

Differential scanning calorimetry study of the effects of heating rate on the $\alpha \rightarrow \beta$ transformation in unalloyed plutonium

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(Received October 4, 1993)

Abstract

The $\alpha \rightarrow \beta$ transformation in plutonium is studied as a function of heating rate by differential scanning calorimetry over the range $0.01 \text{ }^\circ\text{C min}^{-1}$ to $10 \text{ }^\circ\text{C min}^{-1}$. Consistent with the fact that the transformation is controlled by nucleation and growth, the onset temperature and the temperature range of the reaction are shown to depend markedly upon heating rate. By investigating heating rates up to a factor of 100 lower than usual we show:

- (1) Earlier calorimetric measurements report onset temperatures for the transformation which are too high.
- (2) The Kissinger analysis, which predicts the scanning rate parameter to vary linearly with reciprocal temperature, does not fit the results of this study.
- (3) With increased scanning rate, the transformation occurs at higher temperatures, and the growth rate of the β phase at a constant fraction transformed is proportional to this temperature increase.

1. Introduction

Thermal analysis (TA), differential thermal analysis (DTA) and classical calorimetric studies of the allotropic transformations of plutonium date back to 1955 when Jette [1] reported the temperatures and enthalpies of its five solid-to-solid phase transformations. Subsequent thermal investigations through 1970 used TA [2, 3], DTA [4–7], and classical calorimetry [8–10] to expand upon the original work.

More recently, with the availability of computer controlled and analyzed calorimetry experiments, additional thermal studies of plutonium have been reported: differential scanning calorimetry (DSC) by Rolon and Gallegos [11], adiabatic calorimetry by Oetting and Adams [12], and DTA by Foltyn [13].

The $\alpha \rightarrow \beta$ transformation in unalloyed plutonium was investigated in all of the above studies. None, however, systematically investigated how this reaction is affected by heating rate even though it is known to be an important variable, especially when the reaction is controlled by nucleation and growth as for the $\alpha \rightarrow \beta$ transformation in plutonium [14]. In this study, we use DSC to investigate heating rate effects upon the kinetics of the $\alpha \rightarrow \beta$ transformation. By varying the heating rate over a factor of 10^3 , and especially by using rates up to a factor of 100 less than earlier studies, we are able to better characterize the reaction. We find the onset temperature extrapolated to a scanning rate of zero to be significantly lower than previously reported.

Also, we discover that when measured over a wide range of heating rates, the Kissinger scanning rate parameter *vs.* reciprocal temperature plot has marked curvature instead of being linear as predicted.

2. Experimental method

The DSC used in this study was a Thermal Analysis Inc., Model 2910 interfaced to an IBM desktop PC. The temperature range investigated was 20–160 $^\circ\text{C}$. At no time during the study were the samples heated above the temperature range for stability of the β phase.

Temperature and heat changes measured by the DSC were calibrated by melting high purity standards of indium and tin ($T_m = 156.61 \text{ }^\circ\text{C}$ and $231.91 \text{ }^\circ\text{C}$, respectively) at the scanning rates of this study. These standards were chosen because they have melting temperatures close to the $\alpha \rightarrow \beta$ transformation temperature of plutonium ($\sim 120 \text{ }^\circ\text{C}$). Figure 1 shows DSC scans for temperature calibration with indium at various heating rates. Each scan shows the endothermic peak for melting of indium. Note that the peaks are sharp and narrow, ranging from $0.1 \text{ }^\circ\text{C}$ to $0.6 \text{ }^\circ\text{C}$ in width. Also, they are heat-flow limited as evidenced by the linear leading edge of the peak [15].

In Fig. 1 we see that for heating rates of $0.1 \text{ }^\circ\text{C min}^{-1}$ and less the inflection point slopes on the leading edge of the peak are congruent. They all intersect the baseline at $156.27 \pm 0.01 \text{ }^\circ\text{C}$. This onset temperature is

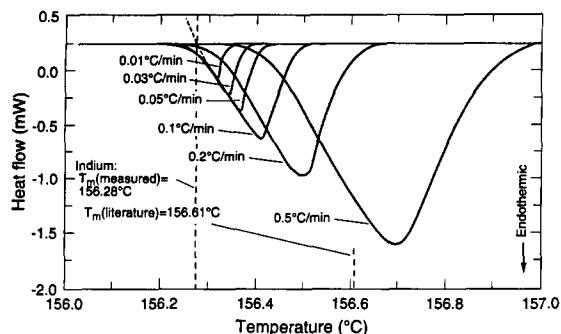


Fig. 1. Heat flow vs. temperature for melting of a 4.67 mg indium standard scanned at six different rates to calibrate temperature.

taken as the melting point. This result combined with the known melting point of indium (156.61 °C) gives a temperature correction of -0.34 °C. Combining this with a similar correction for the melting point of tin provides a linear temperature correction. As a result of these special calibration efforts, the absolute accuracy in temperature measurement is estimated to be ± 0.1 °C.

