THE KINETICS OF THE BETA TO ALPHA
TRANSFORMATION IN UNALLOYED PLUTONIUM
USING DIFFERENTIAL SCANNING CALORIMETRY

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KINETICS OF THE $\beta \rightarrow \alpha$ TRANSFORMATION IN UNALLOYED PLUTONIUM USING DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

Differential scanning calorimetry measurements, both isothermal and on cooling, were made during the $\beta \rightarrow \alpha$ transformation of unalloyed plutonium. The calorimetric measurements, because they directly measure the rate of heat flow, provide a direct quantitative measure of the rate of the reaction. Isothermal measurements at temperatures from 56 °C to 68 °C showed that the reaction required incubation times, presumably for nucleation of the alpha phase, of from 300 to 550 seconds. The reaction rate increased with decreasing temperature in agreement with results of prior studies. The measured value for the heat of the reaction also corroborated earlier findings. The fraction-transformed curves were analyzed using the Johnson, Mehl, Avrami model. Analysis showed clearly that the reaction kinetics do not fit this model. The Avrami exponent, instead of being constant as predicted, decreased continuously (by more than a factor of four) during the first 80% of the reaction. Possible reasons for this apparent deviation from classical transformation kinetics are discussed. Measurements in the temperature-scanning mode were made on a sample consisting of ten separate pieces of plutonium. With successive cooling cycles through the $\beta \rightarrow \alpha$ transformation, the heat release peak changed in shape, width, and position. This effect is believed to be due to changes in the residual stresses in different pieces of the sample.
Introduction

Differential scanning calorimetry (DSC) is an excellent but little-used method for measuring the kinetics of an allototropic phase change. It has the unique advantage of being a direct measurement technique, i.e., it provides an absolute measure of the rate of heat release (or absorption) during a transformation; this is proportional to the rate of the reaction. Thus the kinetics can be determined by a single DSC measurement [1]. Also, if the reaction goes to completion, the rate curves can be integrated to obtain the fraction transformed versus time (or temperature). An additional advantage is that the measurements can be made either isothermally or in the scanning mode, either upward or downward in temperature.

Recently Cost and Salazar [2] reported DSC measurements of the α→β transformation in unalloyed plutonium. Because of the reasons mentioned above, the experiments were able to add new understanding to the thermodynamics and kinetics of this transformation. In the present paper we use the same DSC technique to provide new results about the reverse allotropic phase change, β→α.

The kinetics of the β→α reaction in pure plutonium have been discussed in detail by White in an excellent review [3]. Techniques which previously have been used to investigate the transformation kinetics include density, dilatometry, electrical resistivity, and acoustic transmission. Thermal studies of the β→α reaction [4-8], however, only reported transformation temperatures and enthalpies. Also, these thermal studies were all made more than twenty years ago, before modern DSC techniques were generally available.

Experimental Methods

The calorimeter for these experiments was a Thermal Analysis Inc., Model 2910 used in both the isothermal and the scanning modes. This DSC was enclosed in a glove-box filled with argon as protection against possible oxidation. The temperature and enthalpy calibrations of the DSC have been described previously [2]. No temperature lag corrections were required in the scanning mode of operation of this study since at our maximum scanning rate of -1.0 °C/min the temperature correction was determined to be less than 0.5 °C. After preparation for the DSC, the samples were never annealed at above 160 °C and thus never transformed to any other phase than alpha or beta.

Two calorimetry specimens of plutonium were used, the first for isothermal experiments and the second for temperature-ramped experiments. The first specimen was identified as #1 and the second as #3 in our earlier study [2]. Both were unalloyed plutonium of medium purity with chemistry and isotopic concentrations as previously described. The first specimen was a single equiaxed piece of plutonium (134.93 mg); the second was ten equiaxed pieces of nearly the same size (total weight of 126.63 mg) which were prepared from a single larger piece by crushing at room temperature.

The specimens were protected from oxidation by encapsulation in an argon atmosphere in cold-welded aluminum sample holders. The reference for the DSC measurements was an empty aluminum sample holder. As evidence that the samples were not changed by oxidation or other possible contamination, it was demonstrated that the transformation behavior of sample #1 was unaffected by repeated temperature cycling through the α→β and β→α reactions. In addition to being reproducible, the temperatures for the transformations were in agreement with those from other studies. The transformation behavior of the second specimen was different in that it changed during cycling. This
evolution is believed to occur because the sample consisted of separate pieces which transformed at different rates as will be discussed.

