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MASTER

TRANSFORMATION KINETICS OF PLUTONIUM

PART II - A STUDY OF THE GAMMA TO BETA TO ALPHA AND ALPHA TO BETA TO GAMMA TRANSFORMATIONS

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

By

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Plutonium Metallurgy
Reactor and Fuels Research and Development Operation

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ABSTRACT

The kinetics of the $\gamma \longrightarrow \beta \longrightarrow \alpha$, $\beta \longrightarrow \gamma$, and $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformations were determined with a fluid displacement technique. The rates of formation of the alpha and beta phases from the gamma phase were determined after gamma heat treating and allowing a sample to transform isothermally in the alpha and beta ranges. Isothermal reaction curves were obtained from 160 C to -78 C. The time-temperature-transformation curve of the $\gamma \longrightarrow \beta \longrightarrow \alpha$ transformation was plotted.

The effect of the gamma heat treating time and temperature on the rate of transformation was examined.

Isothermal reaction curves and time-temperature-transformation curves of the $\beta \longrightarrow \gamma$, and $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformations were plotted.

Photomicrographs of specimens having transformed from the gamma range at different rates of transformation are presented.

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INTRODUCTION

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.[1, 2] The beta phase transforms to the gamma phase at approximately 200 C. The crystal structure of the gamma phase is face-centered-orthorombic.

Results of a study of the $\beta \longrightarrow \alpha$ and $\alpha \longrightarrow \beta$ transformations have been presented in a previous report.[3] This report presents and discusses results obtained from a study of the $\gamma \longrightarrow \beta \longrightarrow \alpha$, $\beta \longrightarrow \gamma$, and $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformations.

SUMMARY

The rate of transformation of the $\gamma \longrightarrow \beta \longrightarrow \alpha$, $\beta \longrightarrow \gamma$, and $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformations were determined by fluid displacement measurements. Heating and cooling curves, isothermal reaction curves showing the weight change and fraction transformed as a function of time, and time-temperature-transformation curves were obtained by this technique.

The time-temperature-transformation curves of the $\beta \longrightarrow \gamma$, and $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformations are similar to that of the $\alpha \longrightarrow \beta$ transformation.[3]

The time-temperature-transformation curve of the $\gamma \longrightarrow \beta \longrightarrow \alpha$ transformation is a double C curve showing the $\gamma \longrightarrow \beta$, and $\beta \longrightarrow \alpha$ transformations.

EXPERIMENTAL PROCEDURE

A wafer one-eighth inch thick was cut from a one-inch diameter as-cast plutonium ingot for the study of the transformation of the gamma phase at 75 C and higher temperatures. Wafers .030 to .045 inch thick and one inch in diameter were used to study the $\gamma \longrightarrow \alpha$ transformation at temperatures lower than 75 C. A wafer one-sixteenth inch thick and one inch in diameter was used in studying the $\alpha \longrightarrow \beta \longrightarrow \gamma$ and $\beta \longrightarrow \gamma$ transformation.

The technique of fluid displacement measurements that was used in the present study to determine the isothermal reaction curves is the same as was used in a study of the $\beta \rightleftharpoons \alpha$ transformations.

The volume change, approximately three per cent, associated with the gamma to beta transformation was significantly less than the volume change associated with the beta to alpha transformation so that it was necessary to use a larger sample. It was found that the time required for the gamma to beta transformation was sufficiently long so that a sample one-eighth inch thick did not cause any appreciable error in the results. Wafers were used in preference to a shape such as a thin cylinder because wafers were more conveniently obtained.

Isothermal reaction curves of the $\gamma \longrightarrow \beta \longrightarrow \alpha$ transformations were obtained by gamma heat treating the samples at 260 C for one hour, quenching to temperatures between -78 C and +160 C, and holding isothermally until there was no further apparent transformation. The weight of the sample in a bath of peanut oil was obtained and recorded as a function of time. The isothermal reaction curves of the $\beta \longrightarrow \gamma$ transformation were determined by cold treating fifteen minutes at -23 C, beta heat treating twenty minutes at 180 C, and holding at the desired temperature in the gamma range. Peanut oil was also used as the transformation medium.

The procedure for obtaining the isothermal reaction curves of the $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformation was the same as that for the $\beta \longrightarrow \gamma$ transformation except after cold treating the sample was held at 100-110 C, below $\alpha \longrightarrow \beta$ transformation temperature, for three minutes. Subsequent

to holding the sample at 100-110 C, the sample was held in a bath at the desired temperature in the gamma range. The isothermal reaction curves were obtained in the same manner. The purpose of holding at 100-110 C was to minimize the temperature difference between the sample and the bath and still have the sample be in the alpha phase.

DISCUSSION

Four isothermal reaction curves of the $\gamma \longrightarrow \beta \longrightarrow \alpha$ transformation are shown in Figure 1. The transformation of the gamma phase to the beta and alpha phases is shown by a weight change in a bath of peanut oil. The weight change in solution was a function of the change in density of the metal. At each temperature there was an initial period in which there was no weight change (constant density) and hence no transformation. As the transformation proceeded the weight in solution increased (increasing density). Finally, there was no further weight increase (constant density) which indicated the apparent completion of the transformation.

The density as a function of time was not computed because of the large variation of the density of peanut oil with temperature. Because of the large surface to volume ratio and the oxidation of the sample, the error in computing the density was quite large. There was also a variation of density between samples.

Since the isothermal reaction curves with weight change as the ordinate would have been identical to curves with density as the ordinate it was not worth while to make the necessary density measurements and calculations. Thus only weight changes were recorded and plotted as a function of time.

The curves have the shape of typical sigmoid curves characteristic of nucleation and growth reactions. The curves at 160 C and 100 C show the rate of formation of beta from gamma. Curves at 148 C, 139 C, 137 C, and 122 C were also obtained and found to be similar. The lower temperatures indicated a larger weight change for an apparent 100 per cent transformation. This was due to the larger density of the peanut oil at the lower temperatures.