An additional result of the calibration with indium was that the thermal lag of the instrument was quantified. Thermal lag is the delay of the temperature measured by the sample thermocouple with respect to the actual sample temperature. The magnitude of this temperature lag is predicted to be linear with heating rate [16], and it typically becomes an important correction at scanning rates of 1.0 °C min^{-1} and greater. Our indium results showed the lag to be linear for scanning rates up to 10 °C min^{-1} . The resulting correction is $\Delta T = K \cdot dT/dt$, $K = 0.09$ min, nearly the same as $K = 0.1$ min in ref. 16.

We used similar techniques for calibration of the reaction heat. The heat of melting of indium, ΔH_m , was obtained by integrating the area of each melting peak in Fig. 1. The six melting scans for indium have an average $\Delta H_m = 27.18 \pm 0.34$ J g^{-1} . This average is 3.7% less than the literature value of $\Delta H_m = 28.21$ J g^{-1} [17]. This small difference does not affect our experimental measurements because we are concerned with differences due to scanning rate rather than with absolute values. For the low heating rate calibration scans in Fig. 1, the heat of melting was not affected by scanning rate.

The plutonium used in this study was medium-high purity and unalloyed. The isotopic concentrations and chemical analyses are given in Tables 1 and 2, respectively. Specimen Nos 1 and 2 were each single pieces of irregular shape, cut with a diamond saw from rod. Specimen No. 3 was from the same starting material, but was broken into smaller pieces (roughly ten) by crushing at room temperature. As will be shown, the

TABLE 1. Isotopic concentration of samples

Plutonium isotope	Concentration (atomic %)
238	0.14
239	93.83
240	5.86
241	0.26
242	0.04

TABLE 2. Chemical analysis of samples

Element	Weight (p.p.m.)	Atomic (p.p.m.)
W	250	325
Si	110	935
O	80	1200
Fe	60	255
Cr	50	230
Ni	50	205
Ga	48	165
Am	33	32
C	30	60
Ce, Ta, Zr	<100	≤ 260
Na	<50	<520
La, Re, Y, Hf	<25	≤ 65
Cd, Mg, Cu, Nb	≤ 10	≤ 100
Al, Ti, Pb, B, Sn, Zn	≤ 5	≤ 110
V, Co, Mo, Ca	≤ 3	≤ 20
Mn, Bi	2	≤ 10
others	<1	-
Total	<1250	<5000

results for all three of the specimens were the same within experimental error.

The plutonium specimens, which ranged from 95 mg to 135 mg, were cold-welded into hermetically sealed sample pans (aluminum) while in an argon atmosphere. The reference sample for the differential measurements was an empty set of pans. All measurements were made in a glovebox under flowing argon. Measurements on each of the specimens were reproducible over as many as one hundred scans indicating negligible contamination or competing reactions of the specimens. Prior to each of the DSC scans the sample was cooled to 50 °C or less, and held for at least 1 h, a treatment shown to produce the $\beta \rightarrow \alpha$ reaction. Heating rates in the range from 0.01 °C min^{-1} to 10 °C min^{-1} were investigated.

3. Experimental results

Figure 2 shows the results of typical temperature scans through the $\alpha \rightarrow \beta$ transformation for specimen No. 2. Each of the four curves is an endothermic peak at a different heating rate. Note that, as with the indium

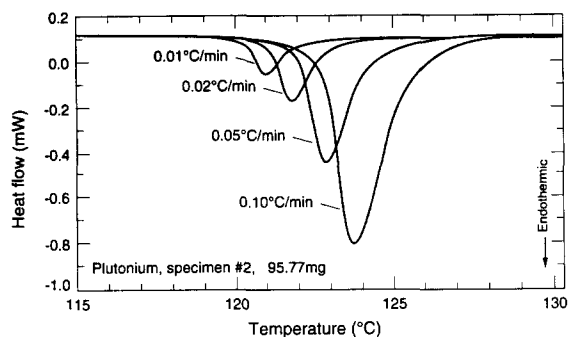


Fig. 2. DSC peaks for $\alpha \rightarrow \beta$ transformation of plutonium specimen No. 2 at various scanning rates.

