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Title: Thermodynamics, Kinetics, and Crystallization of Pt57.3Cu14.6Ni5.3P22.8 Bulk Metallic Glass Forming Alloy.

Abstract Approved:

Ralf Busch

This study utilizes differential scanning calorimetry (DSC) to characterize the thermodynamics, kinetics and crystallization processes of a new Pt57.3Cu14.6Ni5.3P22.8 bulk metallic glass forming alloy. The heat capacity of the alloy is measured for the crystalline, glassy, and supercooled liquid phases. This data is used to obtain thermodynamic driving forces for crystallization and quantify the thermodynamic fragility. The kinetic properties of the alloy are investigated by observing the glass transition under different heating rates. The heating rate dependence of the glass transition is then used to calculate the kinetic fragility and estimate how the material's viscosity varies with temperature. DSC is also used to observe the crystallization event at a variety of temperatures and generate a Time-Temperature-Transformation (TTT) diagram for crystallization. The crystallization results and TTT diagram are compared with thermodynamic and kinetic data using classical nucleation theory, and different models for crystallization are discussed.
Thermodynamics, Kinetics, and Crystallization of Pt_{57.3}Cu_{14.6}Ni_{3.3}P_{22.8} Bulk Metallic Glass Forming Alloy

by

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Benjamin A. Legg, Author
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Sincerely,
Ben Legg
# TABLE OF CONTENTS

1. **Introduction** ......................................................................................................................... 2  
   1.1. **General Introduction** ................................................................................................... 2  
   1.2. **Overview of BMG Systems** ........................................................................................ 2  
   1.3. **Goals of the Study** ...................................................................................................... 4  

2. **Experimental Methods** ........................................................................................................ 5  
   2.1. **Differential Scanning Calorimeter** .............................................................................. 5  
   2.2. **Calibration** .................................................................................................................. 6  
   2.3. **DSC Temperature Scans** ............................................................................................ 6  
   2.4. **Heat Capacity** ............................................................................................................. 9  
   2.5. **Isothermal Crystallization** ........................................................................................ 10  

3. **Background Theory** ........................................................................................................... 14  
   3.1. **Thermodynamics** ...................................................................................................... 14  
   3.2. **Fragility** .................................................................................................................... 16  
   3.3. **Crystallization** ........................................................................................................... 20  

4. **Results** ............................................................................................................................... 23  
   4.1. **Thermodynamics** ...................................................................................................... 23  
   4.2. **Fragility** .................................................................................................................... 24  
   4.3. **Crystallization** ........................................................................................................... 26  

5. **Discussion** .......................................................................................................................... 34  
   5.1. **Thermodynamics** ...................................................................................................... 34  
   5.2. **Fragility** .................................................................................................................... 37  
   5.3. **Crystallization** ........................................................................................................... 42  

6. **Conclusion** ........................................................................................................................ 54  

7. **Appendix** .......................................................................................................................... 56  
   7.1. **Microstructures and X Ray Diffraction** ..................................................................... 56  
   7.2. **Discussion of Crystal Products** ................................................................................. 66  

8. **Bibliography** ..................................................................................................................... 67
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic diagram of a power compensated DSC.</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>A typical DSC heat flow curve, taken at a heating rate of 30 K/min.</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>A typical DSC heat flow curve of the glass transition, taken at a heating rate of 6 K/min.</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Diagram of the heat capacity measurement procedure.</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>Example of a percent crystallization curve based on DSC output.</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>Heat capacity measurements of the Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$ alloy.</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>DSC heat flow curves of the glass transition region in Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>Four isothermal heat flow curves, showing crystallization of the amorphous alloy after heating from the glassy state.</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>High temperature crystallization isotherms.</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>High temperature DSC crystallization isotherms, demonstrating the precrystallization event.</td>
<td>32</td>
</tr>
<tr>
<td>11</td>
<td>Time-Temperature-Transformation diagram for crystallization and relaxation of the Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$ alloy.</td>
<td>33</td>
</tr>
<tr>
<td>12</td>
<td>Enthalpy curve ($\Delta H_{f,s}$) for Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$.</td>
<td>34</td>
</tr>
<tr>
<td>13</td>
<td>Gibbs free energy comparison for six BMG forming alloys.</td>
<td>36</td>
</tr>
<tr>
<td>14</td>
<td>Entropy Curve ($\Delta S_{f,s}$) for Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$.</td>
<td>37</td>
</tr>
<tr>
<td>15</td>
<td>Modified Angell Plot for Pt$<em>{57.3}$Cu$</em>{14.6}$Ni$<em>{5.3}$P$</em>{22.8}$.</td>
<td>38</td>
</tr>
<tr>
<td>16</td>
<td>Predicted Angell plot of viscosity, based upon VFT fit.</td>
<td>39</td>
</tr>
<tr>
<td>17</td>
<td>Entropy vs. temperature for Pt$<em>{55.7}$Cu$</em>{14.4}$Ni$<em>{5.3}$P$</em>{22.5}$, plotted relative to the crystalline state.</td>
<td>41</td>
</tr>
<tr>
<td>18</td>
<td>Comparison of the configurational entropy for several BMG alloys.</td>
<td>42</td>
</tr>
<tr>
<td>19</td>
<td>Comparison of three Avrami crystallization models with experimental results at 553 K.</td>
<td>46</td>
</tr>
<tr>
<td>20</td>
<td>A diagram of the transient time period in relation to temperature.</td>
<td>47</td>
</tr>
<tr>
<td>21</td>
<td>Volmer distribution functions for subcritical nuclei, at four different temperatures.</td>
<td>48</td>
</tr>
<tr>
<td>22</td>
<td>Time-Temperature-Transformation diagram for low temperature isothermal crystallization.</td>
<td>49</td>
</tr>
<tr>
<td>23</td>
<td>Comparison of theoretical and actual DSC isotherms at (a) 568 K, (b) 558 K, (c) 548 K, and (d) 538 K.</td>
<td>50</td>
</tr>
<tr>
<td>24</td>
<td>Time-Temperature-Transformation diagram, with Avrami crystallization predictions extrapolated to higher temperatures.</td>
<td>52</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>The glass transition temperature as measured in eleven different DSC scans at various heating rates</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>Isothermal crystallization times and heat of crystallization, for temperatures below the nose of the TTT diagram</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>Isothermal crystallization times and heat of crystallization, for temperatures above the nose of the TTT diagram</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>Crystallization times at 703 K, taken during eight repetitions with a 4.5 mg Pt alloy sample encased in B$_2$O$_3$ flux</td>
<td>31</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>TTT Diagram for Pt_{57.5}Cu_{14.7}Ni_{5.4}P_{22.5}, completed by L. Shadowspeaker.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>XRD spectra after annealing at 550K for time intervals between 360 s and 3000 s.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>XRD spectra after annealing at 565 K for 600 and 7200 seconds.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Microstructure after annealing for 600 s at 565 K.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Microstructure after annealing for 7200 s at 565 K.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Microstructure after annealing for 7200 s at 565 K.</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>A constant heating rate thermal scan at 0.333 K/s. (20 K/min).</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>X-ray diffraction spectra, obtained after heating glassy samples at 0.333K/s to different maximum temperatures, and rapidly quenching to room temperature.</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>MXRD profile of the glassy sample which is heated to 583 K and rapidly quenched.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Microstructure for sample which was heated to 583 K and rapidly quenched.</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>MXRD profile of the glassy sample which is heated to 650 K and rapidly quenched.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Micrograph of the sample which is heated to 650 K and rapidly quenched.</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>MXRD profile for the sample which was heated to 700K and then quenched.</td>
<td></td>
</tr>
</tbody>
</table>
Thermodynamics, Kinetics, and Crystallization of Pt$_{57.3}$Cu$_{14.8}$Ni$_{5.3}$P$_{22.8}$
Bulk Metallic Glass Forming Alloy
1. Introduction

1.1. General Introduction
Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ is a new type of bulk metallic glass (BMG) forming alloy. BMGs are unique metal alloys that can be cooled into the solid state without crystallization, and instead retain a disordered amorphous microstructure. This amorphous structure leads to physical properties that are not seen in typical alloys, including enhanced yield strength, elastic energy storage, and processability [1][2].

The defining characteristic of a BMG is its glass forming ability (GFA), which describes how easily it can be solidified without crystallization. Poor glass formers crystallize rapidly and must be quenched quickly from the molten state to remain amorphous, while good glass formers can be cooled at moderate rates without crystallizing. For metallic systems, the best GFA has been observed in alloys of palladium with copper, nickel, and phosphorus [3].

Based on the similarities between palladium and platinum, the Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ alloy has been developed as a new BMG. This alloy's GFA is not as high as that of the palladium based alloy Pd$_{40}$Cu$_{30}$Ni$_{15}$P$_{15}$, but it does have many potential benefits over typical platinum alloys, particularly in terms of processability [4]. With a liquidus temperature of only 853 K, it can be processed at relatively low temperatures. Studies on PtCuNiP alloys by Schroers et. al, have also demonstrated the use of superplastic forming, a type of processing that is typically associated with polymers [5].

This study contains an analysis of the thermodynamic and kinetic properties of the Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ alloy, and how these properties vary with temperature. Observations of crystallization are also obtained at different temperatures and explained in terms of the thermodynamic and kinetic data. It is hoped that this study will help to explain the alloy’s glass forming ability, and contribute to a better understanding of metallic glass forming systems in general. The experimental observations may also aid in the development of appropriate processing conditions for this alloy.

1.2. Overview of BMG Systems.
A glass is an amorphous solid formed by quenching from the liquid state. This process of forming a glass is called vitrification. The transition from liquid to glass takes place at a glass transition temperature, designated $T_g$. Above the glass transition temperature, the material is a liquid in equilibrium or metastable equilibrium, but below the glass transition temperature the material is a non-equilibrium solid. As the material is cooled below $T_g$, the kinetics of relaxation become so slow that the material is unable to reach its equilibrium thermodynamic state within laboratory conditions.
timescales. During a DSC temperature scan the glass transition can be observed by a change in heat capacity. The slowing of relaxation kinetics is also displayed by the materials viscosity. At temperatures below \( T_g \) the viscosity becomes so high that the material effectively ceases to flow and is considered a solid.

The first metallic glass was discovered in 1960, in an \( \text{Au}_{75}\text{Si}_{25} \) alloy [6]. These initial glass forming alloys were very poor glass formers, and would crystallize rapidly when cooled below the liquidus temperature. To prevent crystallization, these alloys needed to be quenched to room temperature at rates exceeding \( 10^5 \) K/s. This high “critical cooling rate” dictated that only very small samples of glass could be produced, using techniques such as splat quenching or melt spinning.

In the 1990’s however, new multicomponent alloys were discovered that were far more resistant to crystallization. Among the best of these was the \( \text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20} \) alloy, which can be cooled as slowly as 0.1 K/s and still solidify into an amorphous structure. This low critical cooling rate has enabled larger “bulk scale” samples of material to be produced. By modifying the composition only slightly to \( \text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20} \), and using very small samples treated in a flux of boron oxide, critical cooling rates as low as 0.005 K/s have been achieved [3].

