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A PHYSICAL METALLURGICAL STUDY OF THORIUM-RICH, THORIUM-URANIUM ALLOYS

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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A PHYSICAL METALLURGICAL STUDY OF THORIUM-RICH, THORIUM-URANIUM ALLOYS

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ABSTRACT

Physical property measurements and metallography were performed on thorium-rich, thorium-uranium alloys containing up to 20 w/o uranium. Tensile tests at 500° C indicate that when commercial-grade thorium is alloyed with uranium the ultimate and yield strengths are increased approximately 50 per cent. Hardness data at room temperature are also presented. Photomicrographs indicate that the uranium is dispersed uniformly as fine particles in arc-melted alloys. These fine particles coalesce when the material is annealed; some of the particles coalesce at the grain boundaries. Alloys containing up to five w/o uranium appear to retain very few of the particles which coalesce along the grain boundaries; most of the particles appear in the matrix. The thorium-rich end of the thorium-uranium phase diagram is presented; it is based on electrical resistivity and lattice-parameter measurements. The variation of thermal conductivity with temperature, up to 1100° C, in thorium alloys is calculated and the resultant data are tabulated.

I. INTRODUCTION

The application of materials for nuclear fuels is governed in part by how well the properties of the nonirradiated material correlate to the expected performance of the fuel system. Thorium-uranium alloys are being considered for use in power-reactor fuel systems. This particular use requires alloys which have known pertinent metallurgical properties at high temperatures.

Recent work[1,2,3] provides information on the phase diagram of the thorium-uranium system, the density of the alloys with temperature, and other necessary data. The present effort was conducted to extend and confirm the previous findings. Physical-property measurements and metallograph were employed. Tensile and hardness tests, lattice parameter measurements, electrical resistivity, and metallography were performed on thorium-rich, thorium-uranium alloys containing up to 20 w/o uranium. Both commercial-grade and high-purity materials were used for these measurements.

II. MATERIALS

Two series of alloys were obtained and studied; a commercial-purity series was made by arc melting "Ames" thorium and reactor-grade uranium; a high-purity series was made by arc melting crystal-bar thorium and center-cut, "biscuit" uranium. Each alloy was analyzed for uranium, nitrogen, oxygen, hydrogen, and carbon; other impurities were assumed to have little effect on the parameters measured. The results are tabulated in Tables I and II.

TABLE I

ANALYSIS OF COMMERCIAL-PURITY, THORIUM-URANIUM ALLOYS

w/o Uranium	w/o Carbon	w/o Oxygen	w/o Hydrogen	w/o Nitrogen
0.0	0.040	0.131	0.009	0.008
1.07	0.011	0.129	0.009	0.008
3.17	0.022	0.130	0.010	0.008
5.46	0.020	0.131	0.010	0.008
8.90	0.034	0.124	0.010	0.009
10.46	0.044	0.126	0.010	0.004

TABLE II

ANALYSIS OF HIGH-PURITY, THORIUM-URANIUM ALLOYS

w/o Uranium	w/o Carbon	w/o Oxygen	w/o Hydrogen	w/o Nitrogen
0.0	0.005	0.029	0.002	0.001
0.29	0.005	0.031	0.002	0.002
0.56	0.006	0.031	0.002	0.001
1.06	0.005	0.036	0.002	0.001
2.08	0.005	0.037	0.002	0.001
3.14	0.006	0.040	0.002	0.001
5.28	0.005	0.045	0.002	0.001
8.43	0.013	0.201	0.001	0.001
10.6	0.030	0.154	0.003	0.021
12.4	0.030	0.055	0.002	0.014
15.4	0.030	0.102	0.002	0.015
19.9	0.030	0.108	0.003	0.015

III. EXPERIMENTAL

A. TENSILE TESTS

Tensile tests were performed on both series of alloys. The tensile specimens used during the commerical-purity series were wires with diameters of 42 mils. Wires with diameters of 20 mils were used during the high-purity series. A special jig, which was inserted in the Instron tensile machine, assured a uniform gage length, and also insured that the specimens would break in the gage length and not at the grips. The gage length was 1/2 of an inch. The cross-head speed was 0.02 inches per minute.

Tensile tests were performed at room temperature and at 500° C on the commercial-purity alloys; tests were performed only at room temperature on the high-purity alloys. Several series of alloys which varied in uranium content were tested for strength as a function of heat treatment prior to testing. The resultant data are shown in Fig. 1 and 2. The results indicate a substantial increase in yield strength and ultimate tensile strength in each of the series

