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TRANSFORMATION KINETICS OF PLUTONIUM

PART III

R. D. NELSON

DECEMBER, 1961

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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TRANSFORMATION KINETICS OF PLUTONIUM

PART III

By

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Plutonium Metallurgy
Reactor and Fuels Research and Development Operation
Hanford Laboratories

December, 1961

HANFORD ATOMIC PRODUCTS OPERATION
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TABLE OF CONTENTS

TRANSFORMATION KINETICS OF PLUTONIUM

PART III

INTRODUCTION

Six allotropic forms of plutonium are known. Table I shows the different phases with their crystal structure, densities, and transformation temperatures. The stable phase at room temperature has been designated alpha and is stable up to 112 C.(1-5)

TABLE I

CRYSTAL STRUCTURE, DENSITIES, AND TRANSFORMATION TEMPERATURES FOR PLUTONIUM ALLOTROPES

Phase	Crystal Lattice	Number of Atoms Per Structure Cell	Approximate Transition Temperature to Next Higher Phase	Calculated Density
Alpha	Monoclinic	16	112	19.82
Beta	Monoclinic	34	185	~17.8
Gamma	Face-Centered Orthorhombic	8	316	17.14
Delta	Face-Centered Cubic	4	451	15.92
Delta Prime	Body-Centered Tetragonal	2	480	16.00
Epsilon	Body-Centered Cubic	2	640	16.51

A study of the phase transformations of plutonium is extremely important for an understanding of the fabrication and stability of the alpha phase. The necessity for extensive experimental work can be shown by analogy to the value received from the vast experimental studies on the phase transformations of steel and other metals and alloys. The information obtained from this work has proved to be necessary in providing satisfactory heat treatments.

The 9 per cent volume change associated with the beta—alpha transformation, the low transformation temperature, and the low ductility of the alpha phase has necessitated that the fabrication of plutonium be primarily by casting and machining.(6) Because of these factors, heat treatment of plutonium is limited in many respects, compared to other metals and alloys. On the other hand, because of these same factors and the five higher temperature allotropes, a number of heat-treating variables affect this type of fabrication. Some of them are retained phases (possibly more than one; however, the beta phase is probably the most important), impurities, strain, and void formation

Considerable work has been accomplished on the beta—alpha transformation. Some work has been performed on the alpha—beta—gamma, gamma—beta—alpha, and delta—gamma transformations.(7-29) No detailed information is available concerning the epsilon—delta prime—delta transformations. This report will primarily discuss the beta—alpha and gamma—beta—alpha transformations.

SUMMARY

Isothermal reaction curves and T-T-T curves showing the effect of different variables on the beta—alpha transformations are presented. Time for the start of the transformation at the nose of the T-T-T curve of recent work is five times faster than any previously reported.

Impurity content, stresses, beta heat-treating time and temperature, hydrostatic pressing, specimen size, and thermal cycling influence the kinetics of the beta—alpha transformation in the following ways:

(1) Decreasing the impurity content increases the rate of transformation.
(2) High tensile stress retards the beta—alpha transformation.
(3) Increasing the beta heat—treating time and temperature markedly decreases the rate of transformation.
(4) Hydrostatic pressing at 90,000 psi accelerates the beta—alpha transformation under pressure but decreases any subsequent beta—alpha transformations by as much as two orders of magnitude.

(5) Specimen size has no effect on the start of the transformation but increasing the specimen size from 0.010 to 0.37 inch decreases the rate of completion of transformation several orders of magnitude.

(6) Thermal cycling less than 15 cycles does not affect the rate of transformation.

The density of high purity plutonium during hydrostatic pressing at 180 C and cooling under pressure increases from 19.60-19.65 g/cm^3 to 19.70-19.75 g/cm^3. This increase was shown to be attributed to decreasing the volume of microcracks rather than transformation of any metastable beta phase.

A T-T-T curve of the alpha–beta transformation is given which shows the start of the transformation is 16 hours at 116.5 C with the rate decreasing extremely rapidly with decreasing temperature. The times for the start and completion of the transformation were significantly shorter than the early work reported at Hanford. The faster rate was attributed to less impurities.

The gamma–beta–alpha and alpha–beta–gamma transformations are discussed also. Isothermal reaction curves and T-T-T curves for these transformations are included.

KINETICS OF THE BETA–ALPHA TRANSFORMATION

Isothermal Reaction Curves and T-T-T Curves

Martin and Selmanoff(7, 10) first indicated that the beta–alpha isothermal transformations might proceed according to a "C" curve characteristic of the T-T-T (time-temperature-transformation) curves of many eutectoid alloys. They reported that the maximum rate of transformation was attained in 1-1/2 minutes at room temperature, whereas at -75 C the maximum speed was reached in 4 minutes.

The first extensive quantitative work on the transformation rates of the beta–alpha transformation was performed at Hanford.(11, 24, 25, 26) It was shown that the T-T-T curve (Figure 1) of the beta–alpha transformation has the form of a simple C curve with the maximum rate of transformation

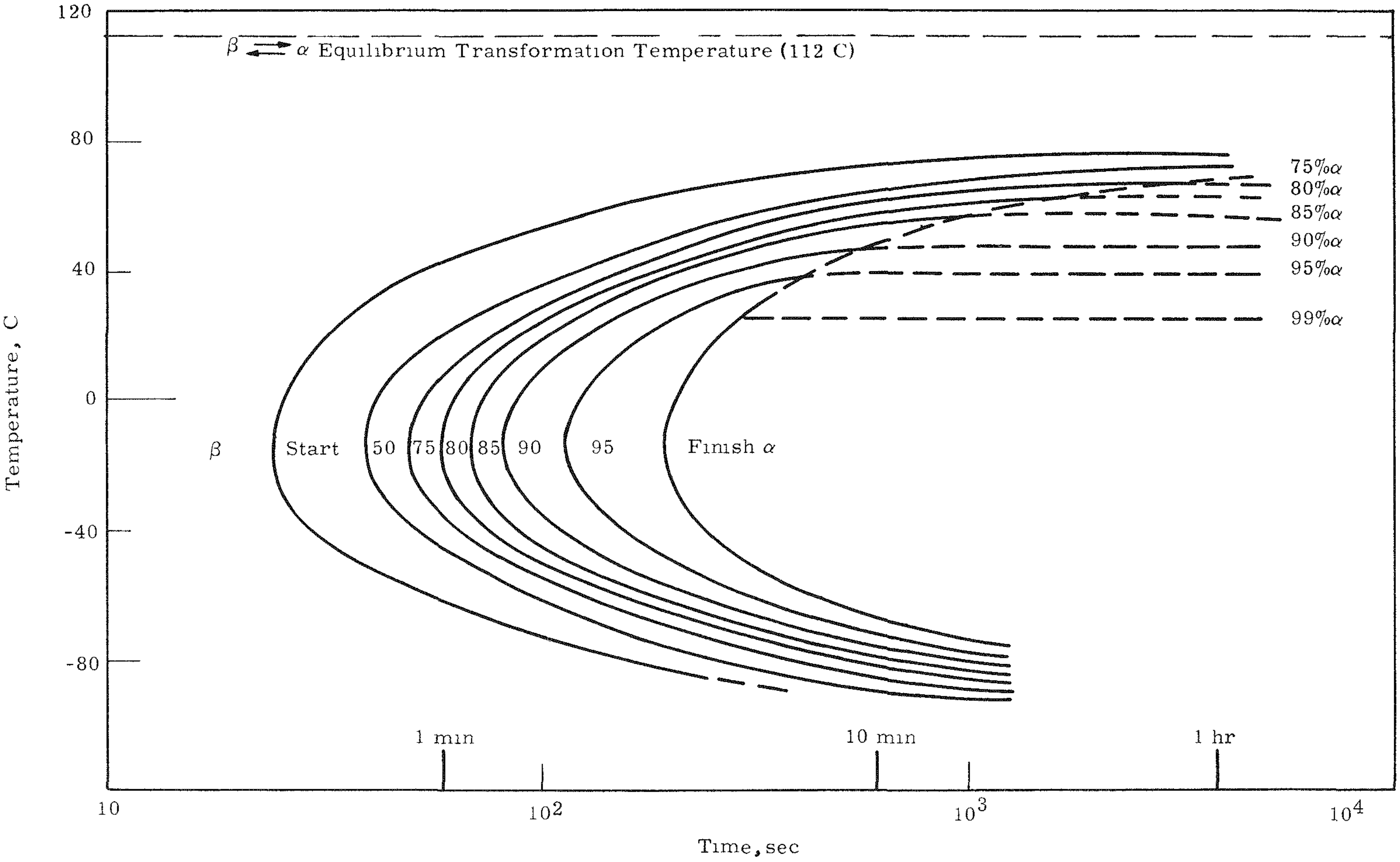


FIGURE 1

Beta–Alpha T-T-T Curve of Nelson(25)

at -20 C. The most significant factors affecting the shape and the position of the curve relative to the time and temperature axes are impurities, stresses, and alloying elements. This will be discussed in greater detail--generally, however, the purer the metal the more rapid the rate of transformation.(26)

Loasby and Lowe(15) have also shown the T-T-T curve to be a typical C curve (Figure 2). The rates of transformation were comparable to Hanford results with the maximum rate also occurring at -20 to -30 C. However, the T-T-T curve given by Loasby and Lowe showed a slightly faster rate of transformation than originally reported at Hanford. The difference between the two sets of results was most likely due either to metal quality or to different beta heat-treating temperature, since the rate of transformation decreases with an increasing beta heat-treating temperature. Also, oxidation of the plutonium did not allow sufficient time for completion of the beta—alpha transformation. More refined fluid displacement techniques, which enable plutonium to be held at any given transformation temperature for 10 to 30 days with insignificant oxidation (less than 0.5 mg increase in a 100-gram sample), have been developed at Hanford. Isothermal transformation curves and the corresponding T-T-T curves obtained by this technique for plutonium of higher purity are given in Figures 3 and 4.

The T-T-T curves of the start of the beta—alpha transformation (Figure 5) show that the transformation rates were approximately ten times faster than those in either the original work at Hanford or the work of Loasby and Lowe. The differences can be attributed to metal quality. The density of the metal is frequently taken as a criterion of metal quality; that is, metal having a density of 19.60 g/cm^3 or better is considered very high quality. However, density alone is not satisfactory for determining the quality of high purity metal due to differences in casting. The densities and impurities of each metal used for obtaining the data (Figures 1, 4 and 8) are listed in Table II, Heats A, B, and C, respectively.

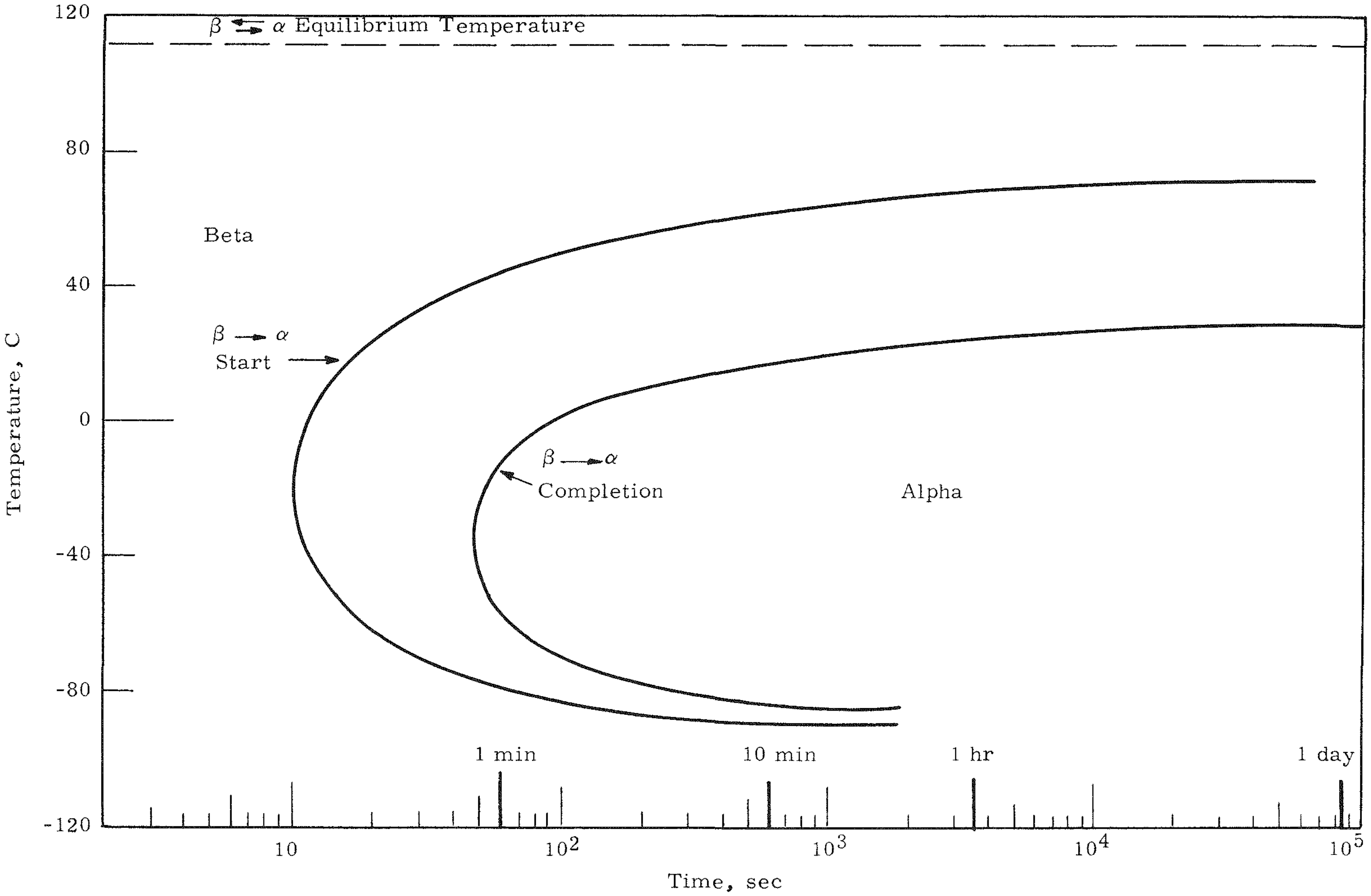


FIGURE 2

Beta–Alpha T-T-T Curve of Loasby and Lowe(15)

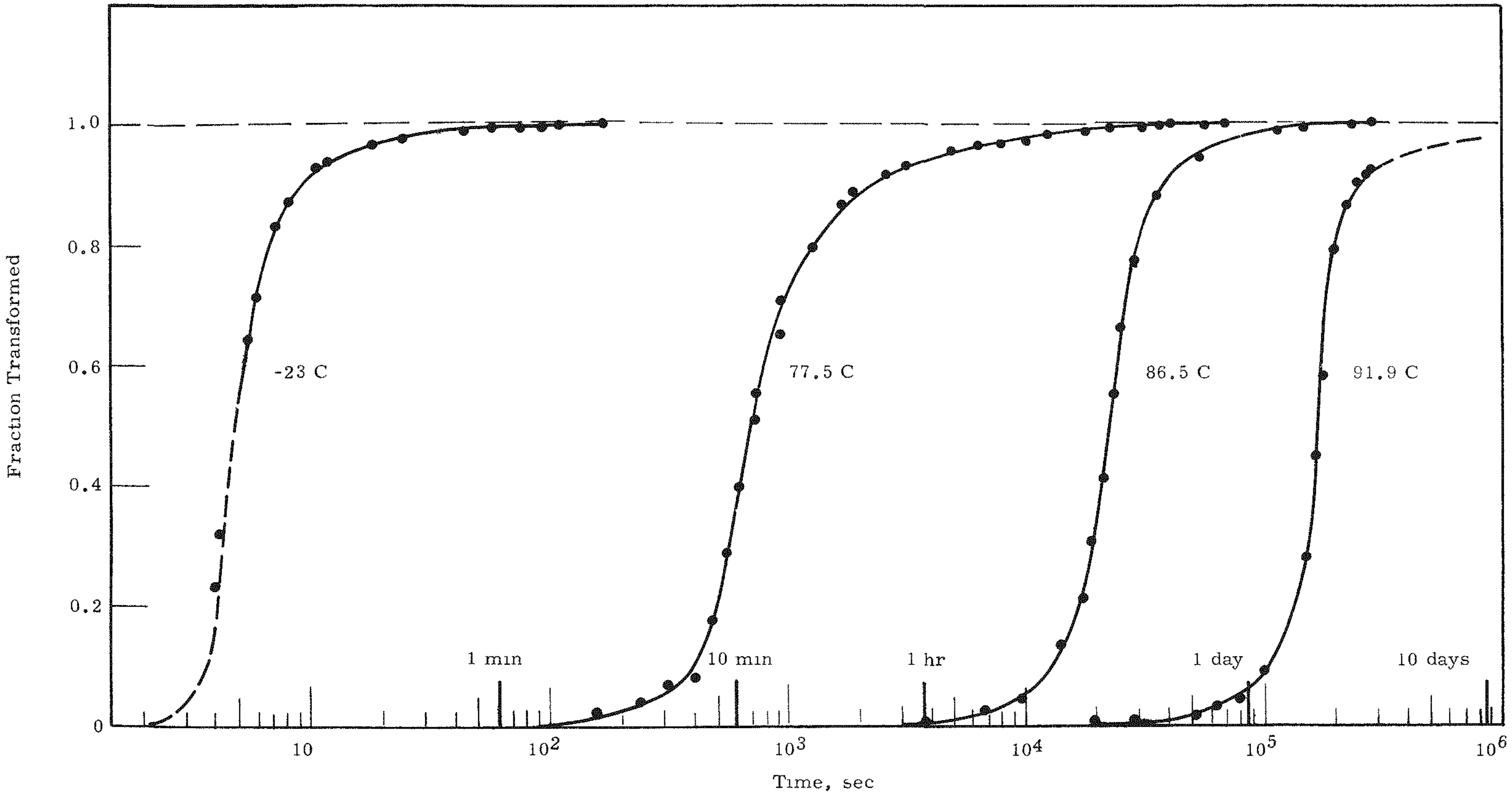


FIGURE 3

Isothermal Reaction Curves of Beta–Alpha Transformation (Heat B)

