Combinatorial temperature resistance sensors for the analysis of phase transformations demonstrated for metallic glasses

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\textbf{A B S T R A C T}

We describe a sensor for measuring the electrical resistance of a conducting thin-film material as a function of temperature and composition. The sensor has excellent sensitivity and can be used at temperatures as high as the melting temperature of the material of interest. The sensor is fabricated by applying a simple lift-off process to a thin film. By combining combinatorial sputtering to fabricate composition spreads with arrays of sensors, the phase transformation behavior of complex alloys can be mapped. We demonstrate this capabilities by using the sensor to determine the glass transition and crystallization temperatures of several PdSiCu-based metallic glasses. We found that in two glass-forming systems, PdCuSi and NiZr, the ratio of the resistance of the crystallized to as-deposited material is correlated with the glass-forming ability. The ability to readily determine glass forming ability, suggests that the sensor is a powerful tool for measuring the glass-forming ability in a high-throughput manner over large compositional spaces. © 2018 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The electrical resistivity of a metal depends sensitively on its microstructure and phase composition. Changes in microstructure and phase composition with temperature are readily revealed by measuring the resistivity of the material as a function of temperature. This technique has long been applied to investigate phase transformations in a broad range of materials, including shape memory alloys \cite{1,2}, metallic glasses \cite{3–5}, materials for phase change memories \cite{6,7}, and superconductors \cite{8}.

Conventional temperature-dependent resistance measurements are usually performed on bulk samples, typically one sample at a time. This approach is effective at determining transformation temperatures for a specific alloy, but ineffective in exploring larger compositional ranges as is required in the materials discovery process. Combinatorial synthesis of materials combined with high-throughput characterization offers a powerful methodology for accelerated materials science and discovery, typically at a fraction of the cost of conventional strategies \cite{8–10}. Deposition of thin-film composition spreads using magnetron sputtering is a convenient method for combinatorial synthesis. Unfortunately, simple methods for measuring the resistivity of a thin film as a function of temperature are not readily available \cite{11}. Recently, Ludwig and colleagues developed a micromachined hotplate sensor that can measure resistance as a function of temperature for combinatorial research on shape memory alloys \cite{12–14}. While this sensor performs well, its widespread use is hampered by a costly and complicated fabrication process, and limited temperature uniformity \cite{12}.

Here, we present a simple sensor that is capable of measuring the resistance of thin-film samples as a function of temperature and composition with excellent temperature uniformity, and that is both inexpensive and easy to fabricate. The key to the simplicity of the sensor lies in the fact that the temperature of the sensors is determined indirectly from the power supplied to the sensor instead of measuring the temperature directly with a thermocouple or thermistor. This approach allows a significant simplification of
the design, fabrication, and application of the sensors. Detailed simulations of the sensor geometry using finite element modeling were performed to ensure optimum temperature uniformity. Arrays of sensors are readily fabricated to explore the behavior of alloy systems using composition spreads. We use this resistance-temperature sensor (RT sensor) to observe the glass transition and crystallization of several PdSiCu-based metallic glasses. We find that the ratio of the resistance of crystallized to as-deposited material is correlated with the glass-forming ability for both PdCuSi and NiZr-based alloys. Thus, the RT sensor may provide an avenue for effective screening of the glass-forming ability of large compositional regions, which are required in metallic glass research [15].

2. Experimental

2.1. Sensor design and fabrication

Fig. 1(a) and (b) illustrate the conceptual design of the RT sensor: a heating element in a four-point measurement configuration patterned on a fused quartz substrate. The heating element consists of a 90 µm wide strip that forms several concentric circles with a 10 µm wide gap in between. The heating element is fabricated out of the material of interest, which serves the dual purpose of heating element/conductor and sample. During the measurement, a current is sent through the sample, which heats up by Joule heating. When the steady-state temperature is reached, the voltage drop along one single circular arc defined by the voltage probes is measured and recorded together with the corresponding current. The resistance of the arc is then calculated using Ohm’s law. If desired, the resistivity can then be calculated from the film thickness and the dimensions of the arc.