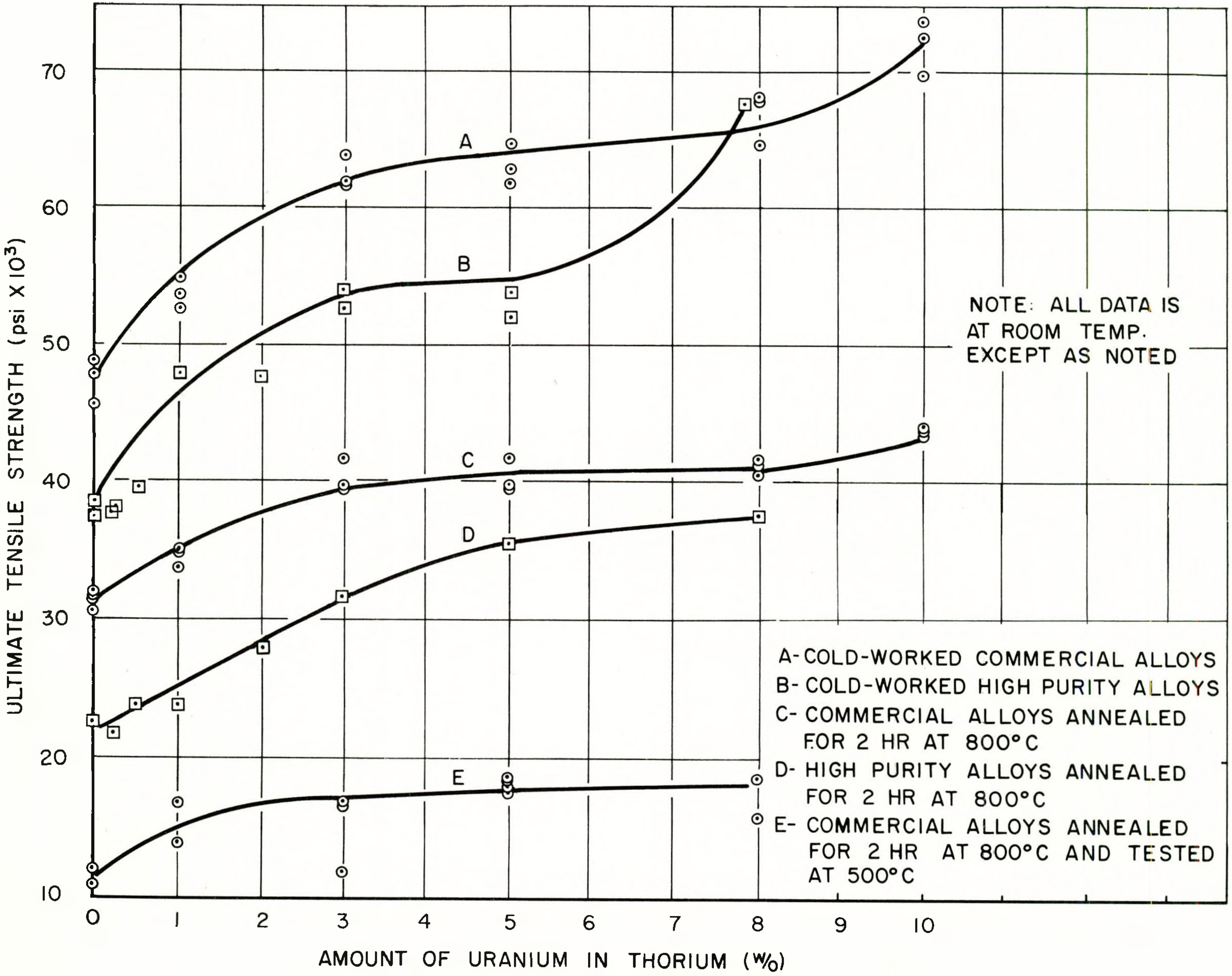


Fig. 1. Ultimate Tensile Strength of Thorium-Uranium Alloys

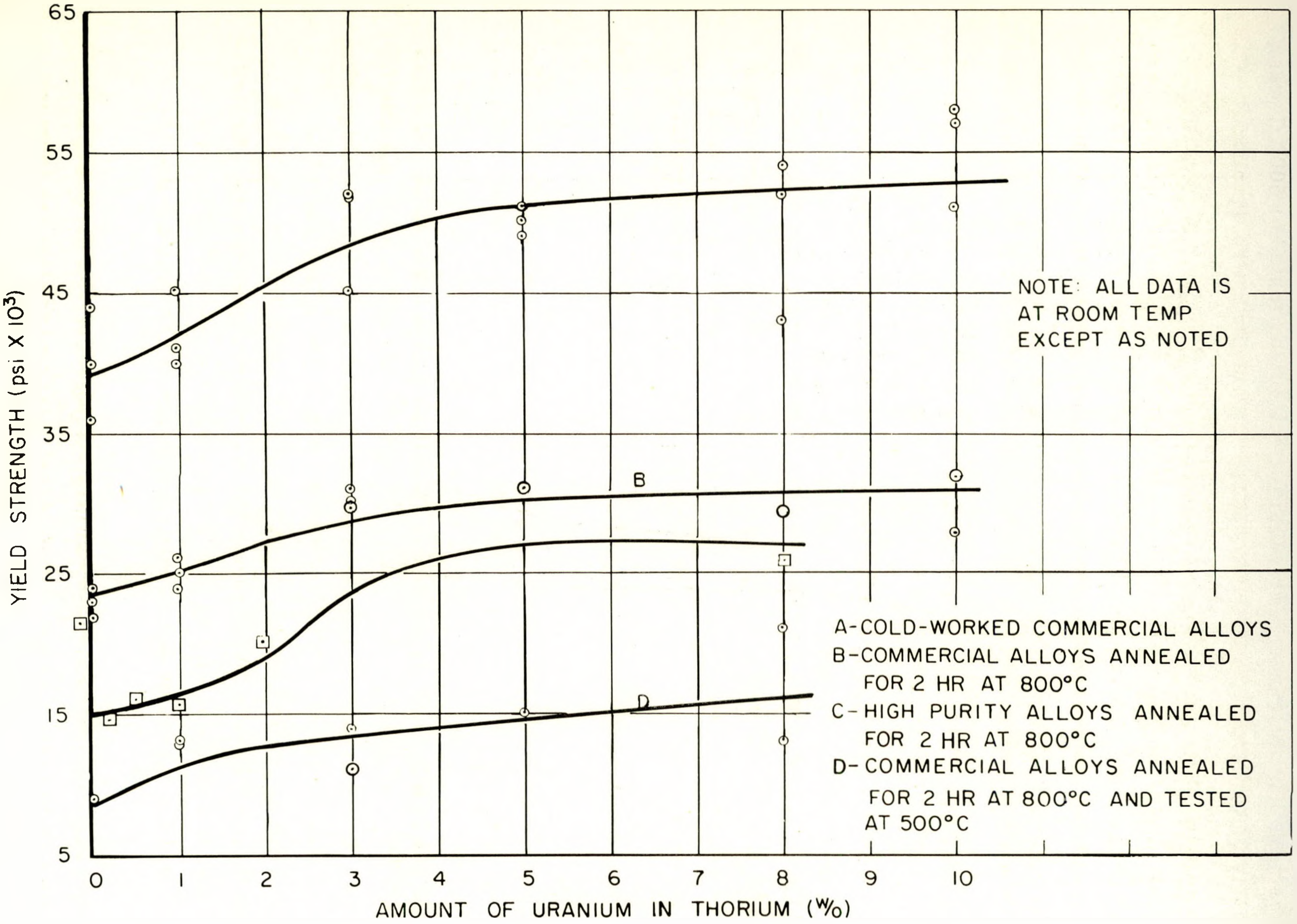


Fig. 2. Yield Strength of Thorium-Uranium Alloys

of alloys tested. This increase in strength for the series tested at 500° C was approximately 50 per cent and was noticeable at and above 3 w/o uranium.

Previous work[5] indicates that impurities in thorium, particularly carbon, cause a yield point to appear in the stress-strain curve. A yield point was also observed during these tests in some of the commercial-purity alloys. The unalloyed thorium and the 1.07-w/o-uranium alloy in the annealed condition showed a yield point. All of the other alloys, including the high-purity material, did not show a yield point.

B. HARDNESS DATA

Figures 3 and 4 represent the accumulated hardness data of the alloys. Each point plotted is the average of four or more impressions. The decrease in hardness with quench temperature of the high-purity alloys is thought to be due to more uranium going into solution and decreasing the amount of fine precipitate in the matrix. Slow cooling produces the maximum amount of this precipitate, as indicated metallographically and as expected from the phase diagram. Apparently other impurities mask this effect in the commercial-purity alloys.

