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TRANSFORMATION KINETICS OF PLUTONIUM

PART I - A STUDY OF THE BETA TO ALPHA AND ALPHA TO BETA TRANSFORMATIONS

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TRANSFORMATION KINETICS OF PLUTONIUM
PART I - A STUDY OF THE BETA TO ALPHA
AND ALPHA TO BETA TRANSFORMATIONS

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Reactor and Fuels Research and Development Operation

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ABSTRACT

The transformation kinetics of alpha and beta plutonium were determined by using a fluid displacement technique. The rate of formation of the alpha phase from the beta phase was determined after beta heat treating and allowing the sample to transform isothermally in the alpha range. Isothermal reaction curves were obtained from -78 C to +90 C. A time-temperature-transformation curve showed the maximum rate of transformation to be approximately -20 C.

The beta phase did not transform completely to the alpha when the transformation was allowed to take place isothermally. A relationship between the fraction untransformed beta and the transformation temperature has been established.

Isothermal reaction curves and a time-temperature-transformation curve of the $\alpha \longrightarrow \beta$ transformation were obtained.

Portions of the time-temperature-transformation curves of the $\beta \longrightarrow \alpha$ transformation of four purities were plotted. The effects of beta heat treating times and temperatures were studied.

Photomicrographs of a specimen having transformed from the beta to the alpha phase at different rates of transformation are presented.

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INTRODUCTION

A program is being performed to study the transformation kinetics of plutonium. The investigation has as its objective a study of the changes occurring in varying phases of plutonium when held in a metastable condition. The information obtained from this investigation will not only give a better understanding of the fundamental nature of plutonium, but will also be particularly useful in the heat treatment of the metal. There are six allotropic forms of plutonium. The stable lattice, alpha, at room temperature is thought to be monoclinic and transforms at approximately 120 C to the beta phase, the crystal structure of which is unknown. ^(1, 2)

The temperature of the maximum rate of transformation is lower than 40 C - 60 C and the rate of transformation occurs more rapidly than had previously been reported. ^(2, 3) Heating and cooling curves, isothermal reaction curves, and time-temperature-transformation curves of plutonium of five purities have been obtained. Also a relationship has been determined showing that at temperatures higher than room temperature the $\beta \longrightarrow \alpha$ transformation may not go to completion isothermally. Photomicrographs showing the effect of the rate of transformation on the microstructure are presented.

It has been found that for high-purity plutonium the transformation of the beta phase at temperatures below the $\beta \longrightarrow \alpha$ equilibrium temperature behaves in a manner similar to the decomposition of metastable eutectoid alloys.

A study of this nature is most satisfactorily accomplished by means of isothermal reaction curves and time-temperature-transformation curves. Isothermal reaction curves are obtained by determining the fraction of alpha or beta transformed as a function of time. The curves have the form of a

typical sigmoid curve shown in Figure 1. The equation for the curve has the general form:

$$f(t) = 1 - \exp(-\pi N G^3 t^4 / 3) \quad (1)$$

$f(t)$ is the fraction transformed

N is the rate of nucleation

G is the rate of growth

t is the time for $f(t)$ to occur

Time-temperature-transformation curves, Figure 2, show the time required for a constant amount of phase transformation as a function of temperature. They can be obtained quite readily from a series of isothermal reaction curves. The appearance of the first detectable trace of the reaction product is taken as the beginning of the reaction, and the time at which nearly all of the transforming product has been transformed is taken as the completion of the reaction. These are conventionally taken as one per cent and ninety-nine per cent respectively.

Phase transformations are of two types, diffusion and diffusionless transformations. The former is a nucleation and growth process in which the transformation will go to completion isothermally if held for a sufficiently long period of time. The latter is quite frequently referred to as a martensitic transformation and is a nucleation and shear process. It may give the appearance of being an athermal reaction (e.g., the formation of martensite in plain carbon steels), it may be an isothermal transformation, as in uranium-chromium alloys, ^(4, 5) or it may be partially isothermal and partially athermal as in the case of some alloy steels. ^(6, 7, 8)

An athermal reaction is a transformation which on cooling begins at a fixed temperature independent of the cooling rate and below which transformation occurs only with decreasing temperature and does not go to completion at constant temperature.