The thickness of the sample/heating element is typically on the order of hundreds of nanometers, while the thickness of the fused quartz substrate is approximately 500 µm. Consequently, the thermal mass of the sample is negligible compared to that of the substrate. In the steady state, the temperature of the sensor is determined only by the balance between input power and heat loss to the environment. Because virtually all heat loss occurs via the fused quartz substrate, there is a one-to-one relationship between input power and temperature that is for all practical purposes independent of the nature of the sample and that is readily calibrated for a given sensor geometry. Details of the calibration procedure are discussed in a later section. Using input power as an indirect
measure for temperature results in a substantial simplification in both the design and fabrication process of the sensor since no separate temperature gauge needs to be incorporated in the sensor.

The sensor was designed based on extensive finite element simulations to achieve optimum temperature uniformity across the area of the material that is being evaluated, i.e., the circular arc between the voltage probes. The voltage probes are much narrower than the current probes to make the sample area as axisymmetric as possible. All the corners of the heating element are filleted to minimize undesirable current crowding and resultant local heating. The positions of the voltage and current pads were carefully arranged to make the temperature distribution as symmetric as possible. The width of the heating element and the gap between concentric arcs were selected based on finite element simulations to ensure good temperature uniformity and manufacturability.

Fig. 1(c) shows a partial cross-section of the sensor. The device consists of three parts: the substrate, the sample/heating element, and a capping layer. Fused quartz is selected as substrate material for several reasons. Fused quartz is readily heated to temperatures as high as 1200 °C without adverse effect, making the sensor capable of high-temperature applications. Fused quartz has a very small thermal expansion coefficient combined with modest stiffness, which makes it resistant to thermal shock and allows steep temperature gradients without fracture. Finally, the relatively low thermal conductivity of fused quartz results in steep temperature gradients outside of the heated zone, shielding adjacent samples from temperature excursions during measurements.

The sensors are fabricated using a conventional lift-off process that is both straightforward and inexpensive. First, 1.5 μm of photoresist (Shipley, 1813, Dow) is coated on a 4-inch fused quartz wafer. The photoresist is exposed (h-line with 405 nm, 120 mJ/cm² dose) through a mask with the desired pattern and developed in CD30 developer for 1 min using standard lithography procedures. The material of interest is then deposited using a physical vapor deposition technique such as evaporation or magnetron sputtering. After deposition, the material is patterned by removing the photoresist in acetone under sonication (Ultra Clean Equipment Inc.) and cleaned in deionized water. In a final step, the material of interest is coated with 100 nm of SiNx using plasma enhanced chemical vapor deposition (Nexx Cirrus 150) to prevent oxidation at elevated temperatures if measurements are performed under atmospheric conditions. If measurements are performed in vacuum, the SiNx coating may not be necessary depending on the material of interest and the fabrication process is further simplified. Fig. 1(d) and (e) show optical images of an as-fabricated sensor and an array of sensors, respectively. The array contains 120 sensors with a spacing of 7 mm arranged on a 4-inch wafer. If the material of interest is not coated with SiNx, RT measurements can be made directly. If the material is coated, an extra mask and etch step may be required to make it possible to contact the pads of the sensor. Given the limited number of measurements in this study, electrical contact with the pads was made possible by scratching the pads with a stylus.

### 2.2. Electrical measurements

Resistance-temperature measurements are performed using a custom-built automated system that probes one sensor at a time (Fig. 2). A four-point probe head is mounted on a vertical piezo-stage (AG-LS25V6, Newport Corp.). The substrate is placed on a 4-inch diameter, 0.25-inch-thick borosilicate glass disc carried by two horizontal translation stages (T-LSM100A, Zaber Technologies Inc.). The motion resolution of the horizontal stages and the vertical stage is 0.05 μm. Two digital microscopes are installed on the base of the system to assist with aligning the probe to the sensor pads and to monitor the sensor. The measurement system is vacuum compatible, making it possible to perform experiments in a vacuum environment.

