TEMPERATURE DISCREPANCIES IN
HIGH TEMPERATURE DIFRACTOMETRY

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Abstract

Measurements using a Pt-Rh heater strip in a high temperature X-ray diffractometer furnace show that the temperature indicated by a two-colour infra-red pyrometer directed at the upper surface of the strip is within ±1 °C of the temperature indicated by a Pt/Pt-10%Rh (type S) thermocouple welded to the lower surface, over the temperature range from 600-1100 °C. However, the temperature of a powder sample on the heater, as indicated by the two-colour pyrometer, is significantly lower than that indicated by the thermocouple. The discrepancy between the two sets of temperature readings depends on the nature of the powder sample, and increases with temperature and with the thickness of the powder sample. The temperature discrepancy is attributed to thermal gradients within the powder sample, caused by cooling of the same surface due to thermal radiation and by the limited area of contact between the powder particles and the surface of the heater strip. Discrepancies between the temperature readings of the pyrometer and the thermocouple also occur for different atmospheres within the furnace chamber, indicating that the two-color pyrometer must be re-calibrated for each particular atmosphere to be used in an experiment.

Introduction

It is common practice in high temperature X-ray diffractometry (HTXRD) to assume that the irradiated surface of a powder sample is at the same temperature as the supporting heater strip. Hence, against all good thermometry practice, the temperature of the heater strip is typically measured by an attached thermocouple, while no direct measurement is made of the actual temperature of the irradiated surface of the powder sample. However, as pointed out by Green [1], a search of the literature revealed large quantities of high temperature diffraction work, but only one other publication [2] dealt with the actual measurement of temperature profiles. These two investigations, together with others presented at a high temperature X-ray diffraction
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heated length of the specimen. The associated (and more significant) problem of temperature gradients through the specimen thickness has also been recognized [3], and a number of suggestions have been made to deal with such, but no investigations have been presented on the magnitude or temperature dependence of the through-thickness gradients. Suggestions to minimize these gradients include: the use of a very thin (mono-particle layer) powder sample; the use of a surround heater maintained at 100-200 °C above the strip heater temperature; the use of an X-ray transparent cover on top of the sample to reduce radiant losses; and the use of a thermally conductive interlayer to support the sample on the heater [3]. The upper surface of this conductive interlayer can also provide an attachment for a second measurement thermocouple, to give a more accurate reading of the specimen temperature [3]. A second measurement thermocouple may be placed within the powder provided, of course, that no reaction takes place and an optical pyrometer may also be used to provide an independent measure of the surface temperature of the sample. A single wavelength pyrometer requires corrections for errors due to the surface emissivity of the sample, absorbance through the sight window, build up of coating on this window, and intensity losses due to mirror reflectance, or prism absorption. The magnitude of these corrections is not easily determined, however, by the average X-ray diffractionist.

Studies in the authors' laboratory have shown that phase transformation temperatures determined by HTXRD are often significantly greater than those determined from physical property changes in the same material [5]. This discrepancy has created a suspicion that the use of a thermocouple welded to the lower surface of a heater strip in a HTXRD furnace may give an inaccurate indication of the actual temperature of the irradiated surface of a powder X-ray sample. To evaluate the veracity and magnitude of this suspicion, the temperature of the irradiated surface of a series of powder samples has been measured by a non-invasive two-colour infra-red pyrometer, under controlled conditions with respect to sample thickness and different furnace atmospheres. The findings of these experiments are presented and discussed below, in order to document them for the information of other researchers who use high temperature diffractometry, but place undue reliance on the temperature readings displayed by the control circuitry of the instrument.

**Experimental**

Experiments were conducted in a Buehler HDK 2.3 high temperature furnace mounted on a Scintag XDS 2000 X-ray diffractometer using the 0:0 geometrical configuration, whereby the sample surface always remains in the horizontal position. At temperatures up to 1400 °C, the primary heating element was a Pt-14%Rh strip approximately 0.1 mm thick and 10 mm wide, which was wrapped around the spring loaded water cooled electrodes. The central 30 mm length of the strip can be heated to the required temperature by the passage of a DC resistive current and/or by radiation from a surround heater made of the same Pt-Rh alloy, as illustrated in Figure 1. The temperature of the heater strip was measured with a Pt/Pt-10%Rh (type S) thermocouple welded to its lower surface and was controlled to ±1 °C (using the same thermocouple) with the aid of a Micristar PID controller, in conjunction with circuitry and software developed by Scintag. In the present experiments, the surround heater was always used in conjunction with the strip heater, but the temperature of the surround heater could not be measured, because the Buehler furnace
As illustrated in Figure 1, the pyrometer was mounted on the inclined viewing port of the diffractometer furnace, using a machined screw thread with double locking ring nuts. An image of the heater strip, or powder sample, is projected on to the detector of the pyrometer by a quartz lens. To focus this optical system, a translucent screen is placed at the location of the detector and the position of the pyrometer case is adjusted by rotating the mounting screw thread until a sharp image of the heater strip is projected on the screen. After the pyrometer case is locked in the focused position, using the locking nuts, and the detector and associated circuitry are re-installed.

