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VISCOSITIES OF Fe-C, Fe-P AND Fe-P-C EUTECTIC LIQUID ALLOYS BY A CAPILLARY METHOD UNDER REDUCED PRESSURE

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INTRODUCTION

Based on the kinetic and thermodynamic points of view, the viscosity is an atomic scale measure of the thermal motion and structure of materials in the liquid state. Therefore, the viscosity has been known to be one of the most sensitive factors controlling the glass forming ability of metallic liquids.

In this study, viscosities and densities of Fe-C, Fe-P and Fe-P-C liquid alloys around their eutectic compositions are measured as a function of temperature and then the glass forming ability of these liquid alloys is discussed in terms of the critical cooling rate associated with experimental viscosities.

EXPERIMENTAL

Nine different kinds of samples as shown in Table 1 were prepared by melting electrolytic iron, reagent-grade carbon and phosphorus in an Ar induction furnace. The chemical composition of the samples was analysed to be identified before and after the viscosity measurement.

The viscosity was measured by the reduced pressure capillary method, in which the apparatus used is shown as a schematic diagram in Fig.1. If a liquid flows through a capillary in reduced pressure atmosphere under the laminar flow condition, its viscosity is calculated from Hagen-Poiseuille's equation as follows

\[ \eta = C_1 (\rho_H - \rho) t - C_2 p t^{-1}, \]  

where \( \eta \) is the viscosity, \( C_1 \) and \( C_2 \) are the constants proper to the apparatus, \( \rho_H \) and \( \rho \) are the densities of mercury and the sample, \( H \) is the difference between the heights of Hg columns in the manometer, \( h \) is the effective mean height of the column of the sample and \( t \) is the flow time of the liquid sample.

The calibration of the viscometer was carried out using Hg(0 and 305 K), Ag(1323 and 1423 K) and a standard organic liquid JS 50(305 K) to determine the values of \( C_1 \) and \( C_2 \) in eq. (1). Quartz capillaries of \( 3 \times 5 \times 10^{-4} \) m in diameter and \( 0.8 \times 1.0 \times 10^{-1} \) m in length were heated up to the experimental temperature in a silicon carbide furnace. The atmosphere gas filling the viscometer is an Ar-5at%H₂ mixture gas, which is chosen to prevent oxidation of liquid samples during the measurement.

Uncertainties in the pressure and time measurements in the present work are less than \( 10^{-3} \) atmospheres and \( 10^{-1} \) seconds respectively. The density was measured using the maximum bubble pressure technique simultaneously together with the viscosity measurement.

RESULT
Experimental results of viscosities for the nine liquid alloys are summarized in terms of the Arrhenius and Vogel-Fulcher relations together with the temperature dependence of densities in Table 1.

Table 1. Experimental viscosities ($\eta$: mPa.s) and densities ($\rho$: $10^3$ g.m$^{-3}$) of Fe-C, Fe-P and Fe-C-P liquid alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>Viscosity</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{33.3}$</td>
<td>26.3</td>
<td>1.016</td>
</tr>
<tr>
<td>Fe$_{33.5}$</td>
<td>27.1</td>
<td>1.011</td>
</tr>
<tr>
<td>Fe$_{34.4}$</td>
<td>27.1</td>
<td>1.009</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.008</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.007</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.006</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.005</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.004</td>
</tr>
<tr>
<td>Fe$_{34.5}$</td>
<td>27.5</td>
<td>1.003</td>
</tr>
</tbody>
</table>

Fig. 2 shows the Arrhenius relation of viscosities, i.e. log $\eta = A + BT$ plots for the nine liquid alloys, from which the activation energy for viscous flow is calculated using the least squares fitting. The values of the activation energy thus obtained are listed in Table 1. It is interesting to note that the activation energy for viscous flow in Fe-P liquid alloys decreases monotonically with increasing P content as shown in Fig. 3. However, the absolute value of isothermal viscosities of Fe-P liquid alloys increases with increasing P content. This result is not in agreement with Dragomir's observation that the viscosity of Fe-P liquid alloys reaches a maximum at the eutectic composition.

Fig. 3 Activation energies of viscous flow in Fe-P liquid alloys.

Isothermal molar volumes of Fe-P, Fe-C and Fe-C-P liquid alloys at 1400 and 1600 K calculated from experimental densities are illustrated as a function of metallic atom content in Fig. 4.

Fig. 4 Isothermal molar volumes of Fe-C, Fe-P and Fe-C-P liquid alloys. The densities of pure iron in the super-cooled liquid state at 1400 and 1600 K are estimated by extrapolating the experimental values of Elliott and Cleiser [7].
The molar volume of Fe-C liquid alloys is much smaller than that of pure liquid iron, while the thermal expansion of Fe-C liquid alloys between 1400 and 1600 K is larger than that of pure liquid iron. Both of the molar volume and thermal expansion of Fe-P liquid alloys decreases with increasing P content. The density of Fe-C-P liquid alloy indicates the intermediate behavior between Fe-C and Fe-P liquid alloys.