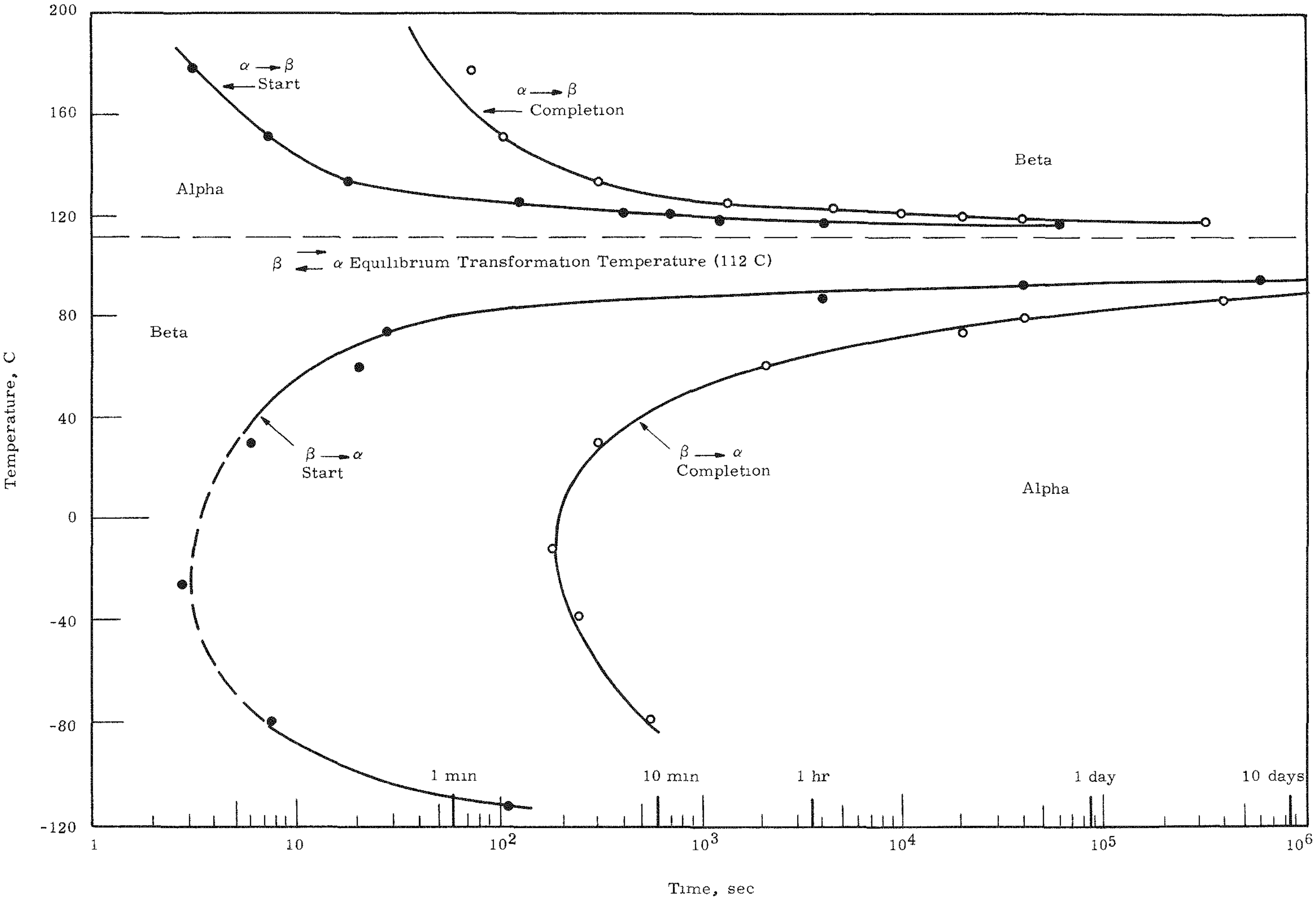


FIGURE 4

T-T-T Curve of Beta–Alpha Transformation (Heat B)

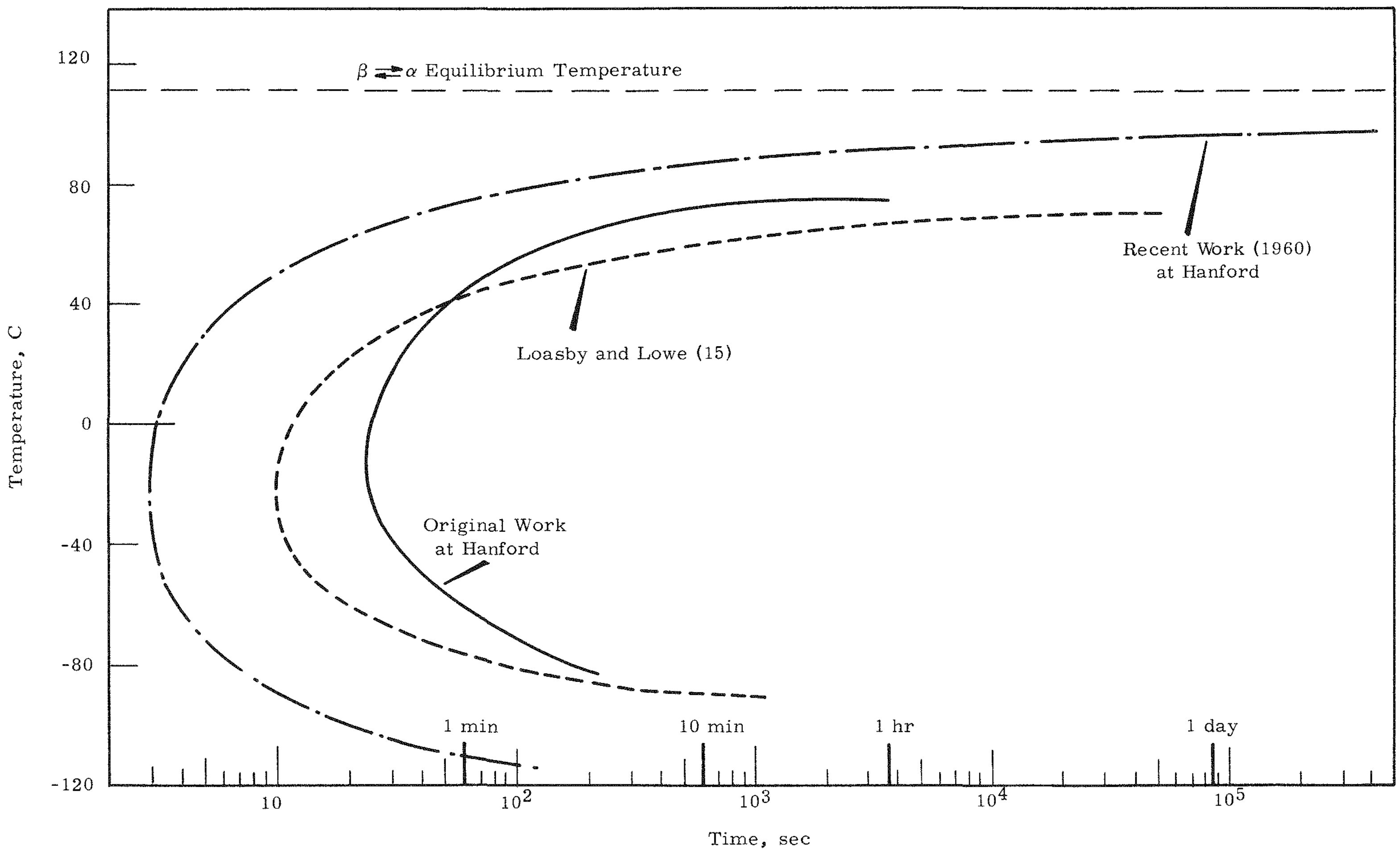


FIGURE 5

Start of Beta–Alpha Transformation of Three Different Qualities of Metal

TABLE II

DENSITY AND IMPURITIES OF PLUTONIUM METAL**

(ppm)

	Heat A	Heat B	Heat C
Density, 25 C	19.50	19.62	19.55
Aluminum	80	20	32
Carbon	130	110	100
Calcium	13	5	20
Chromium	100	16	20
Iron	726	130	260
Magnesium	<10	25	200
Mangenese	40	25	20
Nickel	40	50	50
Columbium	--	50	<10
Silicon	20	--	--
Hydrogen	*	5	8
Nitrogen	*	<0.1	<0.1
Oxygen	*	180	180
Others	<50	<25	<25

* Not determined

** Figures 1, 4, and 8 were plotted from these data.

During the isothermal transformation, the beta phase is initially metastable. The transformation proceeds slowly at first, increasing and leveling off at a maximum rate, then decreasing to a linear rate at which the transformation proceeds very slowly. For example (Figure 3), the transformation was apparently 99 per cent transformed after 2 days at 86.5 C, assuming the transformation goes to completion by cold treating at -23 C for a minimum of 2 hours. The density after transforming at 86.5 C and before cold treating was 19.04 g/cm^3 (19.22 g/cm^3 at room temperature). After cold treating for 2 hours, the density at 86.5 C remained 19.04 g/cm^3. The low density, as compared to the 25 C theoretical density of 19.8 g/cm^3, was due to voids and difference in temperature.

The isothermal reaction curves (Figure 3) have the shape of typical sigmoidal curves charactistic of nucleation and growth reactions to which the Avrami Equation has been applied:(30)

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

or

$$\ell n\, \ell n \left(\frac{1}{1 - f}\right) = A + n\, \ell n t, \text{ (natural logarithms)}$$

where f = fraction transformed,

t = time, and

n, k, A = constants.

The verification of a transformation obeying the Avrami relationship can be obtained by plotting $\ell n\, \ell n \left(\frac{1}{1 - f}\right)$ as a function of ℓn time and determining the linear relationship. For the beta—alpha transformation of plutonium, such a plot shows that the curve is linear for only a portion of the transformation (Figure 6). The Avrami plot of the work of Loasby and his colleagues(21) departed from linearity at only 40 per cent transformation. Thus, the Avrami type of equation is not particularly applicable to the beta—alpha transformation. However, the linear portion of the curve has a slope of 4 to 5. This value of n is greater than the value of 2 to 3 reported by Loasby, et al. For plutonium, the significance of the high value of n is not known at present but is probably due to the high nucleation rate.

Since the transformation consists of more than one step and the rate of transformation varies markedly with temperature, the determination of an activation energy for each step is neither possible nor the total activation energy too meaningful. This can be seen by application of an Arrhenius type of equation of the form:

$$\text{Rate} = \sum_{i=1}^{n} A_i \exp\left(\frac{-Q_i}{RT}\right). \tag{2}$$

Plotting ℓn rate as a function of $1/T$ (absolute temperature) results in a curve with a very rapid change in slope. The activation energy for nucleation is also a function of temperature. Thus, the calculation of the activation

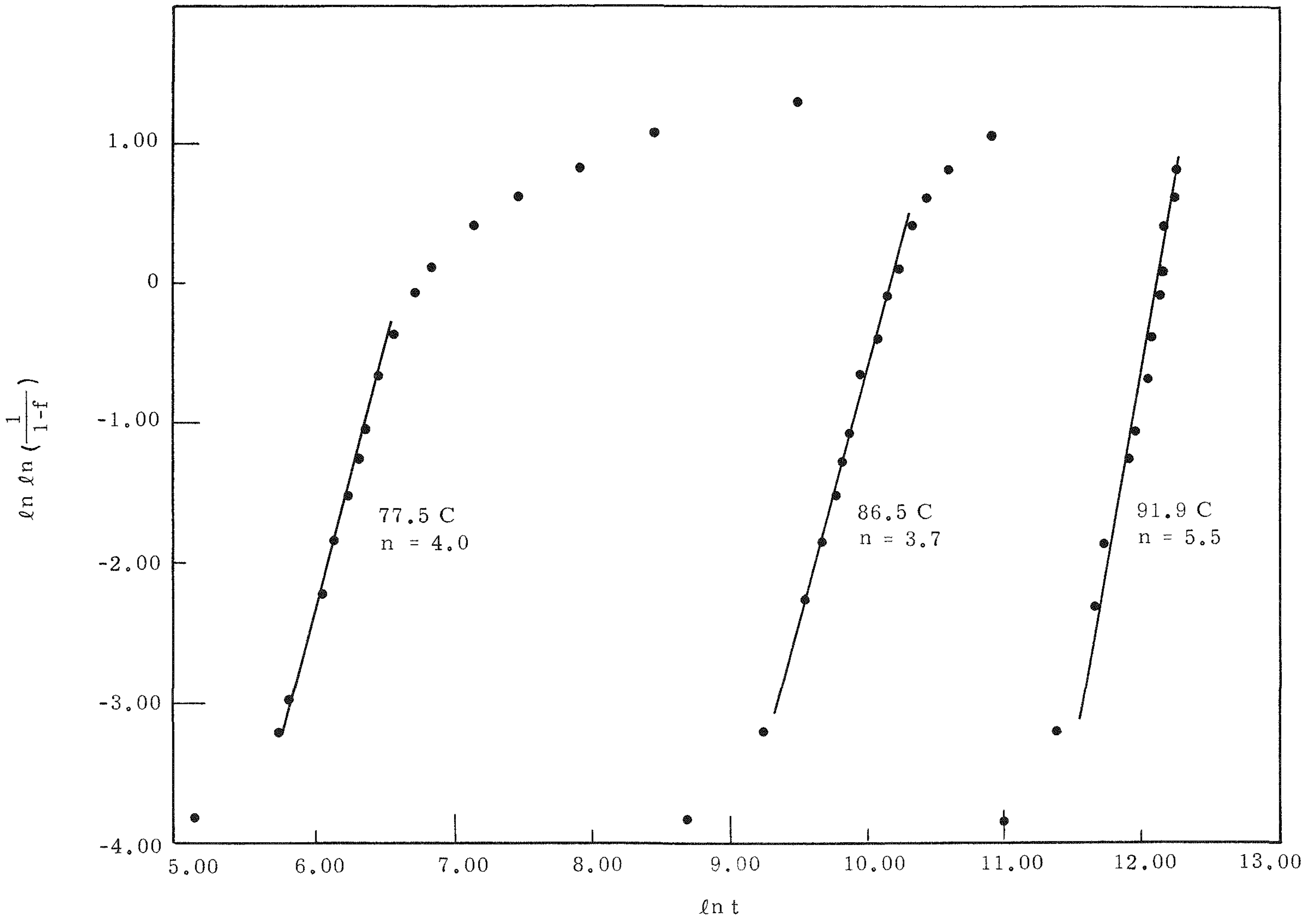


FIGURE 6

Avrami Plot of Beta–Alpha Transformation energy of the beta–alpha transformation is meaningless at present. Hill(1) computed the activation energy to vary from 12.7 to 118 kcal.

Retention of the Beta Phase

The initial work at Hanford(11, 25, 26, 28) and the work of Loasby and Lowe indicated that the beta–alpha transformation may not go to completion isothermally, that is, the transformation may be partially athermal. Between 40 and 70 C, the beta–alpha transformation appeared to go to completion isothermally with some retained beta phase. Subsequent lowering of the temperature reduced the amount of retained beta phase. Although the original work at Hanford indicated that the beta–alpha transformation may be partially athermal, the amount of retained beta phase at any given temperature was significantly less than reported by Loasby and Lowe (Figure 7). Where they showed a linear relationship between the fraction transformed and the isothermal transformation temperature, the Hanford data indicated that the transformation approached 100 per cent completion asymptotically. The detection and analysis of 99.5 per cent transformation compared to 100 per cent transformation was difficult.

Later work at Hanford demonstrated that the transformation of the beta phase to the alpha phase will go to completion if held at the transformation temperature for a sufficient period of time (Figure 3). The completion of the transformation at the higher temperature may require a long time (Figure 8). The chemical composition of this metal is given in Table II, Heat C. The analysis of Heat C was similar to that of Heat B. The transformation was assumed to go to completion by cold treating for 2 hours at -23 C.

The disagreement between the results of Nelson(19, 24) and of Loasby and Lowe(15) concerning the completion of the transformation is believed largely due to specimen size. The specimens used by Loasby and Lowe were 0.16 inch compared with specimens less than 0.040 inch used by Nelson. This can be seen by comparing the two isothermal reaction curves (Figure 8) of two samples which had been machined to 0.060 and 0.375 inch in diameter, respectively. The specimens were adjacent in a 1/2-inch rod. The weights of the specimens were 1.49 and 57.67 grams, respectively.