The materials used for investigating through-thickness thermal gradients in X-ray powder diffractometer specimens were Johnson-Matthey "Specpure" Nb and Mn, and Armco iron. The size of the crushed Nb and Mn powders was ~40 μm, while the Armco iron was in the form of filings with a minimum dimension of ~40μm. No adhesive was necessary for attaching the powders to the heater strip, as the specimens were mounted horizontally. A 10 mm wide strip from the same source of Armco iron was rolled down to ~0.1 mm and cut into 50 mm lengths, to fabricate heater strips that would undergo a known phase transformation for use in temperature discrepancy measurements. Due to the high temperature reactivity of these powder specimens in normal atmospheres, all experiments, except those specifically designed to investigate the effect of different atmospheres, were conducted in a vacuum of 2 x 10⁻⁵ torr, generated by a Levbolt...
Results and Discussion

Calibration Experiments

After focusing the image of the heater strip in the plane of the pyrometer detector, using the procedure described above, the circuitry of the two-colour pyrometer was switched on and allowed to warm up for a period of 2 h, to ensure that the Peltier-cooled electronic components achieved thermal equilibrium. The pyrometer was calibrated against the type S thermocouple welded to the lower surface of a previously cleaned Pt-14%Rh heater strip, under a vacuum of 2 x 10^-5 torr. The heater temperature, as indicated by the thermocouple, was set at 600 °C and allowed to equilibrate. The voltage output from the pyrometer focussed on the upper surface of the heater at this temperature was adjusted, by a fine movement of the "lower-adjust" trimpot, until the output read 600 ±1 mV. The heater temperature was then raised to 1400 °C and the output of the pyrometer was adjusted to read 1400 ±1 mV, by a fine adjustment of the "range adjust" trimpot of the circuitry. On lowering the temperature back to 600 °C, a further fine adjustment of the "lower adjust" trimpot was required to re-set the output to 600 ±1 °C, which in turn required a further small adjustment of the "range adjust" trimpot to return the upper output to 1,400 mV. This iterative adjustment process was continued over a few cycles, until both the upper and lower temperatures indicated by the pyrometer agreed to within ±1 °C of the set temperatures indicated by the thermocouple. This calibration process was repeated on a daily basis, or before each set of experiments. On an occasion when the pyrometer was not re-calibrated over a period of 5 days, the drift in the output mV reading at 600 °C was found to be less than 5 mV, which translates into a drift of less than 5 °C over this time period.

Niobium Powder Samples

After calibrating the pyrometer, Nb powder samples of different thicknesses were heated on the Pt-Rh heater strip, in a vacuum of 2 x 10^-5 torr, to a temperature of 600 °C, which was one of the calibration points of the pyrometer. As indicated in Table 1, although the readings of the thermocouple (TThermo) and the two-colour pyrometer (TPyro) agreed to within ±1 °C when using an uncovered heater strip, when a 1 mm thick layer of Nb powder was placed on the heater strip the temperature indicated by the two-colour pyrometer was 90 °C cooler than the temperature indicated by the thermocouple. Increasing the thickness of the Nb powder layer to 2 mm resulted in only a very slight increase (5 °C) in the discrepancy between the two temperature readings, at the set temperature of 600 °C. However, when the set temperature was raised to 1000 °C, which is within the calibrated range of the pyrometer, the discrepancy between the measured temperatures for a 1 mm powder sample of Nb was further increased to 145 °C. These findings indicate that, even in an evacuated chamber, the temperature of a loosely packed powder specimen on the surface of a heater strip can be significantly lower than the temperature of the heater itself, because of thermal gradients through the thickness of the sample. These gradients arise because of radiation cooling of the surface in directions along the clear path for the incident and the diffracted beams through the radiation shielding and surround heater, and because of the relatively limited area of contact between the underlying powder particles and the upper surface of the heater. The latter
Table 1. Thermocouple and Pyrometer Discrepancies for Powder Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{Thermo}}$ (°C)</th>
<th>$T_{\text{Pyro}}$ (°C)</th>
<th>$T_{\text{Thermo}} - T_{\text{Pyro}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Rh Heater</td>
<td>600</td>
<td>600</td>
<td>±1</td>
</tr>
<tr>
<td>1 mm Niobium powder</td>
<td>600</td>
<td>510</td>
<td>90</td>
</tr>
<tr>
<td>2 mm Niobium powder</td>
<td>600</td>
<td>505</td>
<td>95</td>
</tr>
<tr>
<td>Pt-Rh Heater</td>
<td>1000</td>
<td>1000</td>
<td>±1</td>
</tr>
<tr>
<td>1 mm Niobium powder</td>
<td>1000</td>
<td>855</td>
<td>145</td>
</tr>
<tr>
<td>Armco Heater</td>
<td>930</td>
<td>930</td>
<td>±2</td>
</tr>
<tr>
<td>0.3 mm Armco powder</td>
<td>1014</td>
<td>930</td>
<td>84</td>
</tr>
<tr>
<td>0.6 mm Armco powder</td>
<td>1117</td>
<td>930</td>
<td>187</td>
</tr>
<tr>
<td>0.9 mm Armco powder</td>
<td>1148</td>
<td>930</td>
<td>218</td>
</tr>
</tbody>
</table>

