Viscosity Measurements of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$
Supercooled Liquid Alloys by Using a Penetration Viscometer

T. Yamasaki$^{1,*,1}$, S. Maeda$^{1,*,2}$, Y. Yokoyama$^2$, D. Okai$^1$, T. Fukami$^1$, H. M. Kimura$^2$ and A. Inoue$^2$

$^1$Department of Materials Science & Chemistry, Graduate School of Engineering, University of Hyogo, Himeji 671-2280, Japan
$^2$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Viscosity of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquid alloys having bulk metallic glass forming ability has been measured by using a penetration viscometer with a cylindrical probe under high speed heating conditions at heating rates between 20 and 400°C/min in the temperature range from the glass transition temperatures ($T_g$) up to above the crystallization temperatures. The viscosity of these alloys decreased with increasing the heating rate and tended to saturate at the heating rate of 200°C/min and above. Their viscosity could be well represented by the Arrhenius relation. The activation energies for viscous flow for Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquid alloys were about 350 and 250 kJ/mol, respectively. The viscosity was also fitted by a Vogel–Fulcher–Tammann (VFT) relationship over the entire temperature range.

(Received July 11, 2005; Accepted August 22, 2005; Published December 15, 2005)

Keywords: Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$, Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, supercooled liquid, penetration viscometer, oxygen contamination, activation energies

1. Introduction

It is well known that a number of the multi-component alloys such as Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloys exhibit a bulk glass forming ability.1) In the glass forming process from the liquid, the most important factor is the temperature dependence of the viscosity of the supercooled liquid, and the viscosity is sensitive to the liquid structure at molecular level. In the case of the Zr-based alloys, however, it has been reported that the viscosity of the alloys increased significantly with increasing the solute-oxygen content.2) In addition, the skin effects of oxide might be prominent on the viscosity measurements.3–5) So the viscosity of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ alloys should be measured in short time periods for reducing the influence of oxygen contamination from the measuring atmosphere. The Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloys might have also some problems for measuring the viscosity at high temperatures because of their evaporation of the phosphorus.

In the present study, the temperature dependence of the viscosity of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquid alloys has been measured by using a penetration viscometer with a cylindrical probe under high speed heating conditions at the heating rate of between 20 and 400°C/min in the temperature range from the glass transition temperatures ($T_g$) up to above the crystallization temperatures. The viscosity in the supercooled liquid has been fitted by a Vogel–Fulcher–Tammann (VFT) relationship over the entire temperature range.

2. Experimental Procedures

Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ bulk metallic glass sheets with a thickness of 2.5 mm, a width of 50 mm and the length of 50 mm were prepared by squeeze copper mold casting method in an argon atmosphere. Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ bulk metallic glasses with a length of 100 mm and a diameter of 5 mm were also prepared by high-pressure die-casting of the melt into cylindrical copper molds with an inner diameter of 5 mm. The glassy structures of as-cast samples were examined by using an X-ray diffractometer using the Cu-K$_x$ radiation (40 kV–20 mA). A penetration viscometer$^6,7$ with a cylindrical W-indentation probe with a diameter of 1.0 mm was used to study the viscosity measurements in the viscosity range between 10$^2$ and 10$^3$ mPa·s (cP) as a function of temperature under the high speed heating rate conditions at the heating rate of between 20 and 400°C/min in a high purity He-gas atmosphere (purity: 99.999%). Applied stress of 6.4 kPa were generated by the probe giving the probe to sample area ratio of about 0.03. The samples used for the viscosity measurements are a plate shape with a size of 5 mm × 5 mm with the thickness of 2.5 mm for the Zr-based alloys and a cylindrical shape with φ 5 mm with the thickness of 2.5 mm for the Pd-based alloys. By measuring the penetration depth ($H$) of the indentation probe versus time ($t$), the viscosity of the samples is given by the following equation,

$$F = \eta \cdot 2\pi rH \cdot (dH/dt) + \eta \cdot \pi r^2 \cdot (dH/dt),$$

(1)

where, $F$, $\eta$ and $r$ are applied force for the probe, viscosity of the samples, radius of the cylindrical probe, respectively. The (2$\pi rH$) and ($\pi r^2$) indicate the side face area and the bottom face area of the cylindrical probe, respectively. Both sides of the eq. (1) derived by $\eta$, and then integrated by time, $t$, as follows;

$$Ft/\eta = A \cdot H^2 + BH = K \quad \text{(constant)},$$

(2)

$$\eta = Ft/K.$$

(3)

Relationships between $K$ and $H$ at various temperatures were calibrated by use of standard samples of the NIST-SRL 710a bulk inorganic glass having main compositions of SiO$_2$ (67.55 mass%), Al$_2$O$_3$ (2.10 mass%), Na$_2$O (8.05 mass%), K$_2$O (9.30 mass%), CaO (8.50 mass%), ZnO (3.60 mass%).
3. Results

Figure 1 shows X-ray diffraction patterns of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ bulk metallic glass samples. In the case of the as-cast Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ alloy, the patterns on the front and back sides of the bulk metallic glass sheet with the thickness of about 2.5 mm are shown. As shown in this figure, only broad diffraction peaks can be found for the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ alloy and between 35 and 50° for the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloy, respectively. This is a typical feature of the metallic glass phase.