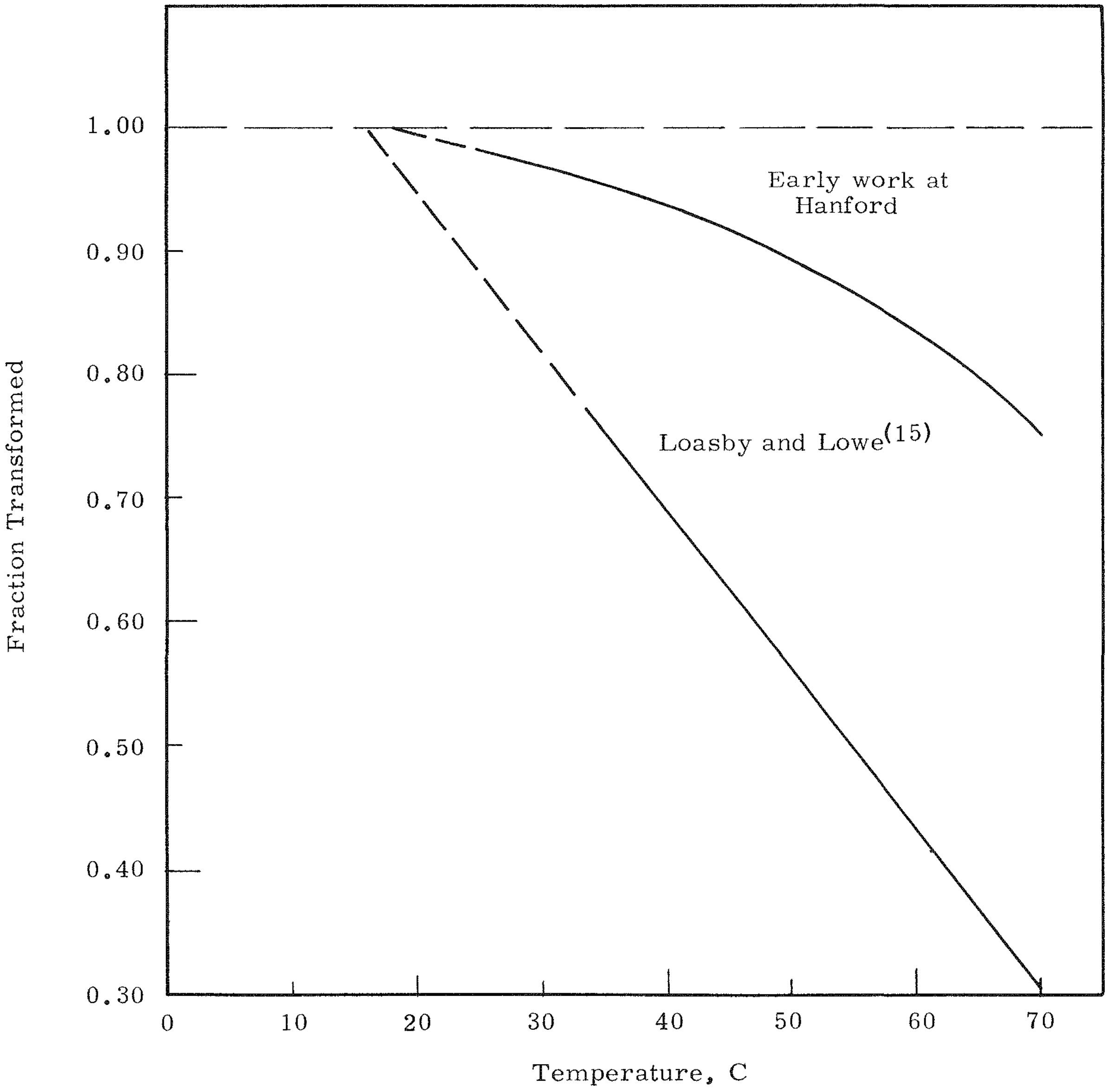


FIGURE 7

Fraction of Transformation Versus Transformation Temperature

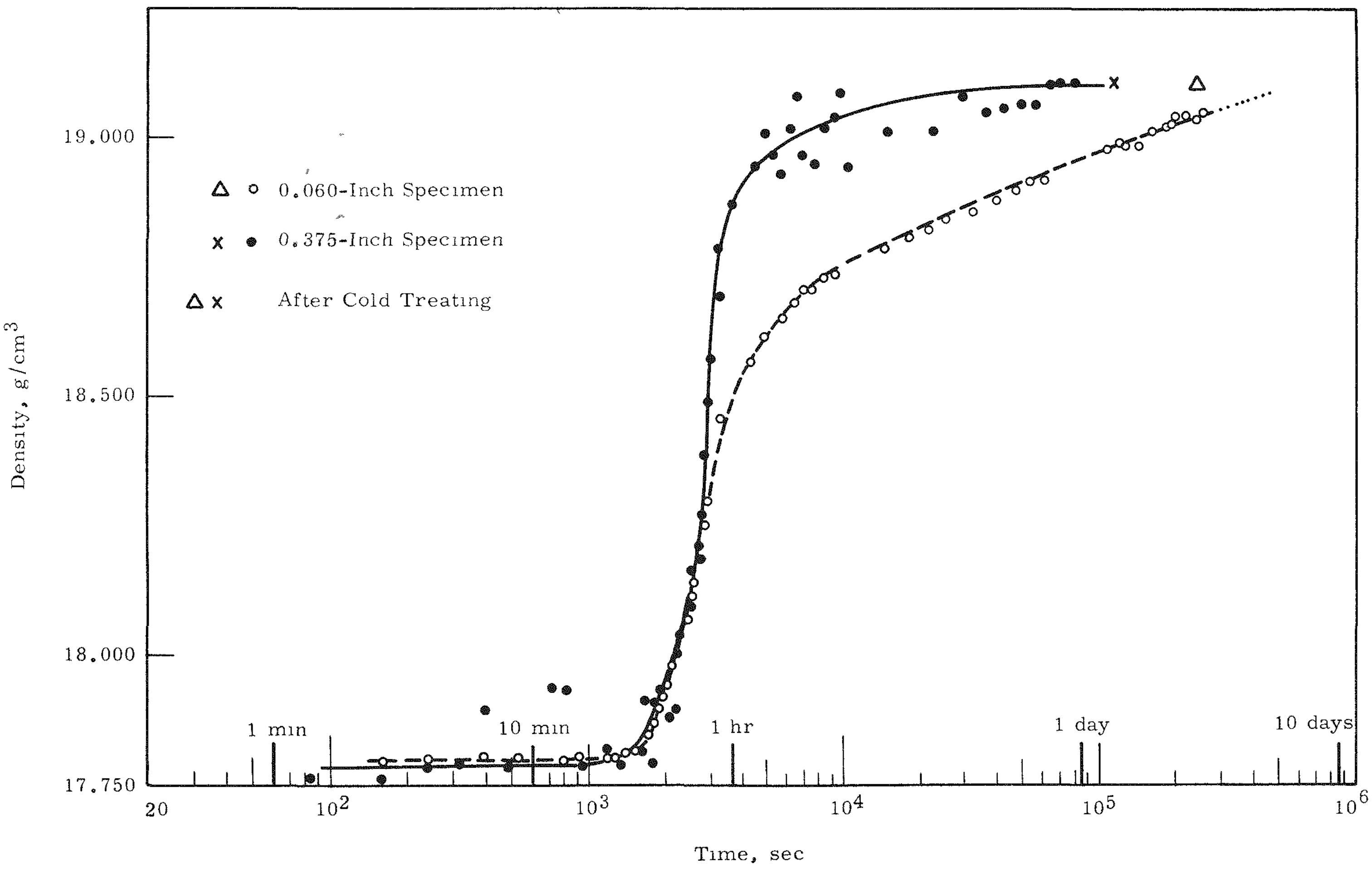


FIGURE 8

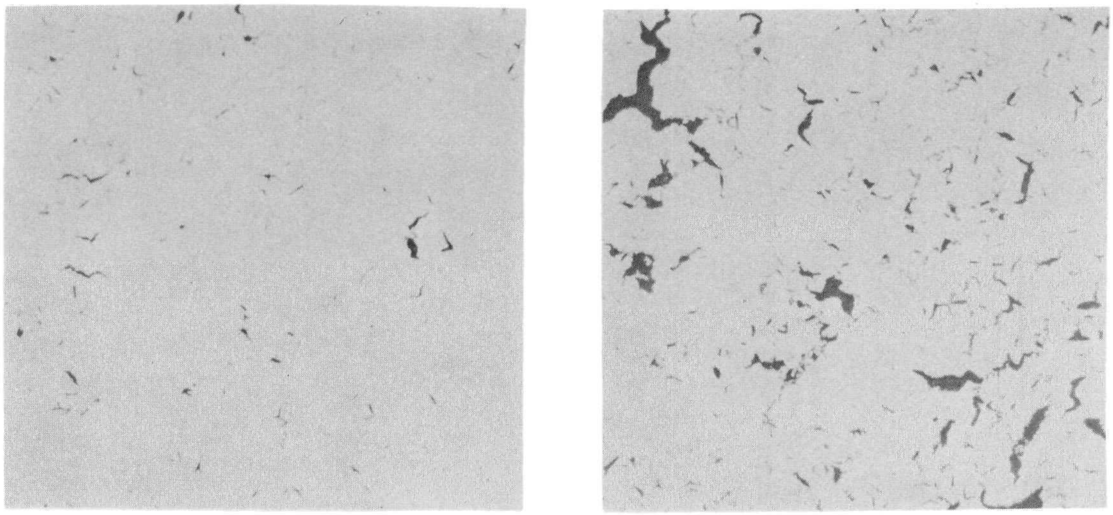
Effect of Specimen Size on Beta-Alpha Transformation at 74.5±0.2C

The two specimens were beta heat treated for 45 minutes at 160 C and were allowed to transform isothermally at 74.5 ± 0.2 C. The isothermal reaction curves were superimposed to about 25 per cent transformation. Beyond this, the transformation of the smaller specimen approached completion much more rapidly than that of the larger one.

The assumption that the transformation goes to 100 per cent completion by cold treating for 2 hours at -23 C may not always be correct; that is, there may be up to 2 per cent retained beta. The subsequent transformation of this small amount of beta phase would be significant in the fabrication of plutonium, since transformation of 1 per cent retained beta will cause an elongation of approximately 3×10^{-4} cm/cm. Whenever alpha plutonium is compressed at 90,000 psi or more, the density increases as much as 0.4 g/cm.(32) depending on the temperature of pressing, microcracks, inclusions, and other imperfections in the metal. Densities up to 19.75 g/cm^3 at 25.0 C have been obtained by hydrostatic pressing at 180 C (beta phase at one atmosphere and alpha phase at 90,000 psi). A small amount of this density increase may be caused by transformation of the retained beta phase but is believed to be due to decreasing the volume of imperfections, particularly microcracks. If 1 per cent of the volume of metal were microcracks and were eliminated during compression, the density would increase 0.2 g/cm^3.

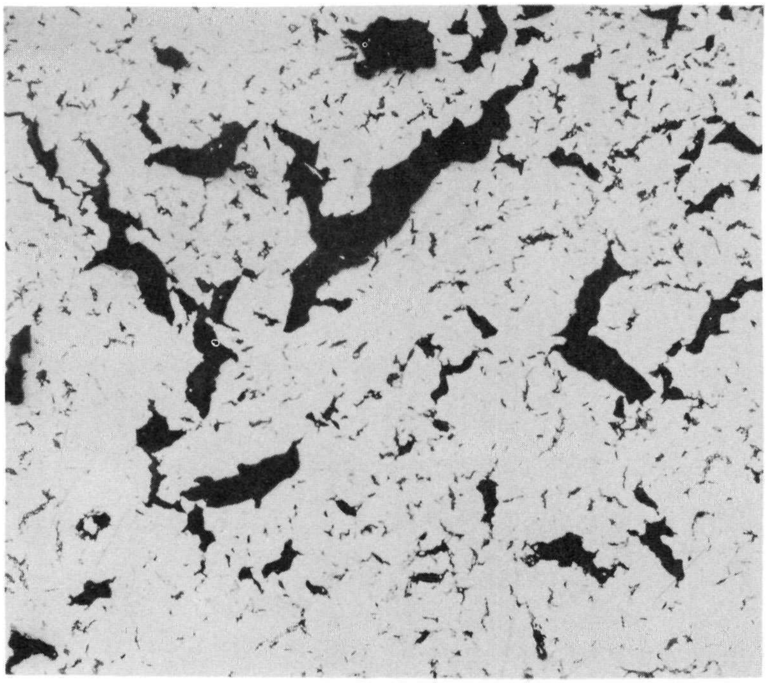
Metallography (Figure 9) revealed that specimens having densities greater than 19.60 g/cm^3 may still contain microcracks. The volume occupied by these microcracks decreased slightly after hydrostatic compression at 90,000 psi and at 90 C. Correspondingly the metal density increases 0-0.02 g/cm^3. Hydrostatic pressing at the same pressure but at 180 C and cooling to the alpha phase under pressure resulted in density increases of 0.10 to 0.15 g/cm^3. The microcracks were only slightly discernible at 250X after this treatment.

The density increase was attributed to decreasing the volume of microcracks and not transformation of retained beta. This was explained on the basis of an experiment performed to compare densities of the beta



As-Cast

One-Cycle



Four-Cycle

FIGURE 9

Photomicrographs of Specimens
Cycled Between Alpha and Beta Phases
50X

and alpha phases before and after hydrostatic pressing at 90,000 psi and a temperature of 190 C. The alpha and beta densities of four as-cast plutonium specimens (more than two weeks after casting) were determined at 84.0 C. The alpha and beta densities were then determined at the same temperature after hydrostatic pressing. The density increases of the plutonium in the beta phase after pressing compared to the density before pressing were 0.14, 0.064, 0.062, and 0.132 g/cm^3. The corresponding density increases of the plutonium in the alpha phase were 0.12, 0.076, 0.065, and 0.136 g/cm^3. The beta densities were determined after beta heat treating 1.5 hours at 170 C and cooling to 84.0 C. The beta—alpha incubation time at this temperature for these specimens was 3 to 5 hours. The reproducibility of density determinations at this temperature was approximately ±0.01 g/cm^3. This comparison shows that the density increases of the beta phase and the alpha phase before and after compressing were comparable. This clearly indicates that the density increase during hydrostatic compression resulted from decreasing the volume of microcracks rather than transformation of retained beta. It can be concluded from this experiment that this metal contained little or no retained beta.

A series of samples of high purity plutonium, 19.52 to 19.67 g/cm^3, were thermally cycled by direct immersion between -75 and +100 C to determine if the transformation of any retained beta could be observed. The results, Table III, show that there was essentially no transformation of any retained beta, which would be indicated by a density increase. Both volume increase and volume decrease were observed. The reproducibility of these determinations was ±0.003 g/cm^3. This also indicates that very little, if any, retained beta is present in high purity plutonium.

TABLE III

EFFECT OF THERMAL CYCLING BY DIRECT IMMERSION TECHNIQUES BETWEEN -75 AND +100 C

Specimen Number	Density Before Cycling, g/cm^3	Density After Cycling, g/cm^3	Density Change, g/cm^3	Number of Cycles
1	19.666	19.672	+0.006	20
2	19.643	19.647	+0.004	20
3	19.575	19.575	+0.000	20
4	19.573	19.572	-0.001	20
5	19.662	19.665	+0.003	1
		19.663	+0.001	2
		19.665	+0.003	3
6	19.614	19.613	-0.001	1
		19.613	-0.001	2
		19.619	+0.005	3
7	19.639	19.643	+0.004	1
		19.633	-0.006	2
		19.639	0.000	3
8	19.516	19.515	-0.001	1
		19.616	+0.000	2
		19.515	-0.001	3
		19.513	-0.003	4
		19.515	-0.001	5
9	19.515	19.508	-0.007	1
		19.512	-0.003	2
		19.510	-0.005	3
		19.508	-0.007	4
		19.509	-0.006	5
10	19.521	19.514	-0.007	1
		19.514	-0.007	2
		19.513	-0.008	3
		19.511	-0.010	4
		19.516	-0.005	5
11	19.532	19.521	-0.011	1
		19.527	-0.005	2
		19.529	-0.003	3
		19.523	-0.009	4
		19.529	-0.003	5
12	19.565	19.567	+0.002	3
13	19.580	19.583	+0.003	3
14	19.584	19.588	+0.004	3

The two factors which tend to increase the amount of retained beta are impurities and tensile stresses. Practically all the studies of transformation at Hanford and that reported by Loasby and Lowe have been with relatively high purity plutonium--densities of 19.50 g/cm^3 or greater. The limited work that has been performed on plutonium with densities of 19.2 g/cm^3 indicate that even at -23 C, which is the nose of the T-T-T curve, months may be required for 99.9 per cent completion of the transformation, or it may never completely transform. Heat treatment by tempering analogous to the tempering of retained austenite in steel may be required for further transformation. In the case of plutonium, the upper limit on tempering is the alpha–beta transformation temperature.

Impurities such as carbon and iron are not believed to have appreciable effects on the transformation, since they form compounds of PuC and Pu_6Fe, respectively. Elements such as zirconium, uranium,(31) and titanium, which form solid solutions with beta plutonium, tend to retard the beta–alpha transformation. Taylor(32) has shown that completion of the beta–alpha transformation of Pu-2 w/o Zr alloy is extremely sluggish above room temperature; that is, the isothermal reaction curves appear to level off before completion of the transformation in a manner similar to that of the plutonium-uranium alloys(31) and the original studies of unalloyed plutonium.(25, 26) Other elements such as aluminum tend to retard the transformation of the delta phase.

Thermal Cycling

The physical damage associated with thermal cycling between any of the low temperature allotropic transformations is very large. Large samples rapidly quenched from either the beta, gamma, or delta phases to -20 C will generally fracture. However, plutonium that is slowly cooled (for instance, 2 C per minute) may form as many as 3 per cent voids per cycle (0.6 g/cm^3 density decrease per cycle). Moreover, the amount of voids formed per cycle depends primarily on the metal quality and secondarily on specimen size.(28)

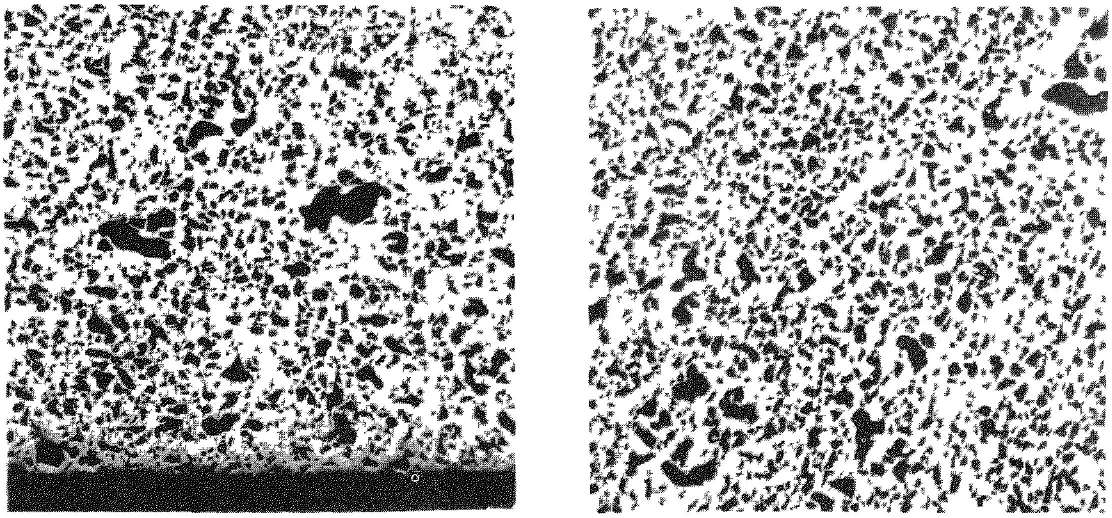
Generally, plutonium with densities of 19.50 to 19.60 g/cm^3 will decrease 0.1 to 0.3 g/cm^3 per cycle when thermally cycled 2 to 50 C per minute through the beta–alpha, gamma–beta–alpha, and delta–gamma–beta alpha transformations. Originally, it was believed that only microscopic voids were formed during the beta–alpha transformation.(4, 5, 6, 11) This was disproved because macroscopic voids have been observed after cycling through any two of the phase transformations regardless of the cycling rate.(28) The density of plutonium at 25 C will decrease from 19.55 to 19.35 g/cm^3 in one cycle, even when the maximum transformation rate is only 2 per cent per minute.