C. METALLOGRAPHY

An electrolytic etchant was developed which produces considerable definition of the thorium-uranium microstructures. The metallographic polishing follows standard procedure: 1 micron diamond paste is the final abrasive used. The etchant solution is glycerine containing 5 volume per cent nitric acid. The conditions are 0.3 to 0.5 amp per cm^2 for 10 to 15 seconds, followed by a rinse in a solution of ethyl alcohol with 8 volume per cent glycerine. All metallographic work utilized this procedure. Figures 5 and 6 represent alloys heated to 1100° C for 2 hours, cooled at 10° C/hour to 450° C, and furnace cooled to room temperature. Figure 7 represents the microstructures of alloys heated to 1100° C for 2 hours, cooled to 1000° C, and water quenched. Figure 8 shows the effects of extended isothermal treatments on the thorium microstructures.

The pepper-like second phase and the larger, light-colored particles are thought to be uranium-rich phase. The larger black particles are thorium

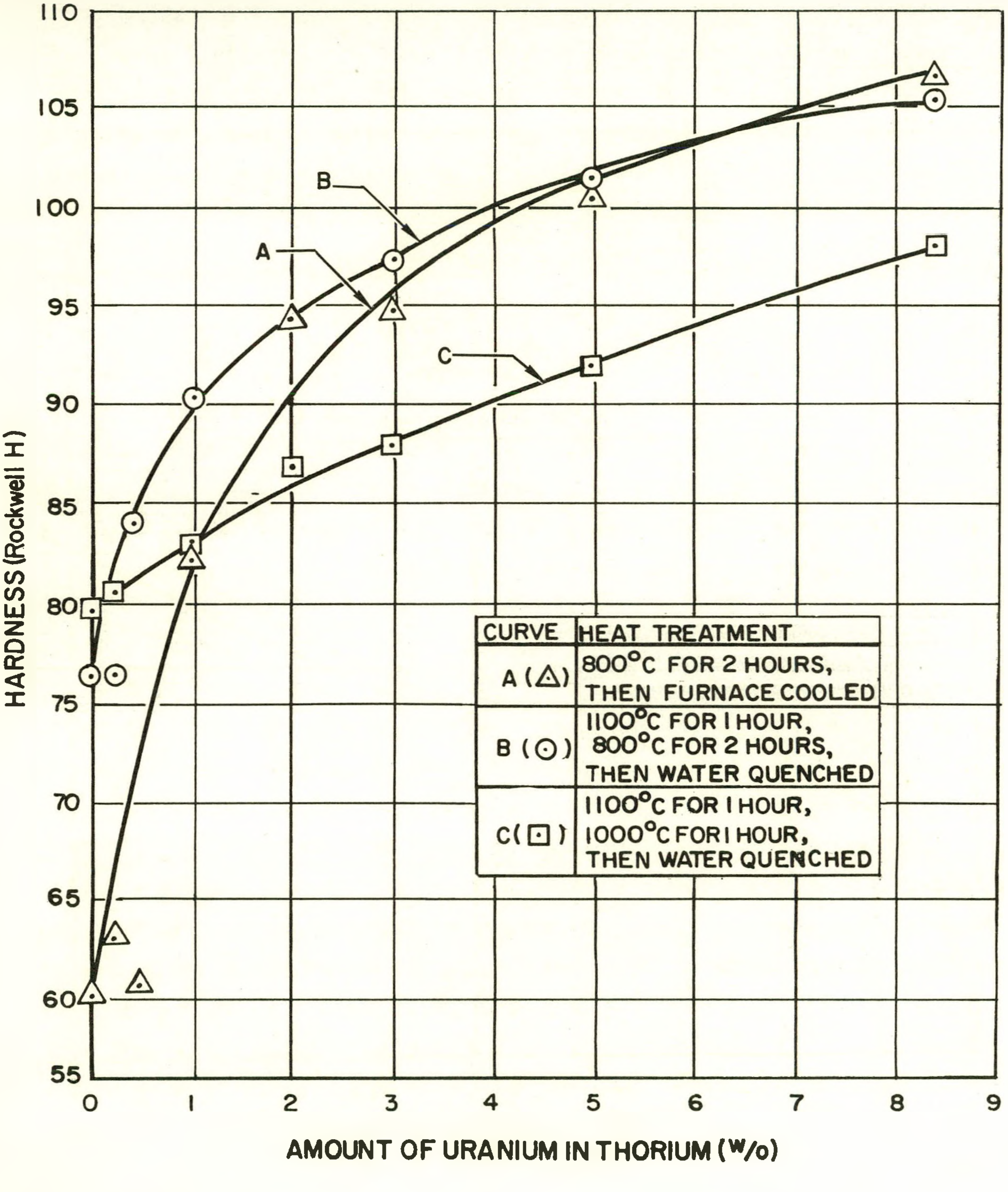


Fig. 3. Hardness of High-Purity, Thorium-Uranium Alloys

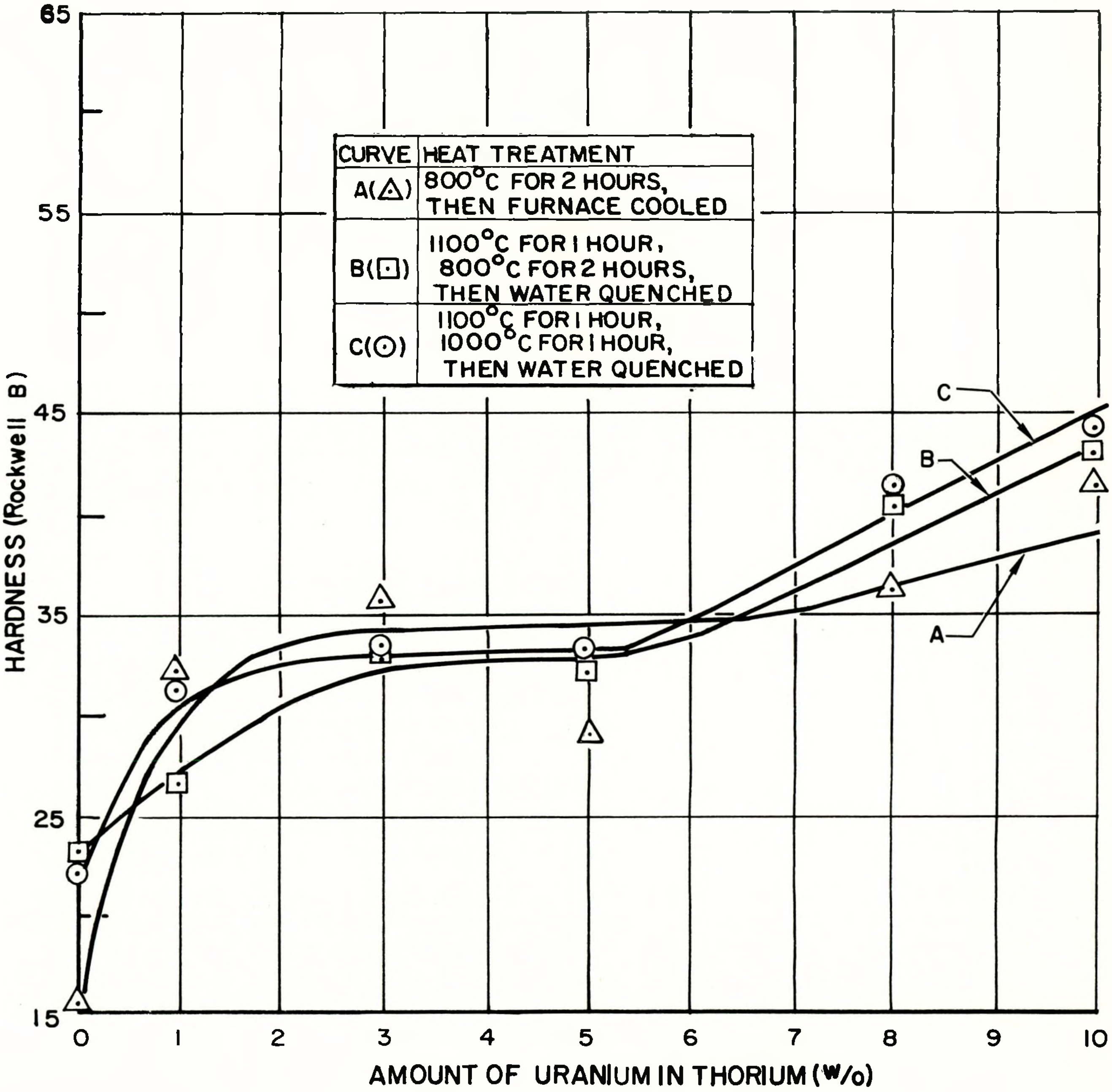
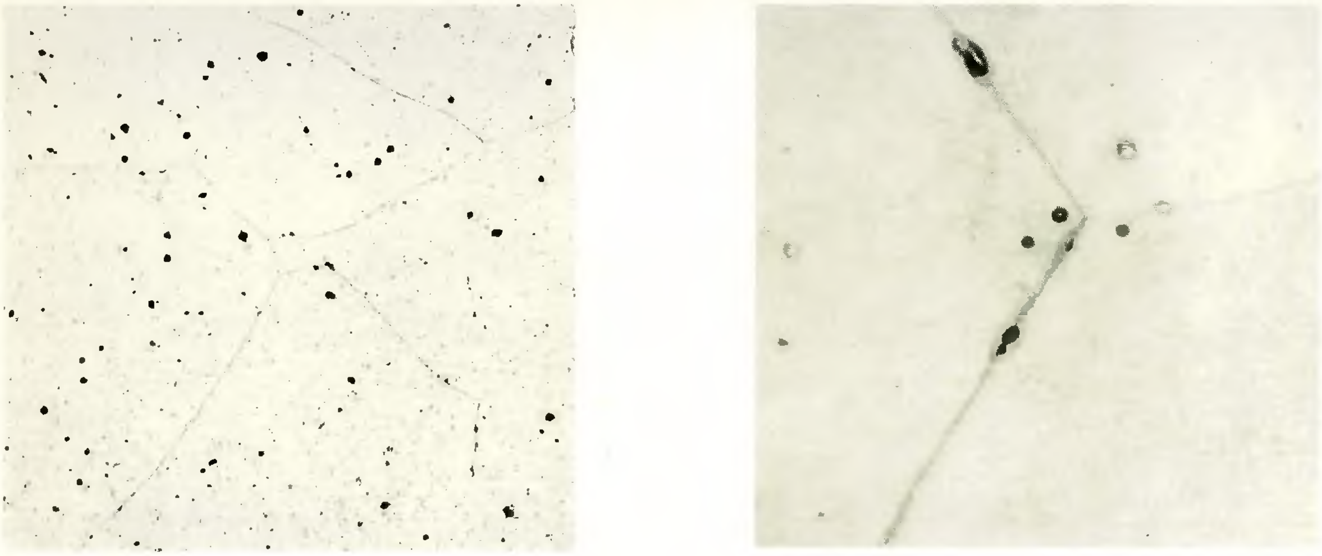