The isothermal reaction curves between 82 C and 90 C may be considered to comprise three stages. Initially there was a period during which the gamma phase transformed to the beta phase. This was followed by an interval during which there was no weight change. Finally, there was a period during which the beta phase transformed to the alpha phase.

The transition period between the $\gamma \longrightarrow \beta$ transformation and the $\beta \longrightarrow \alpha$ transformation is shown on the 88 C curve of Figure 1 as a plateau. The plateau at 82 C appeared only as a change of slope. The time interval of the plateau increased with increasing temperature. The portion of the curve at 100 C that show the apparent completion of the gamma to beta transformation was also a transition between the $\gamma \longrightarrow \beta$ and $\beta \longrightarrow \alpha$ transformations. Had the sample been held for a sufficient time at 100 C the beta phase would have transformed to the alpha phase.

The isothermal reaction curves below 82 C do not show a transition period between the $\gamma \longrightarrow \beta$ and the $\beta \longrightarrow \alpha$ transformations, indicating that the gamma phase may transform directly to the alpha phase. There was also a weight change equivalent to a total volume change of both transformations.

The start and the completion of the $\gamma \longrightarrow \beta \longrightarrow \alpha$ transformation were plotted as a portion of the time-temperature transformation curve shown in Figure 2. The curve has the form of a double C curve. The upper C curve represents the $\gamma \longrightarrow \beta$ transformation and the lower C curve represents the formation of the alpha phase.

The upper C curve shows the rate of formation of beta to increase by lowering the temperature of transformation from 160 C to 100 C. Further lowering of the temperature to 82 C shows a decrease in the rate of transformation of the gamma phase to the beta phase.

The rate of formation of the alpha phase increased quite rapidly below 88 C. It appears that below 82 C the gamma phase transforms directly to the alpha phase without first transforming to the beta phase. To the author's

knowledge the skip transformations of no other high purity metal showing more than two transformations have been studied. The formation of the alpha phase from the gamma phase, by-passing the beta phase, is a skip transformation.

The $\gamma \longrightarrow \alpha$ transformation proceeded too rapidly at -78 C to be measured by the fluid displacement technique. It has been reported that the gamma phase cannot be retained regardless of the quenching temperature or the quenching rate.[4] The present work did not involve a study of the gamma transformation at temperatures lower than -78 C.

A comparison of the formation of the alpha phase from the gamma phase and the beta phase is shown in Figure 3. The time for fifty per cent transformation as a function of temperature was plotted for both transformations. The data for the $\beta \longrightarrow \alpha$ transformation was obtained from previous work.[3] The rate of formation of alpha was considerably higher from the gamma phase than from the beta phase. The difference becomes increasingly great below the nose of the $\beta \longrightarrow \alpha$ T-T-T curve since it appears from the $\gamma \longrightarrow \alpha$ T-T-T curve that the rate of formation of the alpha phase from gamma phase does not pass through a maximum.

A study of the effect of gamma heat treating temperatures has shown that the rate of transformation decreases with increasing gamma heat treating temperatures. This is shown in Figure 4 in which the time for fifty per cent transformation at 127.8 C was plotted as a function of the gamma heat treating temperature.

A variation of the gamma heat treating temperature caused essentially no change of the rate of the $\gamma \longrightarrow \alpha$ transformation. Varying the gamma heat treating time had essentially no effect on either the $\gamma \longrightarrow \alpha$ or the $\gamma \longrightarrow \beta$ transformation rates.

The $\beta \longrightarrow \gamma$ transformation behaved in a manner similar to the $\alpha \longrightarrow \beta$ transformation. The isothermal reaction curves also had the sigmoid shape characteristic of nucleation and growth reactions. Three representative curves are shown in Figure 5.

The T-T-T curve, Figure 6, was plotted from the isothermal reaction curves. The shape of the curve is similar to that of the T-T-T curve of the $\alpha \longrightarrow \beta$ transformation. The reaction started after only five or six seconds and was completed after one and one-half minutes at 25 C. The transformation was quite sluggish at 202 C with the reaction not starting until after thirty minutes and not being completed until approximately four hours.

Isothermal reaction curves, Figure 7, and a T-T-T curve, Figure 8, of the $\alpha \longrightarrow \beta \longrightarrow \gamma$ transformation, transforming to the gamma phase after holding at 100 C, were also determined. The rate of formation of the beta phase from the alpha phase at temperatures between 200 C and 250 C was too rapid to be accurately measured as the time for the completion of the transformation was less than thirty seconds. It appeared that the sample began transforming within less than three or four seconds of the time it was in solution.

The time required for the appearance of the gamma phase after the sample had undergone the latter heat treatment was slightly longer than after the previous heat treatment of holding at 180 C. This could have been due to the larger grain size resulting from the higher temperature at which the beta phase had transformed. It could also have been because a longer time was required to raise the temperature of the sample from 100 C than from 180 C. The two effects could very easily have supplemented one another. The higher the transformation temperature the greater was the difference in the T-T-T curves. The difference at 205 C was negligible. The difference at 240 C was slight but it was apparent. Either of the two reasons could apply but it is thought that the temperature difference is the most likely.

Metallographic studies have revealed that the final grain size is dependent on the rate of transformation of beta to alpha but the final grain size is not dependent on the rate of formation of the beta phase from the gamma phase. Figures 9 and 10 show that the grain size is approximately the same for sample that had been quenched from the beta and gamma phases to 26 C. The final grain size was approximately the same for the sample that had been in the as-cast condition, Figure 11, transformed to beta at 160 C and air-cooled, Figure 12, or had transformed isothermally at 100 C and air-cooled, Figure 13. The nose of the gamma to beta T-T-T curve is at 100 C.