Results and Discussion

Isothermal Measurements

DSC measurements on the first specimen were made in the isothermal mode; this enabled quantitative analysis of the reaction kinetics and comparison with earlier experiments which used other measuring techniques. The heating cycle for all the isothermal experiments was to first ramp the alpha phase to 160 °C at 10 °C/min and thereby transform it to beta. Immediately thereafter the beta phase was cooled at 25 °C/min to the isothermal measuring temperature. It was then held at constant temperature until the β→α reaction was completed.

Typical Results. DSC data from an isothermal measurement at 62.8 °C are shown in Figure 1a. These results are similar to those of our two other isothermal measurements, at 56.6 °C and 67.9 °C. The peak

![Figure 1](image-url)

Figure 1. (a) Heat release peak for the β→α transformation at 62.8 °C. (b) Fraction transformed curve obtained by integrating heat flow peak in Figure 1a.
in the heat flow, which starts roughly 300 sec after the sample has reached the measuring temperature and which lasts until 900 sec, is due to the heat released by the $\beta \rightarrow \alpha$ transformation (following the convention that exothermic is positive). This exothermic peak is expected for the allotropic transformation from the metastable beta phase to the alpha phase, the latter being stable below 117 °C [2]. In Figure 1a we see that the heat flow has a constant baseline, both before and after the transformation. The magnitude of this baseline is nearly the same before and after the reaction because it is determined by the specific heat of the sample, and the specific heats of beta and alpha are the same within 10% at 62.8 °C [9].

The following aspects of the results in Figure 1a are of particular interest:
(1) An incubation time of roughly 300 sec was required before the transformation started. Such relatively long times are consistent with a nucleation and growth mechanism for the transformation. Incubation times and other measurement parameters are listed in Table I.
(2) The time for the reaction, roughly from 300 to 900 seconds, was long enough so that the condition of temperature equilibrium was maintained in the calorimeter during the full extent of the transformation, i.e., the reaction heat was released slowly enough so that the isothermal condition was maintained. This is an important requirement for the kinetic analysis which follows.
(3) The isothermal reaction appears to go to nearly to completion. Thus there is no measurable continuation of the transformation after it tails off to background at roughly 900 seconds. This ignores a small amount of retained beta (less than 5%) which is believed to be present unless the samples are cooled to and held for several hours at room temperature [2].
(4) The heat release peak is not perfectly smooth at its maximum. Instead, the peak appears to consist of two or more superimposed peaks. As will be discussed later, this effect is believed to be due to different portions of the sample transforming at different rates, probably due to dissimilar internal stresses.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Incubation time (sec)</th>
<th>Δt_{25%/75%} (sec)</th>
<th>ΔH_{\beta \rightarrow \alpha} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.9</td>
<td>540</td>
<td>372</td>
<td>13.78</td>
</tr>
<tr>
<td>62.8</td>
<td>330</td>
<td>200</td>
<td>14.27</td>
</tr>
<tr>
<td>56.6</td>
<td>360</td>
<td>70</td>
<td>14.24</td>
</tr>
</tbody>
</table>

Heat of Transformation. The exothermic heat flow peaks for the isothermal $\beta \rightarrow \alpha$ transformation were integrated to obtain the heat of the reaction, $\Delta H_{\beta \rightarrow \alpha}$. As shown in Figure 1a, $\Delta H_{\beta \rightarrow \alpha} = 14.27$ J/g for the measurements at 62.8 °C. The integration of the heat release peaks to obtain $\Delta H_{\beta \rightarrow \alpha}$ was done with good accuracy since the baselines were well established and there was little scatter in the data for the peaks. The average of the isothermal measurements gave $\Delta H_{\beta \rightarrow \alpha} = 14.1$ J/g, in good agreement with the value 14.0 ± 0.1 J/g measured on the same sample for the reverse reaction [2]. As was previously mentioned, this value for the heat of the reaction may be several percent too low because of the small amount of retained beta phase expected for the heating cycles of this experiment.
Fraction-Transformed Curves. The integrated curve for the reaction at 62.8 °C is shown in Figure 1b as the fraction transformed versus time. (Note that the time scale is the same as for Figure 1a.) Also shown in Figure 1b are the results described by White [3] of the isothermal measurement of the $\beta$-$\alpha$ transformation by Davey, Faiers and White (DFW) [10] at 45 °C. Several interesting comparisons can be made between their results and ours. First, the DFW transformations tended to occur less rapidly than ours at a given temperature. Second, the DFW transformations were markedly more sluggish after 65% of the reaction and, in fact, were not shown as going beyond 70% of completion. Third, as will be shown in our later analysis, the parameters describing the reaction kinetics are significantly different.