The current applied to the sensor is generated using a programmable power supply (Rigol DP832a). The voltage across the voltage leads of the sensor is measured using a Keithley 2000 multimeter, while the precise current is obtained from the voltage drop across a 10 Ω precision resistor (Vishay VPR221Z) in series with the sensor using a Fluke 8842 A multimeter. The power supplied to the sensor is determined from the product of the current and the voltage drop across the sensor. The motion of the automated probe and the resistance-temperature measurement are controlled using a LabVIEW program.

### 2.3. Finite element simulations

The temperature distribution in the sensor was determined for a broad range of conditions by solving the coupled heat transfer and Joule heating problem using a commercial finite-element code (COMSOL Multiphysics®). The temperature of the ambient and the edge of the 4-inch substrate were set at room temperature (293.15 K). Both heat loss by natural convection (heat transfer coefficient -5 W/m² K) and radiation were taken into account, but not loss by conduction through air given the low thermal conductivity of air (0.026 W/m-K) [16,17]. The parameters used in the simulations are listed in Table 1. Fig. 3(a) illustrates the steady-state...
temperature distribution in the sensor at a temperature < 1200 K. The temperature distribution is approximately axisymmetric, consistent with the intentions of the design. As a result, the temperature within the sample area, i.e., the circular arc between the voltage probes is very uniform. To quantitatively evaluate the temperature uniformity, we define the relative temperature non-uniformity, \( \delta \), as

\[
\delta = \frac{1}{T_0 - T_a} \frac{1}{S} \int (T_0 - T) dS
\]

where \( T_0 \) is the average temperature across the sample area, \( T_a \) represents the ambient temperature, \( T \) is the temperature at a specific position, and \( S \) is the sample area [18]. The temperature non-uniformity increases nearly linearly with increasing temperature (Fig. 3(b)), but is better than 1% even at the highest temperature.

While it is easy to maintain a constant ambient temperature for the sensor to ensure the power-temperature relationship of the sensor does not change, there is one factor that can have an impact on this relationship — the emissivity of the sample surface. To estimate the effect of radiation loss from the sample surface, we performed simulations using the parameters listed in Table 1, except that the emissivity of the sample was varied from 0.01 to 0.05, typical values for physical vapor deposited metallic films [21,22]. Since radiation heat loss rises with the fourth power of the temperature, the effect of radiative losses from the sample increases rapidly with increasing temperature (Fig 3(c)). Even so, the sensor temperature changes less than 3 K over this emissivity range at elevated temperature (~1200 K), which should be negligible for most screening applications.

### 2.4 Temperature calibration

Before the sensor can be used, the relationship between input power and temperature needs to be calibrated. Since this relationship is independent of the nature of the sample, we use a 200 nm platinum film as sample material for the calibration because of its oxidation resistance. Prior to the calibration, the sensor is heated to 1300 K for more than 20 s to stabilize the microstructure of the platinum. The relationship between input power and temperature is then determined in a two-step process. First, the resistance of the platinum is calibrated to temperature. The sensor is placed on a hotplate and heated from ambient temperature (~293 K) to 640 K in 20 K increments. During this process, the resistance of the platinum sample is measured using a Keithley 2000 multimeter in a four-terminal configuration. This step yields the temperature-resistance relationship for the platinum film. In the second step, the resistance of the same sensor is measured as a function of input power. In a typical measurement, the resistance of the platinum stabilizes within a few seconds from the moment the power is applied, indicating that a steady-state temperature is reached almost immediately. The resistance of the platinum sensor serves as the link between input power and temperature, and makes it possible to determine the steady-state power-temperature relationship. Fig. 4 shows the correlation between temperature, resistance, and heating power. As expected this relationship is very nearly linear with a very slight curvature as a result of radiation losses. The relationship is fitted with the following equation,