**Armco Iron Powder Samples**

When the Armco iron heater strip was used to record diffraction patterns (again in vacuum) at temperatures just above and below the α→γ phase transformation, that occurs at 910 °C [6], it was observed that the temperature $T_{\text{Pyro}}$ of the pyrometer (previously calibrated with respect to the Pt-Rh heater strip) agreed with the accepted transformation temperature to within ±2 °C, while the reading $T_{\text{Thermo}}$ of Pt/Pt-10%Rh thermocouple welded to the Armco strip was 221 °C below the α→γ transformation temperature. This unexpected discrepancy was attributed to poisoning of the Pt-10%Rh thermocouple bead by the diffusion of Fe during the spot welding process. This observation indicates that significant errors can also be expected when using a Pt/Pt-10%Rh thermocouple welded to a Kanthal heating strip [7]. In this context it is recommended that an iron/constantan (type J) thermocouple be used for temperatures up to 760 °C and that higher temperatures up to 1260 °C be measured with a chromel/alumel (type K) thermocouple.

To correct for errors in the Pt/Pt-10%Rh thermocouple due to Fe poisoning (when using the Armco heater strip), the output of the pyrometer previously calibrated with respect to thermocouple measurements made with a cleaned Pt-Rh heater strip was used as the temperature reference, and the accuracy of such $T_{\text{Thermo}}$ measurements was lowered to ±2 °C. The effectiveness of this procedure was confirmed by recording the diffraction patterns of the α, β and γ phases in a powder sample of Mn mounted on the Armco iron heater (again in vacuum) at temperatures just above and below the α→β and β→γ phase transformations. When the calibrated pyrometer was used as the temperature reference for these measurements, the respective transformation temperatures of 725 °C and 1095 °C [8] were obtained to within ±2 °C.

The effect of powder thickness on the discrepancy observed between the $T_{\text{Thermo}}$ and $T_{\text{Pyro}}$ measurements was also investigated (in vacuum) using Armco iron powder specimens mounted on the Armco iron heating strip, as shown by the results included in Table 1. These findings indicate that, for a constant $T_{\text{Pyro}}$ reading of 930 °C (i.e. within the γ-phase region), the recorded
Table 2. Thermocouple and Pyrometer Discrepancies in Various Atmospheres

<table>
<thead>
<tr>
<th>(T_{\text{Thermo}} (^\circ\text{C}))</th>
<th>(T_{\text{Pyro}} - T_{\text{Thermo}} (^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vacuum</td>
</tr>
<tr>
<td>600</td>
<td>±2</td>
</tr>
<tr>
<td>700</td>
<td>±2</td>
</tr>
<tr>
<td>800</td>
<td>±2</td>
</tr>
<tr>
<td>900</td>
<td>±2</td>
</tr>
<tr>
<td>1000</td>
<td>±2</td>
</tr>
</tbody>
</table>

as indicated by the pyrometer. The magnitude of this effect was found to increase from 84-219 °C for sample thicknesses of 0.3-0.9 mm. These temperature discrepancies are again considered to be caused by thermal gradients within the sample, due to thermal radiation along the clear X-ray beam path, and to the relatively low area of contact between the powder particles and the heater strip.

Measurements in Different Furnace Atmospheres

To evaluate the effectiveness of the two-colour pyrometer in non-uniform atmospheres, the pyrometer was first calibrated against the thermocouple output using a clean Pt-Rh heater strip in a vacuum of \(2 \times 10^{-5}\) torr at 600 and 1400 °C, as described above, and then used to measure the temperature of the upper surface of the Pt-Rh heater strip at temperature intervals of 100 °C from 600-1000 °C. As shown by the results in Table 2, measurements of \(T_{\text{Pyro}}\) in atmospheres of flowing dry argon and dry nitrogen were significantly greater than the equivalent measurements of \(T_{\text{Pyro}}\) in vacuum. The magnitude of the discrepancies at the different set temperatures was almost identical in both of these dry atmospheres, and increased from 17-49 °C when the temperature was raised from 600-1000 °C. The inability of the two colour pyrometer to correct for these different atmospheres (compared to vacuum) is considered to be due to the non-uniformity of the atmospheres, caused by convection currents generated by the heater. When this experiment was repeated in moist air, the magnitude of the discrepancy in the measurement of \(T_{\text{Pyro}}\) compared to vacuum, was further increased to 29-59 °C over the range of set temperatures from 600-1000 °C, as shown in Table 2. This increased temperature discrepancy is again associated with convection currents, which would cause increased non-uniformity due to the presence of water vapour. It is also consistent with the known differential absorption of solar infra-red wavelengths by water vapour in the atmosphere [9]. The overall conclusion of this evaluation of the two-colour pyrometer is that, although the use of intensity ratios may be effective in eliminating errors due to sample surface emissivity and to transmission through uniform media, errors due to transmission through non-uniform media are not corrected. This finding means that a two-colour pyrometer must be re-calibrated in the particular atmosphere to be used in any planned series of experiments.
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References