Inoue has listed three “rules” for creation of a good glass forming alloy. These are that a BMG alloy must be a multicomponent alloy (it must include at least three elements), that the size difference between atoms is large (atomic radii should differ by at least 12%), and that there is a large negative heat of mixing among the three main constituent elements [2]. These rules enhance glass forming ability in several ways. They stabilize the amorphous liquid state by increasing its entropy, they destabilize the crystalline state by disrupting crystal structures, and they slow the kinetic process of crystallization by creating densely packed structures with strong interatomic bonding. Another common guideline for producing metallic alloys with high GFA is that the composition should lie near a deep eutectic point in the phase diagram [1]. At these compositions, the liquidus temperature, \( T_l \), is depressed, so that the amount of undercooling required to reach \( T_g \) is minimized. The best glass forming ability is not always at eutectic composition however, because the diffusion processes required to form crystalline compounds must also be considered.

If the above rules are well satisfied, an alloy may display sluggish crystallization rates and high GFA. To obtain a better understanding of crystallization however, it is useful to consider two thermophysical properties: the driving force for crystallization, and the relaxation time [7]. Both of these thermophysical properties, and the crystallization time, can be measured quantitatively using a technique known as differential scanning calorimetry (DSC). The driving force for
Crystallization is a thermodynamic property that can be quantitatively estimated with DSC by calculating the Gibbs free energy difference between liquid and crystal, $\Delta G^\circ$. In general, it is expected that a good glass former will have smaller driving forces for crystallization. The relaxation time is a kinetic property, and it is closely related to other rate processes that control crystallization like viscosity and diffusivity. Good glass formers have long relaxation times, high viscosities and low diffusivities in the supercooled liquid region. A quantity known as the "fragility parameter" is often used to quantify how these kinetic processes vary throughout the supercooled liquid region.

1.3. Goals of the Study.
In order to more fully understand the PtCuNiP system, the kinetics, thermodynamic driving forces, crystallization products, and time for crystallization will be studied throughout the supercooled liquid region. These experiments will be performed using differential scanning calorimetry.

The kinetic fragility of the material will be calculated by measuring heating rate dependence of the glass transition. This fragility can be used to estimate the material's viscosity as a function of temperature. Heat capacity measurements will be used to obtain the thermodynamic functions of entropy, enthalpy, and Gibb's free energy. These thermodynamic functions are used to estimate the driving force for crystallization and to calculate a thermodynamic fragility. The Adam Gibbs relation will be used to compare the thermodynamic fragility with the kinetic fragility.

Isothermal crystallization measurements will be used to observe the crystallization event and generate a Time-Temperature-Transformation (TTT) diagram. These results will be explained with nucleation theory, in terms of the thermodynamics and kinetics.
2. Experimental Methods

2.1. Differential Scanning Calorimeter

The majority of the experimental results cited in this study were obtained by differential scanning calorimetry (DSC). DSC is a powerful tool for the analysis of kinetics, thermodynamics, and phase changes [8][9]. The primary output of a DSC is a heat flow signal, which corresponds to the amount of heat energy produced or received by the sample. All DSC experiments in this study were completed with a power compensated Perkin Elmer Pyris 1 DSC. A schematic diagram of the power compensated DSC is shown in Figure 1.

![Schematic diagram of a power compensated DSC.](image)

The power compensated DSC consists of two small platinum crucibles, each of which is attached to a resistive heater and a thermocouple. One crucible contains the sample under analysis, while the second remains empty or contains a reference material. During an experiment, the crucibles can either be heated at a constant rate or held isothermally. A computer control system is used to monitor the temperature of each crucible, and the power input to each heater is adjusted to keep both crucibles at the same temperature. The power difference between the sample and reference crucible corresponds to the amount of heat flow into or out of the sample. This heat flow signal can be analyzed to obtain very sensitive measurements of a sample's heat capacity or heat of
reaction. The temperature and time at which a reaction occurs can also be determined with a high degree of accuracy.

2.2. Calibration
The heat flow and temperature output of the DSC must be calibrated. These calibrations are performed with high purity reference materials that have known reaction temperatures, heats of fusion, or heat capacities. Zinc reference material of 99.998% purity and indium reference material of 99.999% purity are used to calibrate temperature and heat flow, since these materials have well defined melting temperatures and heats of fusion.

Because the DSC signals depend upon heating rate (with higher heating rates introducing a thermal lag) a separate calibration must be performed for each heating rate used. For measurement of the glass transition temperature (Section 2.3), the machine was calibrated at heating rates of 3 K/min, 6 K/min, 15 K/min, 30 K/min, 60 K/min, and 120 K/min. When isothermal crystallization measurements were performed (Section 2.5), the slowest available calibration rate of 3 K/min was applied. For heat capacity measurements, the indium and zinc temperature calibration was performed at a heating rate of 20 K/mm. However, the heat flow calibration was performed with a sapphire reference of known heat capacity, as described in Section 2.4.

2.3. DSC Temperature Scans
A series of DSC temperature scans was performed at heating rates of 2 K/min, 3 K/min, 6 K/min, 15 K/min, 20 K/min, 30 K/min, 60 K/min, 120 K/min. Each temperature scan involves heating a small piece of the glassy platinum alloy. The sample mass ranged between 9 and 38 mg, and was measured to the nearest 0.01 mg. During the first scan on each sample, the glass transition and crystallization events are observed. Afterwards, the now crystalline sample is cooled and scanned for a second time in order to obtain a crystal baseline. Six of these experiments involved scanning between about 430 K and 850 K. These scans utilized graphite sample pans to prevent undesired reactions with the melted sample. Other scans were limited to temperatures below 750 K and utilized aluminum sample pans.

The DSC temperatures scans were used to obtain a number of important transition temperatures and to measure the heat of fusion and heat of crystallization. Figure 2 shows a temperature scan at 30 K/min, and displays the following important temperatures: onset and completion of the glass transition, the crystallization temperature, the solidus temperature, the melting peak temperature, and the liquidus temperature. The heat of reaction may be calculated from the data in Figure 2 by integrating the appropriate reaction peaks with respect to time.
Figure 2: A typical DSC heat flow curve, taken at a heating rate of 30 K/min. Important temperatures are shown. $T_{g \text{onset}}$ and $T_{g \text{complete}}$ are the glass transition temperatures. $T_x$ marks the onset of crystallization. $T_s$, $T_{\text{peak}}$, and $T_l$ are the solidus temperature, melting peak temperature, and liquidus temperature respectively.

The most important goal of these temperature scans was the measurement of the glass transition temperature at different heating rates. The glass transition temperature is critical for determining GFA, and its temperature dependence gives important insight into other relaxation properties like viscosity and diffusivity. In a DSC temperature scan, the glass transition is observed as a change in heat capacity. The method for determining the onset and completion of the glass transition is
demonstrated in Figure 3. For the purposes of this study, T_g onset will be considered the definitive 
T_g, because it seems to provide the most consistent results.¹

![Figure 3: A typical DSC heat flow curve of the glass transition, taken at a heating rate of 6 K/min. 
During temperature scans the glass transition temperature is marked by a change in heat capacity. 
T_g onset and T_g complete are defined as shown by taking the intersection of tangent lines. T_g max is defined where the heat flow curve has a maximum slope. For this study, the generic glass transition temperature T_g will refer to T_g onset.](image)

¹ASTM Standard E 1356-03 describes some alternative definitions of T_g, and Angell has suggested defining T_g by the so called fictive temperature [10][11]. The use of a fictive temperature seemed inferior to T_g onset however, because it provided less consistent results and left more room for interpretation by the analyst.
2.4. Heat Capacity
In order to calculate the thermodynamic variables such as Gibbs free energy and entropy, the heat capacities of the liquid, glassy, and crystalline state is precisely measured over a temperature range of 600 degrees Celsius. The method used is modified from ASTM standard E1269-05 [12]. The first step of this method is to perform a baseline scan upon empty sample and reference pans. The baseline temperature profile consists of a series of 15 degree temperature scans, conducted at a heating or cooling rate of 20 K/min. Between each temperature scan the pans are held isothermally for 5 minutes. Figure 4 shows an example of two temperature scans and the associated isothermal periods. For the second step, this thermal profile is repeated exactly, but this time the sample pan contains a sapphire calibration reference. In the final step, the profile is repeated again, but the sample pan contains the material of interest. For greatest accuracy, all three steps utilize the same sample and reference pans.

![Diagram of the heat capacity measurement procedure. The dashed line shows the DSC temperature profile. The other lines show heat flow signals after subtraction of the empty pan baseline. $Q_{\text{sapphire}} - Q_{\text{pan}}$ and $Q_{\text{metal}} - Q_{\text{pan}}$ as shown in this diagram can be used calculate the heat capacity.](image-url)
capacity at 383 K. Similar measurements on the second pair of peaks can be used to obtain $\dot{Q}_{\text{sapphire}} - \dot{Q}_{\text{pan}}$ and $\dot{Q}_{\text{metal}} - \dot{Q}_{\text{pan}}$ at the temperature of 398 K.

At each isothermal temperature, the heat flow difference $\dot{Q}_{\text{sapphire}} - \dot{Q}_{\text{pan}}$ or $\dot{Q}_{\text{metal}} - \dot{Q}_{\text{pan}}$ is obtained by subtracting the heat flow required to hold the sample isothermally from that required to heat it at a constant rate, as shown in Figure 4. The heat capacity at the isothermal temperature can then be calculated as

$$c_p(T)_{\text{metal}} = \frac{\dot{Q}_{\text{metal}} - \dot{Q}_{\text{pan}}}{\dot{Q}_{\text{sapphire}} - \dot{Q}_{\text{pan}}} \cdot \frac{m_{\text{sapphire}} \cdot \mu_{\text{metal}}}{m_{\text{metal}} \cdot \mu_{\text{sapphire}}} \cdot c_p(T)_{\text{sapphire}},$$

where $m$ is the sample mass and $\mu$ is the molar mass [13]. The value of $c_p_{\text{sapphire}}$ is obtained from ASTM charts.

For measuring the heat capacity of the glassy phase, this procedure was performed on a 304.11 mg piece of initially glassy material. The starting temperature was 323 K, and it was heated to 743 K in 15 degree increments. Aluminum sample pans were used. The very large sample size was needed to maximize the heat flow signal and increase measurement precision. To obtain the heat capacity of the crystalline state, the same sample (now crystalline) was run through this temperature profile an additional time.

The heat capacity of the supercooled liquid was obtained in a similar method, but with graphite crucibles and a different temperature profile. This time, the sample was heated above the liquidus temperature to a starting temperature of 993 K. The temperature profile then involved cooling in 15 degree increments until crystallization occurred. Further cooling steps were performed in order to double check the crystalline heat capacity.

2.5. Isothermal Crystallization

Isothermal crystallization studies were performed in DSC by bringing a sample of the amorphous material to a given temperature in the supercooled liquid region and then waiting until the exothermic crystallization event is observed. This data is used to generate a Time-Temperature-Transformation (TTT) diagram. DSC carries distinct advantages over other techniques for measuring crystallization because the progression of the reaction through time can be observed. This is in contrast to early undercooling experiments, in which crystallization was observed by recording a change of surface appearance, or an emission of light due to recalescence [14][15] [17].
2.5.1. High Temperature

In the high temperature regime between roughly 693 K and 743 K, crystallization is observed by heating the sample to a melt temperature of 988 K, and then rapidly cooling at 120 K/min to the isothermal temperature where it is held until crystallization occurs. This temperature regime is above the so called “nose of the TTT diagram.” The sample for these experiments consists of a small particle (4.5mg or 6.56mg) of the platinum alloy, held in a graphite DSC crucible with boron oxide flux. The samples were prepared by placing the platinum alloy in a graphite crucible with boron oxide powder and heating in an induction furnace under vacuum. At high temperatures, the boron oxide powder melted and encased the metal sample. This flux was used because it is believed to reduce heterogeneous nucleation [17]. It has the added benefit of protecting a sample from oxidation and allowing samples to be reused in multiple crystallization experiments.