\[
P = h(T_0 - T_a) + B(T_0^4 - T_a^4),
\]

which is the steady-state heat balance for the sensor assuming conductive and convective losses (linear term), as well as radiative losses (quartic term). In this expression, \( P \) is the power supplied to the sensor, \( T_0 \) is the temperature of the sample area, and \( T_a \) is the ambient temperature; \( h \) and \( B \) are used as fitting parameters. This expression fits the data very well and can be used over a broad temperature range.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical conductivity (S/m)</th>
<th>Thermal conductivity (W/m·K)</th>
<th>Heat capacity (J/kg·K)</th>
<th>Emissivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused quartz</td>
<td>( 1 \times 10^{-14} )</td>
<td>1.4</td>
<td>730</td>
<td>0.7</td>
</tr>
<tr>
<td>SiN_x</td>
<td>( 1 \times 10^{-10} )</td>
<td>3.2</td>
<td>700</td>
<td>0.18</td>
</tr>
<tr>
<td>Platinum</td>
<td>( 8.9 \times 10^8 )</td>
<td>71.6</td>
<td>133</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig. 3. Finite element method (FEM) simulation result of RT sensor. (a) Color-coded temperature distribution under stationary condition. The color bar is in Kelvin; (b) Relative temperature non-uniformity at various temperature; (c) Temperature change due to sample emissivity variation. \( \Delta T \) represents the absolute change in average temperature of the sensor as the emissivity of the sample varies from 0.01 to 0.05. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
2.5. PdSiCu deposition and characterization

PdSiCu thin-film samples were deposited on fused quartz wafers with patterned photoresist by means of DC magnetron sputtering from elemental targets (50.8 mm diameter, Kurt J. Lesker Company) using the process parameters listed in Table 2. The depositions were performed at an argon working pressure of 5 mTorr in a high-vacuum system (ATC, 1800, AJA Int.) with a base pressure better than $5 \times 10^{-7}$ Torr. The Pd$_{79.5}$Si$_{16.5}$Cu$_4$, Pd$_{77.5}$Si$_{16.5}$Cu$_6$, and Pd$_{71.5}$Si$_{16.5}$Cu$_{12}$ compositions were selected as examples of good glass formers with known glass transition temperatures [23–25]; in addition, samples with compositions of Pd$_{80}$Si$_{14.3}$Cu$_{5.7}$ and Pd$_{64.5}$Si$_{16.5}$Cu$_{19}$ were also synthesized as part of a composition spread. After deposition, lift off was performed by soaking the substrates in an acetone bath under sonication (Ultra Clean Equipment Inc.) to define the sensors. Finally, all samples were capped with a 100 nm SiNx film using a PECVD process in a Nexx Cirrus 150 system.

The compositions of the samples were determined using an energy-dispersive X-ray spectrometer (EDS) installed in a field emission scanning electron microscope (Zeiss Supra 55 V P). The measurement error of the EDS is approximately 0.5 at%. The critical cooling rates of the selected PdSiCu samples are much lower than the effective cooling rate during sputter deposition (over $10^9$ K/s) [26], resulting in amorphous as-deposited samples. Several samples were also analyzed using nanocalorimetry to determine their glass transition temperatures. Details of the operating principles and measurement procedures can be found elsewhere [19,27,28]. The nominal heating rate during the calorimetry measurements was approximately 5000 K/s. Optical images were taken using a Nikon DXM1200 CCD camera.