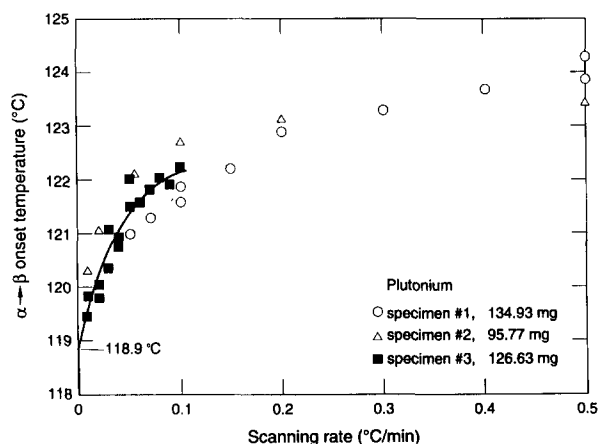


Fig. 3. Onset temperature for plutonium $\alpha \rightarrow \beta$ reaction vs. scanning rate for three different specimens. The onset temperature is defined by the intersection of the low temperature background line and the slope at the leading edge inflection point of the peak.

calibration curves, the base lines, both above and below the peak, are straight and well defined. Thus, it is possible to use the methods discussed by Flynn [15] to obtain integral DSC curves for the analysis.

In Fig. 2 it may be seen that with a decrease in the scanning rate the peak decreases in height, becomes narrower and shifts to lower temperatures. These three effects are all as expected for a first-order transition controlled by nucleation and growth. At lower heating rates the β phase has more time to nucleate and grow at lower temperatures. Also, the reaction kinetics are slowed down because there is less driving force closer to the equilibrium transformation temperature.

3.1. Onset temperature

The onset temperature for the transformation is defined as the intersection of the baseline before the peak and the slope through the inflection point on the leading edge of the peak (same as for the temperature calibration). Our experimental results for the variation of the onset temperature with heating rate are shown in Fig. 3 for three different specimens at rates from

$0.01 \text{ } ^\circ\text{C min}^{-1}$ to $0.5 \text{ } ^\circ\text{C min}^{-1}$. In accord with the results shown in Fig. 2 the onset temperature decreases with the scanning rate. Note that at a given scanning rate there is agreement within roughly $\pm 0.5 \text{ } ^\circ\text{C}$ between the measured onset temperatures for the three different specimens.

In Fig. 3 the curve through the data points for specimen No. 3 (solid squares) is a least-squares fit to a second-order polynomial for the 15 measurements. The standard deviation of the data from this curve is $0.18 \text{ } ^\circ\text{C}$. Extrapolation of the fit curve to a scanning rate of zero gives an onset temperature of $118.9 \text{ } ^\circ\text{C}$. This is significantly lower than the $121.9 \text{ } ^\circ\text{C}$ which was given in the review by Oetting *et al.* [18] as the suggested value for the equilibrium temperature for the transformation, $T_{\alpha/\beta}^0$. It should be mentioned that the true value of $T_{\alpha/\beta}^0$ is most certainly less than the onset temperature we report because close to $T_{\alpha/\beta}^0$ the time for nucleation of the β phase is expected to be long compared with the time-scale of these experiments.

The scanning rates and thus the onset temperatures of this study are considerably lower than those of previous investigations. For example, Rolon and Gallegos [11] scanning at $2.5 \text{ } ^\circ\text{C min}^{-1}$ obtained an onset temperature of $126.45 \text{ } ^\circ\text{C}$ while Foltyn [13] heated at $3.0 \text{ } ^\circ\text{C min}^{-1}$ (and higher) to obtain $127 \text{ } ^\circ\text{C}$. The decrease in the onset temperature with scanning rate shown in Fig. 3 indicates that onset temperatures need to be measured at rates much lower than usually reported. Also, any extrapolation to zero scanning rate is clearly open to uncertainty since the onset temperature decrease is most rapid at the lowest scanning rates and the true shape of the extrapolation curve is not known. Thus, it is expected that if the scanning rate were decreased below the lowest value of this experiment, then a further decrease in the extrapolated onset temperature would be observed.

