prepeak or indication of short range order. These observations are correlated with the enhanced glass-forming ability of metallic melts on microalloying. © 2009 American Institute of Physics. [doi:10.1063/1.3263950]

Bulk metallic glasses (BMG) are a rather new class of materials that have significant scientific and technological importance.1–5 There have been many efforts to develop new BMG with superior glass-forming ability (GFA). However, due to the complexity of glass-formation obtaining a full understanding of GFA remains a challenge and applications of BMG are still limited due to their poor GFA. To describe the GFA of a metallic system several empirical criteria based on structure, thermodynamics, and kinetic have been proposed.1–5 These criteria are based on experimental results of frozen glass itself and are not found to hold in general. Recently it was discovered that certain alloy systems show a dramatic increase in GFA while microalloying.6–8 Thermophysical properties such as density, viscosity, or electrical properties, etc. did not change significantly while microalloying:6,7 The reason for such a huge increase in the GFA has not yet been established.6 Here we investigated such a glass-forming system using quasielastic neutron scattering (QENS) in order to understand the changes in the atomic dynamics while microalloying and the correlation with the GFA.

Recently developed cerium based glass-forming alloys show an exceptionally low glass-transition temperature and excellent GFA.8,9 We chose this alloy system for the following reasons: (1) While microalloying, the critical casting thickness increases up to 80%. For example, replacing 1% of Ce by Nb in Ce70Cu20Al10 the critical casting diameter increases from 2 mm to 10 mm.2 (2) The change in glass transition temperature (Tg), crystallization temperature (Tc), and the liquidus temperature (Tl) in microalloying is only a few degrees Kelvin (see Table I). (3) The reason for the increase in the critical casting diameter cannot be explained by the kinetic or thermodynamic models or empirical relations mentioned above.6 (4) In this alloy systems only the Cu atoms possess an incoherent neutron scattering cross-section, hence the changes in the dynamics of Cu while microalloying can be investigated.

QENS experiments were carried out on the time-of-flight spectrometer FOCUS at the Paul Scherrer Institut, Switzerland. We used a 5.4 Å neutron wavelength providing a wave-number range (q) at zero energy transfer of 0.4 to 2.0 Å−1, with an energy resolution of ≈130 μeV. The q range in our experimental setup was less than structure factor maximum, q0 (q0=2.4 Å−1), hence coherent scattering were suppressed. Thus, the scattered signals in our experiments were dominated by the incoherent scattering from Cu atoms. The resulting self-correlation functions Φ(q,t) represent the mean dynamics of Cu atoms in the melts. The samples were measured at room temperature to obtain the instrumental energy resolution function, close to the melting temperature (Tm), 850 K, and 5 more temperatures up to 1350 K with a step interval of 100 K.

The scattering law, S(q,ω), was determined by normalizing the raw data to a vanadium standard, correcting for self-absorption and container scattering, interpolating to constant q, and symmetrizing with respect to energy with the detailed balance factor. Fourier deconvolution of S(q,ω) and normalization to one for t=0 gives Φ(q,t). Figures 1(a) and 1(b) display Φ(q,t) of the liquid Ce70Cu20Al10 and Ce60Cu20Al10Nb1, respectively, at q=1.09 Å−1. Φ(q,t) in the α-relaxation regime was fitted with Kohlrausch–Williams–Watts (KWW) function,

Φ(q,t) = q fq exp[−t/τq]βαq. (1)

The Φ(q,t) of Ce70Cu20Al10 melt obtained at 850 K can be well fitted with KWW function with a βα value of 0.70 ± 0.04. On increasing the temperature the value of βα increases and at 1350 K its value was found to be 0.90 ± 0.04. Similarly, for liquid Ce70Cu20Al10Nb1, βα varies from 0.50 ± 0.04 at 850 K to 0.88 ± 0.04 at 1350 K. A clear temperature dependence on stretching of structural relaxation is observed in these liquids. Figure 2(a) shows the temperature dependence of βα obtained from the KWW fit in the above melts. Mode-coupling theory gives a microscopic explanation for stretching in terms of a nonlinear coupling

<table>
<thead>
<tr>
<th>Sample</th>
<th>dth (mm)</th>
<th>Tg (K)</th>
<th>Tc (K)</th>
<th>Tl (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce70Cu20Al10</td>
<td>2</td>
<td>341</td>
<td>408</td>
<td>722</td>
</tr>
<tr>
<td>Ce60Cu20Al10Nb1</td>
<td>10</td>
<td>352</td>
<td>412</td>
<td>728</td>
</tr>
</tbody>
</table>

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of density fluctuations caused by feedback effects in dense liquids.\textsuperscript{10} The larger stretching observed for liquid Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} indicates an increase in feedback compared to “pure” Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}. Integrating $S(q, \omega)$ over the elastic line gives structural information at intermediate length scales. Figure 2(b) shows $S(q)$ of both liquids measured at 850 and 1350 K. Neither of the liquids showed any prepeak as we observed in Al-Ni systems.\textsuperscript{11} This indicates that there is no significant short range ordering and the intermediate structure of the liquids did not change while microalloying.