Observations were completed at eight different temperatures between 693 K and 743 K. Observations at 703 K were repeated eight times, in order to assess repeatability and to quantify the variation in onset time.

The crystallization times are measured in terms of the time required to reach 5%, 50%, and 95% crystallization. These times are written as $t_{5\%}$, $t_{50\%}$ and $t_{95\%}$ respectively. The percent crystallization is quantified relative to the total observed heat of crystallization, $\Delta H_c$. As in the measurement of $\Delta H_f$, the value of $\Delta H_c$ is calculated by integrating the isothermal heat flow curve with respect to time. A graphical example of the crystallization calculation is shown in Figure 4.
2.5.2. Low Temperature

For temperatures between 538 K and 568 K, crystallization was observed by heating small pieces of the glassy Pt alloy directly to the isothermal temperature. The method of rapid quenching described in Section 2.5.1 could not be applied here, because the DSC's maximum cooling rate is insufficient to reach this temperature range without the sample crystallizing first.

Each sample was only used once, and weighed between 10 and 40 mg. Larger sample sizes were used for lower temperatures where the crystallization proceeded more slowly. The samples were held in standard aluminum sample pans. After the crystallization event had completed, some samples were heated further to ensure complete crystallization. Following this procedure, a baseline scan was obtained by cooling each sample and running it through the temperature profile.
for a second time. As in the high temperature case, onset and completion of crystallization were measured and reported in terms of \( t_{5\%}, t_{50\%}, \) and \( t_{95\%}. \)
3. Background Theory

3.1. Thermodynamics

3.1.1. Calculation of Thermodynamic Functions

Basic thermodynamic properties such as enthalpy, entropy, and Gibbs free energy are very useful for characterizing a material. A major goal of this study was to quantify the enthalpy difference, \( \Delta H^{l-x} \), entropy difference, \( \Delta S^{l-x} \); and Gibbs free energy difference, \( \Delta G^{l-x} \), between the liquid and crystalline states. Each of these quantities provides useful information.

\( \Delta H^{l-x} \) is important because it corresponds to the thermal energy released upon transformation from the liquid state into a crystalline mixture. This enthalpy difference is what allows phase transformations to be observed using DSC. If complete crystallization occurs, then \( \Delta H^{l-x} \) should be equivalent to \( \Delta H_x \), but \( \Delta H_x \) may be smaller if complete crystallization does not occur.

\( \Delta S^{l-x} \) displays an important relation to structural disorder. The importance of entropy is discussed more fully in Section 3.2, where the Adams Gibbs relation is presented, and it is shown how entropy affects rate processes such as viscosity and relaxation.

In many ways, the most important thermodynamic quantity is \( \Delta G^{l-x} \), which describes the relative phase stabilities. If the crystal has a lower Gibbs free energy than the liquid, than \( \Delta G^{l-x} \) is negative and the crystal is favored to grow. Because of this, \( \Delta G^{l-x} \) represents the driving force for phase change during a polymorphic transformation. It should be noted however, that when phase transformations involves a change of composition, the proper driving force is no longer described by \( \Delta G^{l-x} \), but by the chemical potential difference (\( \Delta \mu \)). Unfortunately, the chemical potential is more difficult to obtain experimentally, and so the driving force is approximated by \( \Delta G^{l-x} \), with the understanding that this is actually a lower limit for the driving force.

While absolute values of the entropy, enthalpy, and Gibbs free energy are not obtained for each phase, it is the relative differences in these values that generally matter. The values of \( \Delta H^{l-x} \), \( \Delta S^{l-x} \), and \( \Delta G^{l-x} \) can be obtained by measuring just three parameters with DSC. These parameters are the temperature of fusion, \( T_f \); the heat of fusion, \( \Delta H_f \); and the constant pressure specific heat capacity of each phase, \( c_p \). Based upon these parameters, the enthalpy is calculated as
\[
\Delta H^{1-x}(T) = \Delta H_f - \int_T^{T_f} \frac{\Delta c_p^{1-x}(T')}{T'} dT'
\]

(2)

the entropy is calculated as

\[
\Delta S^{1-x}(T) = \Delta S_f - \int_T^{T_f} \frac{\Delta c_p^{1-x}(T')}{T'} dT'
\]

(3)

where the entropy of fusion is defined as

\[
\Delta S_f = \frac{\Delta H_f}{T_f}
\]

(4)

and the Gibbs free energy can be calculated as

\[
\Delta G^{1-x}(T) = \int_T^{T_f} \frac{\Delta c_p^{1-x}(T')}{T'} dT' - T \int_T^{T_f} \frac{\Delta c_p^{1-x}(T')}{T'} dT'.
\]

(5)

It is still necessary to make an approximation about \(T_f\), which is properly defined as the temperature at which \(\Delta G^{1-x}=0\). While \(T_f\) is equivalent to \(T_m\) for the case of polymorphic melting, in general \(T_f\) is located somewhere between the solidus and liquidus temperatures. The exact value of \(T_f\) can’t be directly obtained with DSC, so \(T_f\) has been approximated by the temperature \(T_{peak}\), at which the heat flow signal due to melting reaches a maximum, following Glade et al [16].

Having obtained a series of data points for the heat capacity, a set of fitting equations can be generated. For temperatures well above the Debye Temperature, the heat capacity of a crystalline metal and the liquid metal are expected to be well modeled by the equations

\[
c_{p\ crystall} = 3R + aT + bT^2
\]

(6)

and

\[
c_{p\ liquid} = 3R + cT + dT^{-2}
\]

(7)

In these equations, \(R\) is the gas constant and \(a, b, c,\) and \(d\) are fitting parameters [18]. The term \(3R\) corresponds to the approximate phonon heat capacity of Dulong-Petit. It is expected that equations 6 and 7 will be valid, since the similar Pt\textsubscript{60}Ni\textsubscript{15}P\textsubscript{25} alloy has displayed a Debye temperature of only 205K. [19].
3.2. Fragility

3.2.1. Kinetic Fragility Theory

The viscosity of a liquid is not constant, but varies with temperature. It has been found that the temperature dependence of a material’s viscosity is strongly related to glass formability. The most important temperature regime is the area between $T_g$ and $T_r$. In order to compare the viscosity of various glass forming materials, it is convenient to classify materials as either “strong” or “fragile.” If an alloy’s viscosity drops off rapidly when heated above $T_g$, it is referred to as a fragile liquid and is likely to have poor GFA. If its viscosity changes less rapidly, it is called a strong liquid and it is likely to have high GFA. The reason that viscosity influences GFA can be seen in Section 3.3, where it is shown that more viscous materials have slower crystallization kinetics.

A useful tool for comparing the fragility of different liquids is the Angell plot [20]. The Angell plot is a variation of an Arrhenius plot, and displays the log of viscosity vs. inverse temperature. The temperature axis is scaled by the value $T_g'$, the temperature at which a material has viscosity equal to $10^{12}$ Pa s. This forces all viscosity plots to converge at a value of $10^{12}$ Pa s where $T_g'/T = 1$. At the high temperature end, all materials also converge to a theoretical “infinite temperature viscosity”, which is relatively constant.

For a large set of materials, especially strong liquids, it is found that the viscosity can be described by an equation known as the Vogel-Fulcher-Taumen, or VFT equation.

$$\eta = \eta_0 \exp \left( \frac{D^* \cdot T_0}{T - T_0} \right) \quad (8)$$

The variable $D^*$ is sometimes referred to as the fragility parameter. For strong glasses such as SiO₂, $D^*$ is on the order of 100 and the viscosity displays an almost Arrhenius temperature dependence. More fragile glass formers may have values of $D^*$ as low as 2. Most measurements of bulk metallic glasses have shown values of $D^*$ between 10 and 30.

The variable $T_0$ is referred to as the VFT temperature, and at this temperature the viscosity is predicted to approach infinity. The coefficient $\eta_0$ is the infinite temperature viscosity, which is expected to be similar for all materials. It can be calculated as
\[ \eta_0 = \frac{N_A h}{V_m}, \]  
(9)

which is dependent solely on the molar volume, \( V_m \) [21]. The values \( N_A \) and \( h \) are Avogadro's number and Plank's constant, respectively. For most metals, the infinite temperature viscosity can be approximated as \( 4 \times 10^5 \) Pa s.

While the above discussion is focused on viscosity, it is applicable to many other phenomena. A particularly important phenomena is diffusion. Diffusion limits most rate processes and an estimation of the diffusion coefficient is very useful for modeling phase transformations such as crystallization. The Stokes Einstein relation,

\[ D = \frac{k_B T}{3\pi \eta a_0}, \]  
(10)

allows one to obtain an estimate of the diffusion coefficient based on knowledge of the viscosity. This means that a rough estimate of the diffusion coefficient can be obtained if the VFT parameters are known. Unfortunately, this method does have some limitations, since the Stokes Einstein relation has been seen to break down at temperatures below \( 1.2 T_g \) [22][23][24]. There are also issues dealing with multiple component alloys where each element has a different diffusivity.

In addition to viscosity and diffusion, the fragility concept is also strongly related the glass transition, which is also a relaxation phenomenon [24]. In fact, it has been shown that the VFT parameters can be obtained directly by observing the glass transition under different time scales. This is discussed in greater detail in the next section.

### 3.2.2. \( T_g \) Shift Technique

To determine the kinetic fragility of a material by direct measurement would require viscosity measurements to be obtained over a large temperature range. While this has been done for some materials, it is a difficult task. Fortunately, an alternative method for estimating fragility has been developed. This procedure, referred to as the \( T_g \) shift technique, allows for the fragility to be estimated by a simple series of DSC experiments which measure the glass transition temperature at heating rates between 2 K/min and 120 K/min.