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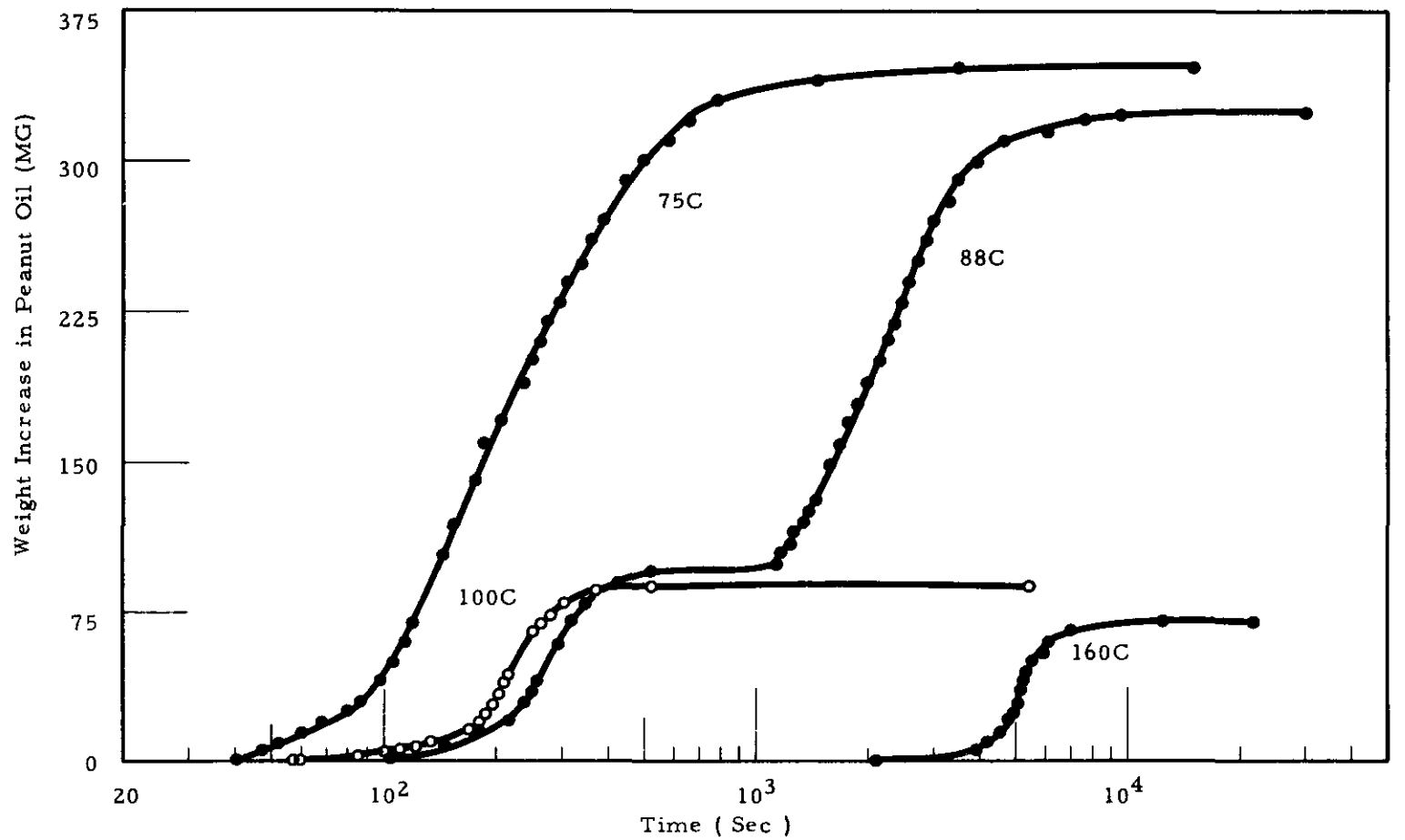