Fig. 4. Hardness of Commercial-Purity, Thorium-Uranium Alloys

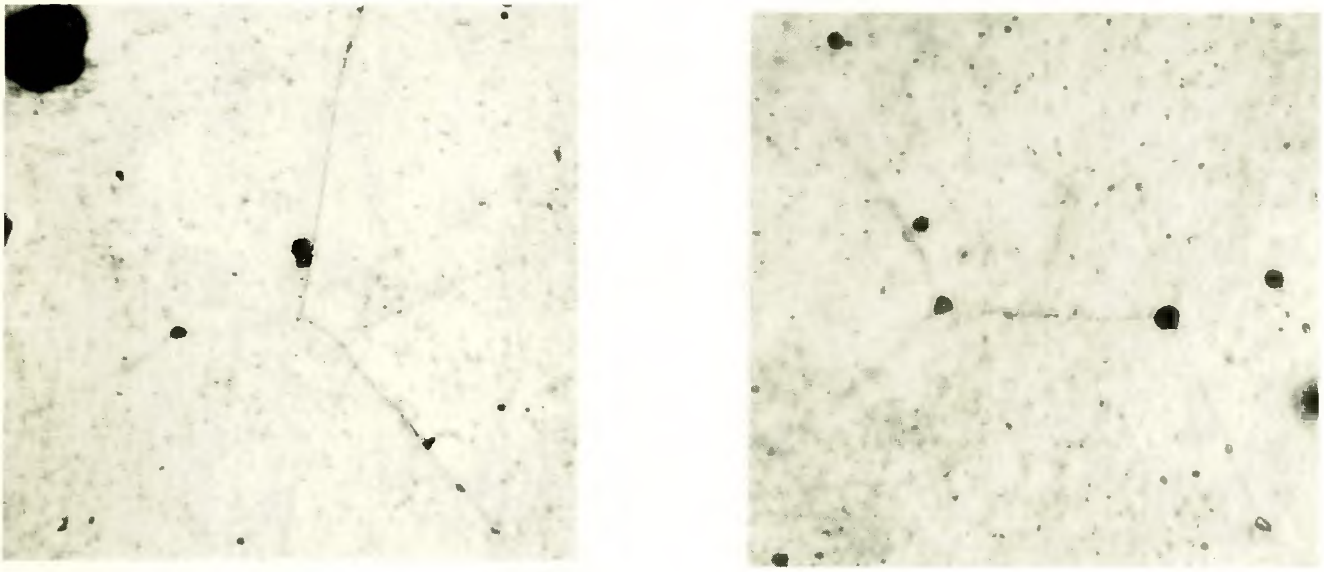


100 X

GRAIN SIZE = 0.5 mm
HIGH-PURITY THORIUM

1000 X

HIGH-PURITY THORIUM



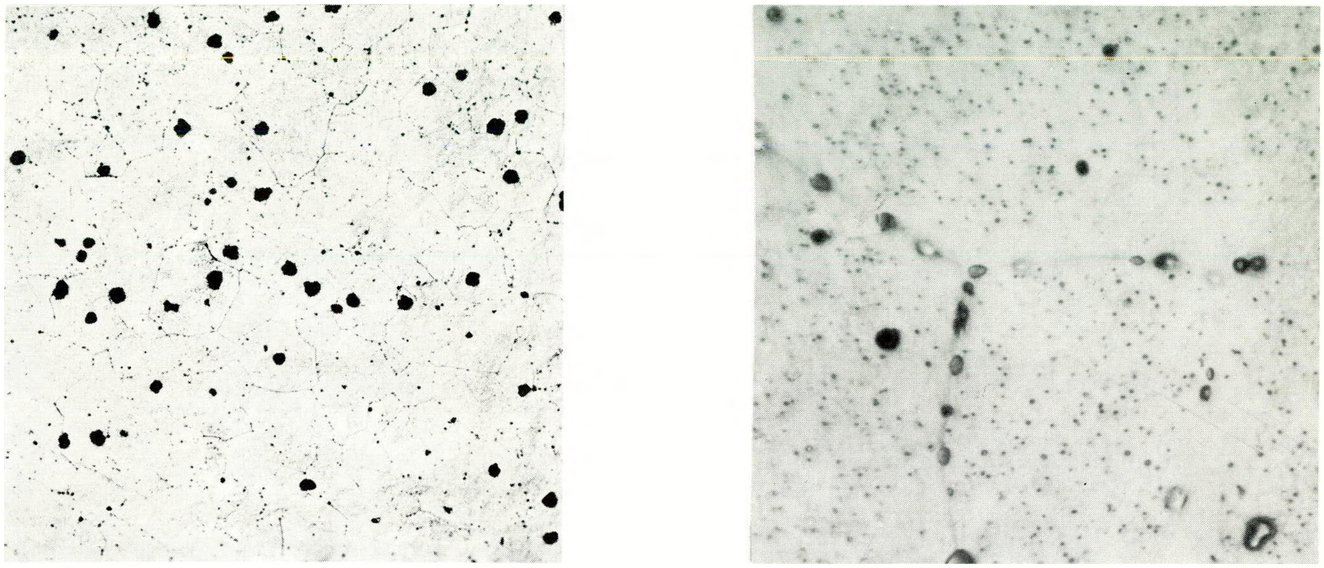
1000 X

THORIUM WITH 1.06 w/o URANIUM

1000 X

THORIUM WITH 2.08 w/o URANIUM

Fig. 5. Microstructure of High-Purity Thorium Alloys Heated to 1100° C for 1 Hour and Slowly Cooled to Room Temperature