Busch and coworkers first demonstrated the \( T_g \) shift technique in studies on \( \text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10} \), and later on \( \text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5} \). In these studies, it was shown that the heating rate dependence of the glass transition was related to the material's fragility [13][25]. Because the glass transition is a relaxation phenomena (on heating, it occurs when the glass relaxes to a liquid state), it is
postulated that the time for the glass transition to occur should also follow a VFT equation similar to that of viscosity. This relation is given as

$$\tau_g = \tau_0 \exp\left( \frac{D^* \cdot T_0}{T_g - T_0} \right),$$

(11)

where \(\tau_0\) is a constant equal to approximately \(2 \times 10^{13}\) s. Experimental measurements of glass transition time can easily be obtained in DSC, by observing the width of the glass transition region, \(\Delta T_g\), at a given heating rate, \(R\) [26]. The glass transition relaxation time is then calculated as

$$\tau_g = \left( T_g^{\text{complete}} - T_g^{\text{onset}} \right) / R = \frac{\Delta T_g}{R}.$$

(12)

In practice it is seen that the onset of \(T_g\) varies significantly, but the value \(\Delta T_g\) is relatively independent of heating rate. Thus, the observed relaxation time becomes inversely proportional to the heating rate, and it is often more convenient to write the VFT equation as

$$\frac{1}{R} = \frac{1}{R_0} \exp\left( \frac{D^* \cdot T_0}{T_g - T_0} \right).$$

(13)

The important point of this discussion is that we can observe very rapid glass transitions or very slow glass transitions by simply adjusting the DSC heating rate. The relaxation time for the glass transition is still a function of temperature however, and faster relaxation events must occur at higher temperatures. By measuring the glass transition temperature at different heating rates, we are able to observe the temperature dependence of the relaxation time, and use this information to characterize fragility. For the platinum alloy, heating rates between \(2 \text{ K/min}\) and \(120 \text{ K/min}\) were used, and \(\tau_g\) was changed by almost 2 orders of magnitude. By increasing the heating rate through this range, the corresponding onset of the glass transition was increased by 20 degrees Celsius. These observations are used in conjunction with equation 13 to obtain best fit values of the VFT parameters \(D^*\) and \(T_0\). The execution of this process is discussed further in Section 5.2.

---

\(^{i}\) Because the VFT equation is meant to predict relaxation times over 12 orders of magnitude, it is desirable to weigh each decade equally. Thus, the least squares fit should be performed with respect to \(\log(\tau_g)\) instead of simply \(\tau_g\). This prevents longer relaxation times from receiving excessive weighting.
It is worth noting that other methods for estimating fragility based upon the glass transition have also been developed. Ito, Moynihan, and Angell have proposed an extremely simplistic method which relates fragility to the single parameter $\Delta T_g / T_g$ [27]. However, errors in the measurement of $T_g$ complete make that method too insensitive for accurately distinguishing between BMG systems.

3.2.3. Thermodynamic Fragility.
While measurements of viscosity or other related relaxation phenomena are the typical method for defining fragility, there has been recent interest in correlating fragility to thermodynamic functions such as entropy. The rational for defining a thermodynamic fragility stems from work by Adam and Gibbs, who developed a theoretical relationship between configurational entropy and structural relaxation times [28]. This relationship is given as

$$\tau = \tau_0 \exp \left( \frac{C}{T \cdot S_c} \right),$$

where $\tau$ is the structural relaxation time, $\tau_0$ is an inverse attempt frequency, $C$ is a constant, $T$ is the temperature, and $S_c$ is configurational entropy. A heuristic explanation for this relationship is that materials with higher configurational entropies can relax more quickly. This is because they have more stable structural configurations and hence more available pathways for relaxation.

Early attempts to use the Adam Gibbs equation to explain the viscosity of glass formers have been promising, but imperfect. One success of the Adam Gibbs model is that it allows for derivation of the VFT equation, in cases where $S_c$ is inversely proportional to temperature.

When dealing with the Adam Gibbs equation, some assumptions need to be made about configurational entropy. Because DSC data does not provide information on configurational entropy.

An alternative and simpler method of fitting the data is to obtain the steepness parameter, $m$. The steepness parameter is defined as

$$m = \frac{d \log \left( \tau_s \right)}{d \left( T_s / T \right)} \bigg|_{T=T_g},$$

and can be obtained by a linear least squares fit to relaxation time data.

Based upon the constraints of the VFT equation, and knowing that the relaxation time varies between about 100 seconds at $T_g$ and the infinite temperature value of $10^{14}$, it can be shown that the fragility parameter $D^*$ is related to $m$ by the simple relationship of

$$m = 16 + 590 / D^*$$

[29]. This method of calculating $D^*$ gives very similar results to those obtained by directly fitting the log of the VFT equation.
entropy, but only relative entropies, a common practice is to assume that the crystalline state has zero configurational entropy. By making this assumption, $S_c$ can be approximated by calculating the so called excess entropy ($S_{\text{excess}} = S_{\text{liq}} - S_{\text{xtal}}$). Although $S_{\text{excess}}$ rarely follows a perfect inverse relationship with $T$, the approximation is not bad.

Unfortunately, by making this assumption that $S_c = S_{\text{excess}}$, the Adam Gibbs relation shows that the Kauzmann temperature, $T_k$ and the VFT temperature $T_0$ should be equivalent. This conflicts with observations of BMG’s, where the Kauzmann temperature tends to be significantly higher than $T_0$. Furthermore, attempts to correlate kinetic fragility with excess entropy have been fairly unsuccessful. Several attempts have been made to rectify this situation [30].

An alternative method has been developed by Bothra et al. to deal with this situation. The assumption is made that configurational entropy of the liquid should go to zero at $T_0$, and that the crystal contains finite configurational entropy $S_{\text{xtal}}$, independent of temperature. This assumption leads to a formula for configurational entropy of the liquid as $S_c = S_{\text{excess}} + S_{\text{xtal}}$. If the $S_{\text{excess}}$ curve has already been calculated through $C_p$ measurements, then relaxation data can be fit using equation 14, with $S_{\text{xtal}}$ and $C$ as fitting parameters. The thermodynamic fragility is then related to the slope of the configurational entropy with respect to temperatures. Bothra has used this technique to calculate configurational entropy curves for a number of metallic glasses, and the results have shown a strong correlation between kinetic fragility and thermodynamic fragility [31].

3.3. Crystallization

One of the most important tools for characterizing a BMG is the TTT diagram. This diagram displays the onset time and completion time for crystallization (or other transformations), as a function of temperature. This information makes an alloy’s TTT diagram very useful for determining appropriate processing temperatures and times. By completing isothermal crystallization experiments with DSC, a large portion of this diagram has been generated for the Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ alloy. DSC is a very powerful tool for this application, because the DSC heat flow curves allow one to determine when a reaction begins, reaches a maximum, and completes. Based upon the thermodynamic and kinetic properties discussed earlier, it is also possible to theoretically derive portions of the TTT diagram, and to explain the DSC heat flow curves.

3.3.1. Crystallization Theory

When a metal is cooled below the liquidus temperature, equilibrium thermodynamics dictate that crystallization should occur. In practice however, the material does not crystallize until a certain degree of undercooling is achieved. The physics behind this crystallization resistance is described by classical nucleation theory.
When solid phase is formed from the liquid state, several competing forces are at work. At temperatures below the melting point, $\Delta G^{kx}$ is negative, which represents a driving force for nucleation of the crystalline state. In order to create a crystalline region however, a solid liquid interface must be formed. This interfacial area has a positive energy per unit area, given as $\gamma_{s1}$. For very small nuclei, the interfacial energy dominates and nuclei are energetically unstable. For the crystal nucleus to become stable, a certain critical size must be achieved. Above the critical nucleus size, the volume related term $\Delta G^{kx}$ dominates and the crystal should grow. For a spherical nucleus, the critical nucleus radius is given as

$$r^* = \frac{2\gamma_{s1}}{\Delta G_v},$$

where $\Delta G_v$ is defined as $\Delta G^{kx} V_m$ and $V_m$ is the molar volume. A critical nucleus with radius $r^*$ will have an associated energy given by

$$\Delta G^* = \frac{16\pi \gamma_{s1}^3}{3\Delta G_v^2}.$$  \hspace{1cm} (16)

The value of $\Delta G^*$ represents the energy barrier that must be overcome in order to form a crystalline region, and is very important in determining the rate of crystallization [32].

Although individual nuclei smaller than $r^*$ are more likely to shrink than to grow, a certain distribution is expected to exist based upon thermodynamic fluctuations. Occasionally, nuclei with radius greater than $r^*$ will be produced, and these nuclei may grow irreversibly. The steady state production rate of critically sized nuclei was calculated by Turnbull [33]. It is convenient to write this expression in terms of $\Delta G^*$ as

$$I_{ss} = \frac{A_v}{\eta} \exp\left(\frac{-\Delta G^*}{k_BT}\right),$$

obtained from reference [34]

It can be seen from equation 17 that $\Delta G^*$ strongly effects the nucleation rate, and for this reason $\Delta G^{kx}$ and $\gamma_{s1}$ are very important in controlling nucleation. Equation 17 also shows how viscosity will control crystallization rates (as a measurement of the material's rate processes). The constant $A_v$ is less important since it relates primarily to the number of atoms in the system.

Once a critical nucleus is formed, it will grow based on one of several mechanisms. Three relevant types of growth include interface controlled growth, diffusion controlled growth, and eutectic growth. Each type of growth is limited by slow atomic motion and promoted by strong...
driving forces. Hence, the growth rate will also be related to $\Delta G^\pm$ and $\eta$. The particular growth modes will be addressed further in Chapter 5.

By characterizing the nucleation rate and growth rate at various temperatures, it is possible to predict both the rate at which a material will crystallize and some characteristics of the microstructure that will form. This allows for theoretical modeling of the TTT diagram, which is discussed further in Chapter 5.

### 3.3.2. Heterogeneous Nucleation

In the prior discussion on nucleation theory, conditions of homogenous nucleation were assumed. Under these conditions, crystals are expected to nucleate randomly from the liquid. However, crystal nucleation does not occur homogenously in most cases, but through heterogeneous nucleation at preexisting particles or surfaces. These heterogeneities can reduce the energy needed to form a critical nucleus and significantly increase nucleation rates. For this reason, the number of impurity particles can strongly influence an alloy's GFA. It is believed that B$_2$O$_3$ flux improves the GFA of some alloys by reducing the number of heterogeneous nucleation sites.

### 3.3.3. Transient Nucleation

In the discussion on homogenous nucleation theory, a steady state nucleation rate was derived. This steady state nucleation rate depends upon having a distribution of sub-critical nuclei existing in the melt. Under steady state conditions, this distribution remains relatively constant, but the nature of the distribution depends strongly upon temperature.

If a material is rapidly quenched from a higher temperature, it will take a certain period of time for this distribution of sub-critical nuclei to accumulate before the steady state nucleation rate of Equation 17 will become effective. Considering the nucleation of liquid particles from a supercooled gaseous phase, Kantrowitz and Probstein conducted early work to estimate the size of this transient period within an order of magnitude [35]. In glassy systems, the transient period should be approximately given by

$$\tau_0 = \frac{n^* a_0^2}{\sigma^* D}.$$  \hspace{1cm} (18)

In this equation, $n^*$ is number of atoms in the critical nucleus, $a_0$ is the average interatomic spacing, $\sigma^*$ is the number of surface atoms in the critical nucleus, and $D$ is the diffusion coefficient, which can be estimated from the viscosity through the Stokes-Einstein relation [37].
4. Results

4.1. Thermodynamics

4.1.1. Heat Capacity

The results of the heat capacity measurements are shown in Figure 6. At temperatures well below \( T_g \), the glass and the crystal have very similar heat capacities. For example, at 353 K the respective heat capacities are 25.5 J/g-atom K and 25.1 J/g-atom K, just slightly above the Dulong-Petit value of 3R. As the glass transition temperature is approached, the heat capacity of glass increases relative to the crystal. By 533 K, the glass is believed to have fully relaxed and achieved the heat capacity of the supercooled liquid state.