3. Results

Fig. 5 (a) shows the temperature-resistance curves for the Pd$_{80}$Si$_{14.3}$Cu$_{5.7}$ sample. The resistance varies slightly with increasing temperature until a sudden drop occurs when the sample crystallizes. Fig. 5 (b) shows a magnification of the low-temperature section before the crystallization process. Evidently, the resistance goes through three distinct stages: Initially, the resistance increases with temperature. Starting at approximately 450 K, the resistance of the sample decreases, which we attribute to low-temperature structural relaxation of the glass. Right before crystallization, the resistance has a brief but distinct increase that starts at approximately 620 K. This type of behavior has been attributed to the glass transition [5]. As the temperature increases further, the sample crystallizes and the resistance drops drastically because of the long-range order of the crystalline phase. The break in the resistance curve, e.g., the sudden change in slope of the resistance curve, prior to a sharp and significant drop in resistance is a typical feature of resistance curves of metallic glasses that may be used to measure $T_g$. On cooling, the resistance decreases monotonically, a behavior typical for a crystalline alloy. Subsequent temperature cycles overlap (red curve) with the cooling curve, verifying that the sample was completely crystalline after the first scan. We further note that the lack of hysteresis on temperature cycling also indicates that the time constant for the sensor to reach the steady-state is small enough to not affect the measurements.

![Fig. 4. Temperature calibration of RT sensor. (a) Temperature as a function of resistance; (b) Resistance as a function of heating power; (c) Heating power as a function of resistance. Experimental data calibrated and uncalibrated to temperature are indicated with blue dots and black triangle marks, respectively. Red lines represent the corresponding curve fits. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)](image_url)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sputtering power (Pd/Si/Cu, Watts)</th>
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<tbody>
<tr>
<td>Pd$<em>{71}$Si$</em>{16.5}$Cu$_{12}$</td>
<td>34</td>
</tr>
<tr>
<td>Pd$<em>{70}$Si$</em>{16.5}$Cu$_{4}$</td>
<td>37</td>
</tr>
<tr>
<td>Pd$<em>{72}$Si$</em>{16.5}$Cu$_{6}$</td>
<td>37</td>
</tr>
<tr>
<td>Pd$<em>{80}$Si$</em>{14.3}$Cu$_{5.7}$</td>
<td>37</td>
</tr>
<tr>
<td>Pd$<em>{64.5}$Si$</em>{16.5}$Cu$_{19}$</td>
<td>37</td>
</tr>
</tbody>
</table>

* Two samples from a composition spread deposited using a single set of process parameters.
Fig. 5. Typical temperature-dependent resistance curves from two successive scans for Pd$_{80}$Si$_{14.3}$Cu$_{5.7}$ (a) and Pd$_{77.5}$Si$_{16.5}$Cu$_{6}$ (e) measured at a heating/cooling rate of 28 K/min. The resistances are normalized with the room temperature resistances of the as-deposited samples. (b) Magnified view of the sections demarcated by the dashed line in (a); Optical microscopy images of an as-deposited (c) and crystallized (d) Pd$_{85.7}$Si$_{1.7}$Cu$_{12.6}$ alloy.
even when one measurement is performed immediately after the other. Fig. 5c and d show optical micrographs of an as-deposited sample and a crystalline sample. The surface of the as-deposited sample is entirely featureless (Fig. 5(c)), while the crystalline sample shows a distinct grain structure (Fig. 5(d)) with a grain size on the order of tens of microns. To confirm that the slight decrease in resistance in the low-temperature range is indeed caused by structural relaxation of the metallic glass, we performed resistance scans on a Pd$_{77.5}$Si$_{16.5}$Cu$_{6}$ sample, shown in Fig. 5(e), in which the sample was not allowed to crystallize. As before, the resistance initially increases with temperature and then starts to decrease at approximately 450 K. On cooling, the resistance does not follow the heating curve, but instead decreases at a rate equal to the initial rate on heating resulting in a permanent decrease of the resistance of the sample at room temperature. This behavior demonstrates that the slight decrease in resistance in the low-temperature range is caused by an irreversible change in the structure of the sample, i.e., by a structural relaxation process that has a direct impact on macroscopic physical properties such as resistivity or viscosity [29].