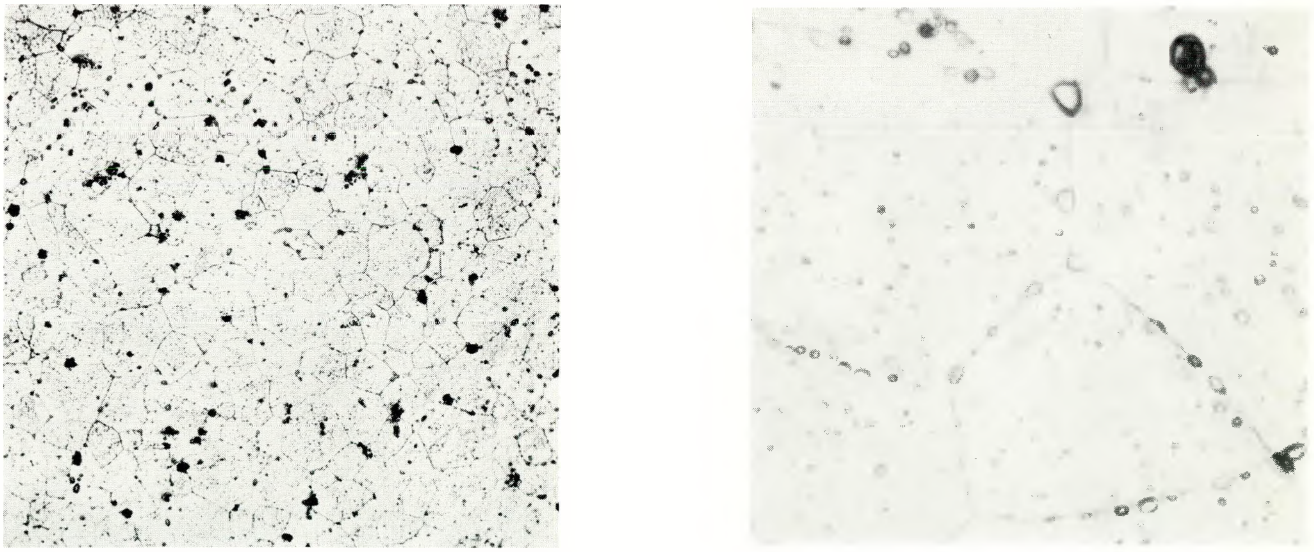


100 X

GRAIN SIZE = 0.1 mm
THORIUM WITH 3.14 w/o URANIUM

1000 X

THORIUM WITH 3.14 w/o URANIUM



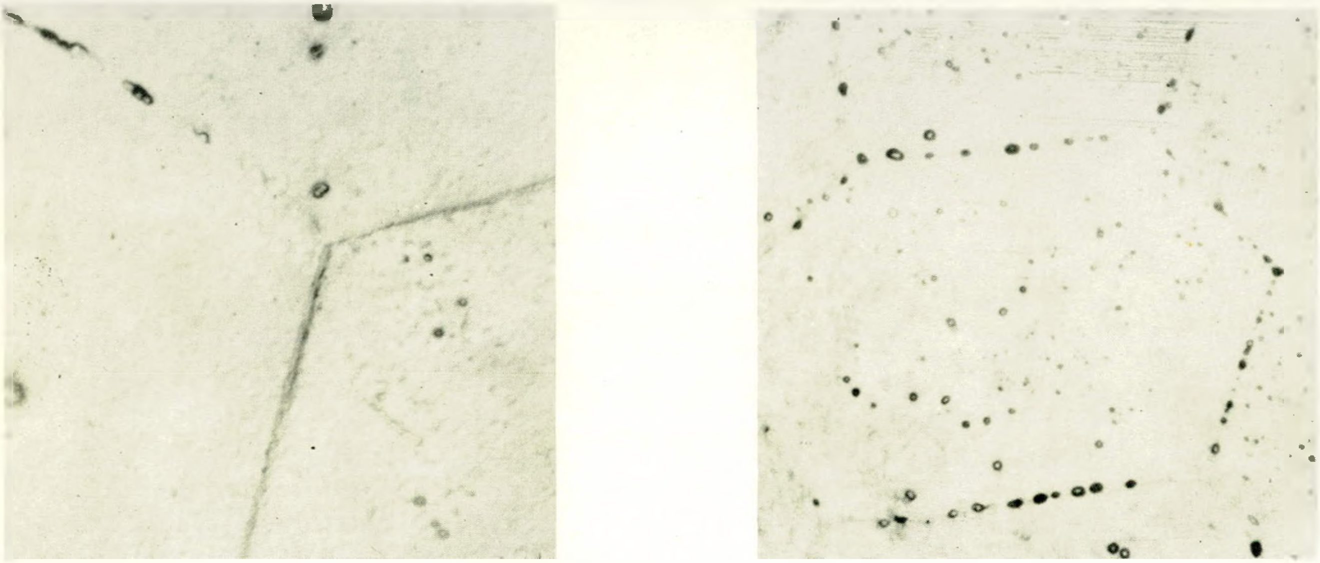
100 X

GRAIN SIZE = 0.075 mm
THORIUM WITH 5.28 w/o URANIUM

1000 X

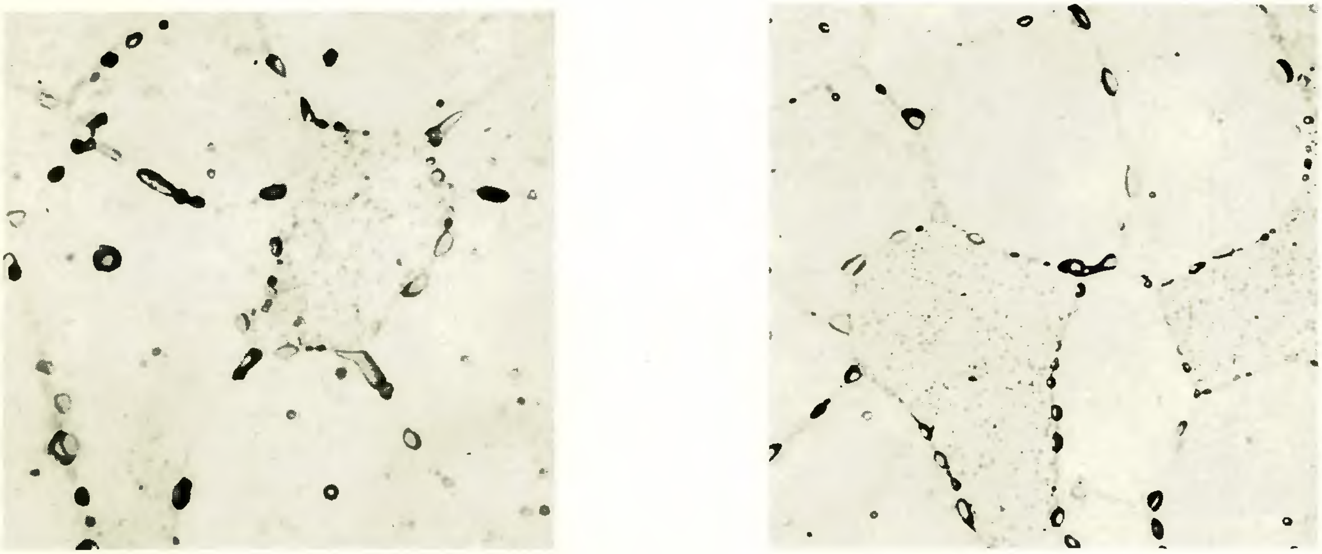
THORIUM WITH 5.28 w/o URANIUM

Fig. 6. Microstructure of High-Purity Thorium Alloys Heated to 1100° C for 1 Hour and Slowly Cooled to Room Temperature