Due to the large volume changes in the $\beta \longrightarrow \alpha$, $\gamma \longrightarrow \beta$ and $\delta \longrightarrow \gamma$ transformations it was proposed that the transformations of the delta, gamma, and beta phases be studied by fluid displacement measurements. Isothermal reaction curves of the $\beta \rightleftharpoons \alpha$ transformation were obtained by this technique.

SUMMARY

The transformation kinetics of the $\alpha \rightleftharpoons \beta$ transformation was studied by means of fluid displacement measurements. Heating and cooling curves, isothermal reaction curves showing the fraction transformed as a function of time, and time-temperature-transformation curves were obtained by this technique.

Time-temperature-transformation curves of the $\beta \longrightarrow \alpha$ reaction have the form of the typical C curve with the maximum rate of transformation at approximately -20 C. The effect of increasing impurities was to shift the T-T-T curve to the right. A time-temperature-transformation curve of the $\alpha \longrightarrow \beta$ reaction was also sketched.

The data indicate that the beta to alpha transformation may not go to completion isothermally unless the temperature is near the nose of the T-T-T curve.

EXPERIMENTAL PROCEDURE

Wafers one inch in diameter and .030 - .045 inch thick were machined from one inch as cast plutonium ingots. A .015 inch hole was drilled near one edge of the wafer so that it could be suspended in solution from the beam of an analytical balance by means of a .005 inch wire. Whenever possible the same sample was used to obtain the data. The effects of variables such as size, composition and casting were minimized by using a single sample.

A sample of each purity was held in a bath of carbon tetrachloride and dry ice at -20 C for a minimum of ten minutes. This resulted in the complete transformation of beta to alpha. Heating curves from 26 C to 175 C of each

sample were then obtained by determining the weight in a bath of peanut oil as a function of temperature. Cooling curves were obtained in a similar manner after holding the samples at 175 C for one hour. Peanut oil was considered the most satisfactory bath because it was necessary to obtain the weight in solution at temperatures as high as 200 C and in a closed hood. Due to the oxidation of the surface and the large surface to volume ratio, the error in making actual density measurements was quite high. Thus only weight changes were recorded.

Isothermal reaction curves of the $\beta \longrightarrow \alpha$ transformation were obtained by solution heat treating at 175 C for one hour, quenching to temperatures between -80 C and +90 C, and holding isothermally until there was no further apparent transformation. The sample was quickly taken from the high temperature bath and suspended from the balance into the low temperature quenching bath.

The weight of the sample was obtained and recorded as a function of time. The time required to obtain the initial weight was approximately ten seconds.

Isothermal reaction curves at temperatures between -80 C and +90 C were obtained in this manner. It was necessary to use carbon tetrachloride at temperatures between +20 C and -22 C as the peanut oil was too viscous in this temperature range. The quenching medium at -39 C and -78 C was acetone.

After the apparent completion of the transformation of beta at each holding temperature the sample was held at -20 C for ten minutes and reweighed at the transformation temperature.

DISCUSSION

A heating curve and a cooling curve of one sample at a heating rate of 40 C per hour and a cooling rate of 20 C per hour are shown in Figure 3. The curves were plotted in the form of weight change as a function of temperature.

Upon heating below the transformation temperature, there occurred two competing effects. The densities of both the plutonium sample and the liquid decreased with increasing temperature. However, the density of the oil decreased at a much faster rate than did the density of the plutonium. This gave a net effect of an increasing weight change.

At the heating rate of 40 C per hour the $\alpha \longrightarrow \beta$ transformation occurred at approximately 135 C, shown in Figure 3 where the weight decreased due to the lower density of beta.