Microcracks (Figure 9) in as-cast plutonium originate during the delta–gamma, gamma–beta, and beta–alpha transformations. The microcracks in as-cast metal become progressively larger during thermal cycling. After two to four cycles, the microcracks become macrocracks leading to fracture. When the as-cast metal contains few detectable microcracks at 100 to 200 magnification, the voids formed by cycling have a more symmetrical shape (Figure 10) than those shown in Figure 9 or in the extreme case of a specimen cycled under a temperature gradient (Figure 11). Certain thermally cycled specimens have had densities decreasing from approximately 19.5 to 7 g/cm^3.

Voids and microcracks generally form uniformly throughout specimens, but large macrocracks have been observed at or near the center of specimens. For example, a 1-1/2-inch sphere thermally cycled eight times at 2 C per minute between 175 and 25 C contained a void 3/8 to 1/2 inch in diameter at the center. Large macrocracks have also been observed at the center of thermally cycled rods.

Increasing the specimen size generally increases the amount of void formation(28) (Figure 12). However, 1/4-inch rods have been shown to have as large a density decrease as 1-inch rods. This indicates specimen size is not as important as metal quality or beta–alpha transformation conditions.

The excellent work of Loasby and Lowe revealed that voids do not occur until after 50 per cent transformation.(15, 22) They plotted the



Edge of Specimen

Center of Specimen

FIGURE 10

Plutonium Rod Cycled 35 Times
Between the Gamma and Alpha Phases
50X

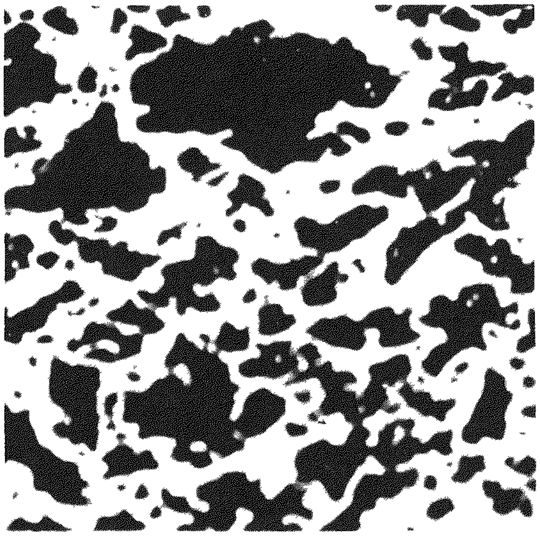


FIGURE 11

Photomicrograph of a Plutonium Rod Subjected to a Thermal Gradient
of 30 to 50 C Per Inch (16 Cycles)
50X

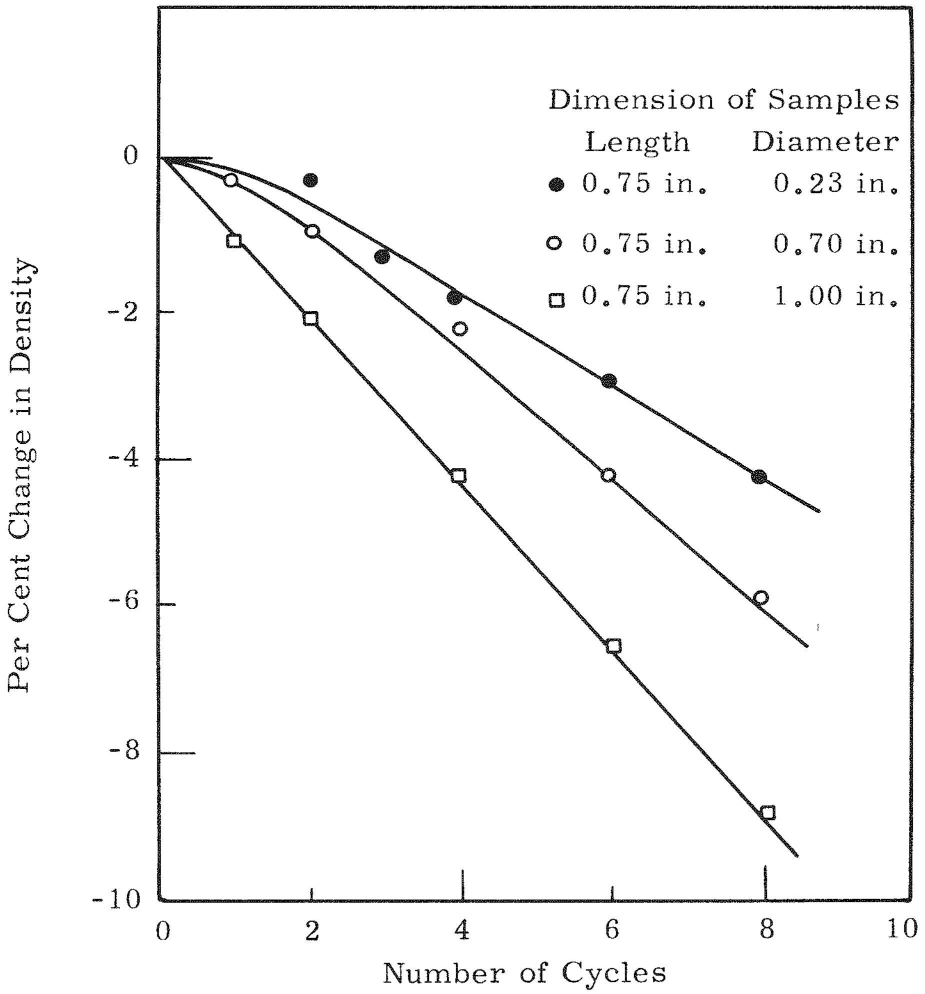


FIGURE 12

Effect of Specimen Size on Density Decrease of Plutonium When Thermally Cycled Through Beta-Alpha Transformation percentage of void against the percentage of transformation and obtained a linear relationship. Above 50 per cent, the amount of void is proportional to the amount of transformation. Data obtained at Hanford essentially confirms this. A plot of the percentage of void as a function of the percentage of transformation (Figure 13) shows no voids formed until 50 per cent transformation. Contrary to the findings of Loasby and Lowe, the relationship between the two is not linear. Other experiments have produced similar curves, but displaced down and to the right. This displacement depends upon such factors as size, isothermal transformation temperature, and metal quality.

Loasby and Lowe showed also that the incubation period for a specimen cycled between 180 C and an isothermal transformation temperature (60 C) in the alpha range decreased from approximately 200 seconds to approximately 15 seconds after 100 cycles. Their data and data obtained at Hanford agreed that thermal cycling 15 times or less has no influence on the rate of transformation.(26)

Investigation has shown that increasing the beta heat-treating temperature decreases the rate of transformation, that is, shifts the T-T-T curve to the right. A specimen was beta heat treated for 1 hour at different temperatures in the beta range, and the isothermal reaction curves were determined. A relationship showing the time for 50 per cent transformation as a function of the beta heat-treating temperature is plotted in Figure 14.

The early work at Hanford(24, 25, 26) showed that for 0.030-inch thick wafers the rate of transformation was essentially not affected by varying the time of beta heat treating, provided the beta heat treatment exceeds 30 minutes. Later work using specimens of 0.37-inch diameter and 0.75-inch long showed that beta heat-treating time at 180 C was significant (Figure 15). The incubation period increased from 1200 seconds at 75.0 C after beta heat treating 30 minutes to 3500 seconds and 60,000 seconds after beta heat treating 4.75 hours and 27 hours, respectively. This effect of beta heating time becomes less significant with lowering of the beta—alpha isothermal transformation temperature.

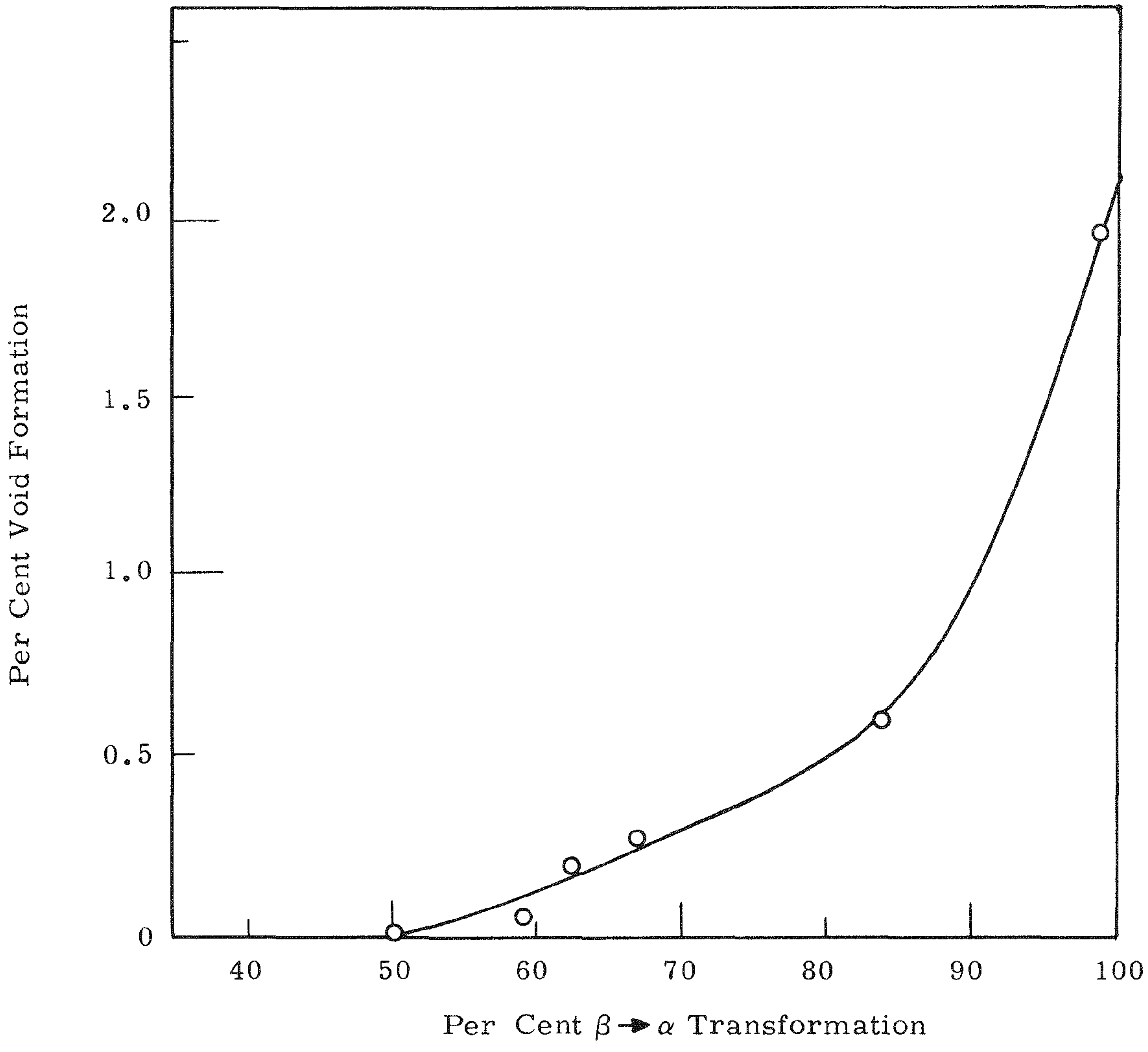


FIGURE 13

Void Formation as a Function of Beta–Alpha Transformation

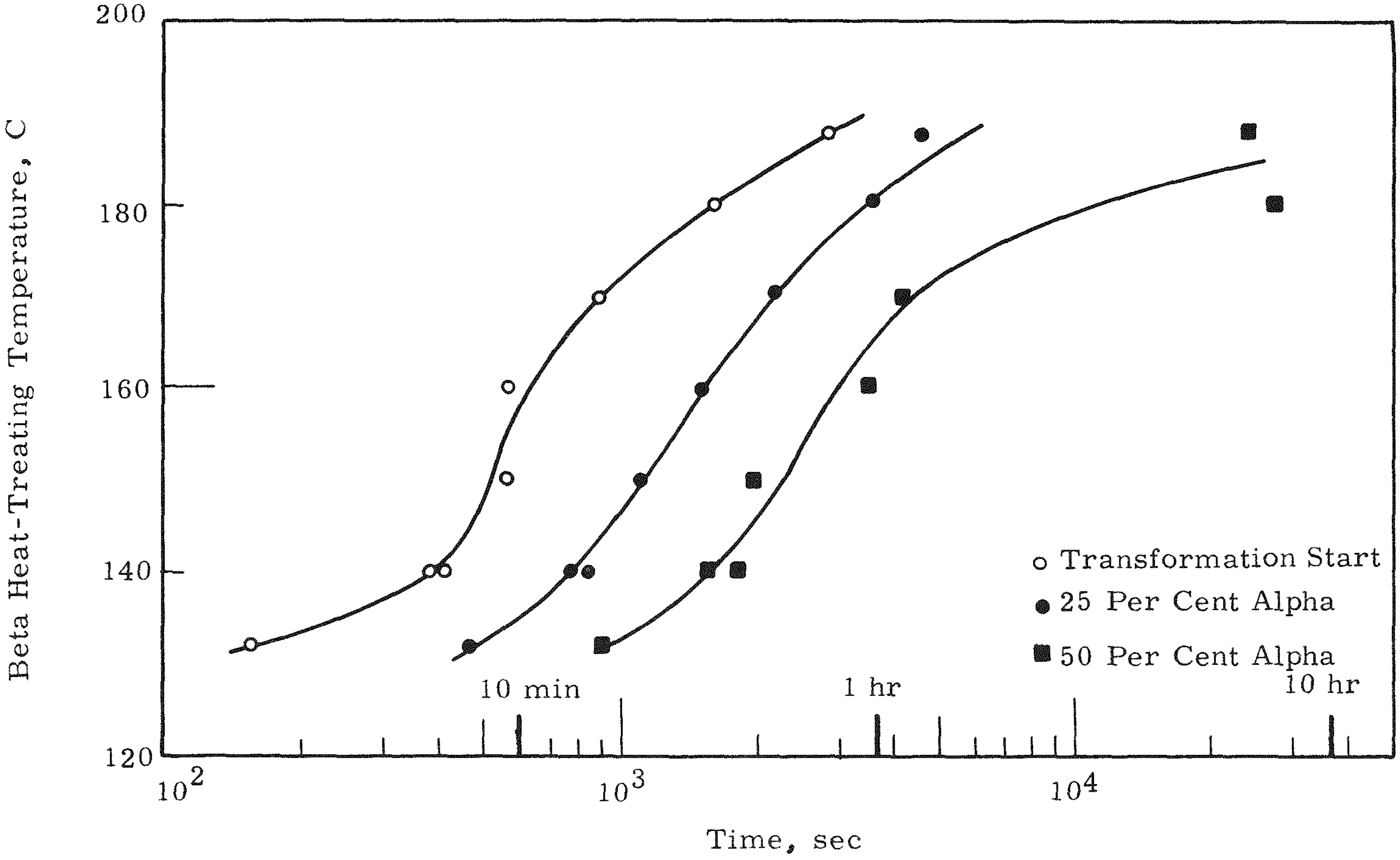


FIGURE 14

Effect of Beta Heat-Treating Temperature (±2C) on Beta–Alpha Transformation (Beta Heat-Treating Time: 90 Minutes; Transformation Temperature: 74.8 ± 0.3C)

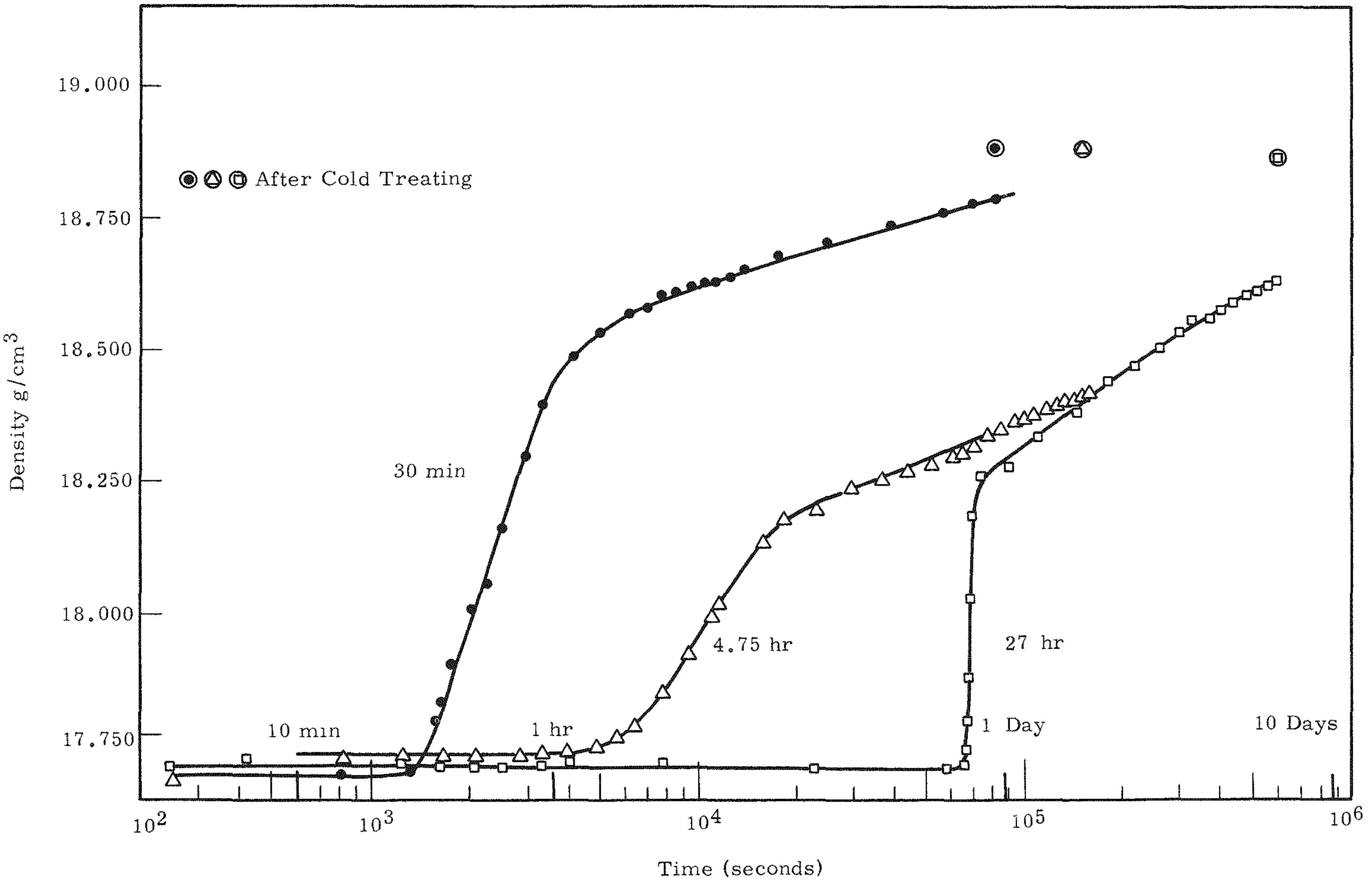


FIGURE 15

Effect of Beta Heat-Treating Time on the Beta–Alpha Transformation
(Beta Heat-Treating Temperature 182 C; Transformation Temperature 75.0C ±0.2)

Effect of Hydrostatic Pressing

The effect of hydrostatic pressing at 180 C is to shift the T-T-T curve to the right upon subsequent beta–alpha transformations. The incubation period of a specimen heat treated 1.5 hours at 170 C was 1000 seconds (Figure 16). The incubation period after hydrostatic pressing at 90,000 psi and 180 C and subsequent beta heat treatment of 1.5 hours at 170 C was 50,000 seconds. After repeating the identical pressing and beta heat treatment, the incubation period increased to 100,000 seconds. Subsequent beta heat treatment and no pressing operation produced a similar isothermal reaction curve as after the second hydrostatic pressing.