FIGURE 1

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

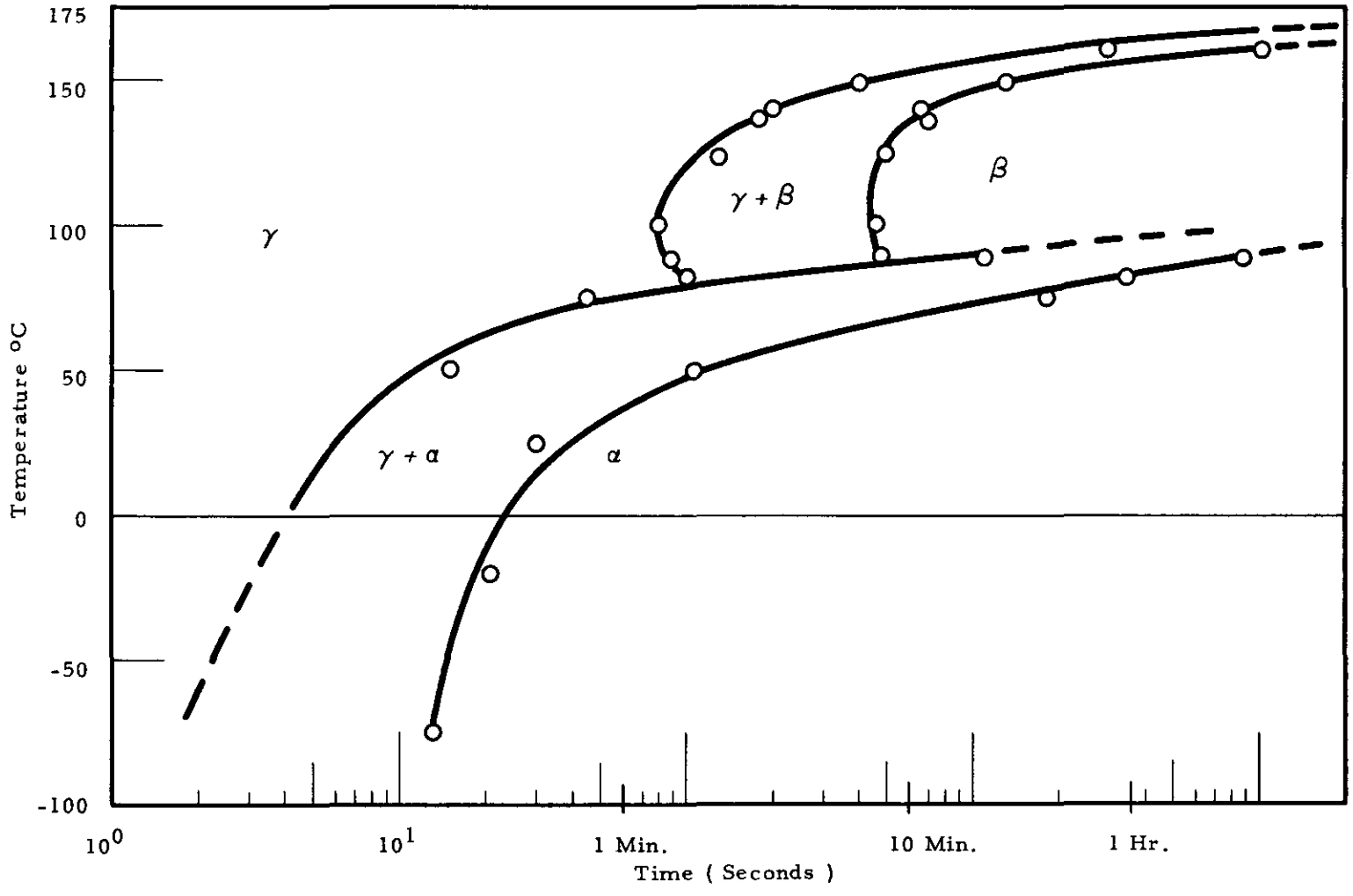


FIGURE 2

T-T-T Curve of the $\gamma \rightarrow \beta \rightarrow \alpha$ Transformation

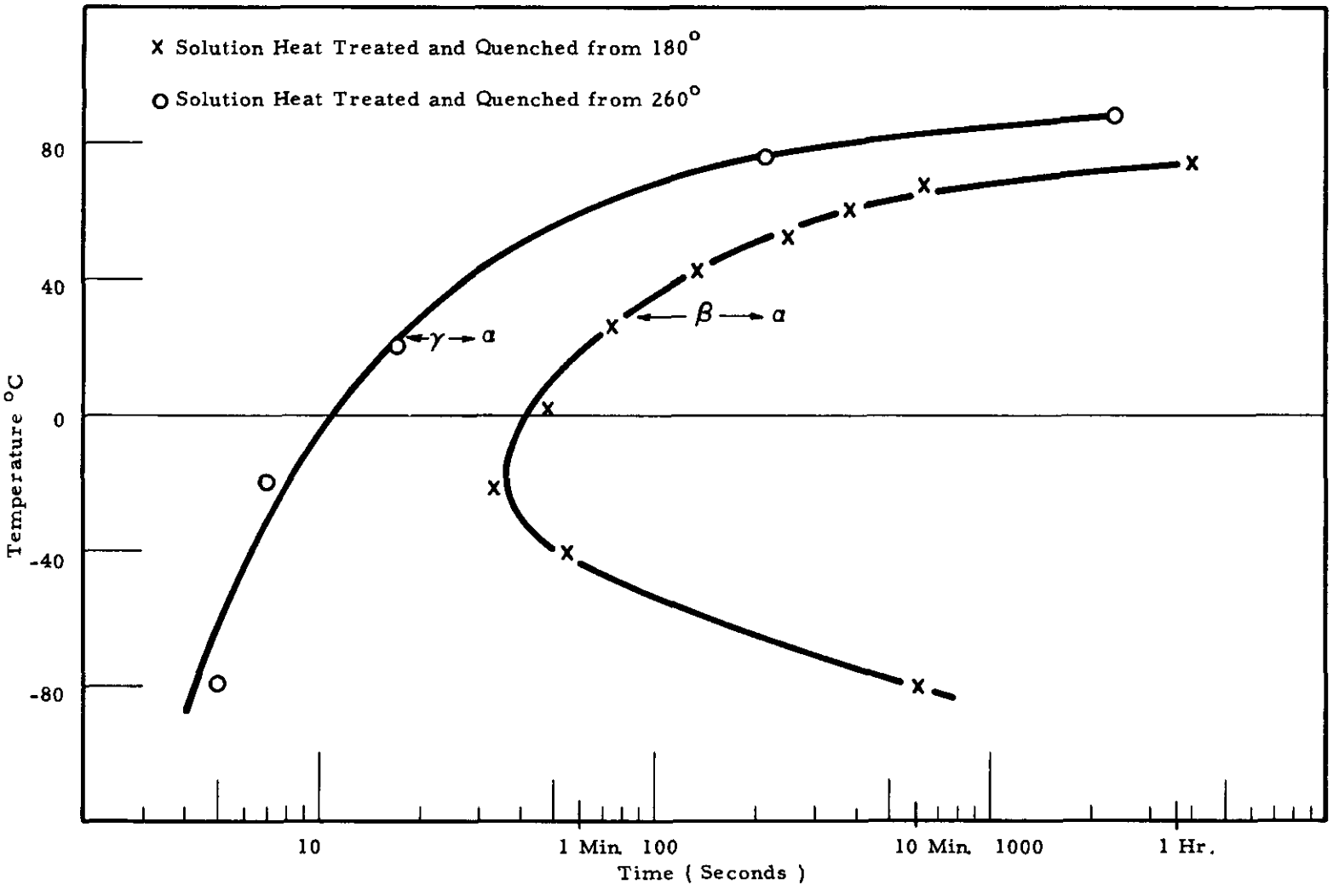


FIGURE 3

Time-Temperature-Transformation Curves (50 Per Cent Alpha) of the $\beta \rightarrow \gamma$ and the $\gamma \rightarrow \beta \rightarrow \alpha$ Transformations

