Frequency Dependence Modulus of Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} Amorphous Alloy around the Glass Transition by Dynamic Mechanical Analysis

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ABSTRACT

Dynamic Mechanical Analyzer (DMA) was used to study the frequency dependence of storage and loss modulus of amorphous Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} alloy over a broad frequency range around its glass transition temperature. The amorphous samples were subjected to two testing conditions: constant frequency with continuous heating and isothermal with frequency sweep. The storage modulus $E'$ exhibited a sigmoidal change from about 90 GPa to a low value of about 0 GPa over the glass transition region. The loss modulus, $E''$, was characterized by an asymmetrical peak with a smaller slope at the low temperature side than at the high temperature side upon heating. These changes in moduli were associated with mechanical relaxation due to atomic motion. Similar results were also obtained under isothermal condition. The Kohrausch-Williams-Watts function was used to fit the data obtained under the isothermal condition. The peak frequencies obtained were then fitted to the VFT equation and the scaling law equation.

I. INTRODUCTION

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. These properties can be expressed via dynamics modulus, the loss modulus and a mechanical damping or internal friction. During dynamic testing, an oscillatory (sinusoidal) strain (or stress) is applied to the material and the resulting stress (or strain) developed in the material is measured and complex modulus can be determined. The complex modulus is a measure of the materials resistance to deformation. It encompasses both in-phase and out-of phase response of the sample, from which one calculates the storage modulus $E'$ and the loss modulus $E''$ respectively, $E^*(\omega) = E' (\omega) + iE'' (\omega)$. The elastic modulus, or storage modulus $E'$ is a measure of the elastic energy stored and the viscous modulus, or loss modulus $E''$ is a measure of the energy lost.

The dynamic mechanical analyzer can provide valuable information about all changes in the state of molecular motion as temperature is scanned. Therefore, this technique is considered to be one of the most effective for studying the structural and mechanical relaxation of glass-forming materials [1, 2].

In this study, the frequency dependence of storage and loss modulus of amorphous Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} alloy was investigated over a broad frequency and temperature range. This alloy is the best metallic glass former known so far. A critical cooling rate of only 0.1 K/s is sufficient to avoid crystallization and to obtain bulk metallic glass castings of up to 72 mm in diameter [3]. Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} combines a deep eutectic composition with a liquidus temperature $T_{liq}$ at only 865 K with a high glass transition temperature $T_g \approx 578$ K. Therefore, in contrast to simple metallic glasses and most alloys, this exceptional thermal stability enables detailed studies of the relaxation dynamics in bulk Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} alloy in both the supercooled liquid region and glass transition region.

II. EXPERIMENTAL

Bulk Pd\textsubscript{40}Ni\textsubscript{10}Cu\textsubscript{30}P\textsubscript{20} ingot was prepared by induction melting of pure Pd (purity 99.95%) and a pre-melted Cu-Ni-P master alloy, which was prepared from a mixture of elements with purity better than 99.95%. Rectangular samples, about 25 x 5 x 1.5 mm, were produced by chilled copper mold casting. The amorphous nature of the samples was verified using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The dynamic mechanical response of the
samples was measured using Dynamic Mechanical Analyzer 2980 (TA Instruments) in the bending mode, with single cantilever geometry. The samples were subjected to two testing conditions: (1) Constant frequency with continuous heating and (2) Isothermal with frequency sweep. The oscillation amplitude used during testing is 3 µm and the ramping rate is 3 K/min. The frequency dependence was described by the Arrhenius law (VFT equation) and the scaling law for the heating and isothermal conditions, and the Kohrausch-Williams-Watts function for fitting the data obtained by the isothermal condition.

III. RESULTS AND DISCUSSION

(1) Constant Frequency with Continuous Heating

Each sample was first annealed at 590 K for 5 mins and cooled at a rate of 3 K/min to 303 K prior to testing to achieve a relaxed state. The samples were then heated at a rate of 3 K/min to 643 K at various frequencies.

Figure 1 shows the real (storage) and imaginary (loss) parts of the complex modulus of Pd_{40}Ni_{10}Cu_{30}P_{20} alloy measured at a heating rate of 3 K/min at frequencies of 1, 10, 50 Hz. During heating, the storage modulus E' exhibited a sigmoidal change from about 90 GPa to a low value of about 0 Pa over the glass transition region. At low temperature (< T_g), the alloy is in its amorphous state with high modulus. As the temperature increases, the alloy undergoes “softening”, resulting in decrease in the modulus. This abrupt drop in the modulus is associated with mechanical relaxation associated with atomic motion (reorganization of the metastable amorphous structure) as the alloy changes from glassy solid state to a viscous liquid in the supercooled region. At a particular temperature, glass transition temperature, a maximum change of E' occurs. This temperature shifted to the higher values as the frequency used to oscillate for testing increases.