![Figure 6: Heat capacity measurements of the Pt_{57.3}Cu_{14.6}Ni_{15.3}P_{22.8} alloy. Liquid data points above 750 K were taken upon cooling from the liquid state. Crystal and Glass measurements were taken upon heating from initially crystalline or glassy states. The two liquid data points taken at 533 K and 548 K were obtained by heating the glass into its supercooled liquid region.](image)
As confirmation of the measurements accuracy, the heat capacity of the crystalline state between 620 K and 690 K was measured by both cooling from the liquid state and heating from the crystalline state. It was seen that these heat capacities varied by less than 1%. Extrapolated heat capacity curves for the liquid and crystal phases were produced using curve fits to equation 6 and equation 7. The fitting parameters for the crystal were $a = -0.0044622 \text{ J/g atom K}^2$, $b = 0.000011977 \text{ J/g atom K}^3$. The fitting parameters for the liquid were $c = 0.0056268 \text{ J/g atom K}^2$, and $d = 5764841.6 \text{ J K/g atom}$.

**4.1.2. Fusion temperature and Heat of Fusion**

The heat of fusion ($\Delta H_f$) is reported based upon DSC temperature scans at a rate of 30 K/min. It was found that $\Delta H_f = 11.4 \text{ kJ/g-atom}$. The fusion temperature, $T_f$, was assumed to equal $T_{\text{peak}}$ as discussed in Section 3.1, giving $T_f = 774.65 \text{ K}$. The entropy of fusion is calculated as $\Delta S_f = \frac{H_f}{T_f} = 14.7 \text{ J/g-atom K}$.

**4.2. Fragility**

**4.2.1. $T_g$ Measurements**

The glass transition was measured in DSC using heating rates between 2 K/min and 120 K/min, as described in Section 2.3. The results of these experiments are shown numerically in and graphically in Figure 7. It is observed that $T_g$ consistently increases with heating rate. The value of $\Delta T_g$ (which is the difference between $T_g$ onset and $T_g$ complete) seems to increase somewhat with heating rate, but overall remains relatively constant at around 20 °K. Some experiments did not yield values of $\Delta T_g$ because deviations from the ideal glass transition shape made accurate measurement of $T_g$ complete impossible.
Table 1: The glass transition temperature as measured in eleven different DSC scans at various heating rates. The onset of the glass transition, $T_g$ onset was recorded using the tangent method shown in Figure 3. $\Delta T_g$ is the difference between $T_g$ onset and $T_g$ complete.

<table>
<thead>
<tr>
<th>Heating Rate (K/min)</th>
<th>$T_g$ onset ($T_g$) (K)</th>
<th>$\Delta T_g$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>492</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>493</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>495</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>496</td>
<td>20.5</td>
</tr>
<tr>
<td>15</td>
<td>498.5</td>
<td>23</td>
</tr>
<tr>
<td>30</td>
<td>502</td>
<td>20</td>
</tr>
<tr>
<td>30</td>
<td>501</td>
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<td>503</td>
<td>Invalid</td>
</tr>
<tr>
<td>60</td>
<td>507</td>
<td>25</td>
</tr>
<tr>
<td>120</td>
<td>513</td>
<td>Invalid</td>
</tr>
<tr>
<td>120</td>
<td>510.5</td>
<td>Invalid</td>
</tr>
</tbody>
</table>
Figure 7: DSC heat flow curves of the glass transition region in Pt\textsubscript{57.3}Cu\textsubscript{14.6}Ni\textsubscript{5.3}P\textsubscript{22.8}, taken at 6 different heating rates. The onset temperature, \(T_g\), is identified and is seen to increase with heating rate. The curves have been shifted along the vertical axis for visibility.

4.3. Crystallization

4.3.1. Low Temperature Crystallization

Isothermal crystallization observations between 538 K and 568 K were performed as described in Section 2.5.2. Selected results from these low temperature studies are shown in Figure 8. From this figure, it can be clearly seen that reaction time decreases with increasing temperature. Furthermore, the shape of the curves is fairly consistent, except for the introduction of a small secondary crystallization event at 568 K.
Figure 8: Four isothermal heat flow curves, showing crystallization of the amorphous alloy after heating from the glassy state. It is clear that crystallization proceeds more rapidly at higher temperatures. Also, a small secondary crystallization event seems to be visible in the 568 K measurement.

The results of all isothermal measurements between 538 K and 568 K are compiled in Table 2. It is important to note that the crystallization enthalpies, $\Delta H$, are lower than would be expected for complete crystallization. After completion of the isothermal experiments, some of these samples were raised to higher temperatures, and were seen to release further heat, which suggests that incomplete crystallization occurs in the low temperature regime. Because of this, the 95% crystallization time $t_{95\%}$ refers to percentage of observed crystallization, not percentage of complete crystallization.
Table 2: Isothermal crystallization times and heat of crystallization, for temperatures below the nose of the TTT diagram. It should be noted that crystallization in this temperature range is incomplete. If longer time scales were allowed, it is likely that $\Delta H_f$ would be larger.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$t_{5%}$ (s)</th>
<th>$t_{50%}$ (s)</th>
<th>$t_{95%}$ (s)</th>
<th>$\Delta H_f$ (kJ/g atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>538</td>
<td>1712</td>
<td>2616</td>
<td>3839</td>
<td>4.1</td>
</tr>
<tr>
<td>548</td>
<td>386</td>
<td>759</td>
<td>1035</td>
<td>4.5</td>
</tr>
<tr>
<td>553</td>
<td>252</td>
<td>456.6</td>
<td>733</td>
<td>4.5</td>
</tr>
<tr>
<td>555</td>
<td>256</td>
<td>385</td>
<td>750</td>
<td>4.5</td>
</tr>
<tr>
<td>558</td>
<td>131</td>
<td>273</td>
<td>654</td>
<td>4.1</td>
</tr>
<tr>
<td>563</td>
<td>72.5</td>
<td>161</td>
<td>559</td>
<td>4.6</td>
</tr>
<tr>
<td>565</td>
<td>80</td>
<td>138</td>
<td>564</td>
<td>4.6</td>
</tr>
<tr>
<td>568</td>
<td>49</td>
<td>98.5</td>
<td>400</td>
<td>4.6</td>
</tr>
</tbody>
</table>

4.3.2. High Temperature Crystallization

Crystallization in the high temperature regime between 690 K and 750 K appears fundamentally different than in the lower temperatures previously presented. It is seen that the material will remain apparently unchanged for long periods of times until a sudden onset of crystallization will take place, after which crystallization will proceed rapidly.

lists the crystallization times and heat of crystallization at temperatures above the nose of the TTT diagram. It can be observed that $t_{5\%}$ varies greatly with temperature, but that the difference between $t_{95\%}$ and $t_{5\%}$ is relatively constant. This can be seen graphically in Figure 9, where the crystallization after onset for various temperatures between 690 K and 750 K is compared.
Table 3: Isothermal crystallization times and heat of crystallization, for temperatures above the
nose of the TTT diagram. Based on measurements of a 6.56 mg Pt alloy sample, encased in
$B_2O_3$ flux.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$t_{5%}$ (s)</th>
<th>$t_{50%}$ (s)</th>
<th>$t_{95%}$ (s)</th>
<th>$t_{95%}-t_{5%}$ (s)</th>
<th>$\Delta H_s$ (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>688</td>
<td>61.44</td>
<td>68.64</td>
<td>84.1</td>
<td>22.7</td>
<td>9.65</td>
</tr>
<tr>
<td>693</td>
<td>78.18</td>
<td>86.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>698</td>
<td>186.3</td>
<td>195.9</td>
<td>216.2</td>
<td>29.9</td>
<td>9.99</td>
</tr>
<tr>
<td>703</td>
<td>308.6</td>
<td>320.2</td>
<td>342.2</td>
<td>33.6</td>
<td>10.14</td>
</tr>
<tr>
<td>708</td>
<td>242.4</td>
<td>258.1</td>
<td>283.4</td>
<td>41.0</td>
<td>10.28</td>
</tr>
<tr>
<td>708</td>
<td>541.5</td>
<td>556.9</td>
<td>596.4</td>
<td>54.9</td>
<td>10.30</td>
</tr>
<tr>
<td>713</td>
<td>1545.6</td>
<td>1557.7</td>
<td>1589.6</td>
<td>44.0</td>
<td>10.31</td>
</tr>
<tr>
<td>713</td>
<td>635.5</td>
<td>649.5</td>
<td>682.3</td>
<td>46.8</td>
<td>10.16</td>
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<tr>
<td>718</td>
<td>1176.6</td>
<td>1188.7</td>
<td>1218.2</td>
<td>41.6</td>
<td>10.48</td>
</tr>
<tr>
<td>718</td>
<td>3289.5</td>
<td>3302.8</td>
<td>3341.3</td>
<td>51.8</td>
<td>9.88</td>
</tr>
<tr>
<td>723</td>
<td>9090.7</td>
<td>9107.0</td>
<td>9173.6</td>
<td>82.9</td>
<td>10.91</td>
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<tr>
<td>743</td>
<td>19894.7</td>
<td>20019.1</td>
<td>20396.9</td>
<td>502</td>
<td>11.15</td>
</tr>
</tbody>
</table>
Figure 9: High temperature crystallization isotherms. Time is measured relative to onset, so that crystallization at different temperatures can be compared. It is seen that $t_{95\%}-t_{5\%}$ varies far less than $t_{5\%}$.

The crystallization times were measured repeatedly at the single temperature of 703 K, in order to assess statistical variation of the crystallization onset time and heat of fusion. The time until onset was found to vary greatly, with an average of 179.9 s and a standard deviation of 77.6 s. After nucleation however, the crystallization proceeds very rapidly and consistently, with $t_{95\%}-t_{5\%}$ accounting for 34 s on average (less than 16% of the total crystallization time) and the standard deviation of $t_{95\%}-t_{5\%}$ at less than 1 s. This suggests a situation of random nucleation followed by rapid growth.
Table 4: Crystallization times at 703 K, taken during eight repetitions with a 4.5 mg Pt alloy sample encased in B$_2$O$_3$ flux.

