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AEC RESEARCH AND DEVELOPMENT REPORT

METALLURGY AND CERAMICS

[redacted] NO.

THE EFFECT OF TRANSFORMATION COOLING RATE ON THE ACTIVATION ENERGY REQUIRED FOR RECRYSTALLIZATION OF BETA QUENCHED URANIUM

BY

H. R. GARDNER AND J. W. RICHES

HANFORD LABORATORIES OPERATION

MARCH 22, 1957

HANFORD ATOMIC PRODUCTS OPERATION

RICHLAND, WASHINGTON

GENERAL ELECTRIC

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H. R. Gardner

Plutonium Metallurgy

and

J. W. Riches

Materials Development
Reactor and Fuels Research and Development Operation

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ABSTRACT

A relationship was established between the lattice strain induced in uranium during quenching from the beta phase and the activation energy required for alpha phase recrystallization.

THE EFFECT OF TRANSFORMATION COOLING RATE ON THE ACTIVATION ENERGY REQUIRED FOR RECRYSTALLIZATION OF BETA QUENCHED URANIUM

INTRODUCTION

In December of 1954[1] it was observed that the coarse, irregular grains in beta quenched uranium* could be converted to fine equiazed grains by a short time alpha anneal in the 610-640 C temperature range. Later studies have shown that this grain refinement is obtained by a recrystallization process.[2] Apparently the strain induced in the orthorhombic alpha uranium lattice during quenching from the beta phase is sufficient to cause recrystallization during subsequent alpha annealing. It is pertinent to note that this phenomenon in itself is rather unusual in metallurgical history; generally the strain requisite to later recrystallization is induced by a cold working or forming process.

Previous work[1] indicated that the recrystallization process was dependent on cooling rate from the beta temperature region; uranium air cooled from the beta phase did not start to recrystallize during a 20-minute anneal at 640 C while beta quenched uranium completely recrystallized within 15 minutes at 640 C. Therefore, because of the interest in this recrystallization process from both the practical and theoretical standpoints, a study of the relation between cooling rate and the recrystallization kinetics of the reaction was initiated.

* Beta quenched uranium refers to a 13-15 minute salt bath heat treatment at 720-740 C followed within 20 seconds by a water quench.

SUMMARY

Uranium, Jominy end quench specimens were used to establish a relationship between the lattice strain induced during cooling from the beta phase and the activation energy required for alpha phase recrystallization. The activation energies obtained ranged from 110,000 calories/mole for a 4.4 C/second cooling rate to 30,000 calories/mole for a 500 C/second cooling rate.

In the Arrhenium equation for rate of reaction, $Ae^{-Q/RT}$, the A values were calculated and ranged from 9.7×10^{22} to 7.7×10^{5} for the 4.4 and 500 C/second cooling rates respectively.

The conclusion was reached that the Avrami nucleation and growth hypothesis for recrystallization does not apply to the observed recrystallization phenomenon.

EXPERIMENTAL PROCEDURE AND RESULTS

To reduce the effect of chemical and casting variables, a single rod of dingot uranium was used. Dingot uranium* is the best quality uranium commercially available, having a density of 19.00 g/cc or greater and a total impurity content of approximately 150 ppm (Table I). The dingot rod was produced by rolling from molten salt** at 620-640 C after the bomb reduction product had been scalped and forged to a suitable size. The rolled rod was salt bath** beta heat treated for 13-15 minutes at 720-740 C and water quenched within 20 seconds after removal from the bath.

Standard one inch diameter Jominy specimens[3] were prepared from the dingot rod and end quenched from 730 C in a Jominy fixture. Cooling curves were taken at a number of positions along the specimens and cooling rates were calculated for the 570-670 C temperature range from each cooling curve and are presented as a function of distance from the quenched end in Figure 1. Details of the heat treatment, thermocouple technique, and cooling rate calculations are presented in Appendix I.

* The term dingot is a contraction of the words "direct ingot" and means that it is formed directly from the bomb reduction without intermediate recasting.

** The salt bath was composed of 46% Li_2CO_3 and 54% K_2CO_3.

Transverse wafers, 0.062 inches thick, were cut from heat treated Jominy specimens at distances from the quenched end listed in Table II with their corresponding cooling rates. The sigmoidal curves establishing the time-temperature relationship for recrystallization at the various cooling rates were determined at temperatures of 580, 595, 620, and 640 C, Figures 2, 3, 4 and 5. All annealing was done in an eight-inch diameter lead pot. For all but the 580 C, 9.4 C/second cooling rate samples and the 580 and 595 C, 4.4 C/second cooling rate samples, bare uranium specimens were annealed in lead with good results. The indicated specimens were sealed in 15 mm I.D. evacuated quartz capsules with a 50×10^{-3} mm Hg initial pressure and then annealed in lead. Since the annealing times for recrystallization of these samples were generally greater than 2 hours, it is not expected that the slower heating rate in evacuated quartz appreciably affected the recrystallization times.

After the annealing treatment, a minimum of 20 mils metal was removed from the surface of the wafers by first grinding on 120 grit emery paper and then polishing on 320 grit cloth. The grain structures were delineated by a hydrochloric acid-water rinse-nitric acid-water rinse macro-etching technique.

Estimates of the percentage recrystallization were made at magnifications of 20 to 60 diameters by a minimum of two observers. Photomacrographs taken at 10 diameters and enlarged to 30 diameters illustrate the 0 and 90 to 100 per cent levels of recrystallization at a particular temperature for each of the cooling rates studied. (Figures 6 and 7).

The average grain diameter at each cooling rate was estimated before and after recrystallization (Table II). The expected grain refining effect of recrystallization was obtained; however, in addition, the data indicate that the recrystallized grain size is either related to effects of cooling rate during end quenching or to the grain size existing in the quenched Jominy specimen prior to recrystallization.

Curves for the activation energy determinations were obtained by plotting the time required for 50 per cent recrystallization, of uranium quenched at a given cooling rate, as a function of the reciprocal of the absolute temperature of annealing. The data for all annealing temperatures and cooling rates are plotted in this fashion in Figure 8. The activation energies (Table II) for the four cooling rates were calculated from the Arrhenius rate equation, $Ae^{-Q/RT}$* or $\log \frac{t_2}{t_1} = \frac{Q}{2.3R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ where t_1 and t_2 are the times required for 50 per cent recrystallization at absolute temperatures T_1 and T_2, Q is the activation energy in calories per mole, and R is the gas constant in calories per mole per ^{o}K.

The relation between cooling rate and time required for 50 per cent recrystallization is presented in Figure 9 for each of the four temperatures studied. The data for the 250 C/second cooling rate do not fit the curves. The most logical explanation is that this particular cooling rate determination is in error Examination of the cooling rate curve for the Jominy specimen (Figure 1) tends to substantiate this explanation. The cooling rate determinations in the region within 0.25-inch from the quenched end have a comparatively wide scatter. A cooling rate of 60-90 C/second would result in a much better fit for the curves drawn in the figure.

In the Arrhenius equation, $Ae^{-Q/RT}$, the value of A in grams recrystallized per second per cm^2 can be computed by taking logarithms of the equation, i.e., $\log \frac{1}{t} = \log A - \frac{Q}{2.3RT}$ where t is the time required for 50 per cent recrystallization at a particular absolute temperature T, Q is the activation energy in calories per mole, and R is the gas constant in calories per mole per ^{o}K. Table II contains the calculated values of A and a sample calculation is included in Appendix III.