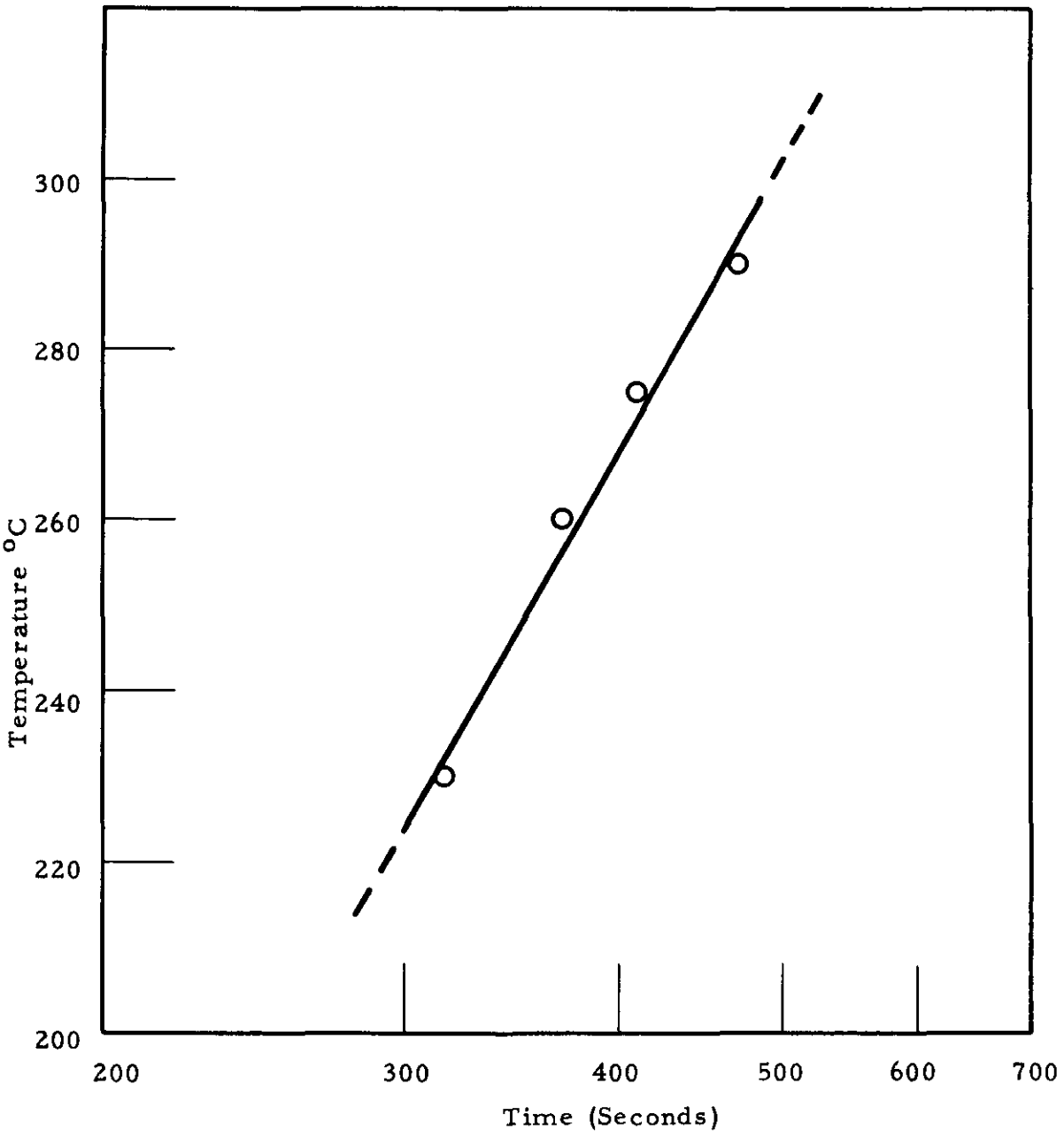


FIGURE 4

Time of 50 Per Cent Transformation at 127.8 C as a Function of the Gamma Heat Treating Temperature