The loss modulus E" is characterized by an asymmetrical peak with a smaller slope at the low temperature side than at the high temperature side upon heating, which is characteristic for the distribution of intrinsic structural relaxation times. The temperature where E" shows its maximum value implies that at this temperature the characteristic relaxation time matches the external imposed frequency. This temperature shifted to higher values with increasing frequency, indicating that at higher frequency, more movement of the atoms will be required to match the imposed frequency, which can be attained with higher temperature.

(2) Isothermal with Frequency Sweep

Figure 2 shows the storage and loss modulus of the sample under isothermal conditions at temperatures 583 K, 587 K, 593 K, 598 K and 603 K respectively. The storage and loss modulus data are fitted with the stretched exponential function or Kohrausch-Williams-Watts function, i.e. the Fourier transform of the response d[exp(-(t/τ_o)^β)]/dt [4, 5, 6], where τ_o is the effective relaxation time and β (0≤β≤1) is the broadening and skewing parameter and is equivalent to the width of the loss peak at half-height.

The plot of loss modulus (E") against log frequency is asymmetric and skewed toward the high frequency side of the maximum. Stretching of correlation functions is generally found to be
more pronounced in fragile glass-forming liquids, characterized by a sharp temperature dependence of viscosity. The non-exponentiality parameter $\beta$ is temperature dependent. The more coupled the atoms is to the motions of its neighbours, the broader the relaxation and the stronger its time and temperature dependence will be. In most of the glass-formers, the value of $\beta$ is found to increase monotonically with temperature. Starting from a value anywhere in the neighbourhood between 0.5 and 0.8 at glass transition temperature, $\beta$ increases and shows a tendency to approach unity at high temperatures [7]. The $\beta$ value found by Meyer et al. [8] for the same system tested in its equilibrium liquid by quasielastic neutron scattering was found to be about 0.76, concluding that metallic bulk-glass forming Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ is a fairly strong glass-forming liquid. However, there is a discrepancy in our $\beta$ value (0.46 – 0.58) as the tests were carried out at a much lower temperature (around the glass transition region). Still, the $\beta$ value increased with temperature.

(3) Fitting of Peak Frequency

Figure 3 shows the peak frequency as a function of temperature obtained from the results in Figures 1 and 2. The TMDSC results obtained by Hu et al. [9] for the same system were also included for comparison. It can be observed from the figure that under the same testing temperature, the peak frequency for the isothermal data is higher than that for continuous heating. This is because the peak frequency then shifts to higher values with slower heating rate and under the isothermal condition, the heating rate can be considered as zero.

The peak frequencies are fitted with the Vogel-Fulcher-Tamman (VFT equation) or the Arrhenius law, $\nu = \nu_o \exp [-B/(T-T_o)]$, where $B$ is a constant and $T_o$, the VFT temperature at which relaxation time shows a divergence. A scaling law is also used to fit the experimental data. Scaling law has the form of $\nu = \nu_1 [(T-T_1)/T_1]^\alpha$, where $\alpha$ is a constant. Both equations are used widely for fitting of glass-transition data, especially in the area of polymers. Table 1 shows the result of the fittings. The values of $T_o$ for continuous heating and isothermal conditions are roughly the same at 431 K and 440 K respectively. Similar results are also obtained for $T_1$ (518 K and 513 K) and $\alpha$ values (14 and 17).

![Figure 2: Plot of storage and loss modulus with frequency at temperatures ( ) 583K, ( ) 587K, ( ) 593K, ( ) 598K and ( ) 603K.](image)

Table 1: A summary of fitting parameters for the VFT and scaling law equations

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\nu_o$ (Hz)</th>
<th>$B$</th>
<th>$T_o$ (K)</th>
<th>$\nu_1$ (Hz)</th>
<th>$\alpha$</th>
<th>$T_1$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>1.43E13</td>
<td>4831.67</td>
<td>430.934</td>
<td>5.79E11</td>
<td>13.70765</td>
<td>518.493</td>
</tr>
<tr>
<td>Isothermal</td>
<td>3.50E14</td>
<td>4832.43</td>
<td>440.218</td>
<td>1.54E14</td>
<td>16.625</td>
<td>512.671</td>
</tr>
</tbody>
</table>
Heating
Isothermal
TMDSC
VFT Fit
Scaling Law Fit

Figure 3: Plot of peak frequency vs $T_{max}$.

Figure 4: XRD plot of Pd-based sample before and after testing.

Subsequent XRD measurements were carried out after the testing confirmed the absence of detectable crystallization in the samples as shown in Figure 4.

IV. CONCLUSION

We have successfully used the dynamic mechanical analyzer to probe the frequency dependence modulus of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ alloy around its glass transition regions. The peak frequencies can be fitted using the VFT and scaling law equation for both the continuous heating and isothermal data, yielding similar results. Kohrausch-Williams-Watts function was used to fit to the storage and loss modulus curves of the isothermal condition giving $\beta$ values of 0.46 to 0.58.

REFERENCE

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