The $\beta \longrightarrow \alpha$ transformation, indicated by a weight increase, did not occur until the temperature had dropped to 65 C. The reaction progressed very quickly below 60 C, and at 55 C there was no further weight increase. Below 55 C there was essentially no weight change upon further cooling, with the cooling curve becoming very nearly horizontal with possibly a very slight weight decrease. This indicated that the reaction may not have gone to completion at temperatures higher than 30 C. If the transformation had gone to completion the cooling curve would subsequently have become very nearly coincident with the heating curve.

Figure 3 shows that at 50 C the difference between the heating and the cooling curve was twelve milligrams, whereas at 30 C the difference was only eight milligrams. The difference between the heating and cooling curve may have been partially due to loss of particles from the surface of the sample.

Isothermal reaction curves showing the weight increase as a function of time for a high-purity sample were plotted in Figure 4. The reaction was not carried to completion at temperatures higher than 78 C.

Isothermal reaction curves showing the fraction of alpha formed from beta as a function of time were plotted in Figures 5 and 6. The fraction transformed was obtained from the relationship:

$$f(t) = \frac{W_t - W_i}{W_f - W_i} \quad (2)$$

W_t = weight in solution at any time

W_i = initial weight in solution

W_f = weight in solution after which there is no further apparent change

The weight W_f was not necessarily the completion of the transformation, for some retained beta phase may have been present. However, W_f did indicate the completion of the transformation at the temperature of holding.

The isothermal reaction curves, Figures 5 and 6, show the rate of reaction to have decreased from -21 C to 67 C and from -21 C to -78 C. The start of the transformation of beta to alpha was approximately 20 seconds at -21 C and 40 minutes at 73 C. The start of the reaction at -78 C was approximately three minutes and the completion of the reaction was approximately fifteen minutes. At temperatures higher than 85 C, the start of the transformation was longer than two thousand minutes.

After the reaction had gone to completion at each temperature, the sample was quenched into a bath of carbon tetrachloride and dry ice and reweighed at the holding temperature. At 26 C and above the weight after quenching to -21 C and reweighing (W_q) was greater than W_f . The ratio $(W_q - W_f)/(W_q - W_i)$, which is an expression of the fraction of untransformed beta, is plotted as a function of temperature in Figure 7. The value of $(W_q - W_f)$ was zero at 0 C.

The lower the temperature the less was the increase in weight, indicating that the sample may have contained some retained beta phase. Another observation was that after repeated cycling between the alpha and beta phases microscopic voids appeared. This also could have accounted for the increase in weight after quenching to -21 C and reweighing at the higher temperatures. This was also in agreement with the fact that the slope of the cooling curve, Figure 3, was very nearly zero between 50 C and 30 C. This phase of the work is being studied in greater detail.

The time-temperature-transformation curve, Figure 8, was sketched (from the isothermal reaction curves shown in Figures 4, 5 and 6). The curve has the form of a C curve common to eutectoid alloys. The temperature of the maximum rate of transformation was approximately -20 C.

Four time-temperature-transformation curves of samples of varying impurity content from 200 ppm to 1500 ppm are sketched in Figure 9. The curves show the rate of transformation to be quite sensitive to impurities and increasing the amount of impurities shifted the curves to the right. It also appeared that there was no apparent shift in temperature of the nose of the curves.

At constant temperatures, it also appeared that the ratio $(W_q - W_f)/(W_q - W_i)$ of Figure 8 would have been increased with lower purity. This gave the effect of shifting the curve to the left.

No attempt has been made to isolate the effects of individual elements. Further work is being accomplished to study the effect of impurities and to particularly determine the temperature of the maximum rate of transformation.

Investigation of the effect of solution-heat treating temperatures in the beta range has shown that increasing the temperature decreases the rate of transformation; i. e., shifts the isothermal reaction curves to the right. A high purity sample was solution-heat treated one hour at different temperatures in the beta range and isothermal reaction curves were obtained

at 52.5 C. Prior to quenching the samples from the higher beta heat treating temperatures to 52.5 C they were quenched to 132 C and held for three minutes. A relationship showing the time of fifty per cent transformation as a function of the beta heat treating temperature is plotted in Figure 10. The rate of transformation was essentially not affected by varying the time of beta heat treating.