3.2. Heat of transformation

The onset temperature, as discussed above, is expected to vary with scanning rate because the reaction kinetics depend upon time and temperature. The heat of the reaction, on the other hand, should, to the first approximation, be independent of scanning rate [19]. Thus, we expect that variations measured in the heat of the reaction are most likely instrumental ones characteristic of the calorimeter.

Endothermic peaks such as in Fig. 2 were integrated to obtain the $\Delta H_{\alpha/\beta}$, the heat of the transformation. This integration used an iterative technique applied to sigmoidal baselines [15] since there was a small step-function difference in the baselines of the α and β phases, as expected from the small differences in the specific heats [20]. Measured values for $\Delta H_{\alpha/\beta}$ are shown for specimen No. 1 as a function of scanning rate in

Fig. 4. Here we note that the measured value of the heat of transformation is roughly constant for rates from $0.05 \text{ }^\circ\text{C min}^{-1}$ to $0.4 \text{ }^\circ\text{C min}^{-1}$. The average value over this range is 14.0 J g^{-1} and the standard deviation is 0.1 J g^{-1} .

As the scanning rate increases up to $10 \text{ }^\circ\text{C min}^{-1}$ in Fig. 4, the measured value of $\Delta H_{\alpha/\beta}$ increases roughly by 10%. This result is in agreement with earlier measurements on other materials using other DSCs which also showed apparent changes in heats of reactions at scanning rates above roughly $2 \text{ }^\circ\text{C min}^{-1}$ [21]. This suggests that our measurements at $0.4 \text{ }^\circ\text{C min}^{-1}$ and less provide a more reliable value for the heat of transformation than those at higher scanning rates.

The value of $14.0 \pm 0.1 \text{ J g}^{-1}$ which we report is in reasonable agreement with $14.34 \pm 0.35 \text{ J g}^{-1}$ quoted as the suggested value [18]. However, it should be recognized that the determination of $\Delta H_{\alpha/\beta}$ is complicated because some of the earlier calorimetric investigations have shown a small prepeak before the main $\alpha \rightarrow \beta$ peak [4, 6], and it is not clear whether to include the heat of this peak in the total. (We did not find evidence for the prepeak in this investigation.) Further studies are in progress which relate to this. It should also be mentioned that our value of the heat is probably several percent too low because in our experiments small amounts of retained β were present in the α phase. This retained β was present because the $\beta \rightarrow \alpha$ reaction requires several hours at room temperature to go to completion rather than the 1 h at $50 \text{ }^\circ\text{C}$ which we used before these scans.

An additional effect which can cause a small change in the heat should also be considered. This is that the heat of an allotropic transformation is expected to vary with temperature because the two phases have different specific heats. Increasing the heating rate causes the transformation to occur at higher temperatures for which the reaction enthalpy will be different. Our experimental results showed that increasing the heating

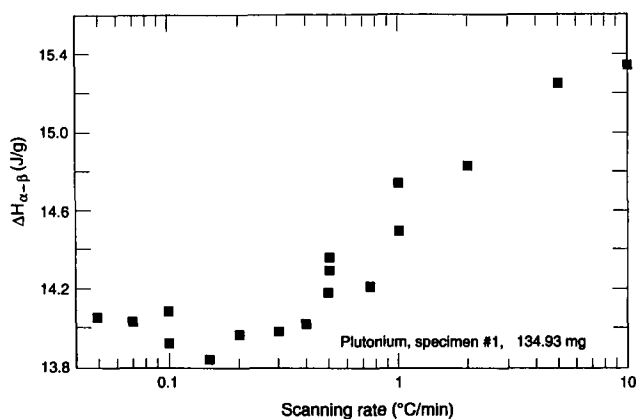


Fig. 4. Heat of the $\alpha \rightarrow \beta$ reaction vs. scanning rate for plutonium sample No. 1.

rate up to $10 \text{ }^\circ\text{C min}^{-1}$ caused the temperature of the reaction to increase by roughly $10 \text{ }^\circ\text{C}$. The calculated change in reaction enthalpy due to this increase based upon differences in the specific heats [20] is -0.14 J g^{-1} . Since the calculated change is too small and of opposite sign, this possible explanation for the results in Fig. 4 must be discounted.