<table>
<thead>
<tr>
<th>t$_{5%}$ (s)</th>
<th>t$_{50%}$ (s)</th>
<th>t$_{95%}$ (s)</th>
<th>t$<em>{95%-t</em>{5%}}$ (s)</th>
<th>ΔH$_i$ (J/g-atom K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102.96</td>
<td>114.54</td>
<td>138.54</td>
<td>35.58</td>
<td>77.44</td>
</tr>
<tr>
<td>146.76</td>
<td>157.20</td>
<td>180.66</td>
<td>33.90</td>
<td>77.92</td>
</tr>
<tr>
<td>120.72</td>
<td>130.56</td>
<td>154.38</td>
<td>33.66</td>
<td>76.84</td>
</tr>
<tr>
<td>242.40</td>
<td>252.60</td>
<td>276.42</td>
<td>34.02</td>
<td>76.96</td>
</tr>
<tr>
<td>320.94</td>
<td>330.24</td>
<td>355.50</td>
<td>34.56</td>
<td>77.10</td>
</tr>
<tr>
<td>237.84</td>
<td>247.50</td>
<td>271.74</td>
<td>33.90</td>
<td>76.89</td>
</tr>
<tr>
<td>144.54</td>
<td>154.62</td>
<td>178.20</td>
<td>33.66</td>
<td>76.79</td>
</tr>
<tr>
<td>122.88</td>
<td>134.22</td>
<td>156.18</td>
<td>33.30</td>
<td>74.79</td>
</tr>
</tbody>
</table>

Average  

<table>
<thead>
<tr>
<th>t$_{5%}$</th>
<th>t$_{50%}$</th>
<th>t$_{95%}$</th>
<th>t$<em>{95%-t</em>{5%}}$</th>
<th>ΔH$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>179.88</td>
<td>190.19</td>
<td>213.95</td>
<td>34.07</td>
<td>76.84</td>
</tr>
</tbody>
</table>

Standard Deviation  

<table>
<thead>
<tr>
<th>t$_{5%}$</th>
<th>t$_{50%}$</th>
<th>t$_{95%}$</th>
<th>t$<em>{95%-t</em>{5%}}$</th>
<th>ΔH$_i$</th>
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</thead>
<tbody>
<tr>
<td>77.62</td>
<td>77.05</td>
<td>77.68</td>
<td>0.71</td>
<td>0.91</td>
</tr>
</tbody>
</table>

At temperatures above 715 K, an interesting and unexpected phenomenon was observed. Shortly before the onset of primary nucleation and growth, a "precrystallization" signal was observed. This was characterized by a small exothermic event, lasting on the order of 1000 seconds. The magnitude of the exothermic signal varied greatly, reaching 0.2 mW at its largest, but typically being much smaller. For greater undercoolings (below 710 K) this precrystallization signal was not observed. Examples of this phenomenon are shown in Figure 10.
Figure 10: High temperature DSC crystallization isotherms, demonstrating the precrystallization event. a) This isotherm taken at 723 K demonstrated the largest precrystallization event, with the precrystallization accounting for 45% of total heat of crystallization. b) This isotherm also taken at 723 K shows a much smaller precrystallization event, near the limits of the DSC detection. c) This isotherm was taken at 743 K. d) This isotherm is typical of those taken below 467K, in that no observable precrystallization event can be seen.

4.3.3. TTT Diagram

Based upon isothermal crystallization results and glass transition measurements, the following Time-Temperature-Transformation (TTT) diagram was generated. A typical TTT “nose shape” is observed. While crystallization times in the nose itself were too rapid to be observed under DSC, data above the nose was collected by cooling from the liquid state (Section 4.3.2) and data below the nose was collected by heating from the glassy state (Section 4.3.1).
Figure 11: Time-Temperature-Transformation diagram for crystallization and relaxation of the Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ alloy. It should be noted that complete crystallization does not seem to occur at temperatures below 575 K, and percent crystallization is reported in terms of the crystallization achievable during laboratory timescales.
5. Discussion

5.1. Thermodynamics
As discussed in Section 3.1, the heat capacity measurements allow for calculation of basic thermodynamic functions such as enthalpy, entropy, and Gibbs free energy. The necessary values of $\Delta c_p$, $\Delta H_f$ and $T_f$ are presented in Section 4.1.

5.1.1. Enthalpy
By utilizing equation 2, a curve for $\Delta H^{f \rightarrow s}$ is produced. In order to assess this curves validity, it was compared with measured values of the crystallization enthalpy, $\Delta H_s$, as shown in Figure 12.

![Figure 12: Enthalpy curve ($\Delta H_{x,s}$) for Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$. The curve is based upon measurements of heat capacity and enthalpy of fusion. Data points represent values of $\Delta H_x$ obtained from isothermal and scanning temperature DSC experiments. Because temperature scans from low temperature display multiple crystallization peaks, the jogged crystallization path is used to represent where each peak occurs.](image)
The curve fit is relatively good, although certain data points deviate from the curve more than would be expected based on measurement error alone. At 703 K, the estimated standard deviation in ΔH was only 1.2% of the mean. Therefore, deviations of ΔH from the predicted curve are most likely real, which indicates that slightly different crystal products may be formed as a function of temperature. Measurements of ΔH obtained from isothermal experiments below the nose were not included in Figure 12 because crystallization in this temperature range is incomplete.

5.1.2. Gibbs Free Energy.
A curve for ΔG is produced by utilizing equation 5. This curve is displayed in Figure 13, where it is compared with the Gibbs free energy curves of various other glass forming metals. Compared with these other metals, the Gibbs free energy curve for Pt573Cu146Ni53P22.8 is much steeper with respect to temperature. The steepness of the Gibbs free curve is due to the relatively large entropy of fusion of 14.7 J/g-atom K. This indicates that the driving force for crystallization increases rapidly on undercooling. Steep ΔG curves generally lead to a large reduction in glass forming ability. The fact the Pt573Cu146Ni53P22.8 is still a reasonable glass former suggests that other factors are limiting the crystallization rate.
Figure 13: Gibbs free energy comparison for six BMG forming alloys. Critical cooling rates are shown in parenthesis.

5.1.3. Entropy.
A curve for $\Delta S^{*}$ is produced by utilizing equation 3. By extrapolating the entropy curve to low temperatures, an estimate of the Kauzmann temperature, $T_k$, can be obtained. The Kauzmann temperature is defined here as the isentropic temperature where both crystal and liquid have the same entropy. Through the Adam Gibbs theory of viscous flow, the Kauzmann temperature is closely related to the glass transition temperature. $T_k$ is found to lie between $T_g$ and $T_0$, as expected. $T_0$ is the VFT temperature where flow is predicted to become infinitely slow, and will be discussed more in Section 5.2. It should be noted that both the entropy of fusion, and the “frozen in” entropy of the glass for $\text{Pt}_{57.3}\text{Cu}_{14.6}\text{Ni}_{5.3}\text{P}_{22.8}$ are among the highest observed in BMG alloys.
Figure 14: Entropy Curve ($\Delta S_{\text{x,1}}$) for Pt$_{57.3}$Cu$_{14.6}$Ni$_{13.3}$P$_{22.8}$. The Kauzmann temperature, $T_k$ is defined where $\Delta S_{\text{x,1}} = 0$. The dashed line represents the "frozen in" entropy that remains after solidification of the glass.

5.2. Fragility

5.2.1. VFT Fitting

The fragility of the Pt$_{57.3}$Cu$_{14.6}$Ni$_{13.3}$P$_{22.8}$ alloy was assessed, using the methods discussed in Section 3.2.2. A nonlinear least squares fit to the expression

$$\ln(R) = \ln(R_0) \cdot \frac{D^* \cdot T_0}{T_g - T_0}$$

was performed, using the $T_g$-heating rate data presented in

to obtain estimates of the VFT parameters $D^*$ and $T_0$. The value of $R_0$ was assumed to have a value $10^{-14}$ s/K. The VFT parameters here calculated at $D^* = 16.4$ and $T_0 = 336.04$ K. The variable $T_g$ is defined as the glass transition temperature at a heating rate of 1 K/min. Based upon
the VFT fit, $T_g'$ has a predicted value of 487.7 K. The results of the VFT fit are plotted along with the original $T_g$ data in Figure 15.

![Figure 15: Modified Angell Plot for Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$. The independent variable (1/R) is plotted along the y-axis.](image)

Because viscosity tends to be a more useful parameter than relaxation time, the VFT data was used to generate a prediction of the alloy's viscosity. The viscosity prediction is obtained applying the VFT parameters of $D^*$ and $T_0$ to equation 8. As described in Section 3.2.1, the pre-exponent $\eta_0$ is assumed to equal $4 \times 10^{-5}$ Pa s. The resulting temperature dependence of viscosity is shown in Figure 16, along with the viscosity profiles of several other glass forming systems. Temperatures are reported relative to $T_g^*$, which is the temperature where viscosity equals $10^{12}$ Pa s. The value of $T_g^*$ is typically similar to $T_g'$ [26].
In this plot, we see that the fragility of $\text{Pt}_{57.3}\text{Cu}_{14.6}\text{Ni}_{5.3}\text{P}_{22.8}$ fits expectations for that of a moderate BMG. The VFT viscosity prediction is useful for determining processing conditions, such as minimum embossing time. Shroers has performed superplastic forming experiments with $\text{Pt}_{55.7}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ to replicate micron scale features [5]. Results from those experiments can be analyzed with the Hagan-Poiseuille equation to obtain a viscosity value of approximately $6.25\cdot 10^7$ Pa s at 543 K. This is very comparable with the VFT prediction for 543 K of $1.5\cdot 10^7$ Pa s.

### 5.2.2. Diffusion Rate Calculation

The Stokes Einstein equation is used to obtain estimates of the diffusion coefficient from the VFT viscosity prediction. Although this technique provides a single diffusion coefficient at each temperature, it should be kept in mind that each atomic species will actually possess a different coefficient. This difference can often be ignored, but it may become significant at temperatures below $1.3T_g$ [24][22]. Once obtained, the diffusion coefficient can be used to calculate diffusion...
lengths and time scales for homogenization. For a given diffusion coefficient and annealing time, the diffusion length is given by

\[ l = \sqrt{Dt} \]  

This equation was used to confirm that sufficient annealing times were applied before crystallization experiments. Before each high temperature isothermal crystallization experiment, the sample was annealed for at least 10 minutes at 983 K. Based on the VFT estimate of viscosity, the diffusion length for this temperature and period should be approximately 0.1 mm. This is on the same order of magnitude as the sample size (about 0.5 mm) and is larger than the observed microstructure. Therefore, it is believed that the annealing time was sufficient, especially since holding for an additional 50 minutes at 983 K did not produce observable changes in the crystallization process.

### 5.2.3. Thermodynamic Fragility [13]

In order to better understand the thermodynamic fragility of this material, the Tg-shift data was fit using an Adam-Gibbs model, instead of the VFT model. The equation used was

\[ \ln(\tau_x) = \ln(\tau_0) + \frac{C}{T(\Delta S_{l-x} + S_{c,x})} \]  

where the fit parameters are C, which is similar to an activation energy, and \( S_{c,x} \), which is the configuration entropy of the crystalline phase. The values of \( \Delta S_{l-x} \) and \( \tau_x \) were obtained from DSC scans, and are defined by equation 3 and equation 12, as discussed previously. The curve fit produced values of C = 204426 J/g atom and \( S_{c,x} = 4.874 \) J/g atom K.

Using these results, the Adam-Gibbs model predicts a Tg temperature of 354 K, at which configurational entropy would theoretically vanish and the viscosity would approach infinity. This value is approximately 18 °C higher predicted by the VFT equation, and suggests a divergence of the two approach at lower temperatures below Tg.
Figure 17: Entropy vs. temperature for Pt$_{55.7}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$, plotted relative to the crystalline state. The dashed line represents the level of zero configuration entropy according to fit of the Adam-Gibbs equation. The entropy of the liquid will should approach this temperature of $T_0=354$K. This is higher than the $T_0$ temperature obtained by fits to the VFT equation.

The configurational entropy of this alloy is compared with other bulk metallic glasses in Figure 18. The thermodynamic fragility can be roughly assessed by noting that stronger materials tend to have more shallow average slopes, and reach a point of zero configurational entropy at lower normalized temperatures. The order of the alloys with respect to thermodynamic fragility is similar to that seen for kinetic fragility in Figure 16.
Figure 18: Comparison of the configurational entropy for several BMG alloys. The number in parenthesis is that material's kinetic fragility parameter of $D^*$. The configurational entropy is normalized relative to its value at the melting point, and the temperature is normalized relative to the melting temperature. Data for other alloys from Bothra [31].