Figure 2 shows the displacement behaviors of the indentation probe on the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ bulk metallic glasses at the heating rate of between 20 and 400°C/min in the temperature range from the glass transition temperatures ($T_g$) up to above the crystallization temperatures. The displacement values of the indentation probe during heating were normalized to the penetration depth for 1 s at each temperature. In the case of the Zr-based alloys, maximum speed of the indenter displacement was largely increased from about 7 to 700 μm/s with increasing the heating rate from 20 to 400°C/min, respectively, indicating that the influence of oxygen contamination from the atmosphere and the skin effects of oxides may be serious. In the case of the Pd-based alloys, the displacement was further increased from about 30 to 1800 μm/s with increasing the heating rate from 20 to 400°C/min, respectively. Surface oxidation of the Pd-based alloys was not observed visibly after the measuring, however, the evaporation effects of the phosphorus and its oxidation in the surface of the Pd-based alloys might be dominant.

Figure 3 shows the viscosity (η) of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquids as a function of temperature at the various heating rate between 20 and 400°C/min. In both alloys, viscosity exhibited relatively high values when the samples were slowly heated at the rate of 20°C/min. With increasing the heating rate, the viscosity largely decreased and tended to saturate. Figure 4 shows the variation of the viscosity measured at various temperatures for the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and the Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquid alloys as a function of heating rate between 20 and 400°C/min. In both alloys, the viscosity decreased with increasing the heating rate and tended to saturate at the heating rate of 200°C/min and above. So, the acceptable values of the viscosity of these alloys can be measured under the high-speed heating conditions at the heating rate of
200°C/min and above. Figure 5 shows the relationships between In η and the inverse absolute temperature of the Zr_{55}Cu_{30}Al_{10}Ni_{5} and the Pd_{40}Cu_{30}Ni_{10}P_{20} bulk metallic glasses. The viscosity of these alloys can be well represented by the Arrhenius relation. The activation energies for viscous flow for the Zr_{55}Cu_{30}Al_{10}Ni_{5} alloy and the Pd_{40}Cu_{30}Ni_{10}P_{20} supercooled liquid alloys were about 350 and 250 kJ/mol, respectively. Table 1 shows activation energies for crystallization and viscous flow of some glass-forming alloys. Activation energies for viscous flow of the Zr_{55}Cu_{30}Al_{10}Ni_{5} and Pd_{40}Cu_{30}Ni_{10}P_{20} supercooled liquids coincided with the activation energies for their crystallization in the supercooled liquid region.

4. Discussion

4.1 Environmental effects

As mentioned above, the viscosity of the Zr_{55}Cu_{30}Al_{10}Ni_{5} and Pd_{40}Cu_{30}Ni_{10}P_{20} supercooled liquid alloys should be measured under the high-speed heating conditions for reducing the oxygen contamination from the atmosphere, the skin effects of oxides and the evaporation of constituent elements such as phosphorus at high temperatures. Myung et al.\(^6\) has also investigated the Zr_{55}Cu_{30}Al_{10}Ni_{5} bulk metallic glass for the viscosity of the supercooled liquid by using the penetration viscometer. They have measured the viscosity under various applied stress conditions between 9.25 and 46.23 kPa and they concluded that the viscosity depended on the applied stress. These stress dependence of the viscosity may be mainly due to the skin effects of oxides. Kueber et al.\(^2\) have investigated the viscosity of (Zr_{30}Cu_{7.5}-Al_{7.5}Ni_{5})_{100-x}O_x (X = 0.2–2.1 at%) supercooled liquids by using the parallel-plate viscometer, and they reported that oxygen contents of less than 0.8 at% do not drastically affect the viscosity of the glassy phase, while the oxygen contents are more than 0.8 at%, viscosity of the supercooled liquid phase increased with increasing solute-oxygen. In the case of the Pd_{40}Cu_{30}Ni_{10}P_{20} alloy, surface oxidation was not observed visually after the measuring, however, the viscosity depended drastically on the heating rate. This may be due to

---

Fig. 4 Variation of viscosity for Zr_{55}Cu_{30}Al_{10}Ni_{5} & Pd_{40}Cu_{30}Ni_{10}P_{20} supercooled liquid alloys at various temperatures as a function of heating rate between 20 and 400°C/min.