* See Appendix II.

DISCUSSION

The process of recrystallization during annealing of strained metals can be described by a nucleation and growth hypothesis. Theories based on this hypothesis have been developed by Johnson and Mehl[4] and Avrami.[5] The theories are quite similar and result in the following equation

$$\ln \frac{1}{1-x} = f(G_x G_y G_z) \int_o^t (t-p)^3 \, N dp \qquad (A)$$

where x is the fraction recrystallized in time t; G_x, G_y and G_z are the growth rates in the x, y and z directions, p is the nucleation period, and N is the rate of nucleation. The main difference between the two theories is in their assumptions as to how N varies with time. Using the Avrami treatment because of its extension to one, two and three dimensional growth which will be discussed later, the rate of nucleation N at time t is given by the equation: $N = \bar{N} e^{-nt}$ where $\bar{N}$ is the number of preferred nucleation sites per unit volume and n is the probability of formation of a nucleus that will exhibit growth. Avrami then substitutes this result into equation A, assumes $G_x = G_y = G_z$ and derives the following equation for the fraction of metal (x) recrystallized isothermally as a function of time, $x_t = 1 - e^{-Bt^k}$. (B) According to Avrami, for k between 3 and 4, polyhedral growth occurs; between 2 and 3, plate-like growth; and between 1 and 2, linear growth occurs. Values for k were obtained by plotting $\log \frac{1}{1-x}$ against time on log log paper for the 16 sigmoidal isothermal recrystallization curves. Straight lines of slope k are obtained, Figure 10 contains those for the 9.4 C/second cooling rate. The general equation of these lines is

$$k \log \frac{t_1}{t_2} = \log \frac{\log \frac{1}{1-x_1}}{\log \frac{1}{1-x_2}},$$

which is merely a modification of equation B.

Table III contains the values of k for the 16 time temperature recrystallization relationships studied. The wide range of k values obtained, 2.6 to 6.4, may seem puzzling; however, inspection of the assumption Avrami made concerning the rates of growth in the x, y, and z directions leads to an explanation. In metals with a cubic structure, it is reasonable to assume, as Avrami did, that $G_x = G_y = G_z$. In the case of the orthorhombic uranium structure with its characteristic anisotropy, the rates of growth along the three crystallographic axes are most certainly not equal; therefore, it is not surprising that a relatively constant k value in the range of 3 to 4, for polyhedral growth, is not obtained. Rather, the conclusion is reached that the Johnson and Mehl, and Avrami simplifying assumption that $G_x = G_y = G_z$ does not apply to metals having a structure other than cubic.

Another description of recrystallization kinetics is that proposed by Cook and Richards[6] which is derived without reference to a nucleation and growth concept. Here recrystallization is described as a first order rate process which depends upon the degree of recovery that has taken place. In their treatment recovery is also regarded as a first order rate process. An equation is derived which is similar to the Avrami equation (B) with k being equal to 2. Clearly this treatment also does not fit the present experimental data.

As illustrated in Table II the activation energy Q required for recrystallization decreases rather markedly as cooling rate increases. Gordon[7] working with high purity copper determined that increasing the strain level up to 39.5 per cent elongation has little or no effect on activation energy. However, Anderson and Mehl[8] in their work on aluminum determined that the activation energy for recrystallization decreased as the amount of strain induced during tensile elongation was increased. An increase from 5 to 15 per cent elongation produced a decrease in activation energy from 64,500 to 52,100 cal/mole. Considering that deformation did not affect the activation

energy for recrystallization of copper and only slightly affected that for aluminum at low deformations; and realizing that the degree of lattice strain induced in uranium during quenching was not determined, it is proposed that the anisotropic nature of alpha phase uranium contributes heavily to lattice strain during quenching resulting in the observed large decrease in activation energy with increasing cooling rate, i.e., strain. An observation which tends to substantiate this proposal is that quench cracking was observed directly on the quenched end of the Jominy specimens indicating that enough strain had been produced during quenching to cause metal failure.

CONCLUSIONS

A definite relationship was established between cooling rate from the beta phase and the activation energy required for alpha phase recrystallization of uranium; as the cooling rate increases, the activation energy decreases.

The phenomenon of inducing sufficient strain by merely quenching to cause subsequent recrystallization is rather unusual in metallurgical history. It is proposed that this process is characteristic of the anisotropic nature of alpha phase uranium.

The Avrami nucleation and growth hypothesis for recrystallization does not apply to the observed phenomenon. Thus the conclusion is reached that the theory should be extended to include anistropic metals.

From a practical standpoint, knowledge of the cooling rate during quenching from the beta phase will yield an estimate of the time-temperature requirements for recrystallization of uranium. This information would be extremely useful in establishing product specifications for production applications.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to K. F. Powell for the excellent assistance provided in all phases of this study. The workmanship of E. Casey in sealing selected specimens in evacuated quartz tubes added greatly to the success of the work. Thanks are due to L. A. Hartcorn and technicians of the Metallography Operation for their fine work on the rather difficult photomacrography of the experimental specimens.

H. R. Gardner

J. W. Riches

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(3) Grossman, M.A., Hardenability of Steel, American Society for Metals, Metals Handbook, 1948 Edition, p. 490.

(4) Johnson, W.A., and Mehl, R.F., Reaction Kinetics in Processes of Nucleation and Growth, Trans. AIME (1939), 135, p.146.

(5) Avrami, M., The Kinetics of Phase Changes, Journal of Chemical Physics, 7 (1939) p. 1103; 8 (1940) p. 212; 9 (1941) p. 177.

(6) Cook, M., and Richards, T.L., Observation on the Rate and Mechanism of Recrystallization in Copper, Journal, Institute of Metals, 73 (1947) p. 1.

(7) Gordon, P., Microcalorimetric Investigation of Recrystallization of Copper, Journal of Metals, Transaction Vol. 7 (1955) p. 1043.

(8) Anderson, W.A., and Mehl, R.F., Recrystallization of Aluminum in Terms of the Rate of Nucleation and the Rate of Growth, Trans. AIME, Vol. 161, (1945) p. 140.

TABLE I

Chemical Analysis and Density of Dingot Uranium Used

Element	Chemical Analysis (ppm)	Method of Determination
H	5.9	Vacuum extraction at 820 C
C	35	Gravimetric
N	11	Gravimetric
Fe	24	Spectrochemical, densitometer
Si	22	Spectrochemical, densitometer
Al	2	Spectrochemical, visual estimate from film
Cr	10	Spectrochemical, visual estimate from film
Cu	0.5	Spectrochemical, visual estimate from film
Mg	5	Spectrochemical, visual estimate from film
Mn	5	Spectrochemical, visual estimate from film
Ni	18	Spectrochemical, visual estimate from film
Density	19.02 g/cm^3	By difference

TABLE II

Cooling Rate, Activation Energy, and Grain Size Corresponding to Distance from Quenched End of Jominy Specimens used in Recrystallization Study

Distance From Quenched End (inches)	Cooling Rate Over 570-670 C Range (° C/second)	Activation Energy Required For Recrystallization (calories per mole)	Value of A (No. of grains Recrystallized per sec. per cm^2)	Average Grain Diameter (mm)	
				As heat treated	Recrystallized
0.005	500 ± 100	30,000	7.7×10^{5}	0.20	0.08
0.060	200 ± 50	52,000	4.1×10^{10}	0.50	0.17
0.625	9.4 ± 2	88,000	7.0×10^{18}	0.55	0.40
1.125	4.4 ± 2	110,000	9.7×10^{22}	0.70	0.50