KINETICS OF THE ALPHA–BETA TRANSFORMATION

Isothermal Reaction Curves and T-T-T Curves

The isothermal reaction curves of the alpha–beta transformation (Figure 17) also have the shape of typical sigmoidal curves. Using the Avrami relationship and plotting $\ell n\ \ell n\ (\frac{1}{1-f})$ versus ℓnt, the value of n has been calculated to be 2 for the original Hanford work and 3.5 to 4.5 for the more recent work (Figure 18).

The T-T-T curve from these isothermal reaction curves has been plotted (Figure 4) in conjunction with the beta–alpha transformation from the same metal, that is, Heat B. The upper portion of the beta–alpha tranformation and the lower portion of the alpha–beta transformation can be extrapolated to intersect at 112 C in agreement with Hill.(1)

The early Hanford rates of alpha–beta transformation, Heat A (11, 25, 26), were significantly slower than the later rates, Heat B. The former alpha–beta T-T-T curve has been included for comparison (Figure 19). These T-T-T curves show that the alpha–beta transformation is quite sluggish below 123 C and that increasing the purity of the metal increases the rate of transformation. Unfortunately, it is difficult to obtain good quantitative data concerning the effect of impurities.

The alpha–beta T-T-T curves (Figures 4 and 19) show that the transformation above 140 C was 99 per cent complete in less than 10 minutes. This is true for all metal with densities greater than 19.45 g/cm^3

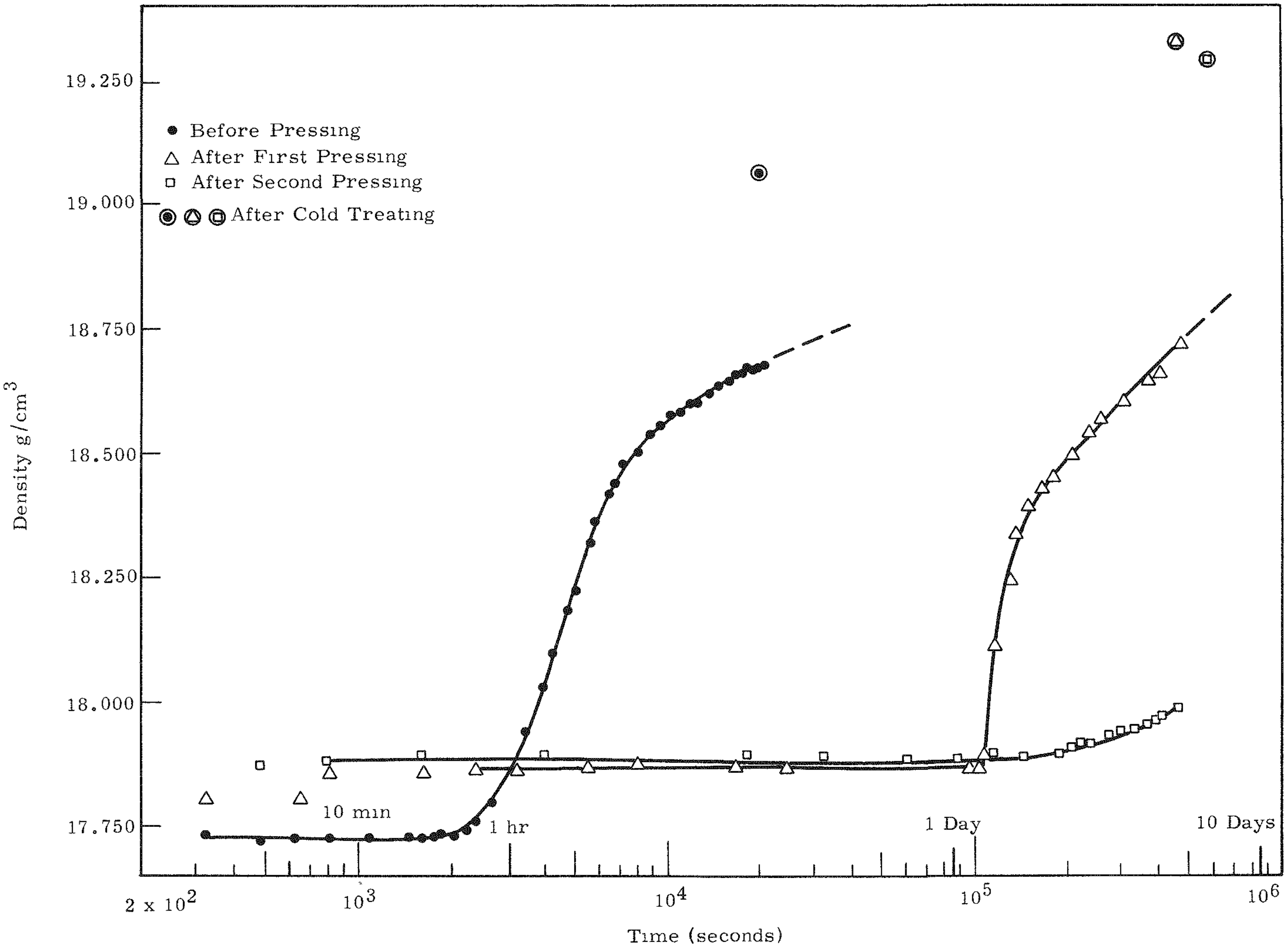


FIGURE 16

Effect of Hydrostatic Pressing
(90,000 psi and a Temperature of 190 C; Cooled Under Pressure)
on the Beta–Alpha Transformation (75.0 ± 0.2 C)

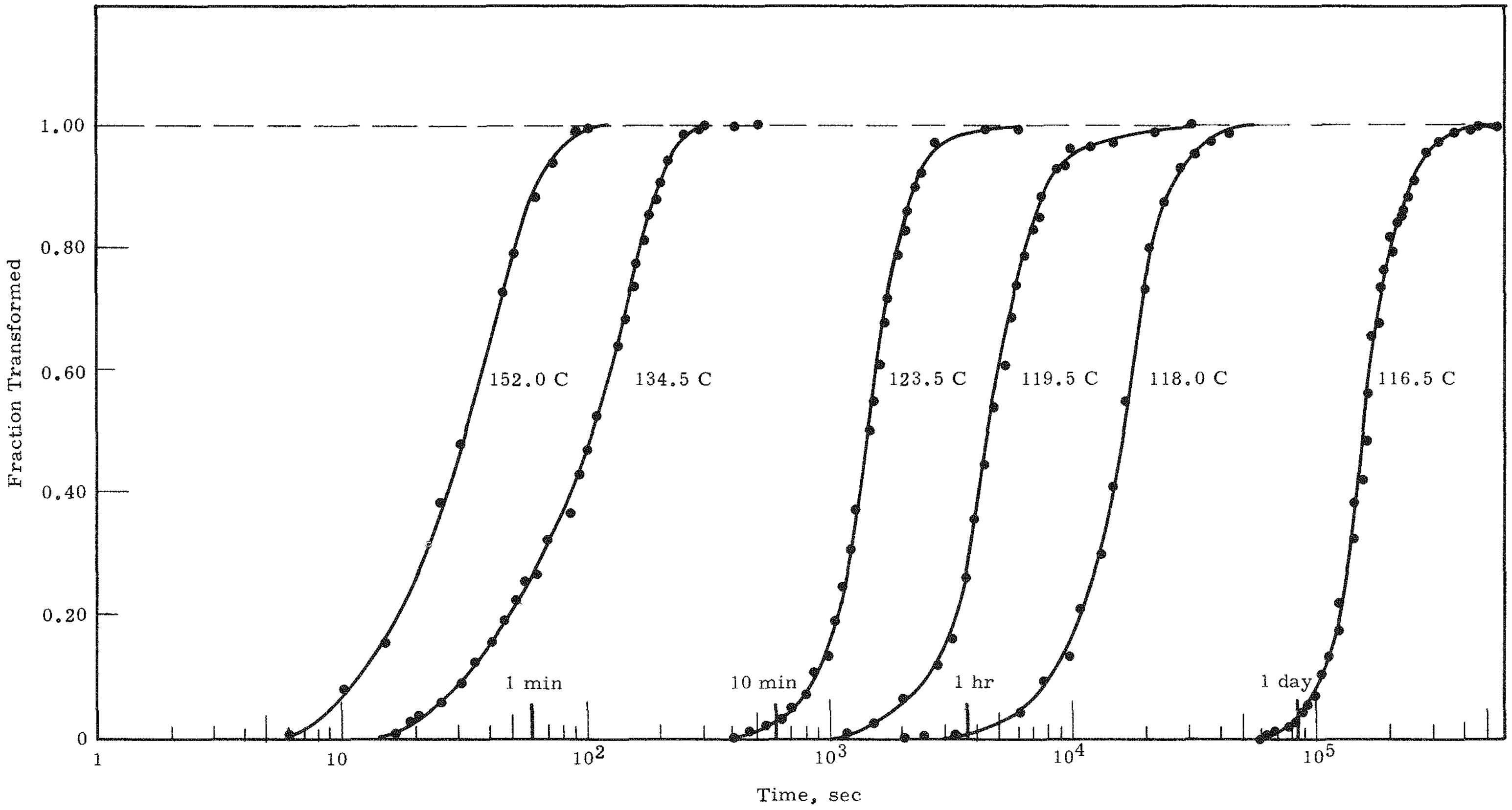


FIGURE 17

Isothermal Reaction Curves of Alpha–Beta Transformation

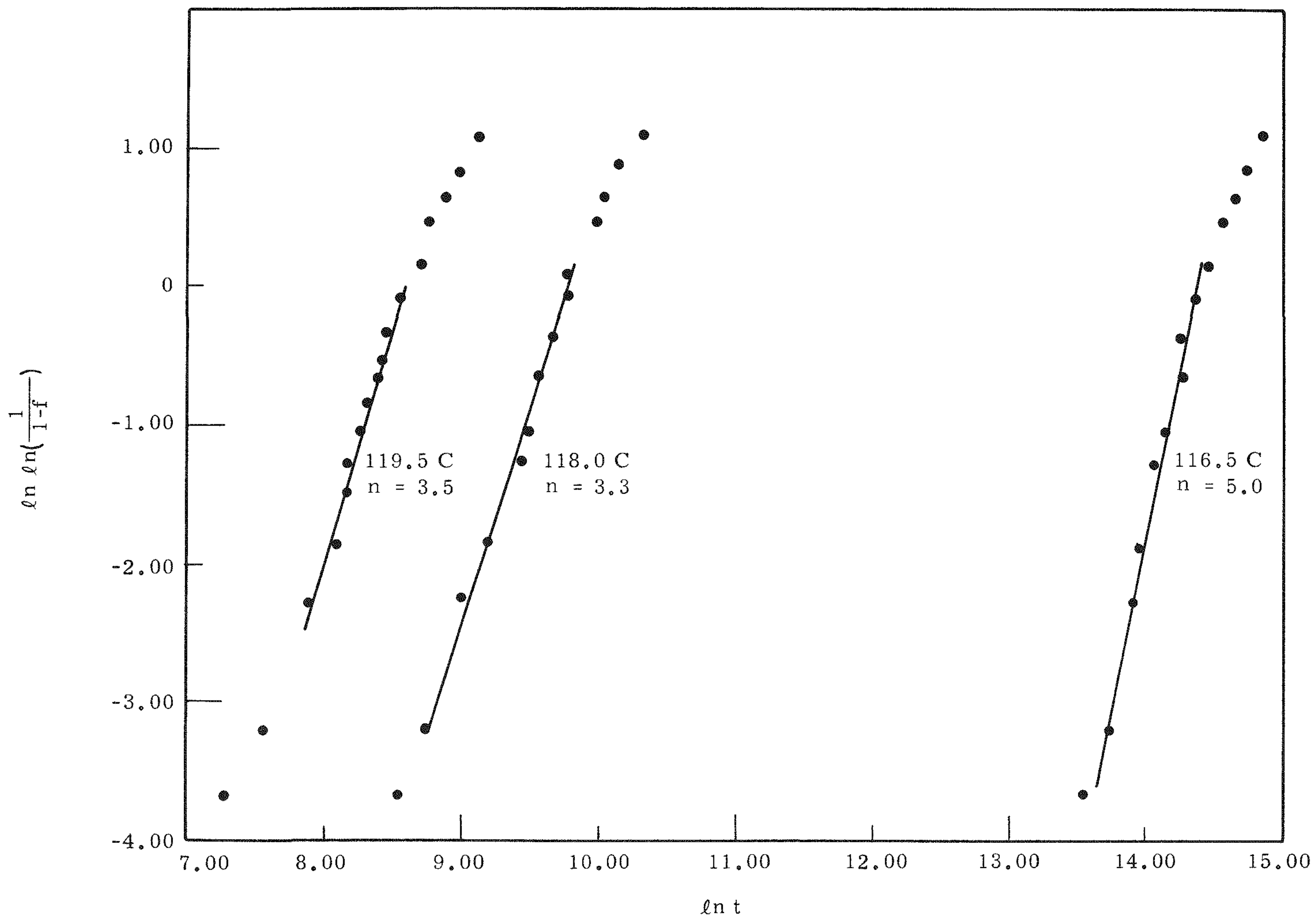


FIGURE 18

Avrami Plot of Alpha–Beta Transformation

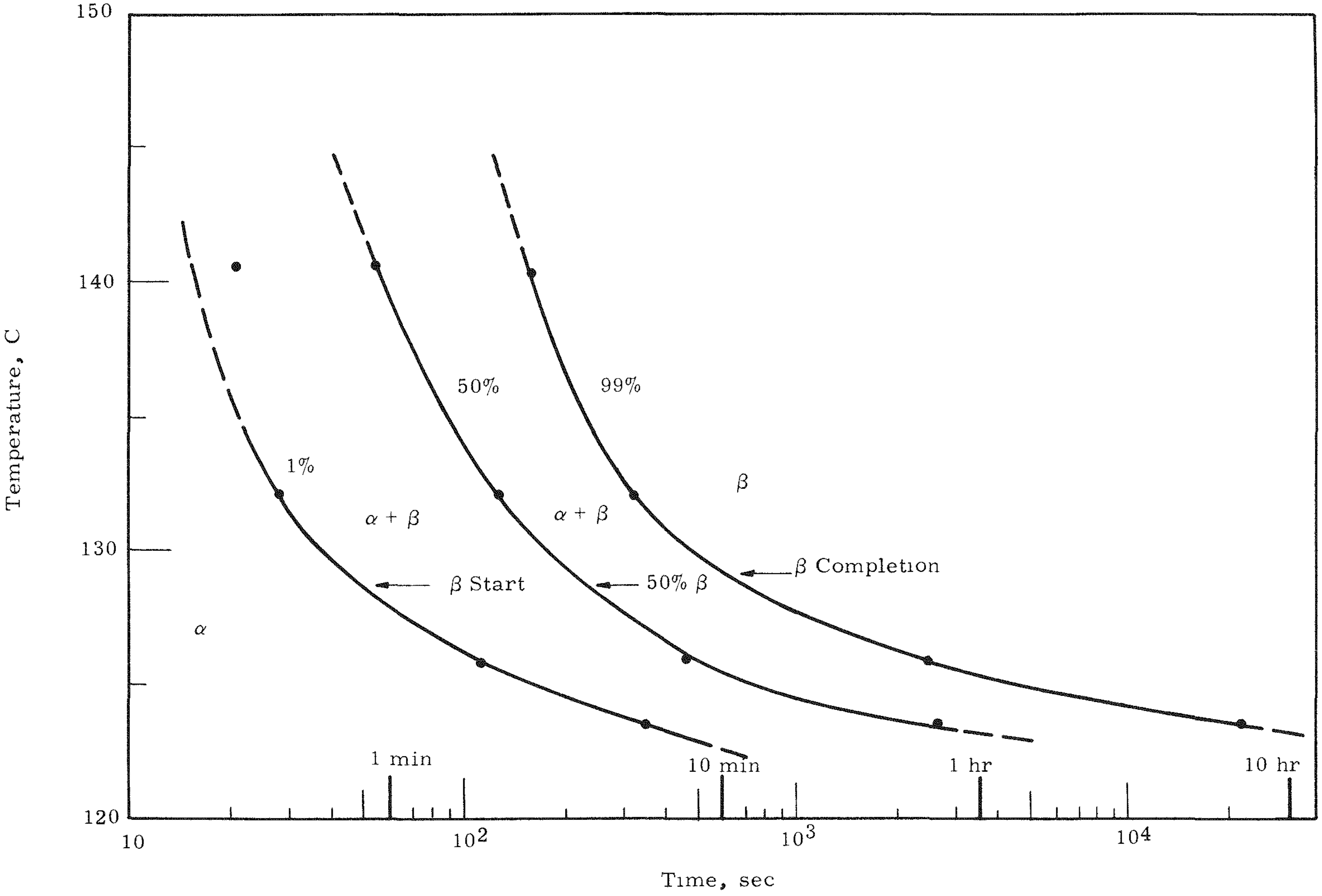


FIGURE 19

T-T-T Curve of Alpha–Beta Transformation
(Early Work at Hanford)

(room temperature), that is, as determined by density changes. However, the solution of impurities may take considerably longer at 130 to 145 C. Although the alpha–beta transformation may be complete at 140 C, longer holding times are required for complete solution of impurities. Horton and Ward(14) found that after direct heating to 140 C and holding 20 minutes, the elongation during tensile testing at this temperature was 2 to 3 per cent, whereas the elongation was 154 per cent after heating to 175 C and cooling to 140 C. They attributed this discrepancy to either incomplete alpha–beta transformation or to solution of impurities during the higher beta heat treatment.