Fig. 5 Relationships between In η and the inverse absolute temperature of the Zr_{55}Cu_{30}Al_{10}Ni_{5} and Pd_{40}Cu_{30}Ni_{10}P_{20} bulk metallic glasses. The viscosity can be well represented by the Arrhenius relation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Below T_g (kJ/mol)</th>
<th>T_g-T_x (kJ/mol)</th>
<th>Above Liquids (kJ/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr_{55}Cu_{30}Al_{10}Ni_{5}</td>
<td>340–350 (viscous flow)</td>
<td></td>
<td></td>
<td>Present study</td>
</tr>
<tr>
<td>Zr_{55}Cu_{17.5}Al_{7.5}Ni_{10}</td>
<td>582 (cryst.)</td>
<td></td>
<td></td>
<td>8)</td>
</tr>
<tr>
<td>Zr_{55}Cu_{30}Ni_{10}</td>
<td>294 (grain growth)</td>
<td></td>
<td></td>
<td>9)</td>
</tr>
<tr>
<td>Zr_{55}Cu_{30}Al_{10}</td>
<td>322 (grain growth)</td>
<td></td>
<td></td>
<td>9)</td>
</tr>
<tr>
<td>Zr_{65}Cu_{27.5}Al_{1.5}</td>
<td>370 (cryst.)</td>
<td>230 (cryst.)</td>
<td>10, 11)</td>
<td></td>
</tr>
<tr>
<td>Pd_{40}Cu_{30}Ni_{10}P_{20}</td>
<td>240–260 (viscous flow)</td>
<td></td>
<td></td>
<td>Present study</td>
</tr>
<tr>
<td>Pd_{40}Cu_{30}Ni_{10}P_{20} (T_x, Kissinger)</td>
<td>236</td>
<td></td>
<td></td>
<td>12)</td>
</tr>
<tr>
<td>La_{55}Al_{20}Ni_{20}</td>
<td>330 (viscous flow)</td>
<td>8–10 (viscous flow)</td>
<td>4, 5, 13)</td>
<td></td>
</tr>
<tr>
<td>Fe_{40}Ni_{40}B_{17}(B_{30})</td>
<td>324 (B_{30}, cryst.)</td>
<td>37 (viscous flow)</td>
<td>3)</td>
<td></td>
</tr>
</tbody>
</table>
the evaporation of the phosphorus and its surface oxidation on the Pd-based alloys.

4.2 Vogel–Fulcher–Tammann (VFT) relationship

In order to obtain information about the temperature dependence of the viscosity over the entire temperature range, the viscosity of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquids has been fitted by a Vogel–Fulcher–Tammann (VFT) relationship.\textsuperscript{14}

\[
\ln \eta = A + B/(T - T_0),
\]

where \(\eta\) [mPas], \(T\) [K] and \(T_0\) [K] are the viscosity, the absolute temperature and the temperature to reach an infinite value of viscosity, respectively. In this case, the viscosity over the entire temperature range was fitted by using the measured-values of the supercooled liquid region. The numerical equations obtained are as follows:

\[
\ln \eta = -3.419 + 5755.8/(T - 364.4),
\]

for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, \(R = 300\, ^\circ\text{C/min}\) \hspace{1cm} (5)

\[
\ln \eta = -2.810 + 7542.5/(T - 431.9),
\]

for Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$, \(R = 300\, ^\circ\text{C/min}\) \hspace{1cm} (6)

They are plotted as shown in Fig. 6. For comparison, the viscosity over the entire temperature range of Zr–Ti–Cu–Ni–Be bulk metallic forming liquids is also shown.\textsuperscript{14} The Zr–Cu–Al–Ni and the Zr–Ti–Cu–Ni–Be bulk metallic glasses behave similar viscosity-temperature relationships over the entire temperature range and their viscosity is much higher than that of the Pd–Cu–Ni–P bulk metallic alloy.

4.3 Strong liquid behavior

It is well known that the silicate liquids usually show high viscosity in their liquid state and the low slope of the Arrhenius relationships in the supercooled liquid region.