TABLE III

Values of k in the Equation $X_t = 1-e^{-Bt^k}$

Cooling Rate °C/second	Annealing Temperature 580 C	595 C	620 C	640 C
500 ± 100	2.7	3.0	4.3	6.4
200 ± 50	4.1	2.6	3.8	4.5
9.4 ± 2	4.3	3.4	4.0	5.9
4.4 ± 2	3.2	4.6	6.4	4.9

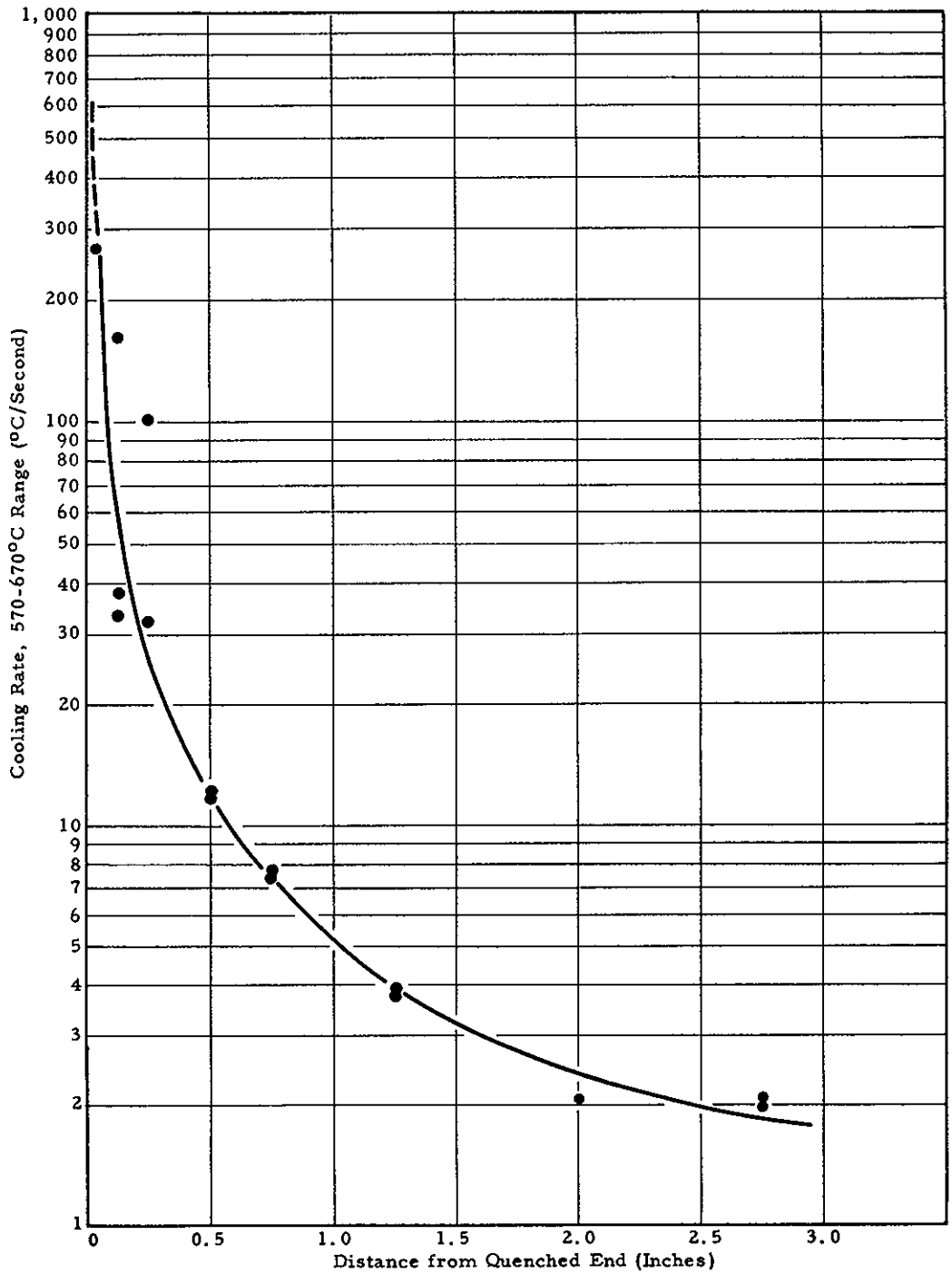


FIGURE 1

Relation Between Cooling Rate and
Distance from Quenched End for a Standard One-Inch Diameter,
Four-Inch Long Uranium Jominy Specimen Quenched from 730 C.

AEC-GE RICHLAND, WASH.