1000 X
THORIUM WITH 1.06 w/o URANIUM

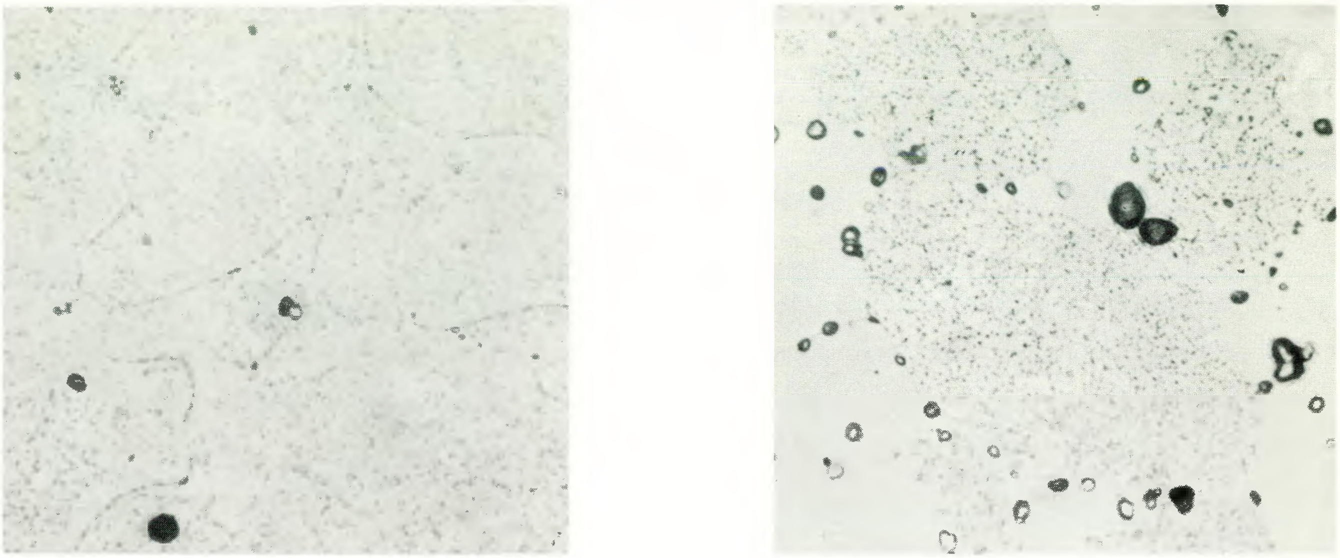
1000 X
THORIUM WITH 2.08 w/o URANIUM



1000 X
THORIUM WITH 3.14 w/o URANIUM

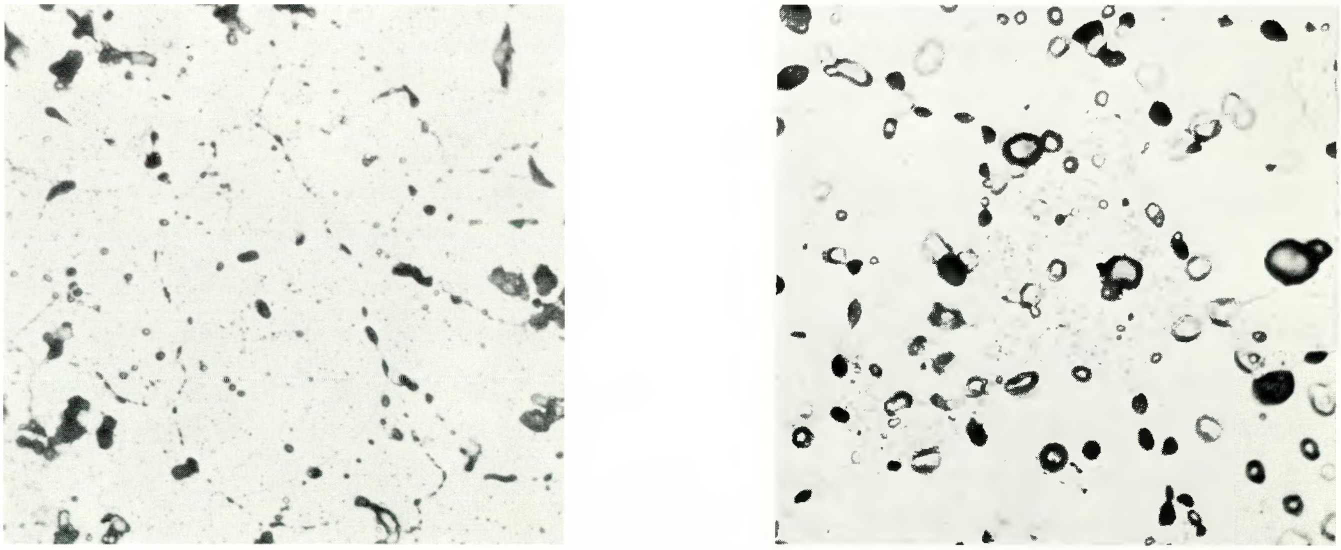
1000 X
THORIUM WITH 5.28 w/o URANIUM

Fig. 7. Microstructure of High-Purity Thorium Alloys Heated to 1100° C for 1 Hour, Slowly Cooled to 1000° C, Held at 1000° C for 1-1/2 Hours, then Water Quenched



1000 X
THORIUM WITH 5.28 w/o URANIUM
MAINTAINED AT 400°C FOR 32 WEEKS

1000 X
THORIUM WITH 5.28 w/o URANIUM
MAINTAINED AT 800°C FOR 39 WEEKS



1000 X
THORIUM WITH 8.43 w/o URANIUM
MAINTAINED AT 400° C FOR 32 WEEKS

1000 X
THORIUM WITH 8.43 w/o URANIUM
MAINTAINED AT 800°C FOR 39 WEEKS

Fig. 8. Microstructure of High-Purity Thorium Alloys Subjected to Lengthy Isothermal Treatment and Furnace Cooled

oxide. The agglomeration of the fine precipitate of uranium eutectic is apparently both concentration and temperature dependent. Diffusion and growth of the preciptate is fairly uniform within individual grains. The reason for agglomeration in isolated grains has not been established. An important features of this agglomeration phenomenon is that the large particles do not form a continuous network at the grain boundaries. The agglomeration of the precipitate of the uranium-rich phase is apparently time, temperature, and concentration dependent.

The solubility of uranium in throium as revealed by metallography is less than 1 per cent at room temperature and more than 1 per cent at 1000° C. This conclusion is based on the presence of a finely divided second phase in the microstructure of the slowly cooled alloy and the near absence of the second phase in the quenched alloy.

D. RESISTIVITY

The resistivity of all of the alloys was measured as a function of temperature. A conventional Kelvin-bridge circuit was utilized. The specimens for the commercial-purity series were 42 mils in diameter and 1-1/2 inches long. Specimens for the high-purity series were 20 mils in diameter and also 1-1/2 inches long. The details of a sample assembly are shown in Fig. 9. Pre-calibrated, 3-mil diameter thermocouples were spark welded to 2-mil tantalum foil which was welded to the sample. Each thermocouple consisted of one pure platinum wire and another wire of platinum with 10 per cent rhodium. The tantalum insert prevented the formation of the platinum-thorium eutectic. Four-mil diameter voltage probes, made from crystal-bar thorium, were welded directly to the sample. They were located by hand and were, nominally, 1/8 of an inch apart. The assembled test specimen (Fig. 9) was placed in a vacuum chamber during heating. The temperature drop due to the 2-mil tantalum insert was measured as a function of temperature and corrections were added to the recorded sample temperature. The temperatures were recorded continuously and were checked occasionally with a calibrated potentiometer. A vacuum of 5×10^{-6} mm or better was maintained during most of the tests. Because the distance between voltage probes was not controlled accurately, the absolute resistance from one alloy to the next could not be compared. The possibility of contamination and the consequences of this on the transformation temperatures were realized. Several samples were retested six times with no