5.3. Crystallization

5.3.1. Low Temp Crystallization

For temperatures below the nose of the TTT diagram, the crystallization rate is highly temperature dependent, with lower temperatures resulting in slower crystallization. Application of the Johnson-Mehl-Avrami-Kolmogorov theory seems to work well in this temperature regime. Using this model, the two factors that control crystallization are the nucleation rate and the growth rate. However, some deviations due to transient nucleation may exist.

5.3.1.1. Johnson-Mehl-Avrami-Kolmogorov theory
The Johnson-Mehl-Avrami-Kolmogorov theory was useful at low temperatures. It assumes that nucleation sites are randomly distributed throughout the material, and that nuclei may grow from these sites until they impinge on each other. The Avrami equation allows the crystallized volume fraction to be calculated as

\[ x = 1 - \exp \left( -\frac{\pi}{3} u^3 I_{ss} t^n \right). \]  

(22)

if there is assumed to be a constant nucleation rate, \( I_{ss} \), and growth rate, \( u \) [34].

Because the Avrami equation is based upon statistical averages, equation 22 should only be expected to hold if the crystallization mechanism involves growth from a large number of nucleation sites. It should also be noted that the exponent \( n \) actually depends on sample geometry and growth mechanism. A value of 4 is assumed to be appropriate for this situation.

By taking the derivative of equation 22, the crystallization rate can be obtained as

\[ \frac{dx}{dt} = \frac{4\pi}{3} u^3 I_{ss} t^3 \exp \left[ -\frac{\pi}{3} u^3 I_{ss} t^4 \right]. \]  

(23)

Assuming that the crystallized volume and heat released are proportional, this curve can be compared directly with DSC isotherms such as in Figure 5. Equation 22 can also be used to model the TTT diagram, by rearranging to solve for time. The time to achieve a crystallization fraction of \( x \) becomes

\[ t = \left( \frac{-3\ln(1-x)}{\pi I_{ss} u^3} \right)^{1/4}, \]  

(24)

making it is easy to obtain values of \( t_{5\%} \), \( t_{50\%} \), and \( t_{95\%} \).

\[ \text{5.3.1.2. Nucleation Rate} \]

The steady state nucleation rate, \( I_{ss} \), was already addressed in Section 3.3.1. There it was shown that \( I_{ss} \) was given by equation 17. If nuclei are assumed to be spherical, this nucleation rate becomes

\[ I_{ss} = \frac{A_s}{\eta} \exp \left( \frac{-16\pi \gamma_d^3}{3k_B T \Delta G_p^2} \right), \]  

(25)

which Löffler et al. have applied to the Pd alloy system [38].
In some prior studies A has been treated as a fitting constant. However, Turnbull’s derivation of the nucleation rate allows A to be calculated from material properties. This is desirable, because it reduces the number of modifiable parameters. A can be approximated as

\[ A_v = \frac{N_v^0 k_b T}{3 \pi a_0^2} \]

if it is assumed that diffusion across the nucleus interface is given by the Stokes Einstein relation [37]. This model has been applied to the Pd_{40}Cu_{30}Ni_{10}P_{20} alloy by Nishiyama and Inoue [39]. In this formulation, \( N_v^0 \) represents the number of free molecules (atoms) per unit volume and \( a_0 \) is the average atomic spacing. For the Platinum alloy we estimate that \( a_0 = 3.1 \times 10^{-10} \text{ m} \) and \( N_v^0 = 96000 \text{ g-atom/m}^3 \). This is determined by taking a weighted average of the atomic radii, and comparing with results for the similar Palladium alloys. At a temperature 550 K, \( A_v \) will have a value of approximately \( 1.5 \times 10^{36} \text{ Pm}^3 \). Thus, with the Gibbs free energy difference and viscosity already characterized, the steady state nucleation rate for this alloy can be calculated purely as a function of temperature and interfacial energy.

### 5.3.1.3. Growth Rate

The growth of a crystal nucleus can be controlled by one of several growth mechanisms. In the low temperature range, the two most likely candidates are interfacial controlled growth, and diffusion controlled growth. Interfacial controlled growth is limited by transfer of atoms across the liquid-crystal interface, while diffusion controlled growth is limited by mass transport of excess impurity atoms away from the growth region. If a composition gradient exists across the growth interface, diffusion controlled growth is expected to dominate. Interfacial controlled growth may still occur though, if the surface of the growing crystal has a low accommodation factor for accepting new atoms [32].

It is very likely that interface controlled exists in the low temperature region. Low accommodation factors are associated with faceted growth, so this hypothesis is supported by micrographs that show long needle like precipitates (see Appendix Figure 10).

Accounting for an accommodation factor of \( f \), the expression for interface controlled growth is given as

\[ u = f \frac{k_b T}{3 \pi a_0^2 \eta} \left[ 1 - \exp \left( -\frac{N_v \Delta G_{\text{f-c}}}{k_b T} \right) \right] \]

(27)
Thus, the growth rate is dependent primarily on $T$, $\Delta G$, and $\eta$ [40]. According to work by Uhlmann, the accommodation factor can be approximated as $f = 0.2 \frac{(T_r - T)}{T_f}$ [42]. At a temperature of 555K this gives $f = 0.057$.

5.3.1.4. Homogenous Nucleation

In Section 3.3.2, the concept of heterogeneous nucleation was discussed. In most situations, heterogeneities are the primary site of crystal growth, and homogeneous nucleation is never observed. However, heterogeneous nucleation can be reduced by dividing samples into very small pieces, so that the statistical probability of each piece containing a heterogeneous nucleation site is reduced [3]. The very slow growth rate seen at low temperatures will have a similar effect by reducing the region of influence for each heterogeneity. This effective isolation is linked to small observed grain size, which is on the order of 0.1 $\mu$m. Therefore, it is possible that homogenous or near homogenous nucleation dominates during low temperature crystallization, and the homogenous nucleation rate of equation 25 is expected to apply.

5.3.1.5. Transient Nucleation

By adjusting the nucleation and growth rates in equation 22, it is possible to control the time scale for crystallization, but not the shape of the crystallization curve. The shape of the curve can be matched more accurately by adjusting the exponent $n$ to values greater than 4, but this does not represent the correct physics. Values of $n$ greater than 4 indicate that an increasing nucleation or growth rate exists, a situation that can be explained by invoking transient nucleation theory. It is proposed that crystallization onset is delayed by an initial transient nucleation period, during which a steady state distribution of sub-critical nuclei must be formed. Until this distribution is achieved, the homogenous nucleation rate would be much lower than predicted by equation 25, and limited growth would occur primarily from heterogeneous nucleation sites. The time scale of the transient nucleation period was given by equation 18. Because this equation is only accurate to an order of magnitude, an adjustment factor of $C_t$ is introduced.

$$\tau_{tr} = C_tr \cdot \frac{n^2a_0^2}{\sigma^*D}.$$  (28)

If heterogeneous nucleation is neglected and homogenous nucleation is assumed to be zero for times less than $\tau_{tr}$, then a new set of crystallization curves can be generated. The resulting improvement in the crystallization curve can be seen in Figure 19.
Figure 19: Comparison of three Avrami crystallization models with experimental results at 553 K.
Curve a) is a best fit of the peak time at 553 K assuming no transient period. Curve b) was is a
best fit of the peak height at 553 K, assuming no transient period. Curve c) is assumes a surface
energy of 0.197 J/m² and a transient period of 196 s. Curve d) is the experimentally observed
curve.

It can be seen that curve c) allows for a more satisfactory approximation of the crystallization
curve shape, by accounting for a transient nucleation period. Accurate understanding of
crystallization in this temperature regime is important, because it defines the time scales for
manufacturing processes such as superplastic forming.

To better understand the transient nucleation process and to assess its viability as a physical
phenomenon, a plot of transient nucleation time vs. temperature was generated using equation 28,
and assuming $C_u=7.9$ and $\gamma_{st}=0.086$ J/m². With the exception of the parameter $C_u$, each variable
in equation 28 can be explicitly calculated from knowledge of $\Delta G$, $\gamma_{st}$, $\eta$, and $V_m$. From Figure
20, it is seen that $\tau_n$ follows a nose shape similar to that of a TTT diagram. Within the low
temperature isothermal region, the transient nucleation time is in the very reasonable range of 10-
1000 seconds, and the time period becomes increasing long at lower temperatures.
Figure 20: A diagram of the transient time period in relation to temperature, assuming $C_w=7.9$ and $\gamma_{st}=0.086 \text{ J/m}^2$. The transient period displays a nose shape similar to that seen with transformation times on a TTT diagram. Between 620 K and 745 K the characteristic time to achieve steady state nucleation is less than 1 second.

There is concern however, that subcritical nuclei obtained while quenching past the nose will negate the existence of a transient nucleation period at lower temperatures. Though it may take 200 seconds to reach steady state conditions at 550 K, it should only take 1 second to obtain a steady state distribution of subcritical nuclei at 620 K. Because it would be difficult to bypass the nose without, this would seem to prohibit observation of a transient time at lower temperatures. Transient nucleation is not excluded from occurring at lower temperatures though, because the subcritical nuclei distribution function is highly temperature dependent. The nuclei distribution function obtained at high temperatures may contain less large nuclei than is necessary to support steady state conditions at lower temperatures.
This can be confirmed by plotting the theoretical Volmer distribution function at different temperatures. It is seen in Figure 21 that the critical nucleus size for 538 K is $n^* = 56$ atoms. The Volmer distribution requires that $6 \times 10^{20}$ nuclei/m$^2$ of this size exist during steady state nucleation at 538 K. At a temperature of 620 K, only $6 \times 10^{17}$ subcritical nuclei/m$^2$ with 56 atoms are present. Even if all nuclei with size greater than 56 atoms are considered, that amounts to just $6 \times 10^{18}$ nuclei/m$^2$. This indicates that a sample that has achieved steady state conditions at 620 K would still have an insufficient distribution of subcritical nuclei for steady state nucleation at 539 K, and a significant transient period may still be expected for samples quenched to temperatures below the nose of the TTT diagram.

![Volmer Distribution Functions](image)

Figure 21: Volmer distribution functions for subcritical nuclei, at four different temperatures.

---

The Volmer distribution function is given as $N_n = N \exp\left(-\frac{\Delta G_n}{k_B T}\right)$ for values of $n < n^*$, and 0 for $n > n^*$. Here $n$ is the number of atoms in a nucleus, $n^*$ is the number of atoms in a critically sized nucleus, $N_n$ is the number of nuclei that contain $n$ atoms. $\Delta G_n$ is the energy of nucleus with $n$ atoms, and $N$ is the total number of atoms in the system. This model is not strictly correct, and a more accurate distribution function would be given by the Becker-Döring distribution function. However, the results are qualitatively similar and the predicted values of $N_{n^*}$ are within a factor of 2 [35].
5.3.1.6. Modeling TTT data

By using a model of primarily homogenous nucleation and incorporating a transient nucleation period, the Time-Temperature-Transformation diagram was modeled computationally. A relatively good fit is obtained by setting the interfacial energy to 0.086 J/m² and assuming that steady state nucleation begins after a transient period of $8\tau_n$. A comparison of this model with the experimental TTT diagram is shown in Figure 22, and a direct comparison of the experimental and theoretical crystallization curves is shown in Figure 23.