Gardner and Mann(13) showed that the elongation after direct heating to 130 C and holding for 30 minutes was 294 per cent. Gardner,(18) in a discussion of Horton and Ward's work, suggested the discrepancy could possibly have been due to impurity effects but was more likely caused by incomplete alpha–beta transformation. The explanation for the incomplete transformation is not known, since all work with plutonium having densities greater than 19.50 g/cm^3 shows 99 per cent or more transformation after 20 minutes at 140 C.

This divergence is most likely caused by a combination of the two effects, but it is extremely difficult to discern between them. For example, at Hanford a specimen was cycled 15 times between the beta and alpha phases (Table IV) after beta heat treating 30 minutes at 140 C. The beta–alpha transformation was complete after casting, 80 per cent complete during the first five cycles, complete during the sixth cycle, 35 per cent complete during the seventh to the tenth cycles, complete during the eleventh and twelfth cycles, 63 per cent complete during the thirteenth cycle, and finally complete. During the first to the sixth cycles, the incubation period progressively increased, whereas after the sixth cycle (during which the beta–alpha transformation was carried to completion) the incubation period again decreased. The progressive increase of the incubation period can be attributed to either retained beta, high stresses, or more impurities going into beta solution after each beta heat treatment since the impurities do not have an opportunity to completely precipitate

TABLE IV

INFLUENCE OF THERMAL CYCLING ON BETA–ALPHA TRANSFORMATION (78 C) AFTER BETA HEAT TREATING 30 MINUTES AT 140 C

Cycle Number	Density of Beta at 77.5 C, g/cm^3	Incubation Period of Beta–Alpha Transformation, sec	Extent of Transformation, Per Cent Alpha
During Casting	---	--	Complete
1	17.66	240	80
2	17.62	320	80
3	17.56	800	80
4	17.52	1100	80
5	---	--	80
6	17.45	1500	Complete
7	17.27	650	35
8	17.29	1200	35
9	17.32	1300	35
10	17.32	1900	35
11	17.33	2300	Complete
12*	17.13	2000	Complete
13**	16.93	1000	63
14**	16.92	2400	Complete
15**	16.66	1350	Complete

* Transformation Temperature: 78.5 C

** Beta Heat Treated at 150 C

out of solution during the 80 per cent beta–alpha transformation. When the beta–alpha transformation was allowed to go to completion after the sixth cycle, the incubation periods of the beta–alpha transformation were decreased from 1500 to 650 seconds. The incubation periods of the beta–alpha transformation again progressively increased from 650 to 2300 seconds during the seventh to the tenth cycles, during which the transformation was taken to 35 per cent completion.

These data also show that an increase in beta density (densification) occurs during the alpha–beta transformation. Plutonium thermally cycled between the beta and alpha phases with the alpha–beta transformation taken to completion and the beta–alpha transformation interrupted prior to the formation of voids, that is, 35 per cent completion, the density of the beta phase progressively increases. The beta density of a specimen cycled five times between the beta phase and 80 per cent alpha decreased from 17.66 to 17.27 g/cm^3. Upon subsequent thermal cycling four times between the beta phase and 35 per cent alpha the beta density increased 0.05 g/cm^3. The density increase occurred because of the high hardness of the alpha phase and the low hardness of the beta phase. Thus, the volume of microcracks was reduced.

Effect of Hydrostatic Pressing

Hydrostatic pressing had less effect on the alpha–beta transformation than it had on the beta–alpha transformation. The alpha–beta isothermal reaction curve at 124.0 C after hydrostatic pressing is displaced to the right by a factor of approximately 5 compared to the isothermal reaction curve before pressing (Figure 20). The reason the curves are closer together at the completion of the transformation is because of densification during the first alpha–beta transformation. After hydrostatic pressing the volume of microcracks was nearly eliminated, hence, there was no densification of the beta phase.

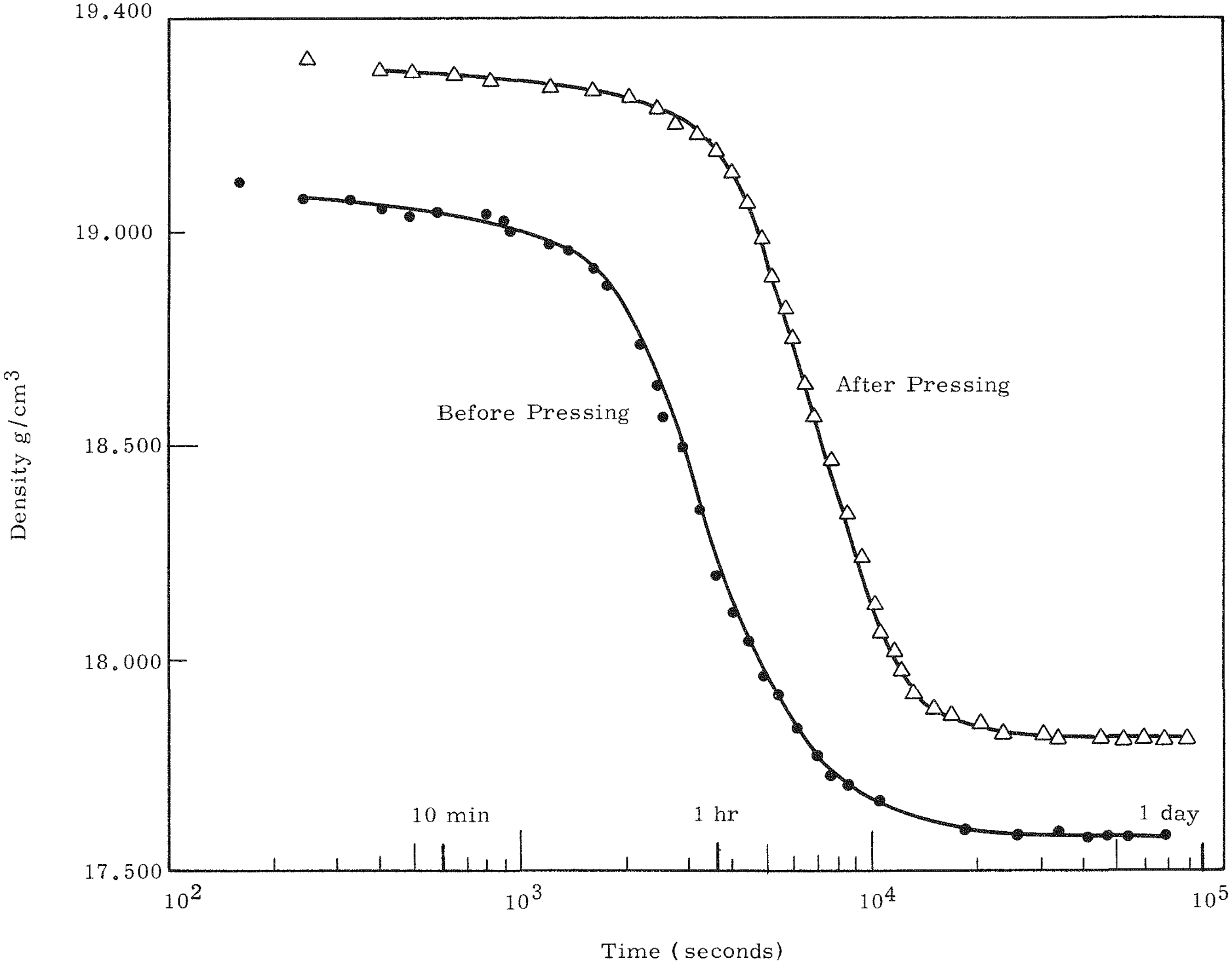


FIGURE 20

Effect of Hydrostatic Pressing
(90, 000 psi and a Temperature of 190 C; Cooled Under Pressure)
on the Alpha–Beta Transformation (124.0 ± 0.3 C)

Elevated Temperature Microscopy

The isothermal reaction curves indicated that the alpha–beta transformation is a nucleation and growth process. This was also shown by elevated temperature metallography (Figure 21). Photomicrographs showed the beta phase forming as islands within the alpha matrix. The total elapsed time between the start and completion of the alpha–beta transformation was 15 minutes.

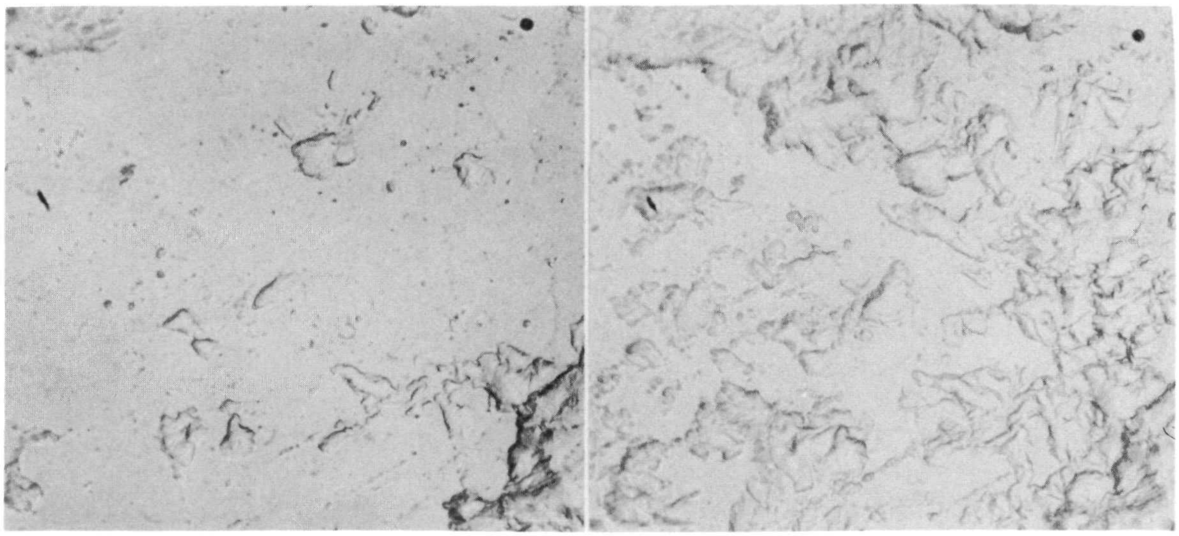
Figure 21 shows that there was considerable upheaval on the surface of the specimen during the transformation. The large surface distortion made it difficult to observe the subsequent transformations.

KINETICS OF THE GAMMA–BETA–ALPHA TRANSFORMATION

The gamma–beta–alpha transformation was studied in a similar manner as the beta–alpha and alpha–beta transformations.(24, 27) A complete T-T-T curve was obtained using the same metal, Heat A, as was used to obtain the beta–alpha and alpha–beta T-T-T curves (Figures 1 and 19).

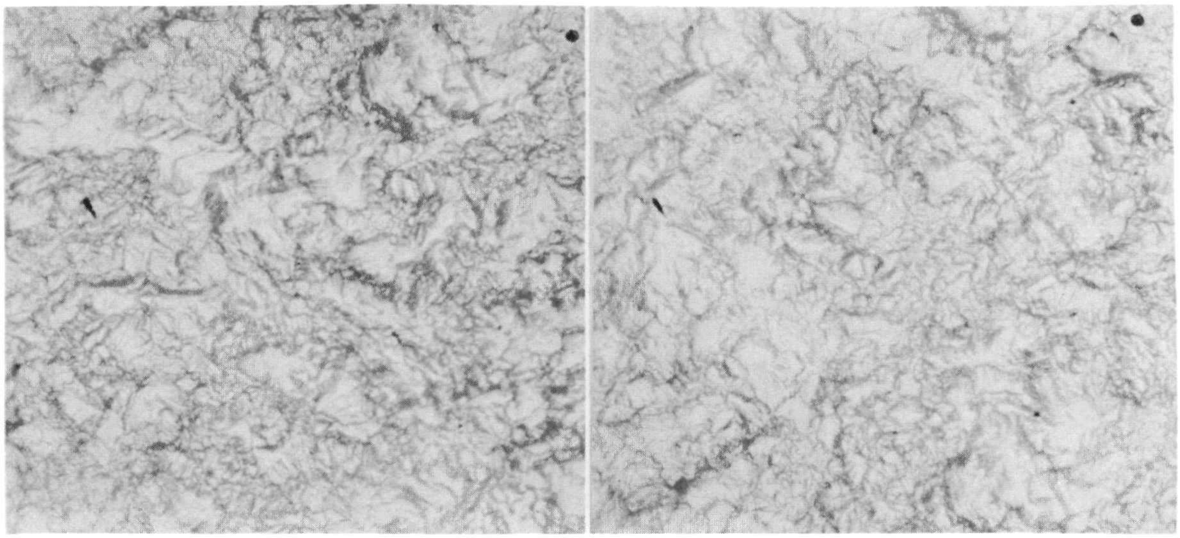
Isothermal reaction curves (Figure 22) were obtained of the transformation of the gamma phase when held at temperatures below the gamma–beta transformation temperature of 185 C and after gamma heat treating for 30 minutes at 260 C. The curves had a shape similar to the isothermal reaction curves of the beta–alpha transformation, except in the temperature range of 82 to 112 C. The curves in this range showed a plateau which increased in magnitude with increasing temperatures. The plateau represented a transition period of no reaction following the end of the gamma–beta transformation and preceding the beginning of the beta–alpha transformation at the same temperature. At 82 C, the plateau appeared only as a change of slope of the isothermal reaction curve.

The shape of the isothermal curves in the range of -80 to 160 C is reflected in the shape of the T-T-T curves for the gamma–beta–alpha transformations (Figure 23). The T-T-T curve of the gamma–beta–alpha transformations was a double C curve. The upper C curve



Start of Alpha–Beta Transformation

Approximately 50 Per Cent Transformed



Completion of Alpha–Beta Transformation

Completion of Beta–Alpha Transformation

FIGURE 21

Photomicrographs Showing Alpha–Beta Transformation and Subsequent Beta–Alpha Transformation 200X