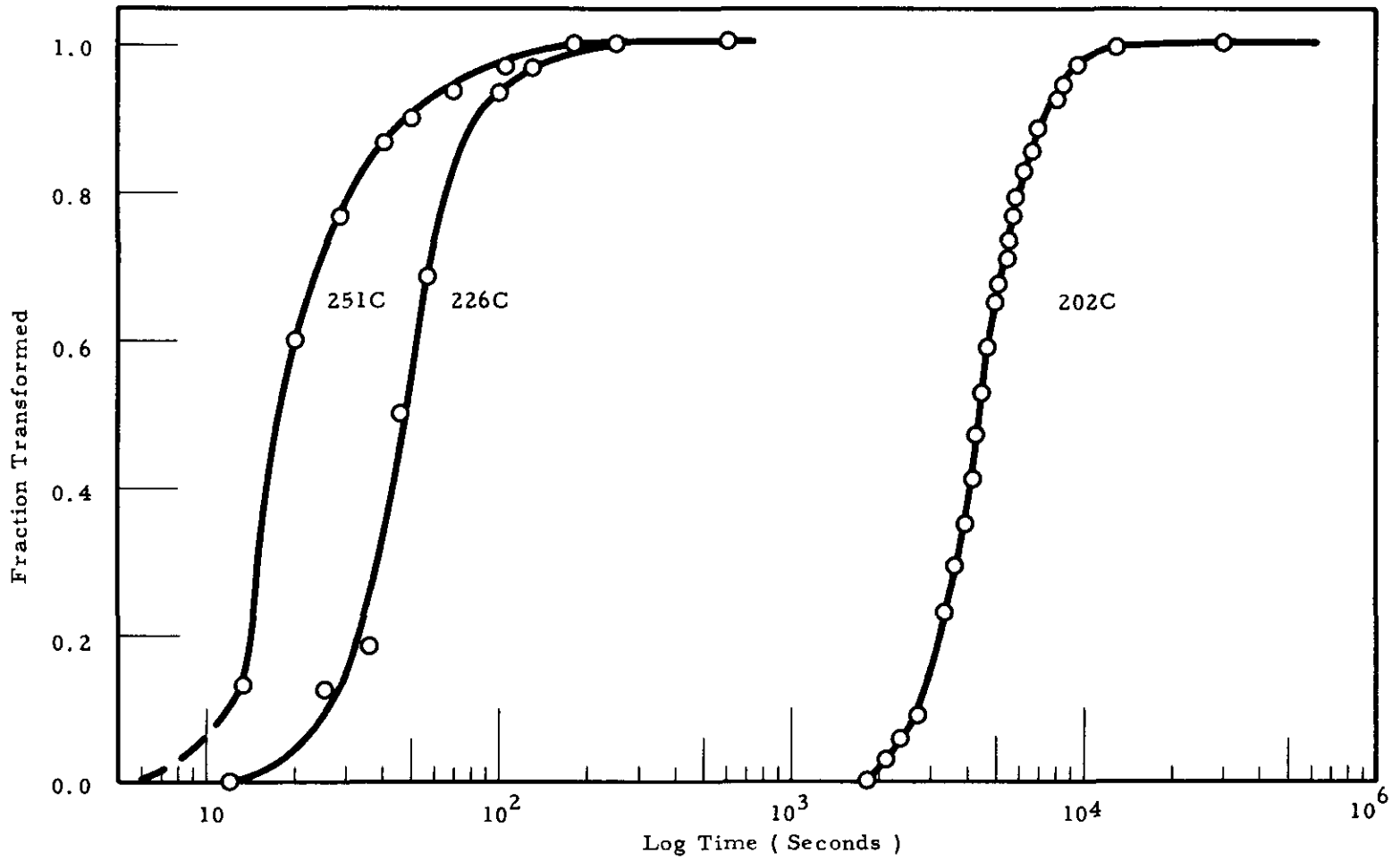


FIGURE 5

Isothermal Reaction Curves of the $\beta \longrightarrow \gamma$ Transformation

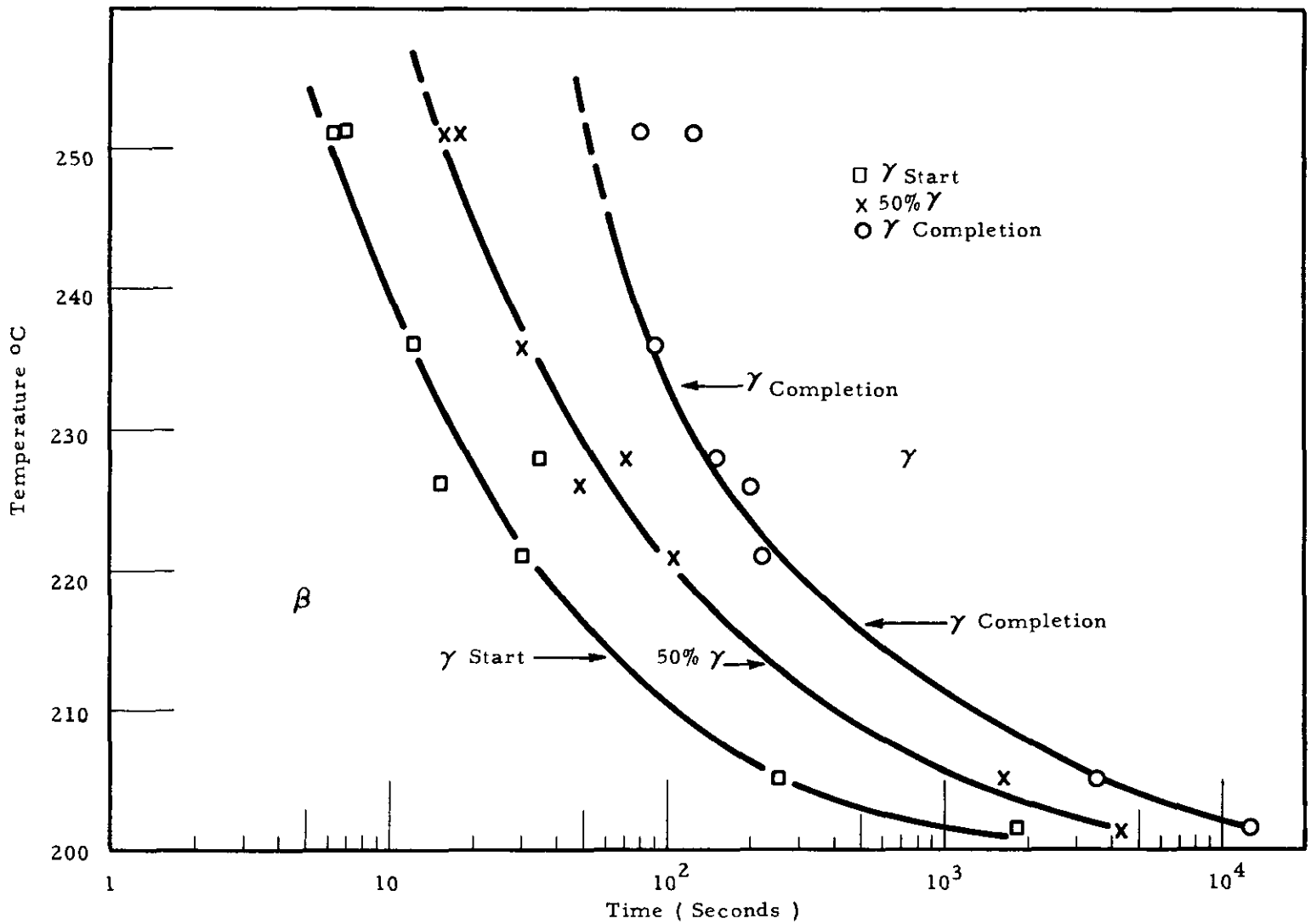


FIGURE 6

T-T-T Curve of the $\beta \rightarrow \gamma$ Transformation

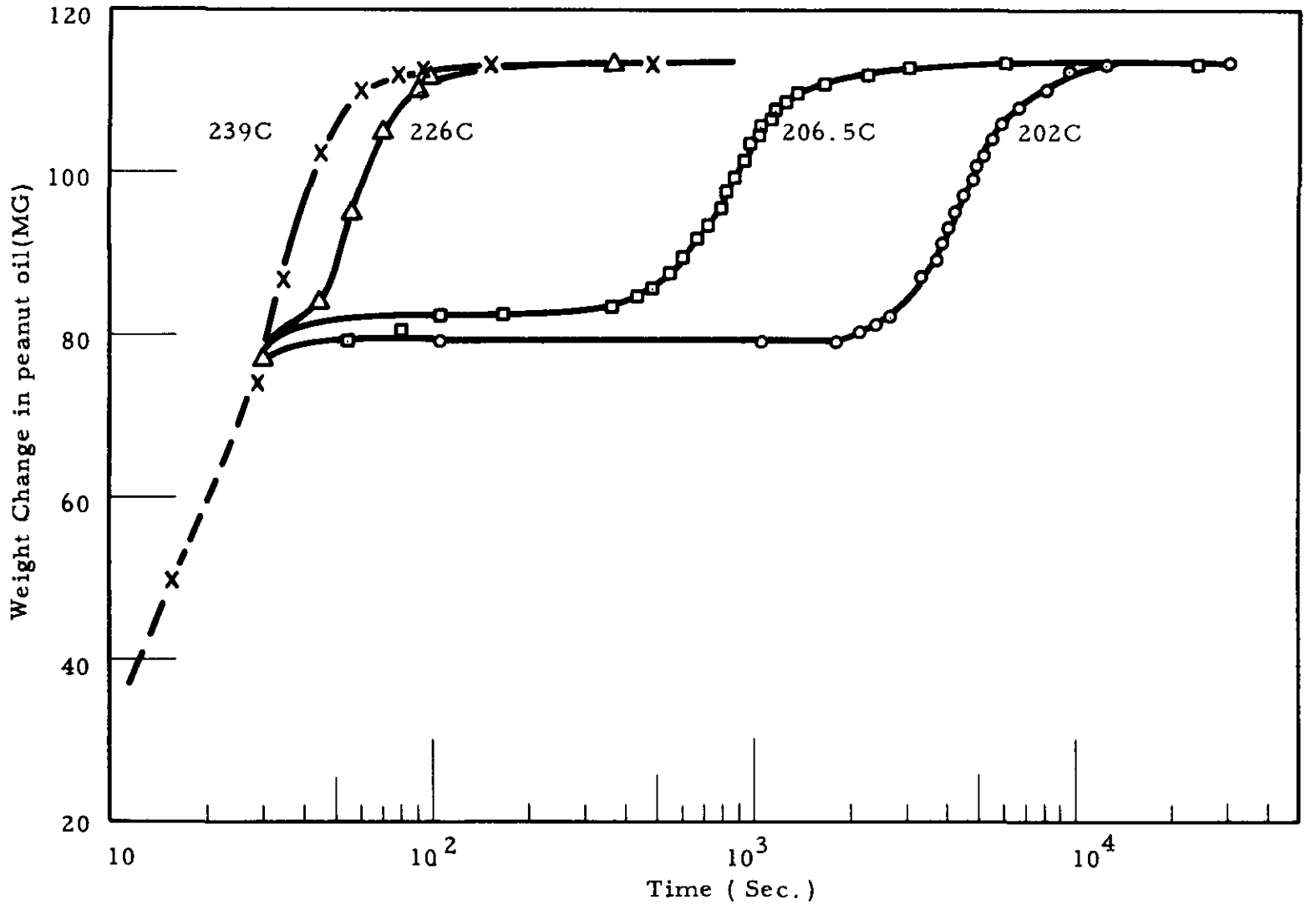


FIGURE 7

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

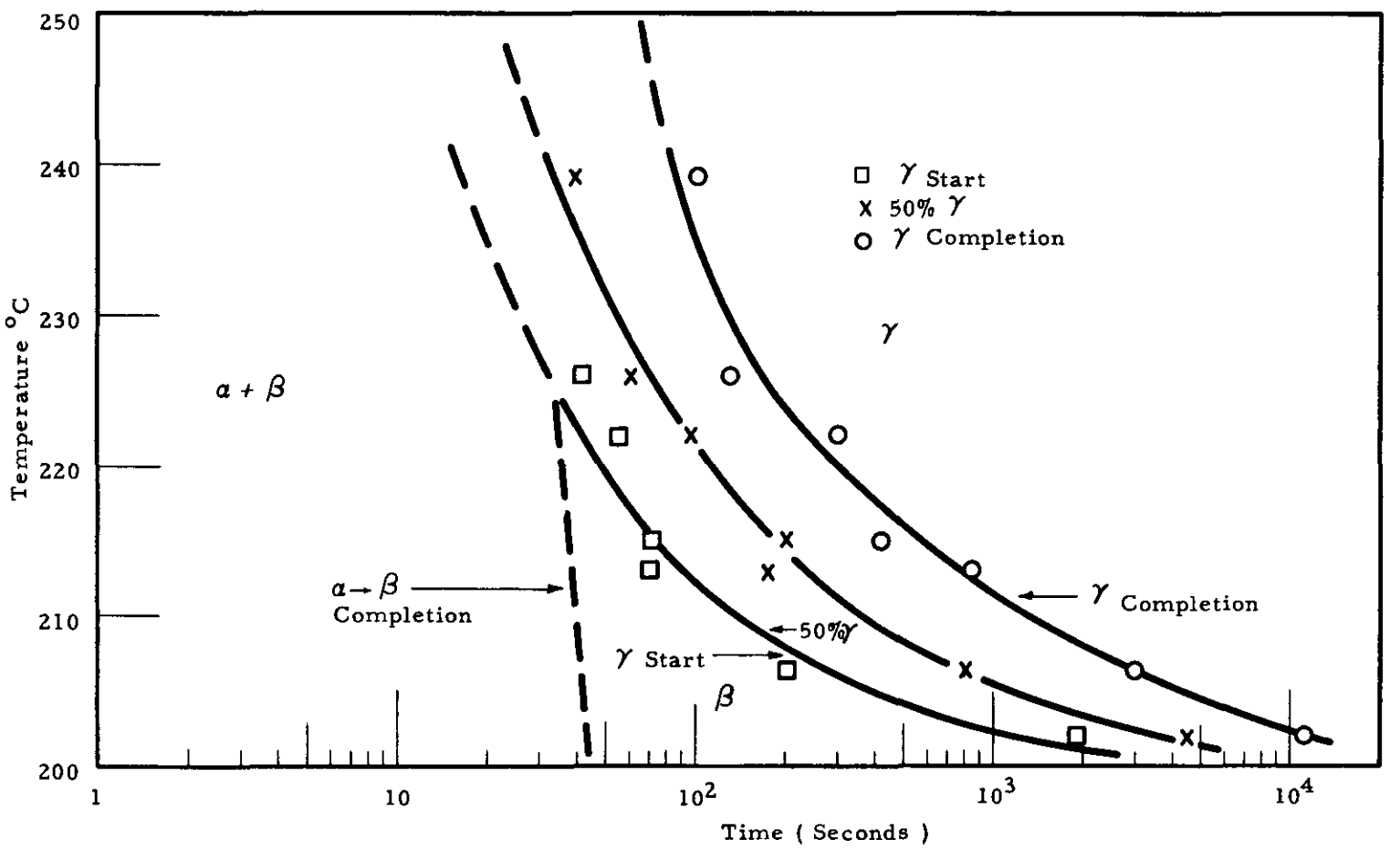


FIGURE 8