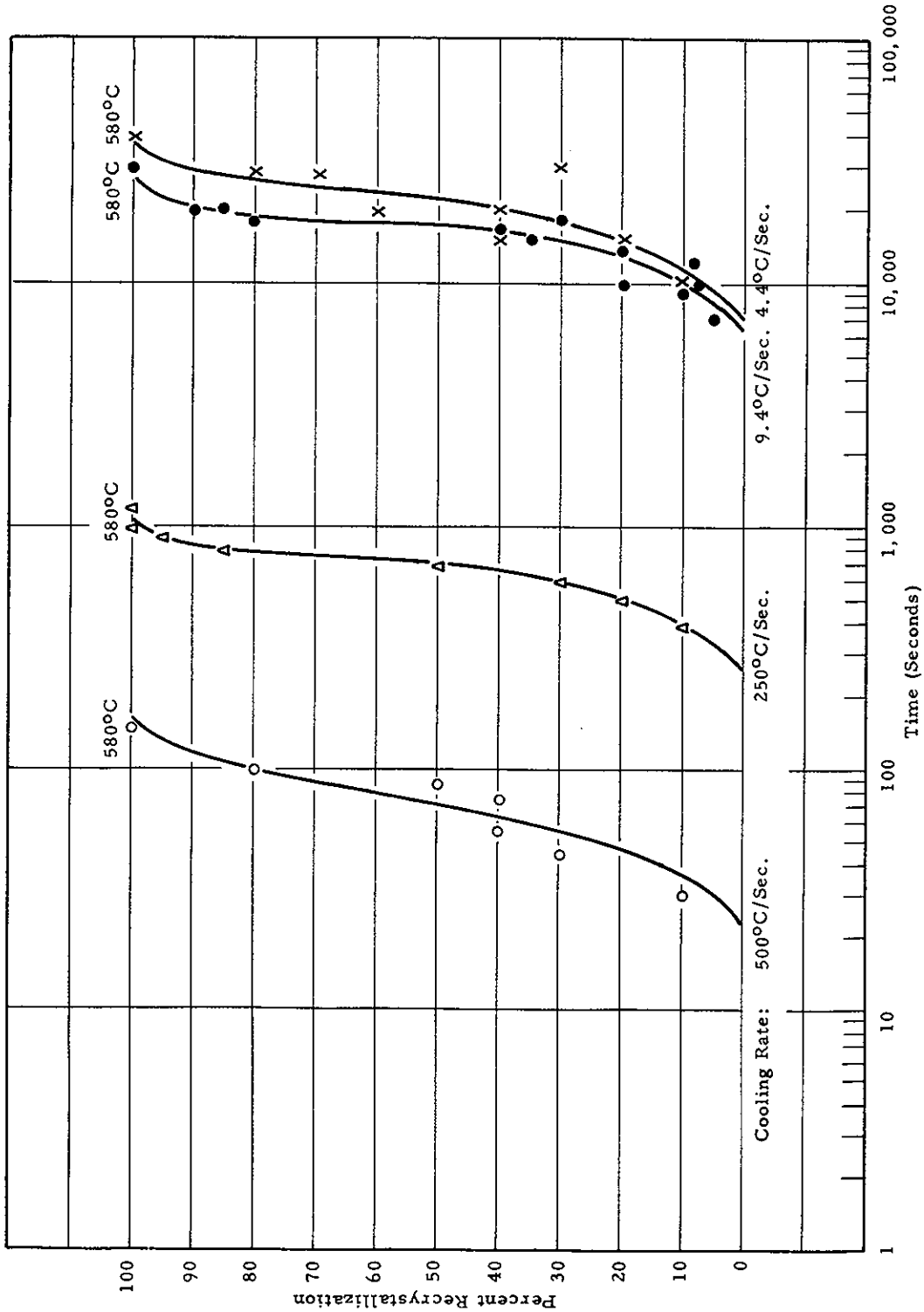


FIGURE 2

Per Cent Recrystallization
as a Function of Time at Temperature for Indicated Cooling Rates

AEC-GE RICHLAND, WASH.

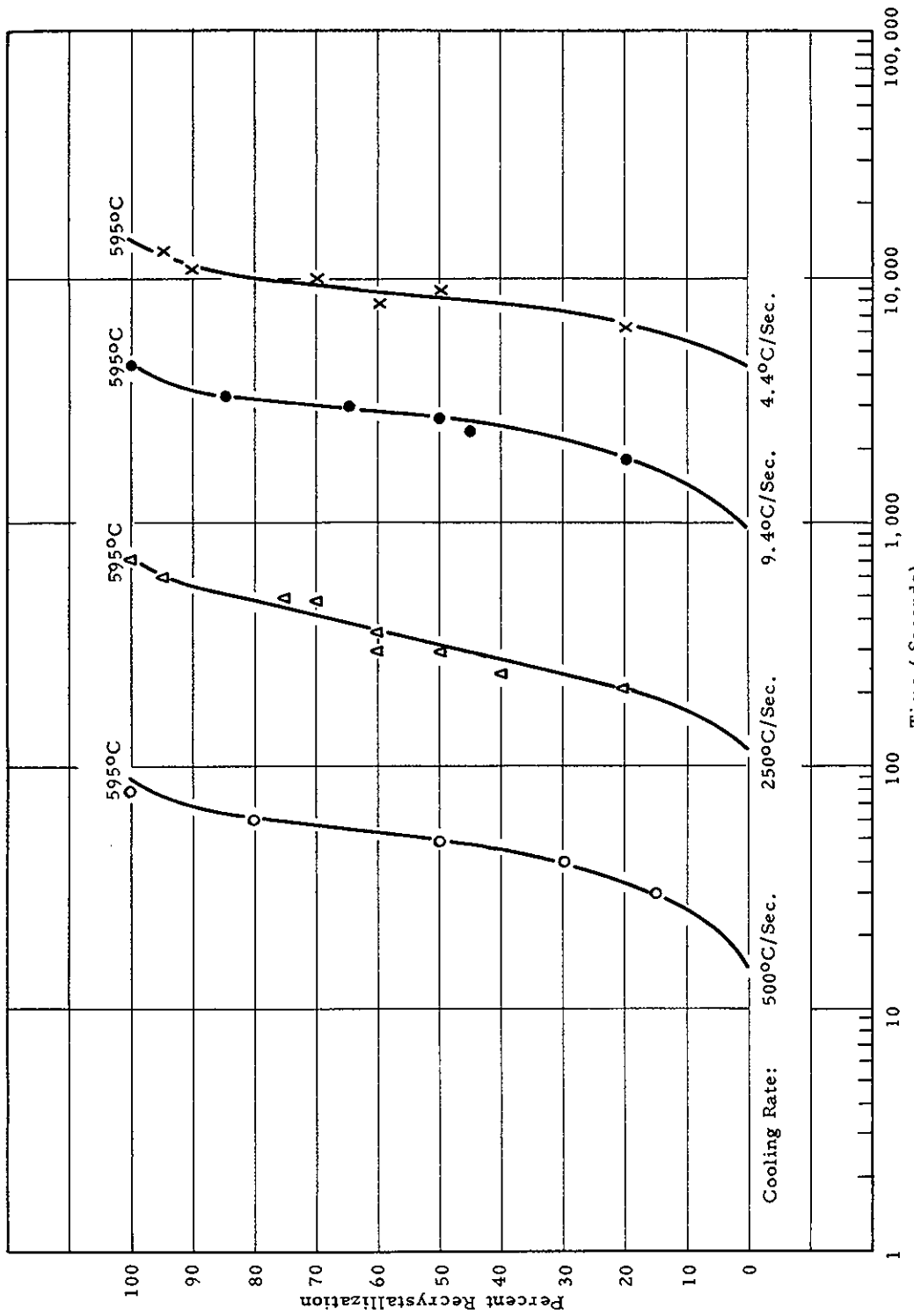


FIGURE 3
Per Cent Recrystallization
as a Function of Time at Temperature for Indicated Cooling Rates

AEC-GE RICHLAND, WASH.