3.3. Kinetic analysis

At temperatures just above the equilibrium transformation temperature the free energy decrease for an allotropic transformation is approximately proportional to $\Delta T = T - T_{\alpha/\beta}^0$. From this it can be shown that near $T_{\alpha/\beta}^0$ the growth rate of the β phase is also nearly proportional to ΔT [22]. Since the output of the DSC is proportional to the growth rate, it follows that a plot of DSC output at any given fraction transformed should vary linearly with ΔT . Figure 5 shows such a plot where the DSC output at the low temperature inflection point, T_{inf} , is plotted vs. $\Delta T = T_{\text{inf}} - T_{\alpha/\beta}^0$ with $T_{\alpha/\beta}^0 = 118.9 \text{ }^\circ\text{C}$ (see Fig. 3). From Fig. 5 it may be seen that the predicted proportionality holds reasonably well for the range of scanning rates of this study. Also, the intercept at low ΔT , which corresponds to a slowest possible scanning rate has a heat flow, and thus a growth rate, approaching zero. It is of interest that the growth rate vs. ΔT proportionality holds for this study since it was derived for an allotropic phase change on cooling; we believe that this is the first time that this prediction has been demonstrated for a transformation during heating.

Thermally activated reactions measured by DSC at various heating rates are most often analyzed by the Kissinger method [23]. The Kissinger analysis predicts that a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ should be linear with slope of Q/k_b . Here β is the scanning rate, T_p is the absolute temperature of the peak, Q is the activation

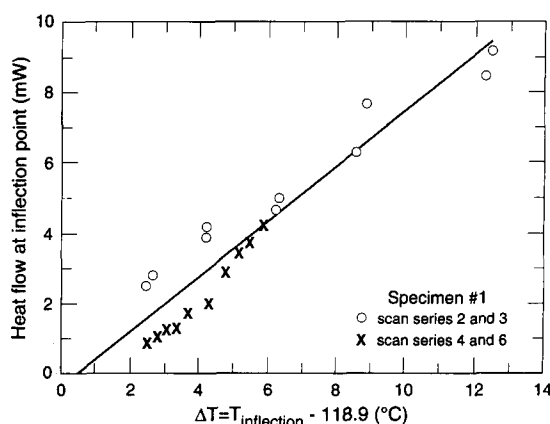


Fig. 5. Heat flow at the leading edge inflection point vs. ΔT , the increase in the temperature of the inflection point caused by increasing the scanning rate. The heat flow is proportional to the rate of the $\alpha \rightarrow \beta$ reaction.

energy for the process, and k_b is Boltzmann's constant. Numerous discussions of the assumptions and uses of the Kissinger analysis have shown it to be correct for solid state DSC studies such as crystallization of amorphous solids and recrystallization of deformed metals [24]; however, it has not to our knowledge been shown to be applicable to allotropic transformations.

Figure 6 is a Kissinger plot of our results covering a factor of 10^3 in β . Corrections for thermal lag were made in determining T_p as discussed earlier [16]. In Fig. 6 the results for specimen No. 1 at scanning rates of $0.5 \text{ }^\circ\text{C min}^{-1}$ and above show excellent reproducibility between scan series 2 and 3, *i.e.* the two data points at each scanning rate almost superimpose, see the open circles.

The Kissinger plot of Fig. 6 shows obvious downward curvature instead of the predicted linear behavior. Note that the slope (absolute value) for the results from specimen No. 1 continuously increases as the heating rate is decreased. Also, the plot appears to have two regions, one at higher and one at lower scanning rates, which are close to being linear. For example, a linear fit to the data of scan series 2 and 3 taken at heating rates above $0.5 \text{ }^\circ\text{C min}^{-1}$ (see upper solid line) gives an apparent activation energy of 2.5 eV (240 kJ mol^{-1}), a reasonable value for the activation barrier for an allotropic transformation. On the other hand, the results from scan series 4 and 6 for the same sample, but at much lower scanning rates, are also nearly linear but with a much steeper slope, having an apparent activation energy of 8.0 eV (769 kJ mol^{-1}), considerably larger than might be expected.