To validate the accuracy of the sensor, we performed additional resistance-temperature measurements on Pd$_{78.5}$Si$_{16.5}$Cu$_{4.0}$, Pd$_{77.5}$Si$_{16.5}$Cu$_{6.0}$, and Pd$_{71.5}$Si$_{16.5}$Cu$_{12.0}$ samples, which are good glass formers with known glass transition ($T_g$) and crystallization ($T_x$) temperatures [23–25]. Nano-calorimetry was then employed to verify the findings from the resistance measurements. The resistance-temperature curves and heat-flow curves are depicted in Fig. 6 and results collected from the curves are listed in Table 3. In general, the $T_g$ and $T_x$ results obtained from the RT sensors are in good agreement with the values reported in the literature, while the nanocalorimetry results are systematically higher because of the orders-of-magnitude higher heating rate used in these measurements and the finite kinetics of the phase transitions. We note that any residual stresses in the thin-film samples or any impurities incorporated in the samples as a result of the deposition process may affect the precise values of the glass transition and crystallization temperatures compared to the bulk values. Comparison of the data in Table 3 shows that any such effects are quite small, especially compared to the effect of the heating rate during the measurement. In fact, the shift in the crystallization temperature of the Pd$_{72.5}$Si$_{16.5}$Cu$_{6}$ is in good agreement with the range of activation energies obtained by Chen et al. [30].

4. Discussion

The ability to measure $T_g$ and $T_x$ in a potential high-throughput manner is very powerful. The knowledge of $T_g$ and $T_x$ allows estimation of the two most important processing-related characteristics: the glass-forming ability [31] and thermoplastic forming ability [32]. Using the RT sensors, $T_g$ and $T_x$ of large ranges of metallic glass-forming compositions can be readily quantified. To the best of our knowledge, this is the first report of the detection of glass transition temperatures in thin-film samples using electrical resistance measurement. The glass transition does not result in a very pronounced change in structure of a material [33] and can therefore be quite difficult to detect, especially for nano-scale samples. The most widely used technique for studying the glass transition is differential scanning calorimetry (DSC). For nano-scale samples, micromachined calorimetry sensors are necessary. While these calorimetry sensors can provide a wealth of information on the thermodynamics and kinetics of phase transformations in nano-scale samples [27,34–36], they are quite fragile, expensive and difficult to fabricate. Compared to nano-calorimetry, electrical resistance measurements are straightforward to implement with high resolution and accuracy, and are cost-effective for screening large numbers of samples.

If the RT response of a material can be correlated with its glass-forming ability, the resistance sensor arrays can also be used in combination with composition spreads to identify compositions of good glass formers. Fig. 7(a) shows the normalized resistance-temperature curves for several PdSiCu alloys with known critical cooling rate [23,37,38]. Since the curves are normalized by the room-temperature resistance of the as-deposited sample, the ratio between the resistance of the as-deposited ($R_a$) and the crystallized
Table 3
Experimental glass transition and crystallization temperatures for several PdSiCu alloys. The average heating rate for nano-calorimetry experiments, resistance-temperature experiments, and references were 300,000 K/min, 35 K/min, and 20 K/min, respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Parameter</th>
<th>Nano-calorimetry</th>
<th>Reference [23–25]</th>
<th>This work</th>
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<tr>
<td>Pd64.5Si16.5Cu19</td>
<td>$T_g$ (K)</td>
<td>n/a</td>
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<td>603 ± 5</td>
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<tr>
<td></td>
<td>$T_x$ (K)</td>
<td>n/a</td>
<td>n/a</td>
<td>651 ± 5</td>
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<tr>
<td>Pd71Si16.5Cu12</td>
<td>$T_g$ (K)</td>
<td>678 ± 10</td>
<td>652</td>
<td></td>
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<tr>
<td></td>
<td>$T_x$ (K)</td>
<td>760 ± 10</td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>Pd77.5Si16.5Cu6</td>
<td>$T_g$ (K)</td>
<td>608 ± 10</td>
<td>637</td>
<td></td>
</tr>
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<td></td>
<td>$T_x$ (K)</td>
<td>771 ± 10</td>
<td>678</td>
<td></td>
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<tr>
<td>Pd79Si16.5Cu4</td>
<td>$T_g$ (K)</td>
<td>656 ± 10</td>
<td>635</td>
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<td></td>
<td>$T_x$ (K)</td>
<td>769 ± 10</td>
<td>675</td>
<td></td>
</tr>
<tr>
<td>Pd80Si14.3Cu5.7</td>
<td>$T_g$ (K)</td>
<td>n/a</td>
<td>n/a</td>
<td>611 ± 5</td>
</tr>
<tr>
<td></td>
<td>$T_x$ (K)</td>
<td>n/a</td>
<td>n/a</td>
<td>676 ± 5</td>
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</tbody>
</table>