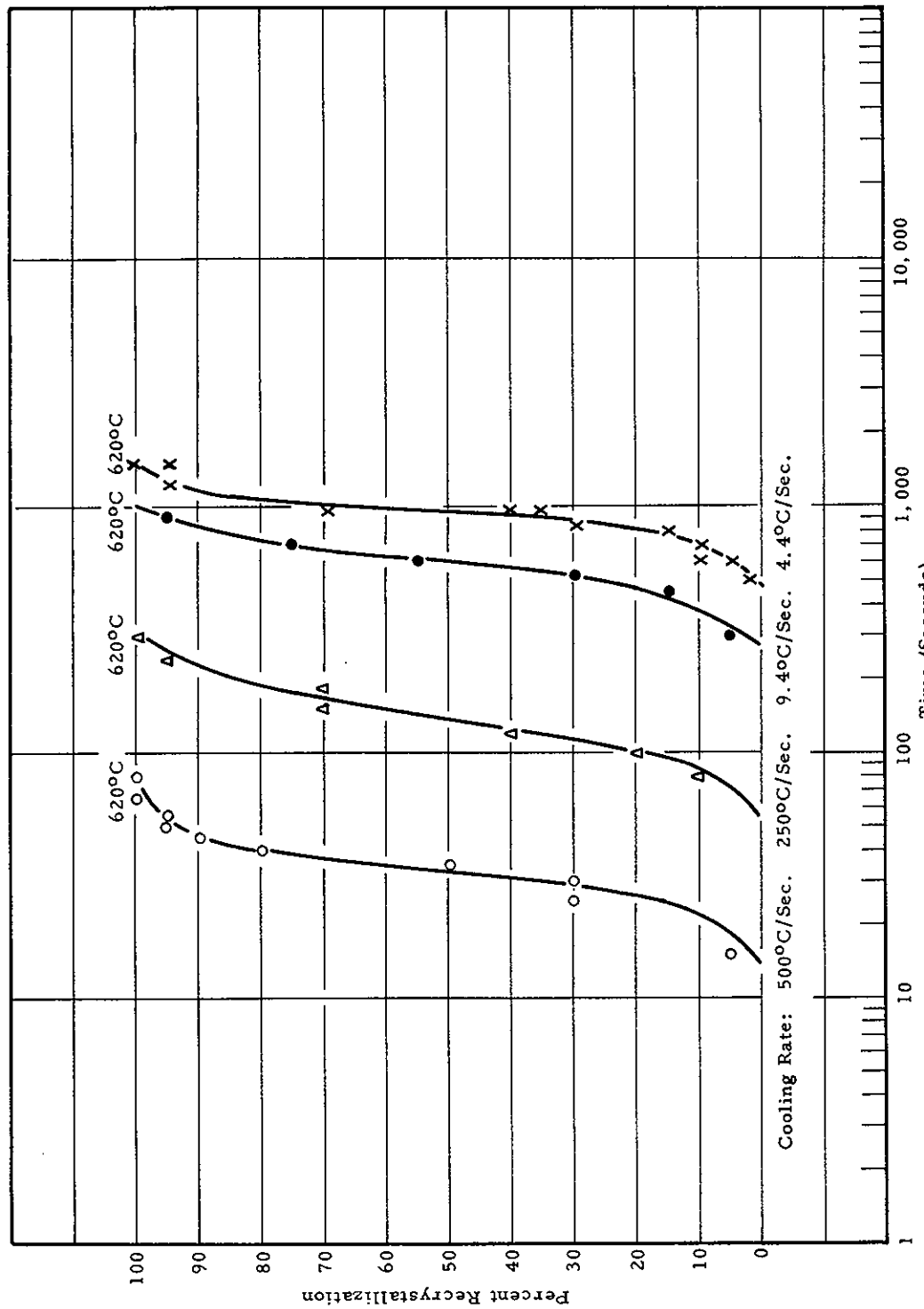


FIGURE 4
Per Cent Recrystallization
as a Function of Time at Temperature for Indicated Cooling Rates

AEC-GE RICHLAND, WASH.

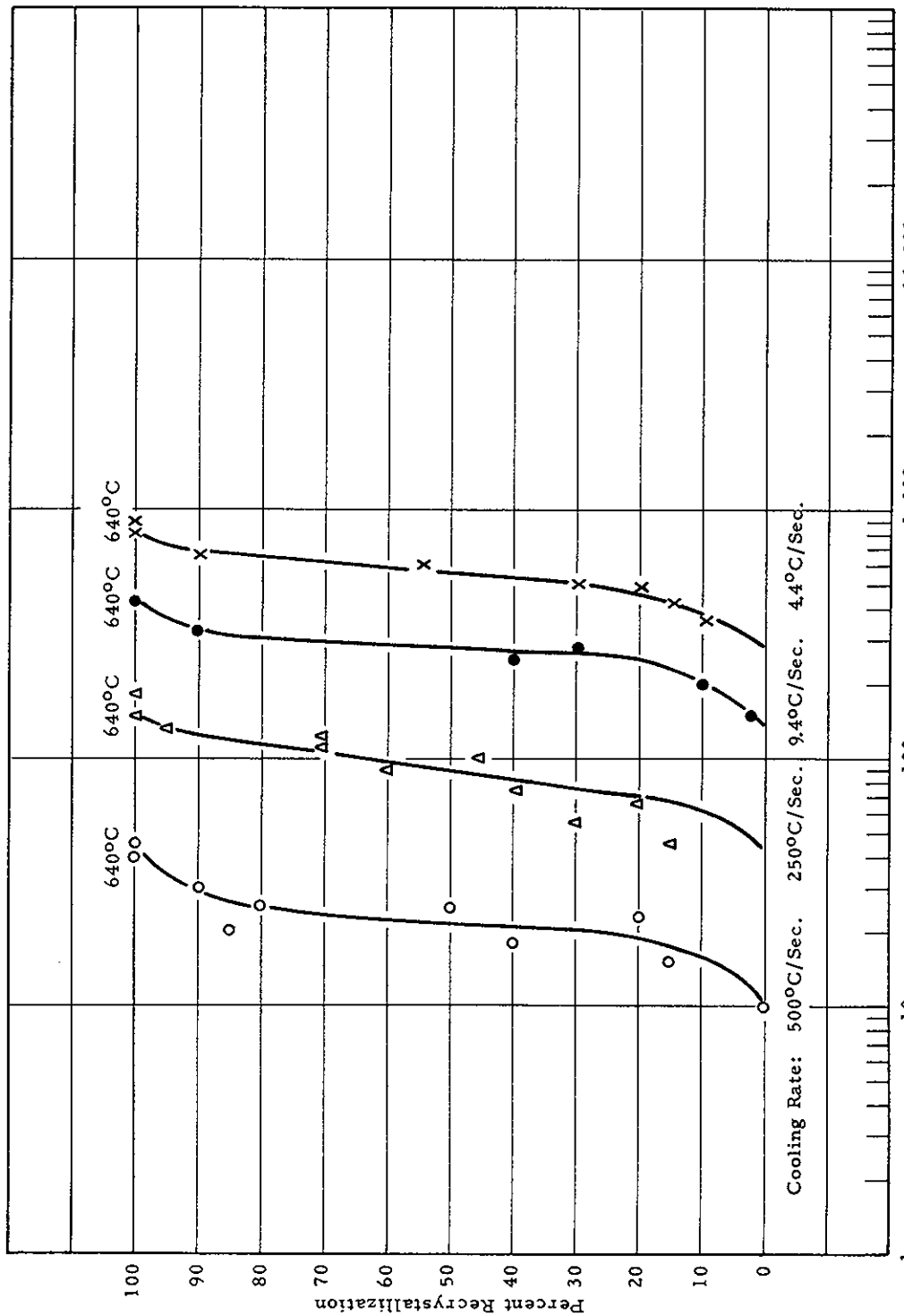
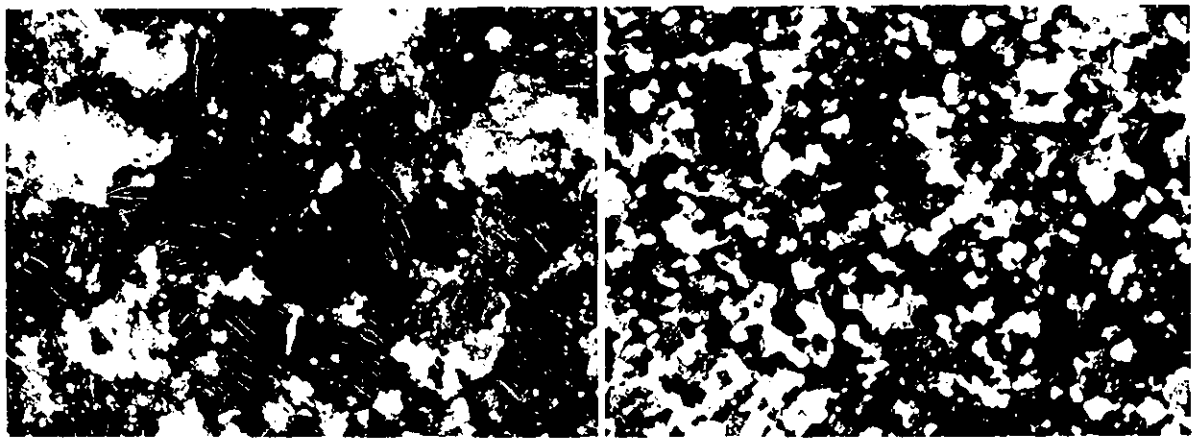


FIGURE 5
Per Cent Recrystallization
as a Function of Time at Temperature for Indicated Cooling Rates

AEC-GE RICHLAND, WASH.