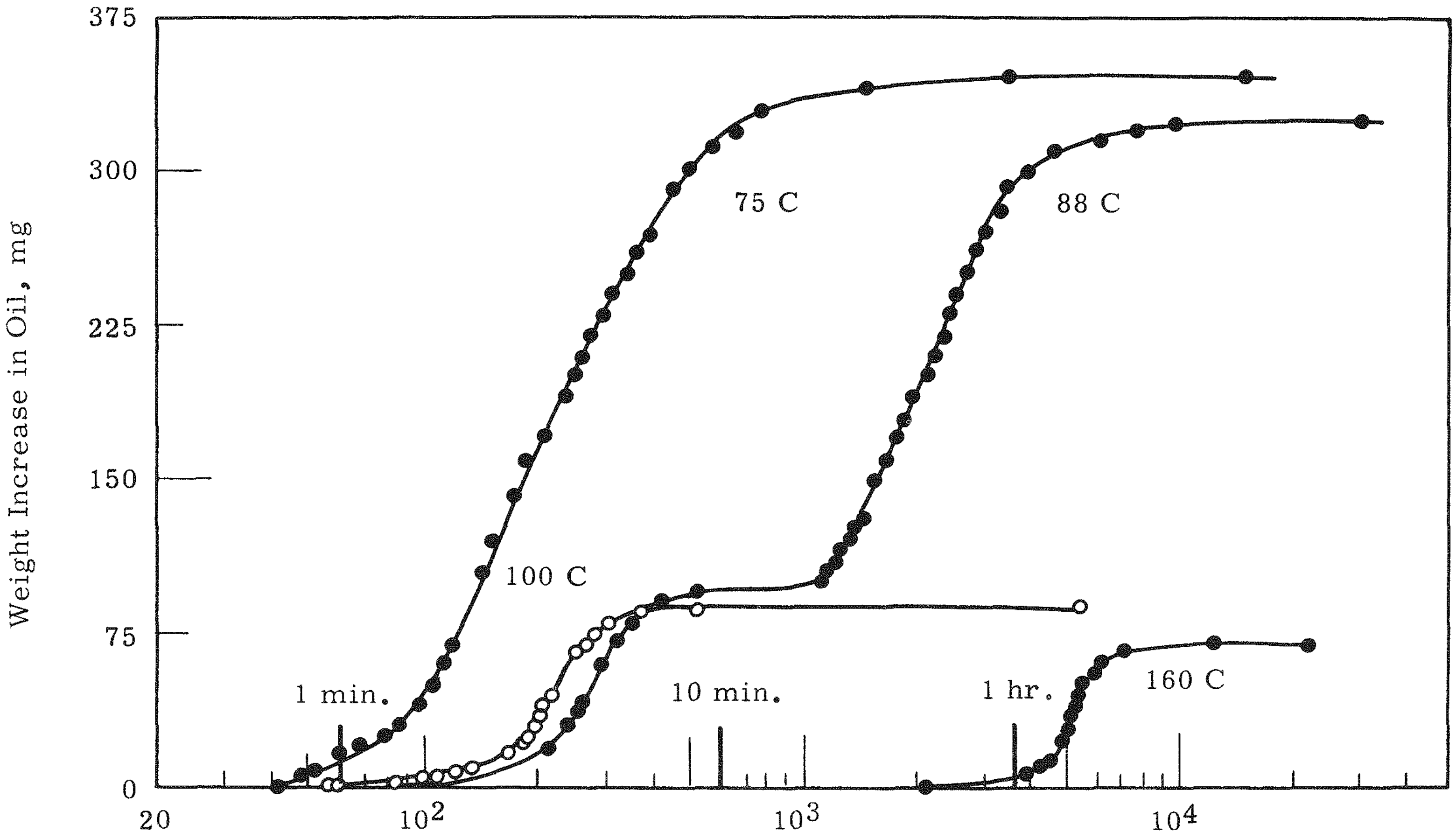


FIGURE 22

Isothermal Reaction Curves of the Gamma–Beta–Alpha Transformation

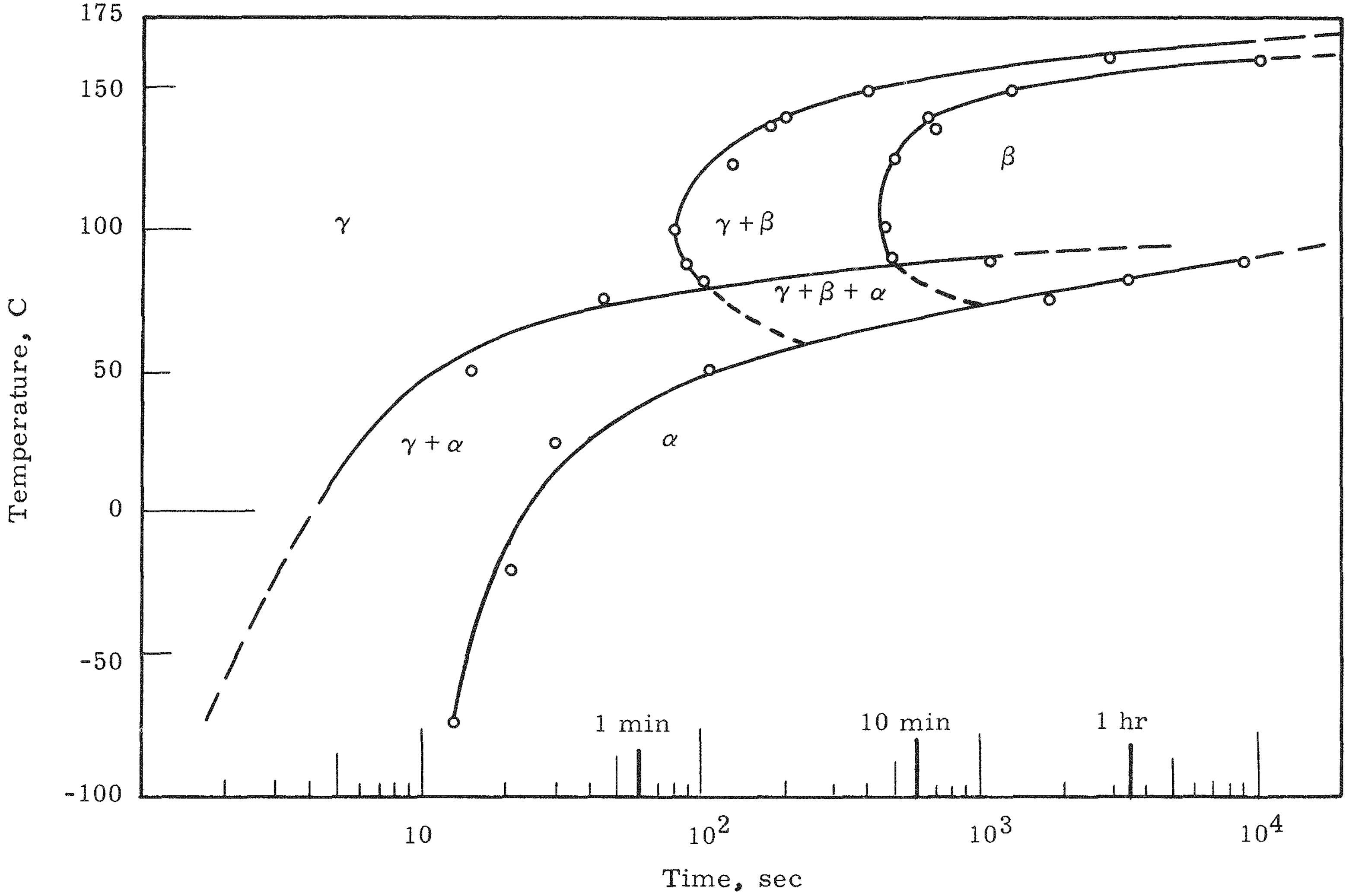


FIGURE 23

T-T-T Curve of Gamma–Beta–Alpha Transformation represents the gamma–beta transformation and the lower C curve represents the beginning and completion of the formation of alpha.

The rate of formation of alpha, when the plutonium metal had transformed directly to the alpha phase from the gamma phase, was greater than when the metal was quenched from the beta range (Figure 24). The time for 50 per cent transformation as a function of temperature is plotted for both transformations. The rate of formation of alpha was considerably higher from the gamma phase than from the beta phase. The difference becomes increasingly greater below the nose of the beta–alpha T-T-T curve, since it appears from the gamma–beta–alpha T-T-T curve that the rate of formation of the alpha phase from the gamma phase does not pass through a maximum. The shapes of the T-T-T curves are similar, except that the curve showing the transformation of alpha after quenching from the gamma range was shifted to the left. The rate of transformation of alpha was greater even at temperatures in the alpha range (82 to 112 C) where the gamma transformed completely to the beta phase before the appearance of alpha.

The rate of gamma–alpha transformation at -78 C was too rapid to be determined by this technique. It appeared that the gamma phase had completely transformed in less than 10 seconds. These data show that any retained beta phase can be avoided by rapidly cooling from the gamma phase, thus skipping the gamma–beta transformation and forming the alpha phase directly from the gamma phase. Retention of the gamma phase does not seem to occur, although careful experimental work is needed to determine if a small percentage of the gamma phase can be retained.

A study of the effect of gamma heat-treating temperatures has shown that the rate of transformation decreases with increasing temperatures. The time for 50 per cent transformation at 127.8 C, which was slightly above the nose of the gamma–beta T-T-T curve, was plotted (Figure 25) as a function of the gamma heat-treating temperature.

Variation of the gamma heat-treating temperature caused essentially no change of the rate of the gamma–alpha transformation. Varying the gamma heat-treating time had essentially no effect on either the gamma–beta or the gamma–alpha transformation rates.

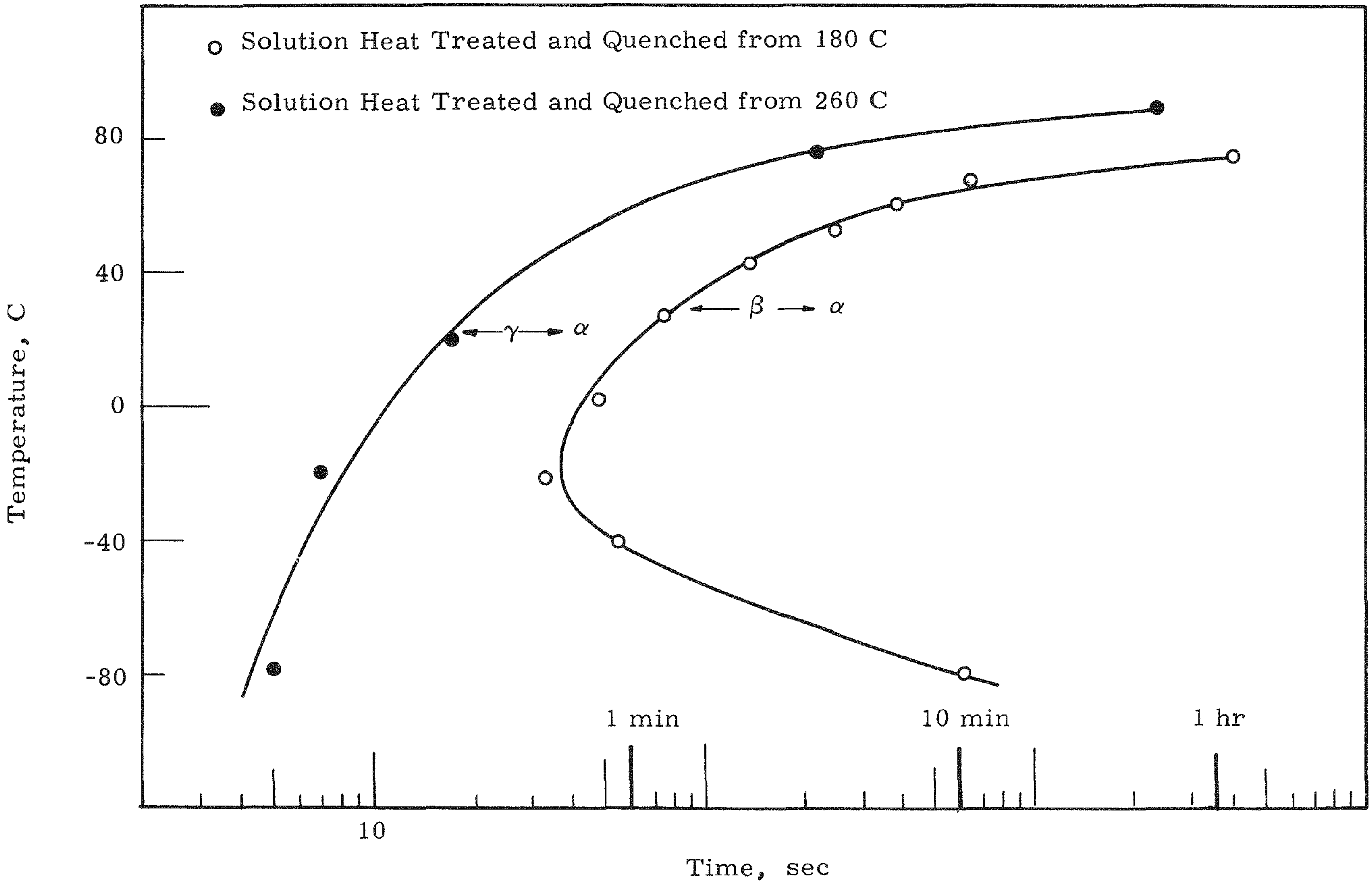


FIGURE 24
T-T-T Curves (50 Per Cent Alpha) of Beta–Alpha and Gamma–Beta–Alpha Transformations

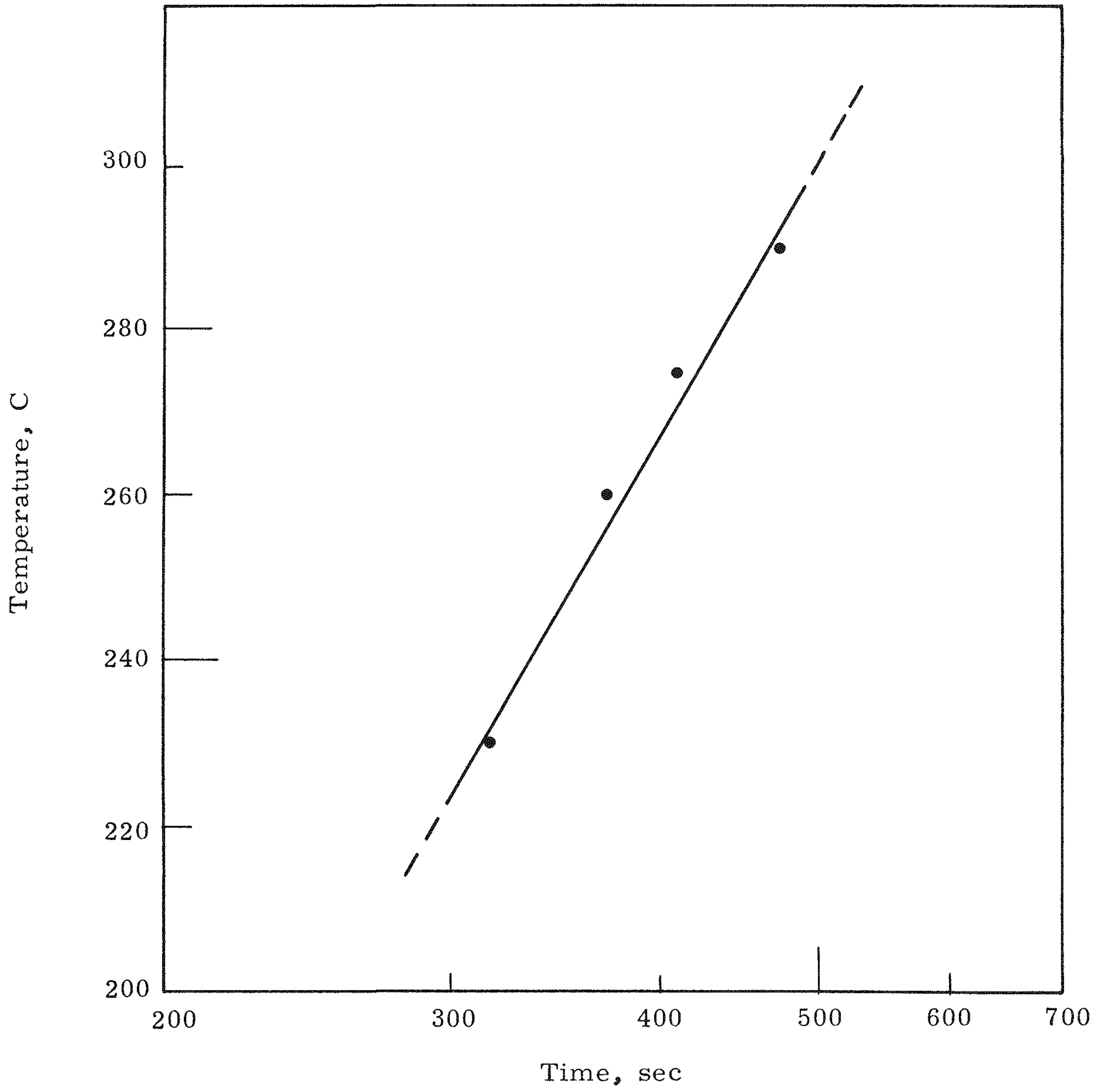


FIGURE 25

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

ALPHA–BETA–GAMMA TRANSFORMATION

The beta–gamma transformation behaved in a manner similar to the alpha–beta transformation. The isothermal reaction curves (Figure 26) also had the sigmoidal shape characteristic of nucleation and growth reactions.

The shape of the beta–gamma T-T-T curve (Figure 27) is similar to that of the alpha–beta transformation. The reaction started after only 5 or 6 seconds and was completed in 1-1/2 minutes at 250 C. The transformation was quite sluggish at 202 C--the reaction did not start until after 30 minutes and was not completed until approximately 4 hours. The beta–gamma equilibrium temperature was reported by Hill(1) to be 185 C.

Isothermal reaction curves (Figure 28) and a T-T-T curve (Figure 29) of the alpha–beta–gamma transformation, transforming to the gamma phase after holding at 100 C, have also been determined. The rate of alpha–beta transformation at temperatures between 200 and 250 C was too rapid to be accurately measured--the alpha–beta transformation started in less than 3 or 4 seconds and was completed in less than 30 seconds.

The time required for the appearance of the gamma phase after the sample had undergone the 100 C heat treatment was slightly longer than after the previous heat treatment of holding at 180 C. This may have been due to (1) larger grain size resulting from the higher temperature at which the beta phase had transformed, or (2) the longer time 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 is is thought that the temperature difference is the most likely.