A study of the $\alpha \rightarrow \beta$ transformation was made by a similar technique. The metal sample was cold treated at -21 C for ten minutes, held at 110 C for three minutes, and allowed to transform isothermally at temperatures between 123 C and 150 C. The isothermal reaction curves are shown in Figure 11 and are similar to the isothermal reaction curves of the $\beta \rightarrow \alpha$ transformation. A time-temperature-transformation curve, Figure 12, was plotted from these curves.

The curves show that above 140 C the transformation was 99 per cent completed in less than three minutes. At temperatures below 123.5 C the transformation was not completed until after five hours.

A metallographic study has shown the temperature of the $\beta \rightarrow \alpha$ transformation to have a pronounced effect on the grain size. Decreasing the temperature of transformation resulted in a finer grain structure. Photomicrographs showing grain structure after quenching at -21 C, 26 C, and 73 C are presented in Figures 13 - 15 inclusive. The resulting grain size at 73 C was significantly larger than after allowing the sample to transform at 26 C or -21 C.

The same specimen, 0.20 inch in diameter and 3/8 inch long, was used for all metallographic examinations. It contained approximately 500 parts per million of impurities. Also, constant solution time and temperature, thirty minutes at 175 C, were used for all transformations.

The metallographic polishing procedure was the standard technique utilizing 600 alundum on billiard cloth after grinding on the 3/0 paper. The final lap polish was Linde B on microcloth. An electrolytic etchant of 20

parts tetraphosphoric acid, 30 parts water, and 50 parts 2-ethoxyethanol was used. The metallographic samples were examined under polarized light illumination.

CONCLUSIONS

The results of this investigation showed the transformation of beta to alpha to have the form of a typical C curve, with the reaction being quite sluggish above 80 C, proceeding quite rapidly below 50 C, reaching a maximum rate at approximately -20 C. More detailed work will be accomplished to determine the exact temperature at which the maximum rate of transformation occurs.

The influence of impurities has been shown to have a significant effect on the rate of transformation; increasing the amount of impurities shifts the T-T-T curve to the right.

The information obtained suggests that there may be retained beta after isothermal transformation below the equilibrium temperature.

The rate of transformation of alpha to beta was quite sluggish below 124 C and was quite rapid above 135 C.

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FIGURE 1

Isothermal Reaction Curve
(Schematic)

FIGURE 2

Time-Temperature Transformation Curve
(Schematic)

FIGURE 3

Heating and Cooling Curves of Plutonium Metal

FIGURE 4

Isothermal Reaction Curves of the Transformation of Beta Plutonium
Showing the Weight Change as a Function of Time

FIGURE 5

Isothermal Reaction Curves of the Transformation of Beta Plutonium
Showing the Fraction Transformed as a Function of Time

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FIGURE 6

Isothermal Reaction Curves of the Transformation of Beta Plutonium
Showing the Fraction Transformed as a Function of Time

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FIGURE 7

Fraction of Weight Increase after Cold Treating
and Re-weighing of a Sample Having 500 ppm Impurities

FIGURE 8

Time-Temperature-Transformation Curve of the $\beta \rightarrow \alpha$ Transformation

FIGURE 9
Time-Temperature-Transformation Curves (50 Per Cent Transformed)
Showing the Effect of Impurities

FIGURE 10

Time of 50 Per Cent Transformation at 52.5 C as a Function
of the Beta Heat Treating Temperature

FIGURE 11

Isothermal Reaction Curves of the $\alpha \rightarrow \beta$ Transformation

FIGURE 12

Time-Temperature-Transformation-Curve of the $\alpha \rightarrow \beta$ Transformation

FIGURE 13

Plutonium Metal
Solution Heat Treated 45 Minutes at 175 C
and Quenched to -21 C. 300X

FIGURE 14

Plutonium Metal
Solution Heat Treated 45 Minutes at 175 C
and Quenched to 26 C. 300X

FIGURE 15

Plutonium Metal
Solution Heat Treated 45 Minutes at 175 C
and Quenched to 73 C. 300X

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