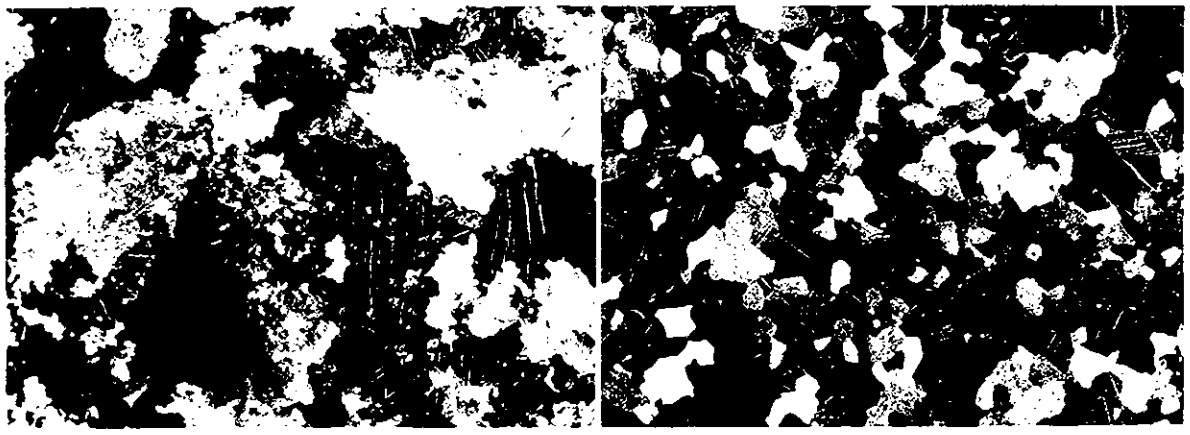


(a)

Grain structure at 500 C/second cooling rate prior to recrystallization. Average grain diameter 0.20 mm.

(b)

Grain structure at 500 C/second cooling rate after recrystallization. Average grain diameter 0.08 mm.



(c)

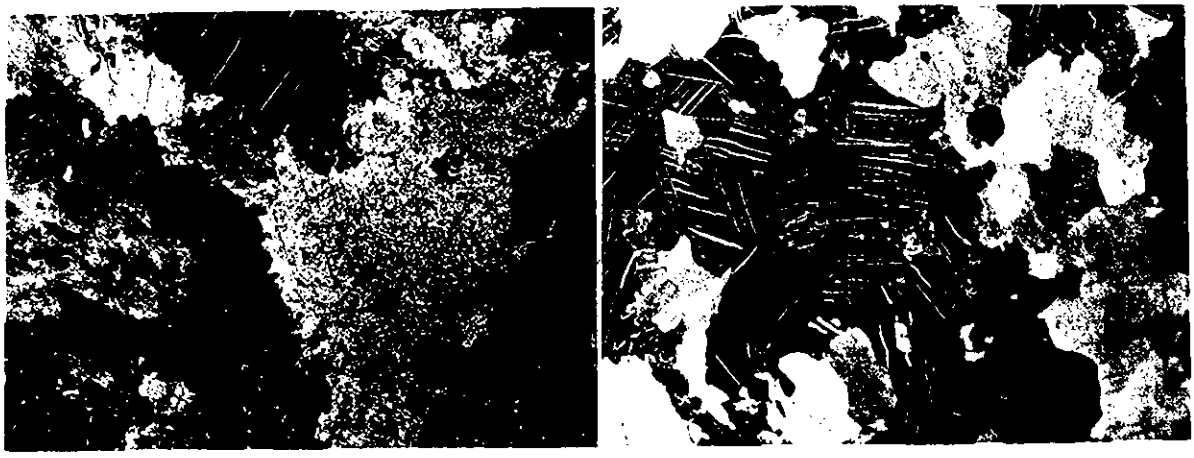
Grain structure at 250 C/second cooling rate prior to recrystallization. Average grain diameter 0.50 mm.

(d)

Grain structure at 250 C/second cooling rate after recrystallization. Average grain diameter 0.17 mm.

FIGURE 6

Photomacrographs (30X) of Macroetched Grain Structure at Indicated Cooling Rates Illustrating the Effect of Recrystallization. Standard HCl, HNO_3 Macroetch.

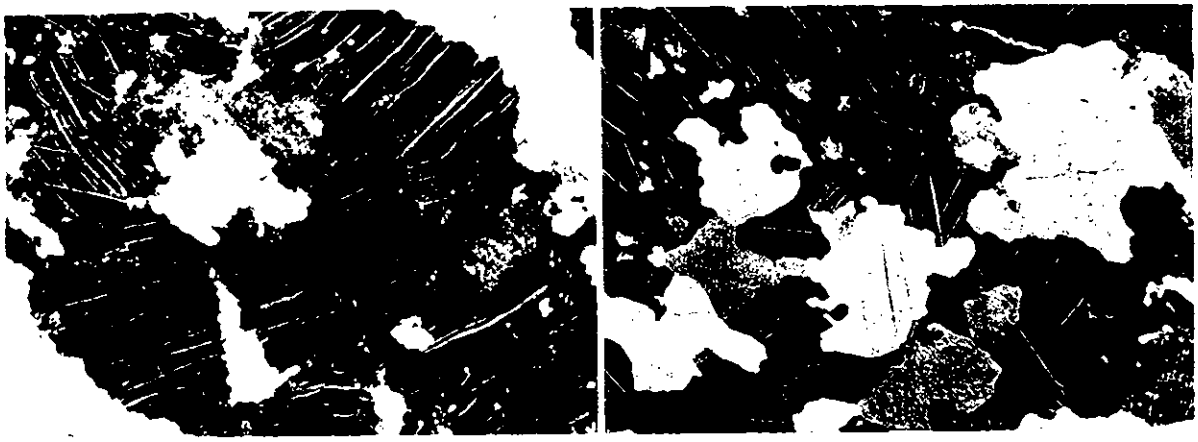


(a)

Grain structure at 9.4 C/second cooling rate prior to recrystallization. Average grain diameter 0.55 mm.

(b)

Grain structure at 9.4 C/second cooling rate after recrystallization. Average grain diameter 0.40 mm.



(c)

Grain structure at 4.4 C/second cooling rate prior to recrystallization. Avarage grain diameter 0.70 mm.

(d)

Grain structure at 4.4 C/second cooling rate after recrystallization. Average grain diameter 0.50 mm.

FIGURE 7

Photomacrographs (30X) of Macroetched Grain Structure at Indicated Cooling Rates Illustrating the Effect of Recrystallization. Standard HCl, HNO_3 Macroetch.