$R_C$ sample can be obtained from the terminal points of the cooling curves, which are shown in the inset. Fig. 7(b) shows the critical cooling rate of the samples as a function of the resistance ratio $R_C/R_a$. The critical cooling rate is correlated with the resistance ratio and the sample with the lowest critical cooling rate, i.e., the best glass-forming ability, has the highest resistance ratio. We attribute this correlation to the observation that good glass formers have fine microstructures after crystallization and thus high electrical resistance, at least compared to other compositions in the same materials system. We believe there are several reasons for this observation. Good glass formers typically occur in the vicinity of deep eutectic compositions, which tend to develop fine microstructures on crystallization, and hence have only modest reductions of their electrical resistance on crystallization. Good glass formers also have a dense atomic packing and low free volume with concomitant low atomic mobility [39–41], which hinders grain growth [42]. Finally, good glass formers often have many competing crystalline phases [43] that can form on crystallization, which again leads to fine, complex microstructures with relatively higher electrical resistance. To confirm this hypothesis, we used optical microscopy to investigate the grain structure of several crystallized samples (Fig. 8). It is evident from the micrographs that the composition with the lowest critical cooling rate indeed has the finest microstructure. Similar trends are also found in other materials systems. For instance, resistance ratios for as-deposited and crystallized samples were reported by Altounian et al. [4] for the NiZr alloy system. Fig. 9(a) shows these resistance ratios as a function of composition. Fig. 9(b) shows data on the glass forming ability parameter $\gamma = T_x/(T_x + T_l)$ for the corresponding NiZr compositions, along with the number of phases observed experimentally for this system [23,43]. Clearly, the resistance ratios and the $\gamma$ parameter are correlated; results of a regression analysis between $\gamma$ and resistance ratio $(R_C/R_a)$ are shown in Fig. 9(c). Thus, similar to the PdSiCu system, there exists a correlation between the glass forming ability and the resistance ratio for the NiZr system. We believe that similar correlations exist for other materials systems. Since measuring the resistance ratio is straightforward experimentally, the relationship between glass-forming ability (GFA) and $R_C/R_a$ makes it possible to measure glass-forming ability over large compositional regions, a long-sought goal in metallic glass research.

5. Conclusions

We have designed a sensor with the capability of measuring the resistance of a thin-film sample, as a function of temperature and composition, from room temperature up to its melting point. By tailoring the shape of the heating element, temperature uniformities within the sample area of better than 1% are achieved over a temperature range from ambient to about 1200 K, allowing sensitive detection of structural changes in the samples. The sensors have been used to investigate the temperature-resistance behavior of thin-film PdSiCu samples, and we have been able to detect the glass transition and crystallization temperatures. Further, we have found that the ratio of the resistance after and before crystallization ($R_C/R_a$) makes it possible to measure glass-forming ability over large compositional regions of potential glass formers.

Fig. 7. (A) Normalized resistance as a function of temperature for several PdSiCu glass forming alloys with known critical cooling rates. The inset shows a magnified view of the sections demarcated by the dashed line; (b) Regression analysis for correlation between critical cooling rate and $R_C/R_a$. 
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