T-T-T Curve of the $\alpha \rightarrow \beta \rightarrow \gamma$ Transformation

Quenched to 26 C.

Electropolished 250X

Polarized Light

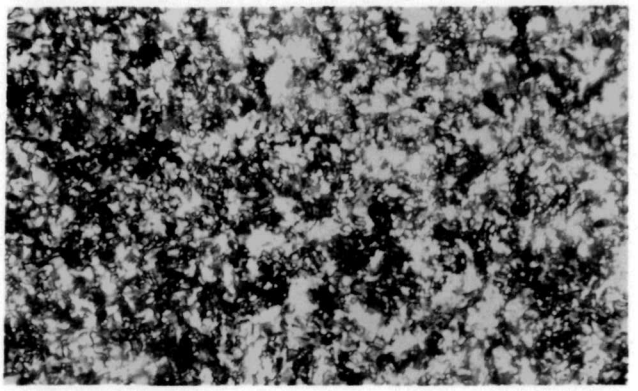
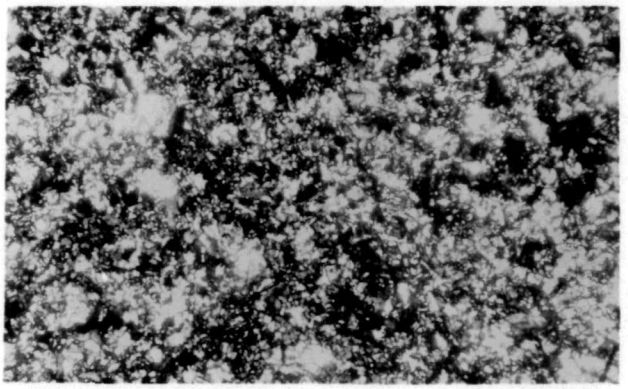


FIGURE 9

Beta Heat Treated 45 Minutes at 175 C,



Quenched to 26 C.

Electropolished 250X

Polarized Light

FIGURE 10

Gamma Heat Treated 45 Minutes at 260 C,

Electropolished 250X

Polarized Light

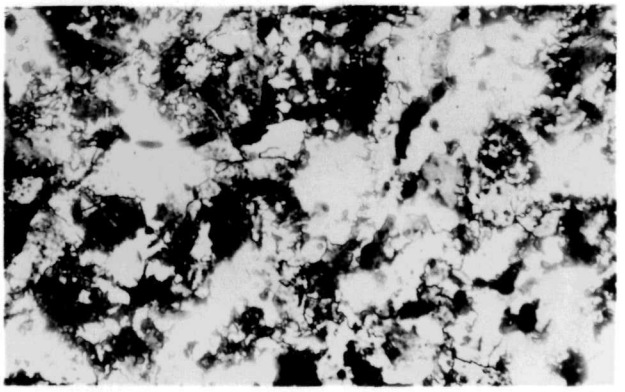