As was found in earlier studies, the rate of the $\beta$-$\alpha$ reaction is strongly temperature dependent. This may be seen in Table I where $\Delta t_{25^\circ_C/75^\circ_C}$, the time for the middle 50% of the reaction, increases by a factor of more than five between our lower and the upper isothermal reaction temperatures. The fraction transformed versus time curve of DFW in Figure 1b measured at 45 °C was the closest in transformation rate to our measurements at 62.8 °C. It shows $\Delta t_{25^\circ_C/75^\circ_C} = 330$ sec compared to 200 sec for our study. At the highest isothermal measurement temperature of DFW, 52 °C, $\Delta t_{25^\circ_C/75^\circ_C} = 970$ sec, again a much slower reaction rate than ours and also a significant slowing of the reaction with increasing temperature.

The reason that DFW found the latter third of the reaction to occur much more slowly than we did is not apparent. The explanation may have to do with their use of the resistivity method and the likelihood that the end-point resistivity of the alpha phase was not reproducible because of structural changes induced by repeated cycling of the reaction. The purity of the plutonium could also play a role. Certainly, additional studies are needed to give evidence to White's claim that “between 80 °C and 40 °C the reaction is essentially self-stopping before completion of the $\beta$-phase transformation.” It is not clear when the self-stopping occurs or why measurements in the DFW study were not continued beyond 70% completion? Such additional measurements would have provided information concerning the extent and circumstances of the markedly decreased reaction rates.

Kinetic Analysis. The isothermal results of have been analyzed using the Johnson, Mehl, Avrami (JMA) model. The fraction transformed is given by

$$f = 1 - \exp (-Kt^n), \tag{1}$$

where $t$ is the starting time for the transformation, $n$ is a constant (the Avrami exponent) determined by the geometry of the nucleation and growth of the new phase and $K = K_0 \exp[-Q/(kT)]$ is the thermally-activated rate constant determined by a pre-exponential frequency constant $K_0$ and an activation energy $Q$. For isothermal experiments the values of $n$ and $K$ are determined by the slope and intercept, respectively, of a plot of $\log[\log[1/(1-f)]]$ versus $\log(t)$, which, if the JMA model is correct, will give a straight line. Figure 2 shows such a JMA plot of our results from Figure 1 at 62.8 °C.

It is quite clear that our results in Figure 2 do not fit the straight line predicted by the JMA model. Instead, the slope continuously decreases during the transformation. Effective values of $n$ measured from these slopes are plotted versus the extent of the reaction in Figure 3. Here we see that the apparent value of $n$ changes during the reaction from roughly $n = 12$ at the start to $n = 2.7$ at completion. According to the JMA theory $n > 4$ occurs if the nucleation rate is increasing [11]. Thus, if we force our results to fit the JMA model, we must conclude that our continuously decreasing value of $n$ indicates that during the transformation the nucleation rate is continuously increasing, but at an ever-decreasing rate. We also must conclude that the nucleation rate is increasing until $n$ becomes less than 4, which is after 80 % of
Figure 2. Johnson, Mehl, Avrami plot of $\beta\rightarrow\alpha$ transformation measured at 62.8 °C by DSC in this study and at 45 °C by resistivity [3].

Figure 3. Avrami exponent versus fraction transformed for results of this study at 62.8 °C (see Figure 1) and White at 45 °C [3].
the reaction. That this is much further into the reaction than is realistic is strong evidence that the JMA model is incorrect for our results. Clearly further investigation of possible reasons for this apparent deviation from traditional transformation kinetics is desirable.

Also shown in Figure 2 are the results of White at 45 °C replotted from his Figure 3 of Reference [3]. These results are a good straight line fit to the JMA kinetic model for the first 50% of the reaction, but the fit becomes poorer as the reaction continues. The results of a local slope analysis of these data to obtain n versus fraction transformed are shown in Figure 3. Here it can be seen that DFW also find a continuous decrease in the value of the Avrami exponent as the transformation proceeds; i.e., White's values for n decrease roughly from n=1.8 at the start to n=1.2 at 70% (the highest percent of the reaction reported).

The situation is even more complicated when the temperature dependence of n is considered. White reports that the value of n increases with decreasing reaction temperature becoming constant at n=7.8 for reactions occurring at 10 °C or less. Thus, by decreasing the transformation temperature by just 35 °C, he finds values of n which are not much different from those of this study. This agrees qualitatively with the results from density change measurements of Nelson [12] who reported n=4.7 over the temperature range of our study but found the value to increase to 8 and 9 as the transformation temperature decreased to 0 °C and below. Considering the results of all of these investigations it appears that n > 4 is not uncommon, especially at lower measuring temperatures; however, large variations for n during a single reaction have only been found in our experiments. As will be discussed, this finding that n is not constant may be a real effect, but one which is only observed in this study because the DSC method provides a more direct and reliable measure of the transformation curve.