They are called strong liquids. On the other hand, fragile liquids show low melt viscosity and an abrupt change of the kinetics close to the glass transition.\textsuperscript{15,16} Figure 7 shows the viscosity of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ supercooled liquids in comparison with some metallic and non-metallic glass forming liquids.\textsuperscript{15,16} In this case, the normalized glass transition temperatures (\(T_g\)) at the viscosity of 10\(^{12}\) Pa-s and the VFT-temperatures (\(T_0\)) are calculated by above mentioned VFT-equations of (5) and (6), i.e., \(T_g = 636\, \text{K and } T_0 = 431.9\, \text{K for Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_{5}\text{alloy, and } T_g = 519\, \text{K and } T_0 = 364.4\, \text{K for Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}\text{alloy, respectively. Fragile glass formers show a VFT-temperature near the glass transition temperature, as well as low melt viscosity, however, the difference between } T_g \text{ and } T_0 \text{ of these alloys exhibited large values of about 200 and 150°C for these Zr-based and Pd-based alloys, respectively. The normalized curves for the Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_{5}\text{ and Pd}_{40}\text{Cu}_{30}-\text{Ni}_{10}\text{P}_{20}\text{ supercooled liquids exhibited almost similar shapes.}

The strong/fragile behavior of the supercooled liquids can be classified with dimensionless parameters, \(m\) and \(D\). The former is defined as the slope of the viscosity curve shown in Fig. 7 at the vicinity of \(T_g\):

\[
m = [d(\log \eta)/d(T_g/T)]_{T=T_g},
\]

where the fragility is high when \(m\) is high. \(D\) is the fragility parameter entering the modified VFT-equation:

\[
\eta = \exp[DT_0/(T - T_0)],
\]

where the \(DT_0\) replaces the parameter B in conventional expression of eq. (4). Strong glasses present high value of \(D\) (\(D = 100\) for SiO\(_2\)), whereas for the fragile ones \(D\) is small.

Table 2 shows the some \(m\) and \(D\) fragility parameters for metallic and non-metallic glass formers\textsuperscript{15} containing the present results of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloys. These alloys behave closer to the strong glasses than the fragile glasses.

5. Conclusions

The viscosity of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$
alloys can be measured under the high-speed heating conditions at the heating rate of 200°C/min and above for reducing the oxygen contamination from the measuring atmosphere. The viscosity of the supercooled liquid and liquid phases has been fitted by a Vogel–Fulcher–Tammann (VFT) relationship as follows;

\[
\ln \eta = -3.419 + 5755.8/(T - 364.4),
\]

for Pd_{40}Cu_{30}Ni_{10}P_{20}, \( R = 300°C/min \)

\[
\ln \eta = -2.810 + 7542.5/(T - 431.9),
\]

for Zr_{55}Cu_{10}Al_{10}Ni_{5}, \( R = 300°C/min \)

where, \( \eta, T \) and \( R \) are viscosity of the liquid [mPa-s], absolute temperature [K] and the heating rate [K/min], respectively. The activation energy for viscous flow of the Zr_{55}Cu_{10}Al_{10}Ni_{5} and Pd_{40}Cu_{30}Ni_{10}P_{20} supercooled liquid alloys exhibited the very high-value of about 350 and 250 kJ/mol, respectively. In order to compare the measured viscosity of different glass forming systems the viscosity is normalized to the temperature where the viscosity of the respective alloy is \( 10^{12} \) Pa-s. These alloys behave closer to the strong glasses than the fragile glasses.

**REFERENCES**


**Table 2** Fragility parameters of the \( m \) - and the \( D \)-values for some metallic and non-metallic glass formers\(^{(15)}\) containing the present results of Zr_{55}Cu_{10}Al_{10}Ni_{5} and Pd_{40}Cu_{30}Ni_{10}P_{20} alloys.

<table>
<thead>
<tr>
<th>Glass</th>
<th>( m )</th>
<th>( D )</th>
<th>( T_{g}/T_{0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>20</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Zr_{46.75}Ti_{13.25}Cu_{17.5}Ni_{10}Be_{22.5}</td>
<td>33</td>
<td>22.7</td>
<td>1.72</td>
</tr>
<tr>
<td>Mg_{95}Cu_{5}Y_{10}</td>
<td>45</td>
<td>22.1</td>
<td>1.58</td>
</tr>
<tr>
<td>Pd_{40}Ni_{10}P_{20}</td>
<td>46</td>
<td>18.1</td>
<td>1.44</td>
</tr>
<tr>
<td>Zr_{55}Cu_{10}Al_{10}Ni_{5}</td>
<td>50</td>
<td>17.5</td>
<td>1.47</td>
</tr>
<tr>
<td>Pd_{40}Cu_{30}Ni_{10}P_{20}</td>
<td>54</td>
<td>15.8</td>
<td>1.42</td>
</tr>
<tr>
<td>Fe_{66}Ni_{16}P_{14}B_{6}</td>
<td>69</td>
<td>10.1</td>
<td>1.28</td>
</tr>
<tr>
<td>Al_{49}Ni_{5}Ce_{6}</td>
<td>127</td>
<td>5.6</td>
<td>1.15</td>
</tr>
<tr>
<td>O-Terphenyl</td>
<td>81</td>
<td>6.8</td>
<td>—</td>
</tr>
</tbody>
</table>

*Present study*