The mean relaxation time from the KWW fitting obtained by

\begin{equation}
\langle \tau_q \rangle = \int_0^\infty \Phi(q,t)/f_q = \tau_0 \beta_q^{-1} \Gamma(\beta_q^{-1}),
\end{equation}

where $\Gamma$ is the gamma function. $\langle \tau_q \rangle$ is proportional to $q^{-2}$ as expected in the hydrodynamic limit for $q \ll q_0$.\textsuperscript{12} This enables us to determine the average self-diffusivity.

\begin{equation}
D = \frac{1}{q^2 \langle \tau_q \rangle}
\end{equation}

Figures 3(a) and 3(b) show $q^2$ dependence of $\langle \tau_q \rangle$ of $\alpha$-process and the data points are fitted with a straight line and the slope gives the $D$. Figure 4 shows the self-diffusivity of Cu in the liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1}. At the highest measured temperature (1350 K), the value of $D$ shows $3.33 \pm 0.16 \times 10^{-9}$ m$^2$ s$^{-1}$ and $4.04 \pm 0.16 \times 10^{-9}$ m$^2$ s$^{-1}$, and at 850 K, $D=8.85 \pm 0.16 \times 10^{-11}$ m$^2$ s$^{-1}$ and $3.46 \pm 0.16 \times 10^{-10}$ m$^2$ s$^{-1}$, in liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1}, respectively. It is surprising that while adding only 1% of Nb the $D$ near to the melting temperature decreases by about 74%. Such a large

**FIG. 1.** (Color online) The self-correlation function $\Phi(q,t)$ of Cu atoms in liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} at three different temperature and the solid lines are fit with KWW function.

**FIG. 2.** (Color online) (a) The temperature dependence of stretching exponent $\beta_q$ obtained from the KWW fitting to the $\Phi(q,t)$. (b) The intermediate structure factor of liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} obtained by integrating $S(q, \omega=0)$ over the elastic line.

**FIG. 3.** (Color online) $q^2$ depends on inverse of $\langle \tau_q \rangle$ of Cu atoms in the liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} obtained for six different temperatures. At $q$ values, $q \ll q_0$ shows a linear dependence. The straight lines are the linear fit and the slope gives the self-diffusion coefficient.

**FIG. 4.** (Color online) The self-diffusion of Cu atoms in the liquids Ce\textsubscript{70}Cu\textsubscript{20}Al\textsubscript{10} and Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} derived from the QENS data. The “straight broken” line is the Arrhenius fit to the self-diffusivity of Cu in liquid Ce\textsubscript{20}Cu\textsubscript{20}Al\textsubscript{10} and dotted curve is the $\tau$-scaling fit to the self-diffusivity of Cu in Ce\textsubscript{69}Cu\textsubscript{20}Al\textsubscript{10}Nb\textsubscript{1} with $T_c=423$ K and $\gamma=2.7$. 

The self-correlation function

$$
\frac{\langle \Phi(q,t) \rangle}{\langle \Phi(q,0) \rangle} = \frac{1}{\tau_q} \exp\left(-q^2 \beta_q t\right)
$$

where $\tau_q$ is the characteristic relaxation time of the $q$-dependence structural correlation function $\Phi(q,t)$.
change in diffusivity while microalloying was not previously observed. For example, the glass forming Ni$_{50.5}$Nb$_{49.5}$ melts while adding up to 5.2% of Sn changes the GFA, but $D$ did not show any significant changes.\(^\text{13}\) Moreover, in Pd$_{40}$Ni$_{60}$P$_{20}$ replacing Ni by 30% Cu, say in Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$, enhances the GFA significantly but $D$ measured using QENS shows a similar value at a given temperature.\(^\text{14}\) An additional surprising effect that we observed was the changes in the temperature dependent self-diffusivity. In the liquid Ce$_{70}$Cu$_{20}$Al$_{10}$, $D$ shows an Arrhenius behavior but in liquid Ce$_{70}$Cu$_{20}$Al$_{10}$Nb$_1$ it becomes non-Arrhenius and can be well described by a $\tau$ scaling law of mode-coupling theory, $D \sim [(T-T_c)/T_c]^{\gamma}$. Figure 4 displays the self-diffusivities of Cu observed in these liquids in an Arrhenius plot. The dotted line is the $\tau$-scaling law fit to the measured self-diffusion coefficients in the liquid Ce$_{70}$Cu$_{20}$Al$_{10}$Nb$_1$ with $(T_c=1.2T_c \ T_c=425 \, \text{K}$ and $\gamma =2.7$, the value for hard-sphere liquids.\(^\text{15}\) The large slowing down of self-diffusivity and transition from Arrhenius to non-Arrhenius behavior while microalloying cannot be explained by changes in the thermophysical properties or changes in the intermediate structure of the melt. However there is a clear correlation between the self-diffusivity at $T_m$ and the larger GFA of these metallic melts.

We suggest that the huge changes in self-diffusivity and GFA due to microalloying can only be explained by a dramatic change in the elastic stress distribution in the medium range order. A 1% change in the alloy would neither change the chemistry or the electronic system of the liquids. Elastic long range fields are known to have a large influence in the dynamic properties.\(^\text{16}\) The so called elastic stress field or compatibility stress surrounding a plastically deformed region is extremely sensitive to atoms with smaller or greater atomic ratio (Ce, Nb). These local atomic stresses are believed to create long range stress field modifications which are seen in the dynamics as well as in the GFA.

In conclusion, we have investigated dynamics in liquids Ce$_{70}$Cu$_{20}$Al$_{10}$ and Ce$_{70}$Cu$_{20}$Al$_{10}$Nb$_1$ using QENS. We observed surprising effects on relaxational dynamics while microalloying the glass-forming Ce$_{70}$Cu$_{20}$Al$_{10}$ liquid. The decay of self-correlation function extended over a wider time range. The self-diffusivity close to the melting temperature decreased by about 74% and its temperature dependence changed from Arrhenius to non-Arrhenius behavior. A detailed understanding of the reason for the above results requires new experiments and theoretical investigations concerning the elastic stress fields. However, we can show that these observations are correlated with the enhanced GFA of metallic melts.

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\(^{3}\) W. L. Johnson, MRS Bull. 24, 42 (1999).