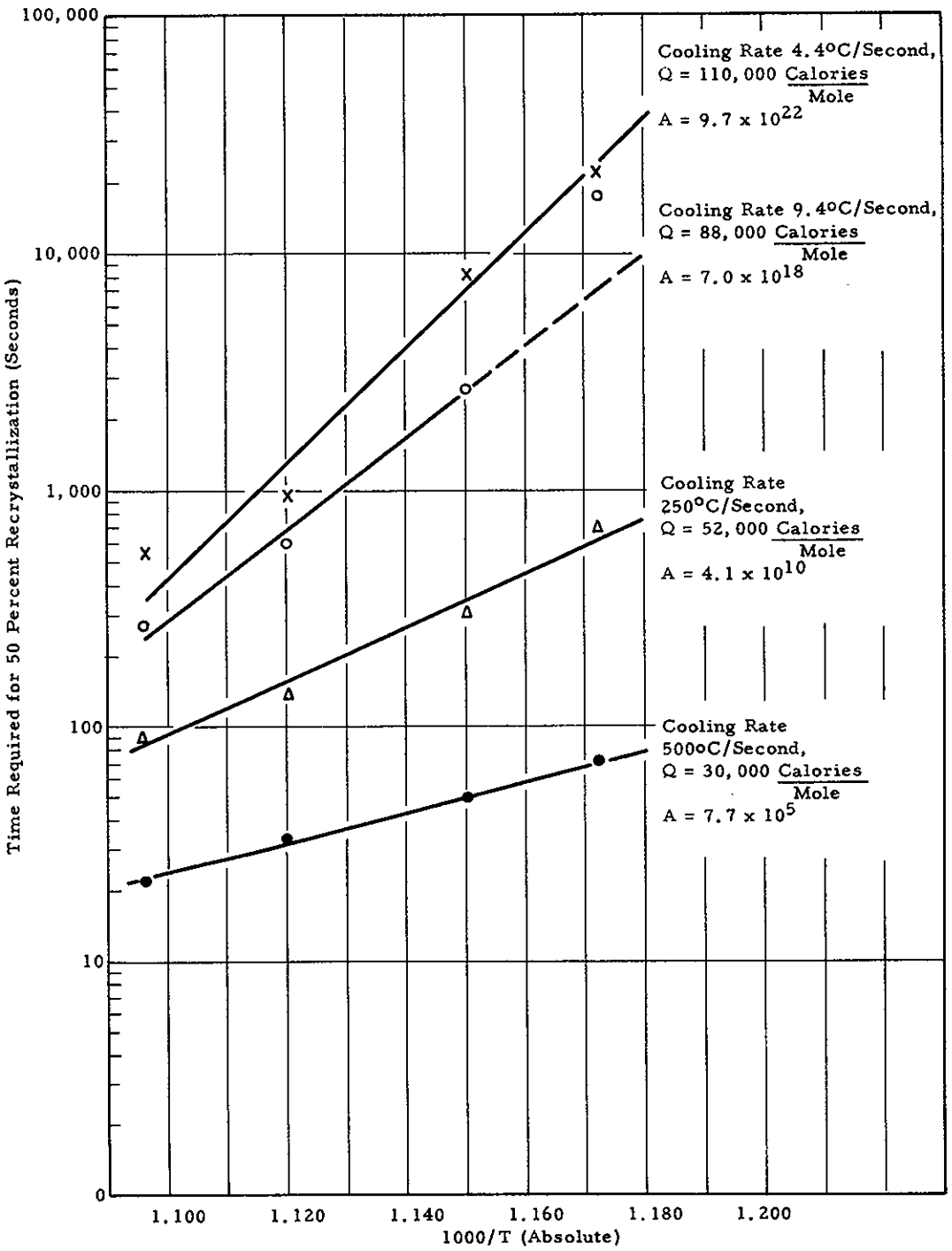


FIGURE 8

Relation Between Time Required for 50 Per Cent Recrystallization and Annealing Temperature with Cooling Rate as a Parameter

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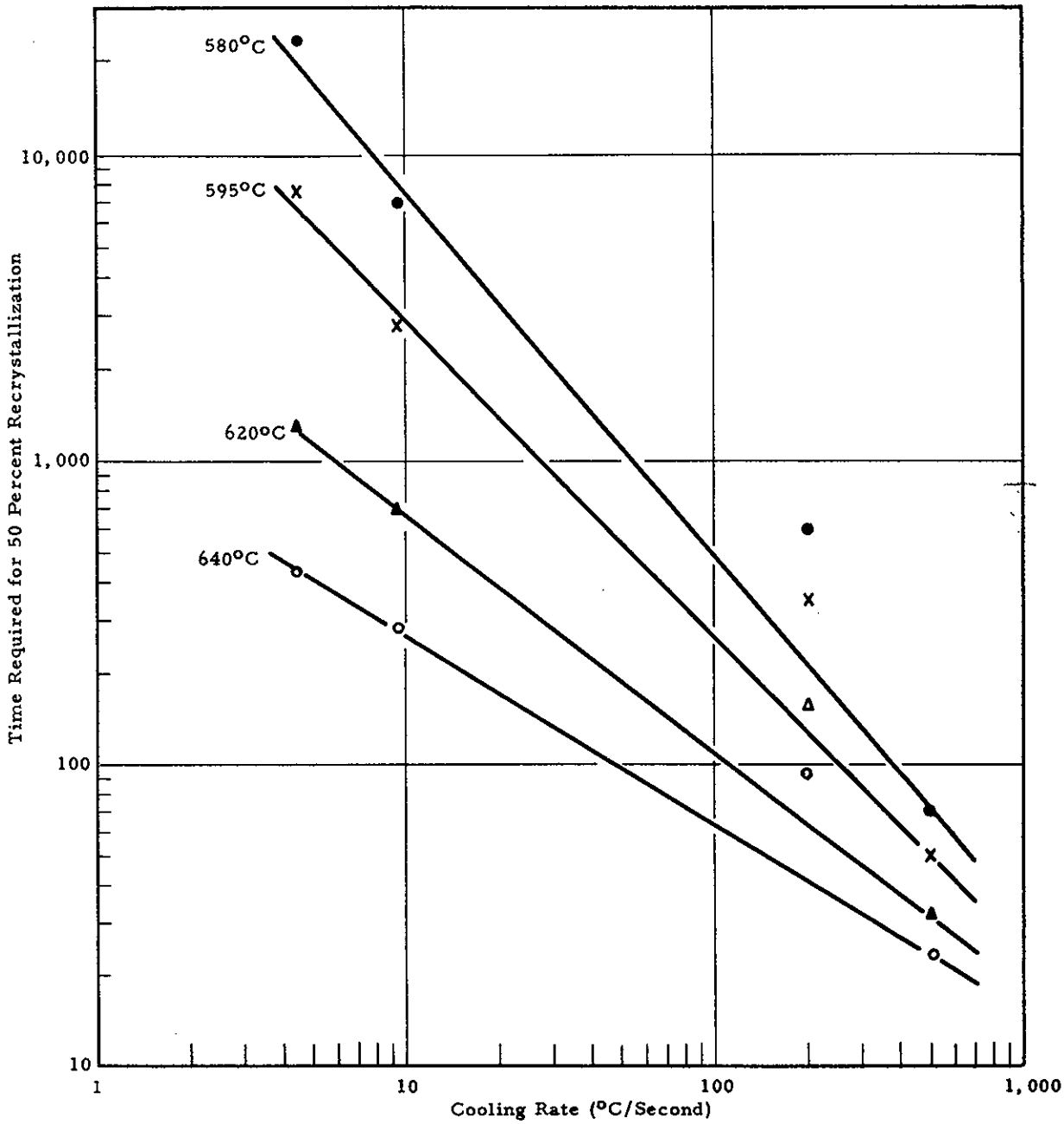