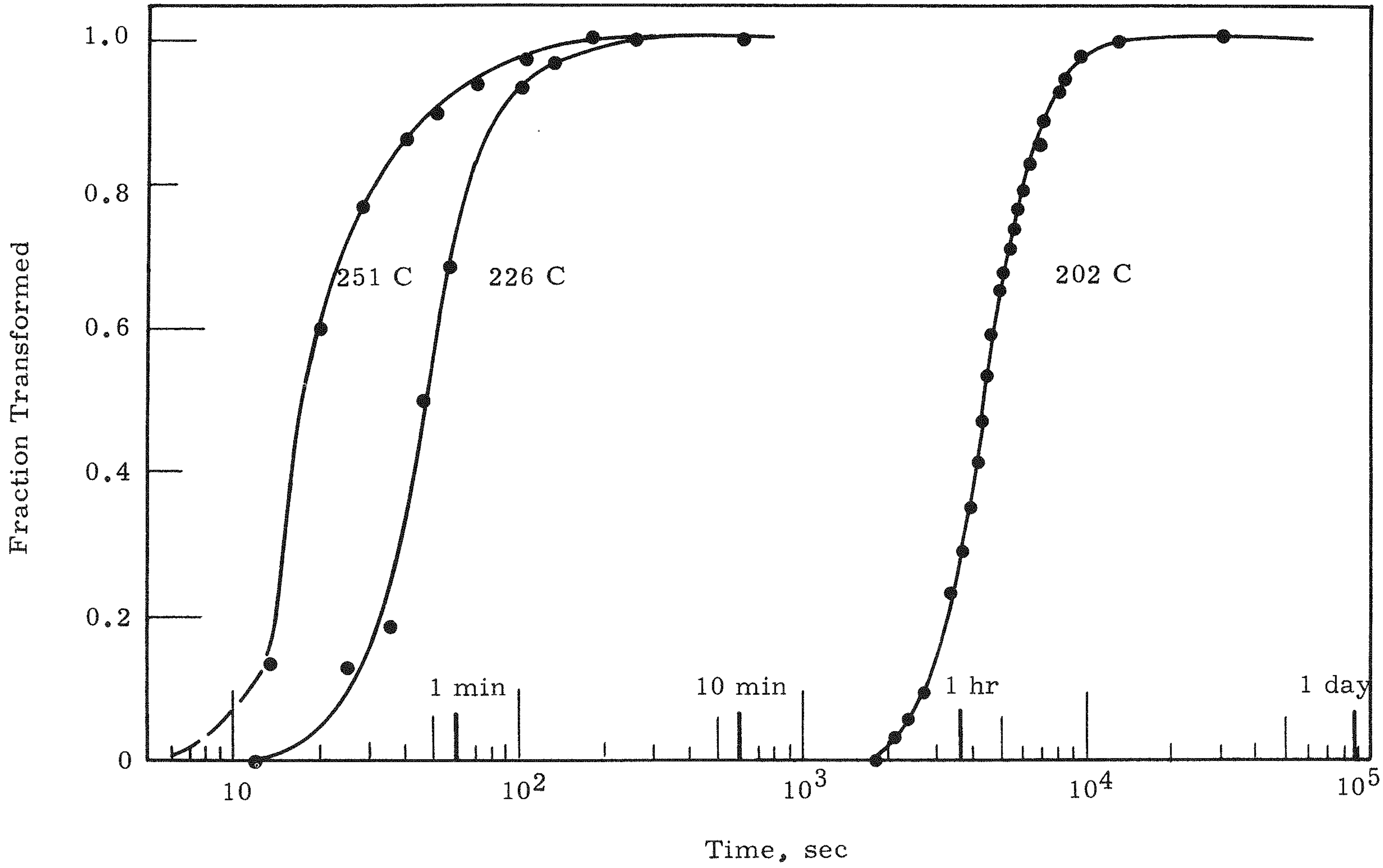


FIGURE 26

Isothermal Reaction Curves of Beta–Gamma Transformation

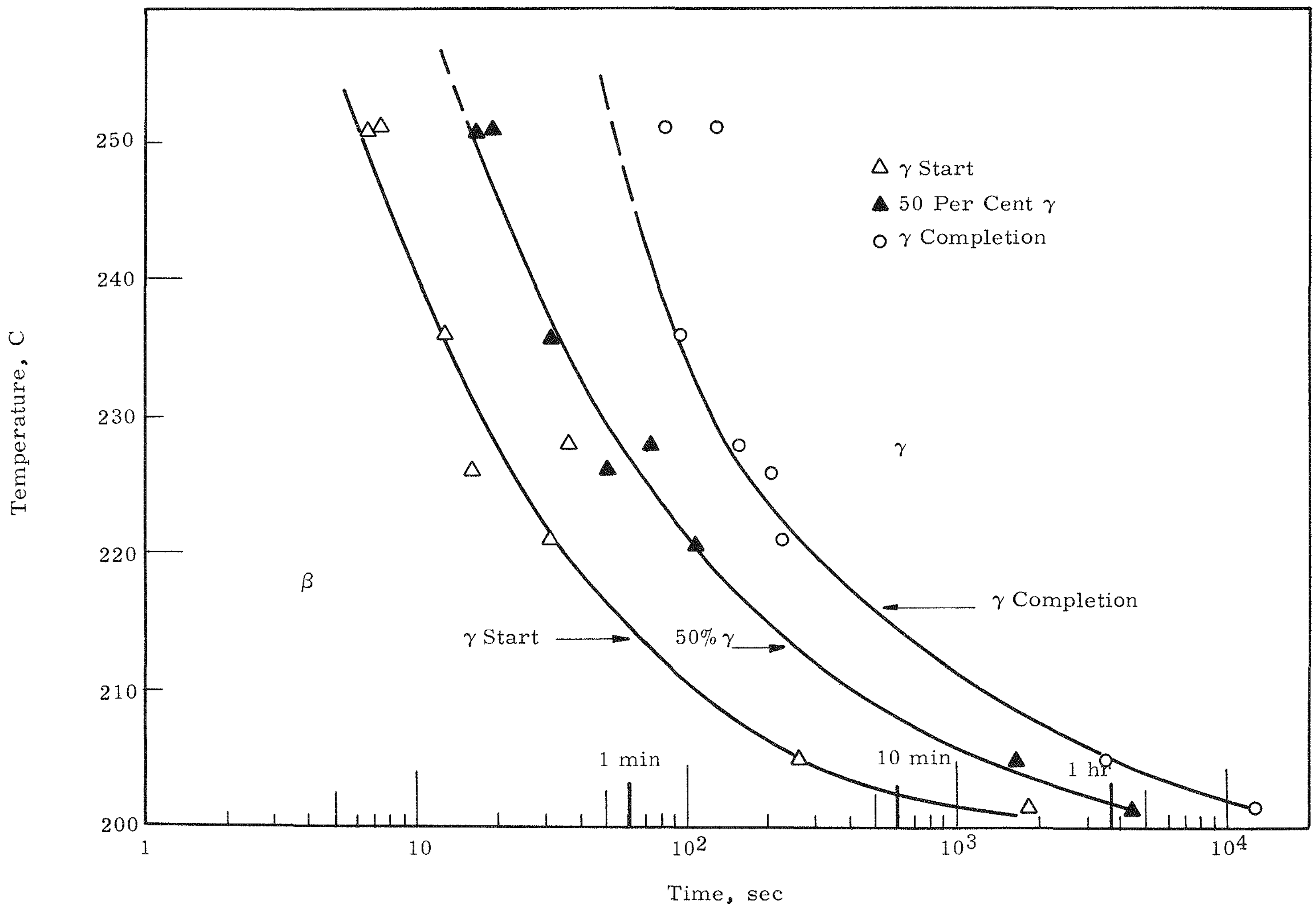


FIGURE 27

T-T-T Curve of the Beta–Gamma Transformation

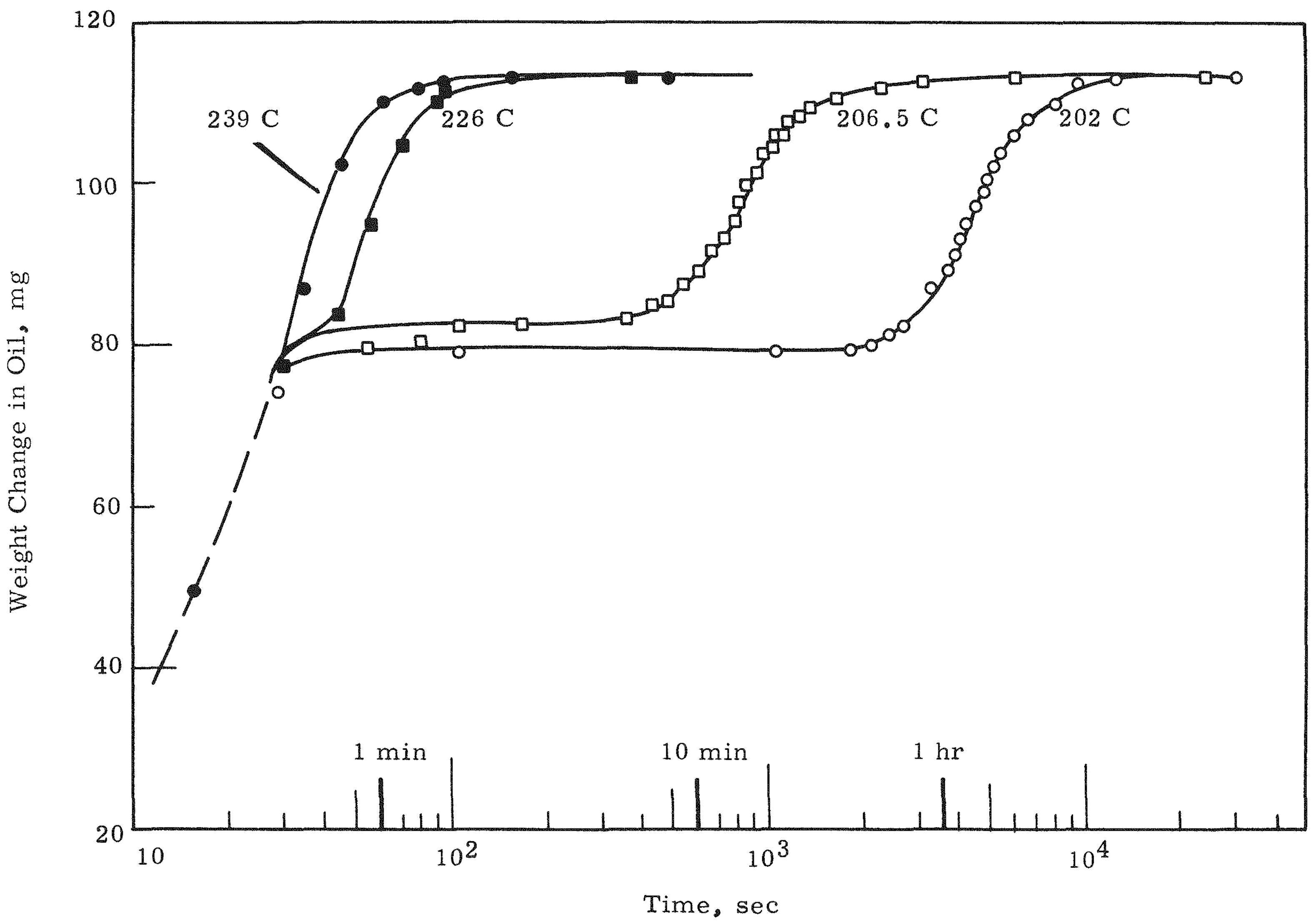


FIGURE 28

Isothermal Reaction Curves of Alpha–Beta–Gamma Transformation

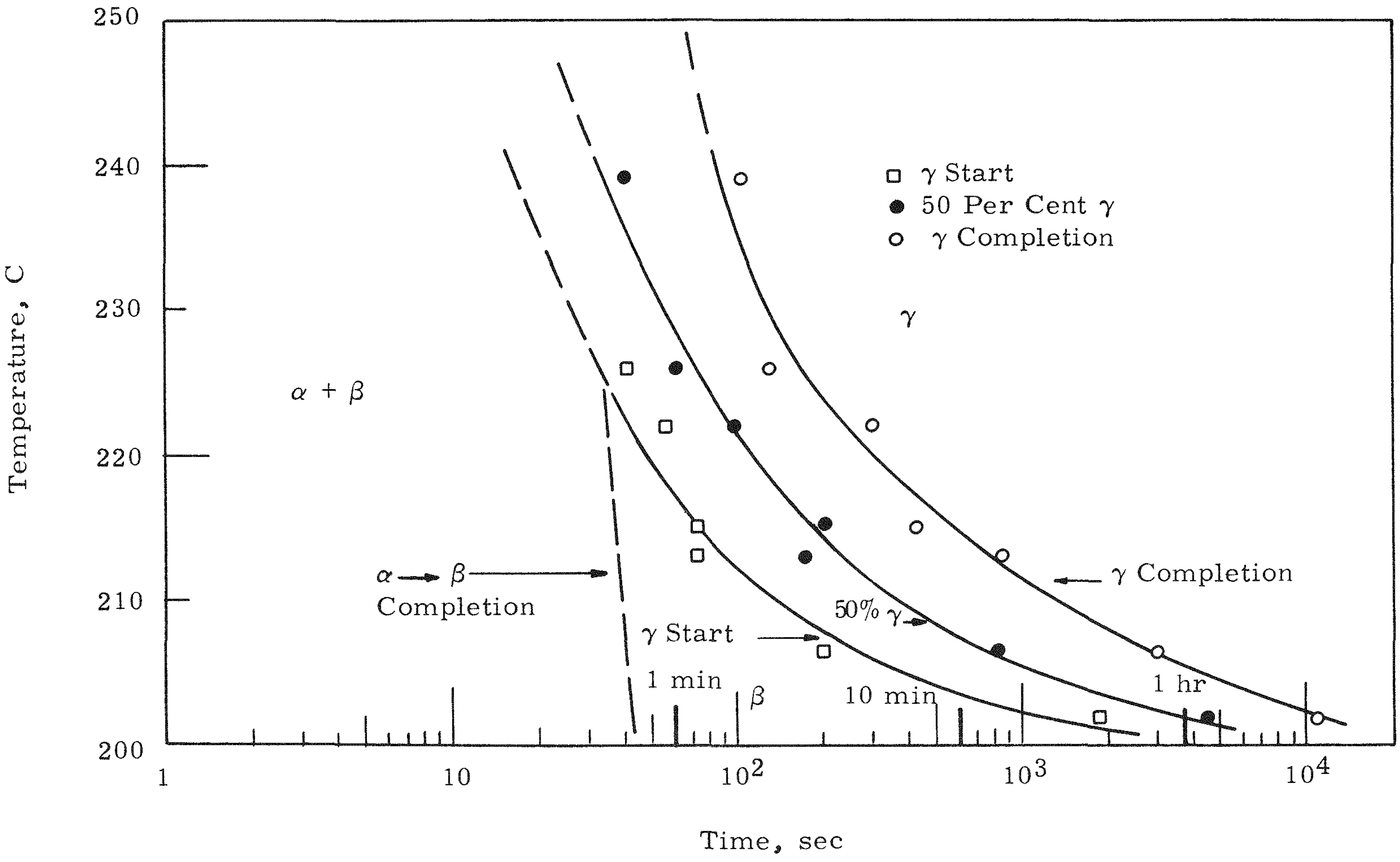


FIGURE 29

T-T-T Curve of Alpha–Beta–Gamma Transformation

COMBINED T-T-T CURVES OF THE ALPHA–BETA–GAMMA AND GAMMA–BETA–ALPHA TRANSFORMATIONS

The T-T-T curves of the alpha–beta–gamma and gamma–beta–alpha transformations (Figures 1, 19, 23, and 27) were combined into one T-T-T curve (Figure 30). These T-T-T curves were all determined from metal of the same casting, Heat A of Table II. The effect of individual impurities is an area which requires extensive investigation.

This composite T-T-T curve represents the earlier work performed at Hanford. The higher purity metals used in more recent studies of the beta–alpha and alpha–beta transformations have not been used to study the gamma–beta and gamma–alpha transformations in great detail. However, preliminary data showed that the T-T-T curves (Figure 4) were shifted to the left with increased purity, but the magnitude of the shift on the gamma–beta, gamma–alpha, alpha–gamma, and beta–gamma transformations was not as large as the shift of the beta–alpha transformations.

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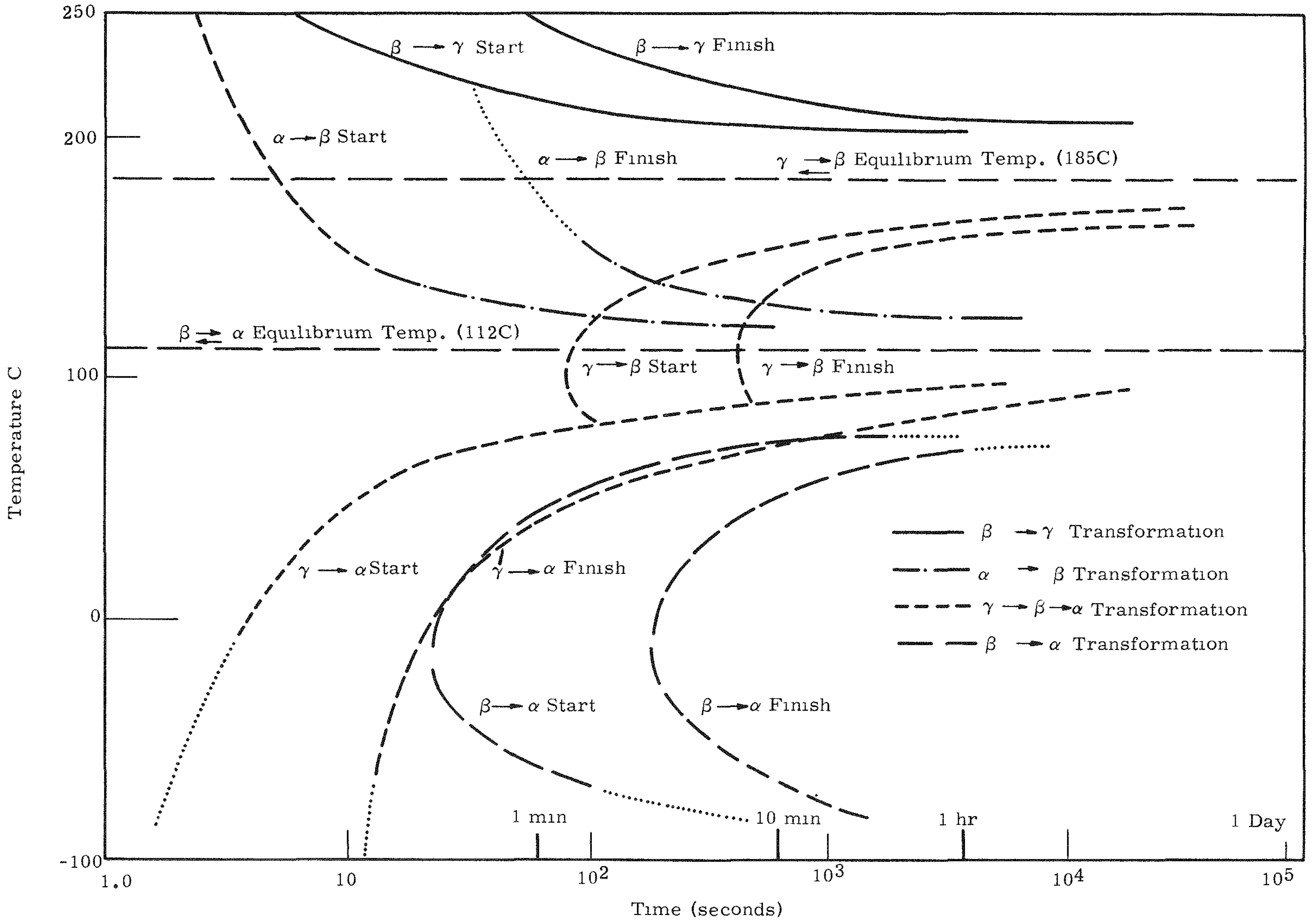

FIGURE 30

Composite T-T-T Curve of the Alpha–Beta–Gamma Transformations of Plutonium

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