DISCUSSION

We define approximately the dynamic free volume $\Delta V_f(T)$ contributing to the viscous flow in the liquid alloy as follows

$$\Delta V_f(T) = V_1(T) - V_{am}(RT), \quad (2)$$

where $V_1(T)$ and $V_{am}(RT)$ are the molar volumes of the alloy in the liquid state at $T$ K and in the amorphous state at room temperature [8], respectively.

According to the pioneered works by Batschinski/2/ and Macleod/3/, the relations between $\log \eta$ and $\left(\frac{\Delta V_f(T)}{V_{am}(RT)}\right)^{-1}$ for Fe-P liquid alloys are plotted in Fig 5. This figure shows that the viscosity of Fe-P liquid alloys increases with increasing P content, if the dynamic free volume is kept constant. When Fe-P liquid alloys have a same value of the viscosity, the dynamic free volume increases with increasing P content.

The characteristic behavior of the viscosity of Fe-P liquid alloys mentioned above can be interpreted in terms of the cluster model/4/, which describes that Fe and P atoms strongly interact to form molecule-like clusters even in Fe-P liquid alloys. Namely, with increasing P content, the concentration of clusters increases in Fe-P liquid alloys and the weak interaction between clusters becomes a predominant factor dominating the viscous flow. Therefore, Fe-P liquid alloys with high P content show the high viscosity value accompanied with the large dynamic free volume and low activation energy of the viscous flow, compared with Fe-P liquid alloys with low P content.
Fig. 6 shows the TTT curves of Fe-17.3 at% C and Fe-13 at% P-7 at% C eutectic liquid alloys calculated by Uhlman's method using the experimental Vogel-Fulcher relations between the viscosity and temperature as shown in Table 1. The delay of crystallization for Fe-13 at% P-7 at% C alloy is about 60 times longer than that for Fe-17.3 at% C alloy. The dotted line (n) shows TTT curve for Fe-17.3 at% C alloy which is calculated by use of viscosity of Fe-13 at% P-7 at% C alloy. The dotted line (Tm) shows TTT curve for Fe-17.3 at% C alloy which is calculated by use of melting point of Fe-13 at% P-7 at% C alloy. These results show that the delay of crystallization, which corresponds to glass formability, is dependent on melting point and viscosity. The critical cooling rate \( R_c \) is defined as

\[
R_C = \frac{(T_m - T_n)}{t_n}^{-1},
\]

where \( T_m \) is the melting point, and \( T_n \) and \( t_n \) are the temperature and time at the nose point in the TTT curve.

The calculated \( R_c \) are summarized in Table 2 together with the experimental \( R_c \) and \( \frac{R_c}{6} \). There are intimate relations between the viscosity and critical cooling rate for metal-metalloid liquid alloys as shown in Fig. 7.

Table 2 | Melting point (\( T_m \)), glass transition temperature (\( T_g \)), viscosity at melting point (\( \eta_m \)), nose temperature (\( T_n \)), nose time (\( t_n \)), viscosity at nose point (\( \eta_n \)), calculated critical cooling rate (\( R_c \)) and experimental critical cooling rate (\( \frac{R_c}{6} \)).
<table>
<thead>
<tr>
<th>Alloy</th>
<th>( T_m )</th>
<th>( T_g )</th>
<th>( \eta_m )</th>
<th>( T_n )</th>
<th>( \eta_n )</th>
<th>( R_c )</th>
<th>( \frac{R_c}{6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe13P7C</td>
<td>1218</td>
<td>900</td>
<td>2-0</td>
<td>945</td>
<td>3-6</td>
<td>6.3</td>
<td>&gt;6.5</td>
</tr>
<tr>
<td>Fe17.3C</td>
<td>1423</td>
<td>500</td>
<td>1-1</td>
<td>945</td>
<td>3-6</td>
<td>2-2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

CONCLUSIVE REMARKS
The viscosity and density of Fe-C, Fe-P and Fe-P-C liquid alloys around their eutectic compositions were measured as a function of temperature and composition. Based on the examination of a correlation between experimental viscosities and dynamic free volumes, the formation of molecule-like clusters may be considered to provide a predominant contribution to the viscous flow in Fe-P liquid alloys. The critical cooling rate of these liquid alloys was obtained from the TTT curves calculated by Uhlman’s kinetic analysis using experimental viscosities. It was confirmed that there is an intimate relation between the critical cooling rate and viscosity for metal-metalloid liquid alloys.

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