FIGURE 11

As-Cast

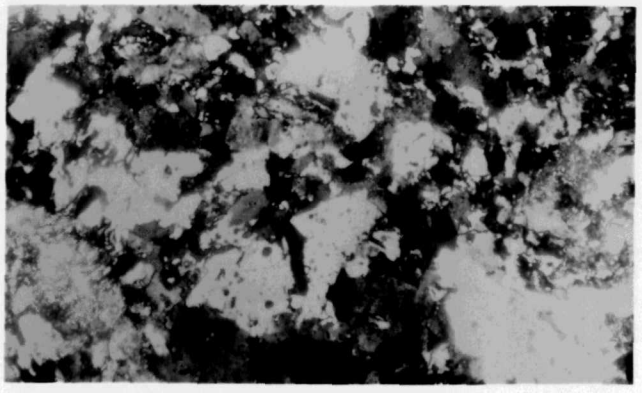


FIGURE 12

Gamma Heat Treated 45 Minutes at 260 C,
Quenched to 160 C, Held 24 Hours, Air-Cooled.
Electropolished 250X Polarized Light

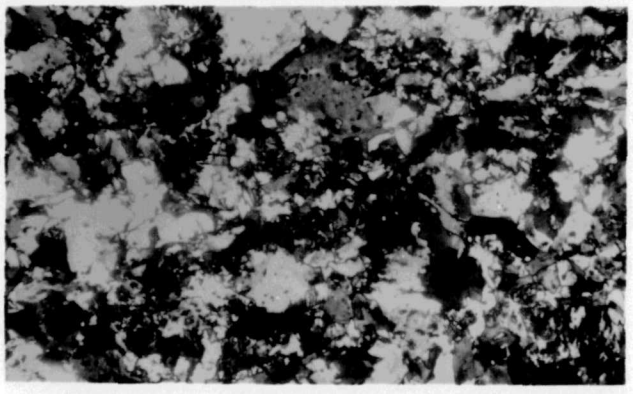


FIGURE 13

Gamma Heat Treated 30 Minutes at 260 C,
Quenched to 100 C, Held 3 Hours, Air-Cooled.
Electropolished 250X Polarized Light

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