**Evaluation of Measuring Methods.** Reasons for the remarkable differences between our results and those discussed by White [3] in his review need to be understood. It is quite possible that the explanation for these differences depends upon intrinsic dissimilarities in what is measured by the resistometric, length change, density, hot stage microscopy, and calorimetric methods. A second, but less likely, explanation may have to do with the purity of the plutonium.

For reliable kinetic analysis it is essential to measure the transformation curves using a technique for which the measured parameter is exactly proportional to the fraction transformed. This is particularly true for a material as anisotropic as plutonium.

Measurements which use the resistometric method are open to question on the following grounds:

a. Microcracks which form during the transformation may change the starting or end-point resistivities.

b. With repeated cycling from one phase to the other, there may be changes in the preferred orientations of the phases thereby changing the electrical resistance since it is so strongly anisotropic.

c. During the transformation the electrical resistance of the sample will depend upon the connectivity of the two phases as well as the fraction transformed. Thus measured resistance at a given fraction transformed will be different depending upon whether the newly-forming α-phase tends to be in series or in parallel with the current flow direction.

d. Oxidation of the resistivity specimen may occur while it is at temperatures above 100 °C unless a protective atmosphere is provided. It is not clear that silicone oil at 160 °C, as was used by DFW, would prevent oxidation.
While the DSC technique as it was used in this study avoids the above difficulties, it is not without possible complications. Some of these are as follows:

a. It is necessary to carefully calibrate the DSC for both temperature and enthalpy before and after experiments.
b. It is important to operate the instrument at scanning rates which minimize temperature lag; this is not a problem in isothermal measurements unless reaction heats are given off so fast that temperature can not be maintained constant.
c. The DSC technique tends to not be sensitive to very slow reactions. This is because it directly measures the reaction rate, rather than changes in a property. Because of this a reaction may occur so slowly that it is not measured. Checks as to whether this occurs can, however, be made by measuring reaction heats for the reverse reaction as a function of annealing time.

**Scanning Measurements**

The DSC was operated in the scanning mode to examine the $\beta \rightarrow \alpha$ transformation during ramp cooling. The specimen consisted of 10 separate pieces of unalloyed plutonium which were originally alpha phase and which were formed by crushing at room temperature. The thermal treatment of this multiple sample was to transform to the beta phase by heating at 1 °C/min to 150 °C, immediately cool at 10 °C/min to 80 °C, and then cool to at 1 °C/min to 50 °C. The interesting evolution of the shape, width, and temperature of the DSC peak with repeated cycling of the $\alpha \rightarrow \beta \rightarrow \alpha$ reactions is shown in Figure 4. The first cooling scan resulting in the $\beta \rightarrow \alpha$ reaction is shown in Figure 4a. The heat release peak is seen to be craggy and to occur over a wide temperature range, 72 °C to 55 °C. The cause for the peak being jagged is believed to be that the different pieces of the plutonium are transforming at different temperatures and thus showing separate peaks which superimpose. This is probably because of disparate residual stresses in the different pieces. Presumably very little deformation occurred during the crushing because of the brittleness of the alpha phase.

The results from the second cooling scan are shown in Figure 4b. The heat release peak is much less jagged and starts at a higher temperature indicating that the transformation of the different pieces is happening more homogeneously and also requiring less driving force in the form of undercooling. Figure 4c shows the transformation on the fifteenth cycle with an intervening anneal of four days at room temperature. The peak has narrowed, is smoother, and has shifted to a lower temperature. In this figure we see the $\beta \rightarrow \alpha$ peak nearly in its fully evolved state, i.e., as it typically appears after many $\alpha \rightarrow \beta \rightarrow \alpha$ cycles. Apparently the separate pieces have developed the same microcrack structure and built up similar residual stresses so that the peaks superimpose and the driving forces as evidenced by the undercooling are the same.

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Figure 4. DSC measurements of the $\beta \rightarrow \alpha$ transformation of a specimen consisting of ten pieces of plutonium. The ten pieces were simultaneously cooled through the transformation at roughly 1 °C/min. (a) First $\beta \rightarrow \alpha$ transformation of as-received pieces. Measurements are during cooling immediately after the $\alpha \rightarrow \beta$ reaction on heating to 150 °C. (b) Second $\beta \rightarrow \alpha$ transformation of same samples upon cooling from 150 °C. (c) Fifteenth $\beta \rightarrow \alpha$ transformation of same samples after 14 cycles of $\alpha \rightarrow \beta \rightarrow \alpha$ transformation with intervening anneal for four days at room temperature.
References

1. J. R. Cost, to be published.