FIGURE 9

Relation Between Cooling Rate and Time Required for 50 Per Cent Recrystallization with Annealing Temperature as a Parameter

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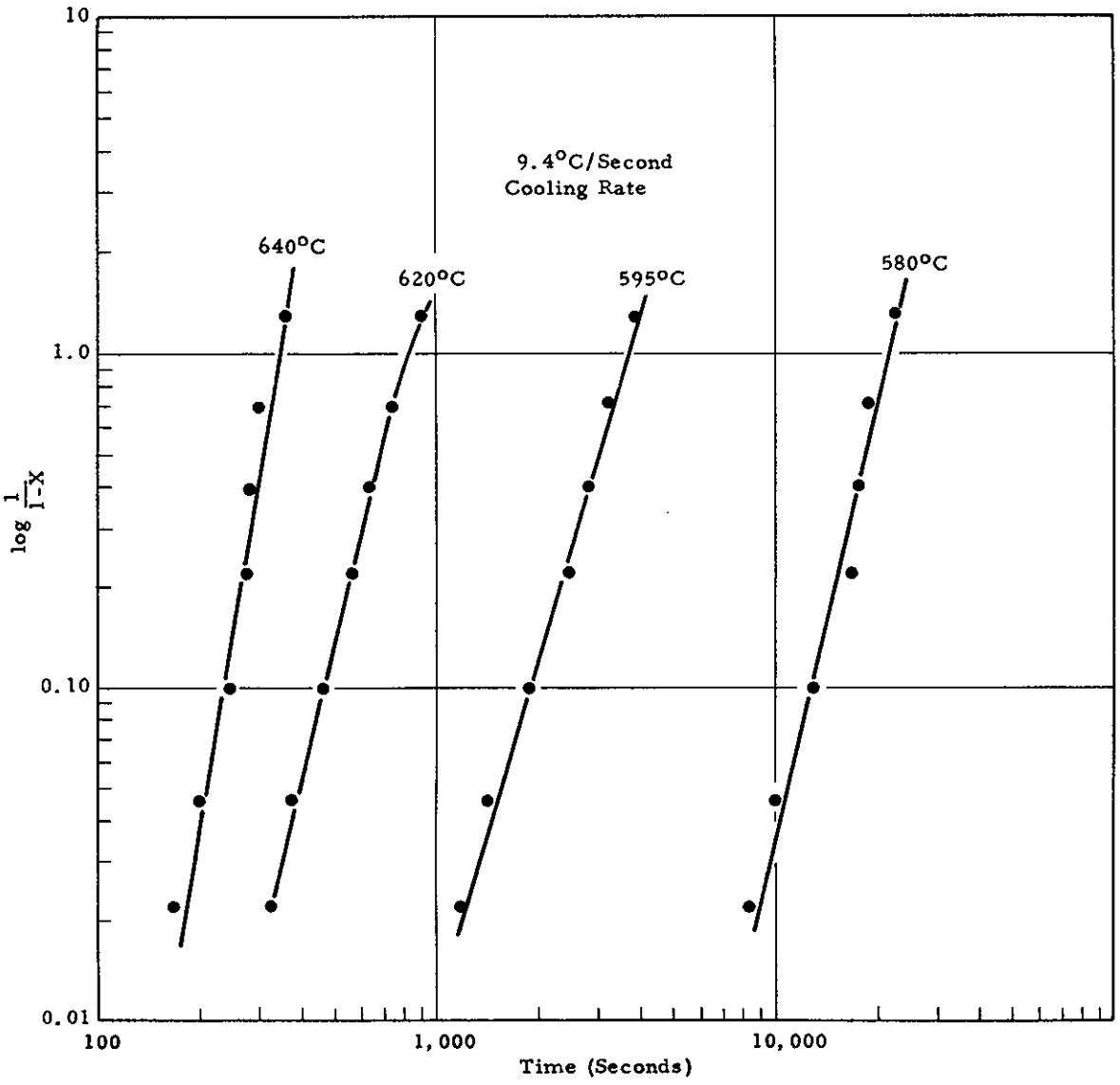

FIGURE 10

Plot of Recrystallization Parameter, log $\frac{1}{1-x}$ vs Annealing Time

AEC-GE RICHLAND, WASH.

APPENDIX I

Jominy End Quenching Technique and Cooling Rate Calculations

Standard one-inch diameter, four-inch long Jominy specimens were fabricated from dingot uranium. The specimens were annealed for ten minutes at 730 C in a Houghton 980 chloride salt bath composed of 24 per cent NaCl, 28 per cent KCl, and 48 per cent $BaCl_2$, and end quenched with 15 C water in a standard Jominy fixture.

Two thermocouple techniques were used for cooling curve determinations with equally good results. The simplest and most economical was to spot weld thermocouples to the specimen surface. The second, involved enclosing the thermocouples in an 18 inch long, 3/16" O.D., 1/16" I.D. stainless steel tube; powdered Houghton 980 salt was added at the sleeve-uranium interface and powdered tin surrounded the thermocouple bead to insure good heat transfer from uranium to thermocouple. The sleeves enclosing the thermocouples were centered at a depth of 5/32 inch from the specimen surface at several positions. During heat treatment, the open top end of the sleeve was kept above the salt bath level to prevent salt attack on thermocouple insulation and possible shorting. The cooling curves were recorded on a Leeds and Northrup Speedomax with a chart speed of 0.475 inches/second.

Cooling rates were calculated on the basis of the time required for cooling from 670 to 570 C; thus, the cooling rate determined is an average over this temperature range.

APPENDIX II

Sample Calculation of Activation Energy

Using the cooling rate of 250 C/second and the data presented in Figure 7, the following calculation of activation energy can be made by application of the Arrhenius rate equation.

Rate of reaction = $\frac{1}{t} = Ae^{-Q/RT}$, where A is a constant, R is the gas constant, and T the absolute temperature.

Taking logarithims, $\ln \frac{1}{t} = \ln A - \frac{Q}{RT}$. Applying this equation at two temperatures, T_1 and T_2, and subtracting, the equation is translated into the useful form $\ln \frac{t_2}{t_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ or $\log \frac{t_2}{t_1} = \frac{Q}{2.3R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Selecting temperatures of 582 C (855 K) and 628 C (901 K) with times for 50 per cent recrystallization of 580 and 120 seconds, respectively, and substituting into the equation:

$$\log \frac{580}{120} = \frac{Q}{2.3R}\left(\frac{1}{855} - \frac{1}{901}\right)$$

The calculated activation energy Q is 52,000 calories/mole. In a similar manner activation energies for the other three cooling rates can be calculated.

APPENDIX III

Sample Calculation of A

As indicated in the text the value of A in the Arrhenius equation $Ae^{-Q/RT}$ can be calculated from the logarithmic form of the equation, $\log \frac{1}{t} = \log A - \frac{Q}{2.3RT}$.

For the 500 C/second cooling rate with an activation energy of 30,000 calories/mole and a time for 50 per cent recrystallization of 32 seconds at 893 K (620 C) the value of A is computed as follows:

$$\log \frac{1}{32} = \log A - \frac{30,000}{(2.3)(1.987)(893)},$$

$$\log 0.0316 = \log A - 7.388$$

$$\log A = 5.888, \quad A = 7.7 \times 10^5 \text{ grains recrystallized/sec/cm}^2.$$