Figure 22: Time-Temperature-Transformation diagram for low temperature isothermal crystallization. Circles represent experimental measurements and the lines represent the calculated fit based on Avrami theory.
Some interesting observations can be made from these figures.

First, there is significant deviation of $t_{95\%}$ from theory at temperatures greater than 552K. This is not unexpected, because the isothermal transformation curves suggest that a secondary crystallization peak is becoming active in this temperature regime. This second peak would be governed by different physical constraints.

Second, experimental values of $t_{5\%}$ occur slightly before theoretical predictions. This is most likely due to growth from heterogeneous nucleation sites that was not incorporated in the theoretical model. Support for this viewpoint comes from the measurements taken at 565 K and 555 K. These two experiments were performed at a later date using slightly different sample
material. It is possible that the sample material for these two tests contained less preexisting nucleation sites, and was therefore more adequately modeled by steady state homogenous nucleation.

Finally, the model appears to slightly overestimate crystallization times at high temperatures and underestimate crystallization times at low temperatures. This may be due to a change in crystallization mechanism. It may also be related to an overestimation of the transient period at high temperatures, which could occur if a significant preexisting nuclei distribution was established when the sample was originally quenched to the glassy state.

The value obtained for $\gamma_{sl}$ is on the order of magnitude that would be expected. Avarami style nucleation and growth models on PdCuNiP alloys have found comparable surface energies of 0.067 J/m$^2$ to 0.079 J/m$^2$ [38][34]. If anything, the interfacial energy of the platinum alloy is expected to be greater because of its larger entropy of fusion. According to interfacial models, a metal's solid-liquid interfacial energy is proportional to its entropy of fusion.$^6$ The interfacial energy is also very comparable with those seen in monatomic metals such as Cd, with $\gamma_{sl} = 0.058$ J/m$^2$ and Al with $\gamma_{sl} = 0.108$ J/m$^2$ [41].

It is useful to compare the expected crystallization times and relaxation times, because both parameters affect manufacturing processes like superplastic forming. For temperatures between 500 K and 550 K, the time scale for crystallization is roughly 4 orders of magnitude greater than the relaxation time. For example, at 540 K the 50% crystallization time is approximately 1700 s, but the projected relaxation time for the glass transition is just 0.1 s. This large difference in the timescales for relaxation and crystallization is what allows the material to be formed without crystallizing.

The extrapolation of the Avrami nucleation and growth model to higher temperatures is shown in Figure 24. This figure displays the theoretical TTT-diagram for Avarami type crystallization. It is seen from the nose of the TTT diagram that $t_{50\%}$ reaches a minimum of about 10 s at a temperature near 620 K. This value should be important in determining the maximum glass forming ability that can be achieved. However, the prediction vastly overestimates crystallization times at temperatures above the nose. This will be discussed in the following section on high temperature crystallization.

$^6$ One concern however, is that we have assumed a constant value for surface energy, whereas theoretical models of surface energy predict a temperature dependence.
5.3.2. High Temp Crystallization.

While the Avrami theory appears to be relevant at low temperatures, a different model is necessary for temperatures above the nose of the TTT diagram. The very large statistical scatter in crystallization onset, combined with the very consistent period for $t_{95\%}-t_{5\%}$, suggests that crystallization begins a random nucleation event, from which crystals grow rapidly throughout the sample.

The onset of nucleation is most likely due to heterogeneous nucleation. Using a surface energy of 0.086 J/m², the homogenous steady state nucleation rate at 703 K is expected to be $2 \times 10^{17}$ m$^3$/s$^1$. This means that homogenous nucleation can be safely ignored, with an expectation time to form one nucleus in a 5 mg sample at over $10^{26}$ s. Experiments at 703 K show an average onset time of just 177 s, which suggests that the nucleation energy barrier for heterogeneous nucleation is significantly smaller.
Many other questions about high temperature growth remain to be answered. At temperatures above 715K, the precrystallization event documented in Figure 10 suggests that initial crystal growth proceeds by a relatively slow process, and that this eventually triggers a more rapid growth mechanism. One possibility for the more rapid growth mechanism is eutectic growth, which has been documented in the Pd alloy [43]. However, micrographs of Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.5}$P$_{22.8}$ solidified from the liquid state have not revealed a eutectic microstructure, but have displayed long needlelike precipitates. The actual microstructure and growth mechanism probably varies significantly as a function of temperature and cooling rate. Evidence for this is provided by the presence of multiple crystallization peaks at 708 K in Figure 9. Further evidence for a temperature dependence of microstructure exists in the deviation of $\Delta H_\alpha$ from predicted $\Delta H^{\text{ex}}$ curves (seen in Figure 12).
6. Conclusion

The thermodynamics, kinetics, and crystallization of Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ were studied using differential scanning calorimetry (DSC).

From a thermodynamic perspective, the entropy of fusion for this alloy is remarkably high. This leads to a high driving force for crystallization, and explains why the GFA of Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ is inferior to that of PdCuNiP alloys. In terms of kinetics, Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ displays the characteristics of a typical BMG. The estimated value of D$^*$=16.4 is neither remarkably high nor low. Its viscosity and diffusion rates appear to be similar to those of PdCuNiP alloys. The alloy is also typical of other BMG's using the Adam-Gibbs model for thermodynamic fragility.

At temperatures below the nose of the TTT diagram, the crystallization of Pt$_{57.3}$Cu$_{14.6}$Ni$_{5.3}$P$_{22.8}$ appears to be characterized by classical homogeneous nucleation and interfacial controlled growth. This results in a very fine microstructure with prismatic precipitates. A delay in the onset of crystallization may occur because of a transient nucleation period. The Avarami equation was used to model the TTT-diagram and crystallization curves in this temperature range. The best fit was obtained using a solid-liquid interfacial energy of 0.086 J/m$^2$, which is a reasonable value and is slightly higher than believed to exist for most alloys.

At temperatures above the nose of the TTT diagram, the crystallization process is significantly different. The onset of nucleation displays significant statistical scatter. Crystallization appears to be initiated by a random heterogeneous nucleation event, and crystal growth proceeds rapidly throughout the sample. The actual nucleation and growth mechanism is undetermined, and is likely to depend upon the exact temperature of transformation.
7. Appendix

7.1. Microstructures and X Ray Diffraction
This section consists of experimental studies on the Pt$_{57.3}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.8}$ alloy conducted by Ludi Shadowspeaker. Glassy samples were annealed at various temperatures below the nose of the TTT diagram using a differential scanning calorimeter. After the samples had partially crystallized, the resulting microstructures were viewed using transmission electron microscopy and x-ray diffraction was performed in order to identify the resultant crystal products.

![TTT Diagram](image)

Figure 1 TTT Diagram for Pt$_{57.3}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.8}$, completed by L. Shadowspeaker. The open circles represent the onset, the half filled circles represent the peak, and the filled circles represent the end of the exothermic DSC event that is characteristic of crystallization. At temperatures above 560 two crystallization events can be observed. (Inset is on a log scale)
Figure 2: XRD spectra after annealing at 550K for time intervals between 360 s and 3000 s. This data indicates that the order of formation is first P$_2$Pt$_5$ (♦) and CuP$_2$ (●), then NiP$_2$ (■), and lastly NiPt (□).

Figure 3: XRD spectra after annealing at 565 K for 600 and 7200 seconds. This data indicates that P$_2$Pt$_5$ and CuP$_2$ form first, followed by NiP$_2$, then Cu$_2$P$_7$. 
Figure 4: Microstructure after annealing for 600 s at 565 K.
Figure 5: Microstructure after annealing for 7200 s at 565 K.
Figure 6: Microstructure after annealing for 7200 s at 565 K. This micrograph shows a P$_2$Pt$_3$ precipitate with in a predominantly nanocrystalline Cu$_2$P matrix.
Figure 7: A constant heating rate thermal scan at 0.333 K/s (20 K/min). Indicates the glass transition onset (T_g), Crystalization onset (T_x), and three major crystalization peaks at 583 K, 592 K, and 668 K.

Figure 8: X-ray diffraction spectra, obtained after heating glassy samples at 0.333K/s to different maximum temperatures, and rapidly quenching to room temperature. It is seen that the degree of crystallinity increases in relation to the maximum temperature that is reached.
Figure 9: MXRD profile of the glassy sample which is heated to 583 K and rapidly quenched. This temperature is approximately the maximum of the first exothermic crystallization peak observed at 0.333 K/s. Based upon the labeled peaks, it appears that $P_2Pt_5$ and $CuP_2$ are the initial crystalline products that form upon heating.
Figure 10: Microstructure for sample which was heated to 583 K and rapidly quenched. The long needle-like crystal structures have been identified as CuP$_2$ and P$_2$Pt$_5$. The surrounding matrix is likely still glassy.
Figure 11: MXRD profile of the glassy sample which is heated to 650 K and rapidly quenched. This temperature is between the second and third exothermic crystallization peaks. In addition to \( P_2Pt_5 \) and \( CuP_2 \), a signal appears that corresponds to the \( Ni_2P \) crystal structure. The \( Ni_2P \) microstructure was also detected using NBD.
Figure 12: Micrograph of the glassy sample which is heated to 650 K and rapidly quenched. This temperature is between the second and third exothermic crystallization peaks. In addition to $P_2Pt_3$ and $CuP_2$, a signal appears that corresponds to the $Ni_2P$ crystal structure. Some of the remaining glass matrix is still visible.
Figure 13: MXRD profile for the sample which was heated to 700K and then quenched. This temperature exceed the highest observed exothermic peak. In addition to P$_2$Pt$_5$, CuP$_2$, and NiP$_2$, there is a signal corresponding to the P$_2$Pt crystal structure. This differs from the final crystallization product of Cu$_2$P$_7$ that occurred at low temperature.

7.2. Discussion of Crystal Products.

Several studies have been completed on the microstructure and crystal products of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ and Pd$_{23}$Cu$_{27}$Ni$_{10}$P$_{20}$ alloys. The constant heating rate curves for these alloys look remarkably similar to that of Pt$_{57.5}$Cu$_{14.7}$Ni$_{53}$P$_{22.5}$, except that a second crystallization peak is somewhat less prominent in PdNiCuP alloys [43].

Löffler, Schroers, and Johnson have shown that Cu$_3$Pd dendrites form at temperatures of 700 K (above the nose of the TTT diagram). They also detect this phase at lower temperatures. In addition to Cu$_3$Pd, phosphides of Ni and Pd, and Pd$_2$Ni$_3$P are detected [38]. This crystallization scheme is remarkably different than in Pt$_{57.5}$Cu$_{14.6}$Ni$_{53}$P$_{22.8}$, where phosphorus compounds dominate the early phase formation, and PtCu structures are not detected. PtNi structures are detected in Pt$_{57.3}$Cu$_{14.6}$Ni$_{53}$P$_{22.8}$, but only as one of the last crystal structures to occur.

At high temperatures, Schroers and Johnson determined that a eutectic microstructure formed in PdCuNiP [43]. Micrographs of Pt$_{57.5}$Cu$_{14.6}$Ni$_{53}$P$_{22.8}$ samples that were crystallized during continuous cooling have been obtained, but are not displayed here. They have not displayed a eutectic structure, but rather a course needle-like structure.
8. Bibliography


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