Also shown in Fig. 6 are the results for specimen No. 2 which were taken at scanning rates of $0.5 \text{ }^\circ\text{C min}^{-1}$ and less. These results, in agreement with those

from specimen No. 1 for the same scanning rates, show very little curvature. In addition, the plot has a steeper slope, giving an apparent activation energy of 10.7 eV (1029 kJ mol^{-1}), which is again appreciably higher than expected. A possible explanation for the two nearly linear regions with different slopes in Fig. 6 is that the mode of growth of the β phase changes near $125 \text{ }^\circ\text{C}$. For example, the growth mechanism might change from one-dimensional growth (to form needles) to two- or three-dimensional. This possibility would also explain the change in the apparent activation energy. This is because it is predicted that for growth in more than one dimension the apparent activation energy will be the activation energy for growth multiplied by a function of the Johnson–Mehl–Avrami exponent which, in turn, is determined by the dimensionality of the growth mechanism [25].

It is interesting to question why the peak temperatures for the different scan series of specimen No. 1 in Fig. 6 are not the same. For the scanning rate of $0.5 \text{ }^\circ\text{C min}^{-1}$, the results from scan series 2 and 3 are in close agreement but have peak temperatures roughly $3 \text{ }^\circ\text{C}$ lower than those from scan series 4 and 6. The reason for this is most probably due to differences in the maximum temperature to which the specimen was heated while in the β phase. For scan series 2 and 3 the specimen was heated to $170 \text{ }^\circ\text{C}$, while for series 4 and 6 the specimens were only heated to $130 \text{ }^\circ\text{C}$. Evidently heating to a higher temperature in the β phase causes T_p to decrease. The reason for this is not clear, but it suggests that the phase transformation reaction does not go to completion either on heating or cooling so that the residual metastable phase can act as nucleation sites and thus affect the reaction kinetics.

The full details of the nonlinearity of the Kissinger plot are not clear from Fig. 6. On the one hand there may be continuous curvature over the full range of heating rates, and on the other there may be two nearly linear regions with a marked change of slope at roughly $0.5 \text{ }^\circ\text{C min}^{-1}$. The fact that there is a definite increase in slope from point to point for the highly reproducible data taken at heating rates of $0.5 \text{ }^\circ\text{C min}^{-1}$ and above (see open circles) is good evidence that the slope varies continuously. If this is correct then it would appear that the Kissinger formalism does not apply. This may be because the assumption of the Kissinger analysis that the rate constant follows Arrhenian behavior over the full temperature range investigated is not applicable below $T_{\alpha/\beta}^0$ where the β phase is not thermodynamically stable or just above the transformation temperature where the free energy for the reaction is proportional to ΔT as discussed earlier.

It is noted that these are apparently the first DSC experiments of an allotropic transformation in which

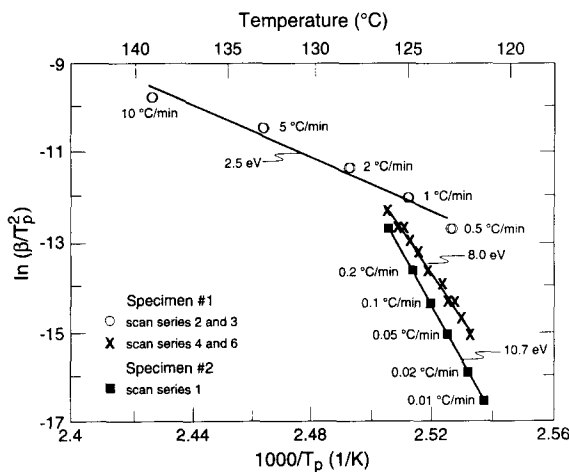


Fig. 6. Plot of the Kissinger parameter, $\ln(\beta/T_p^2)$, vs. reciprocal temperature where β is the scanning rate and T_p is the peak temperature. The Kissinger analysis predicts this plot to be linear with a slope proportional to the activation energy for the reaction.

the heating rate has been systematically varied in the range below $1.0 \text{ }^\circ\text{C min}^{-1}$. Experiments at low rates have important advantages which will make them attractive for future investigations. First, and specially important, the thermal assumptions of calorimetry are well satisfied, e.g. there is no problem with thermal lag for the sample or the reference because heating is too rapid. Second, at very slow scanning rates such as in this study, the reaction occurs over a relatively narrow temperature range so that to a first approximation the reaction may be treated as isothermal. For example, in Fig. 2 for a scanning rate of $0.01 \text{ }^\circ\text{C min}^{-1}$ the peak width for the transformation is less than $2 \text{ }^\circ\text{C}$.

Acknowledgments

We wish to thank Jose Archuleta and Ray Martinez for their expert installation of the DSC into the glovebox. Appreciation is also expressed to S.D. Soderquist and J.T. Stanley for critical reviews of the manuscript.

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