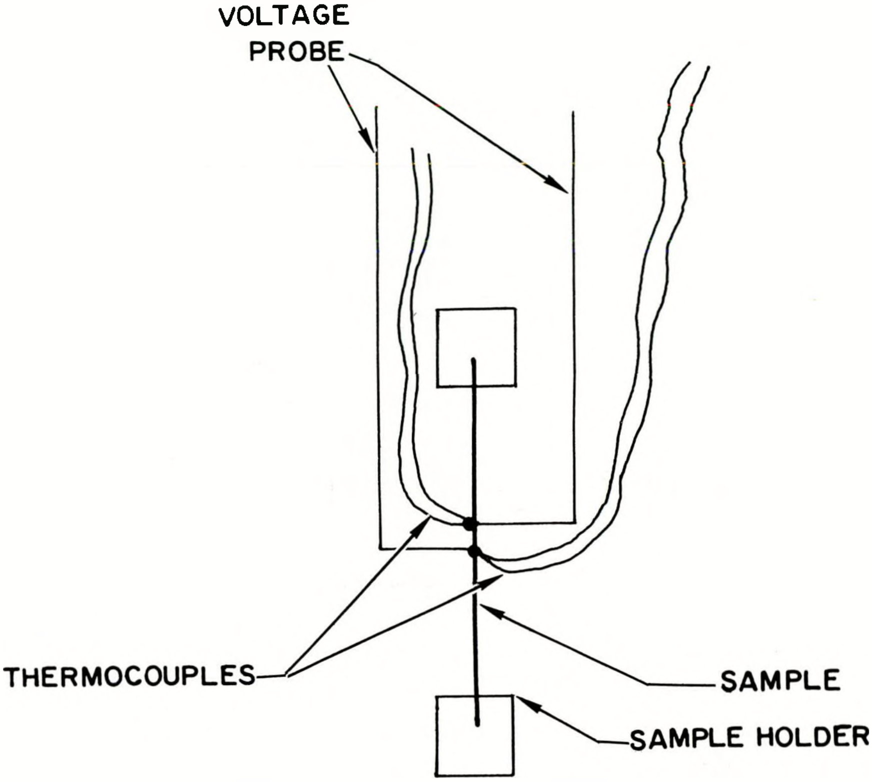


Fig. 9. Resistivity Measurement Apparatus

measured change in the transformation temperatures. A minimum of 3 samples which had similar transformation temperatures (within 5° C) were tested for each alloy. These three samples always represented the minimum transformation temperatures of a given alloy. The heating rate was varied from 5 to 125° C per minute and the beginning of transformation was not affected.

A typical plot of resistance vs temperature is shown in Fig. 10. The sudden change of slope has been proven[1, 5] to indicate a transformation point, i.e., the beginning of transformation of the face-centered-cubic lattice of thorium to the body-centered-cubic lattice. The beginning of transformation is point A, and the end of transformation is point B, Fig. 10. None of the curves of resistance vs temperature show an effect of the uranium transformations or eutectic melting. The beginning and end of transformation are plotted on the phase diagram, Fig. 11, as squares; only the transformations of the high-purity alloys are plotted.

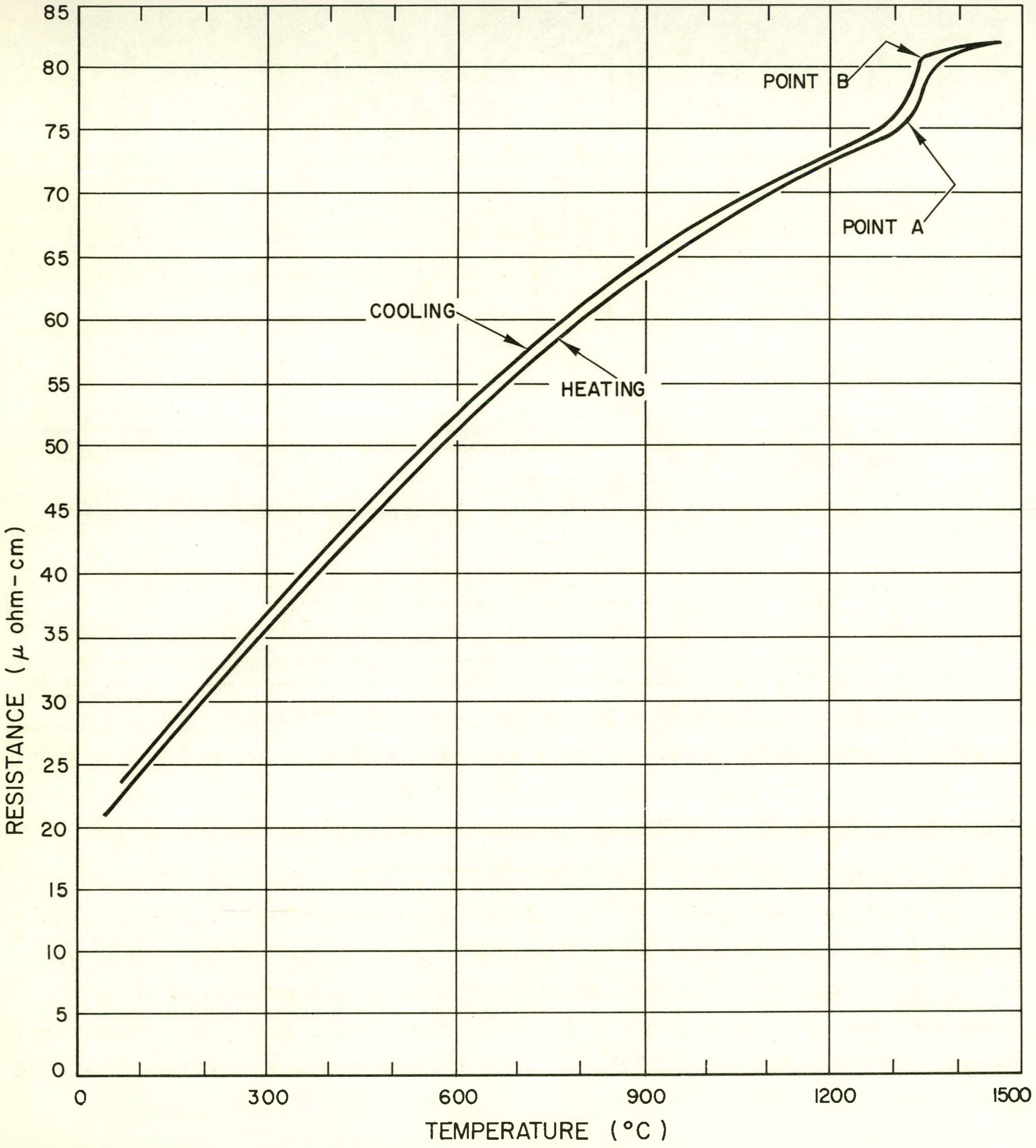


Fig. 10. Variation of Resistance with Temperature for Thorium Alloy with 0.26 w/o Uranium

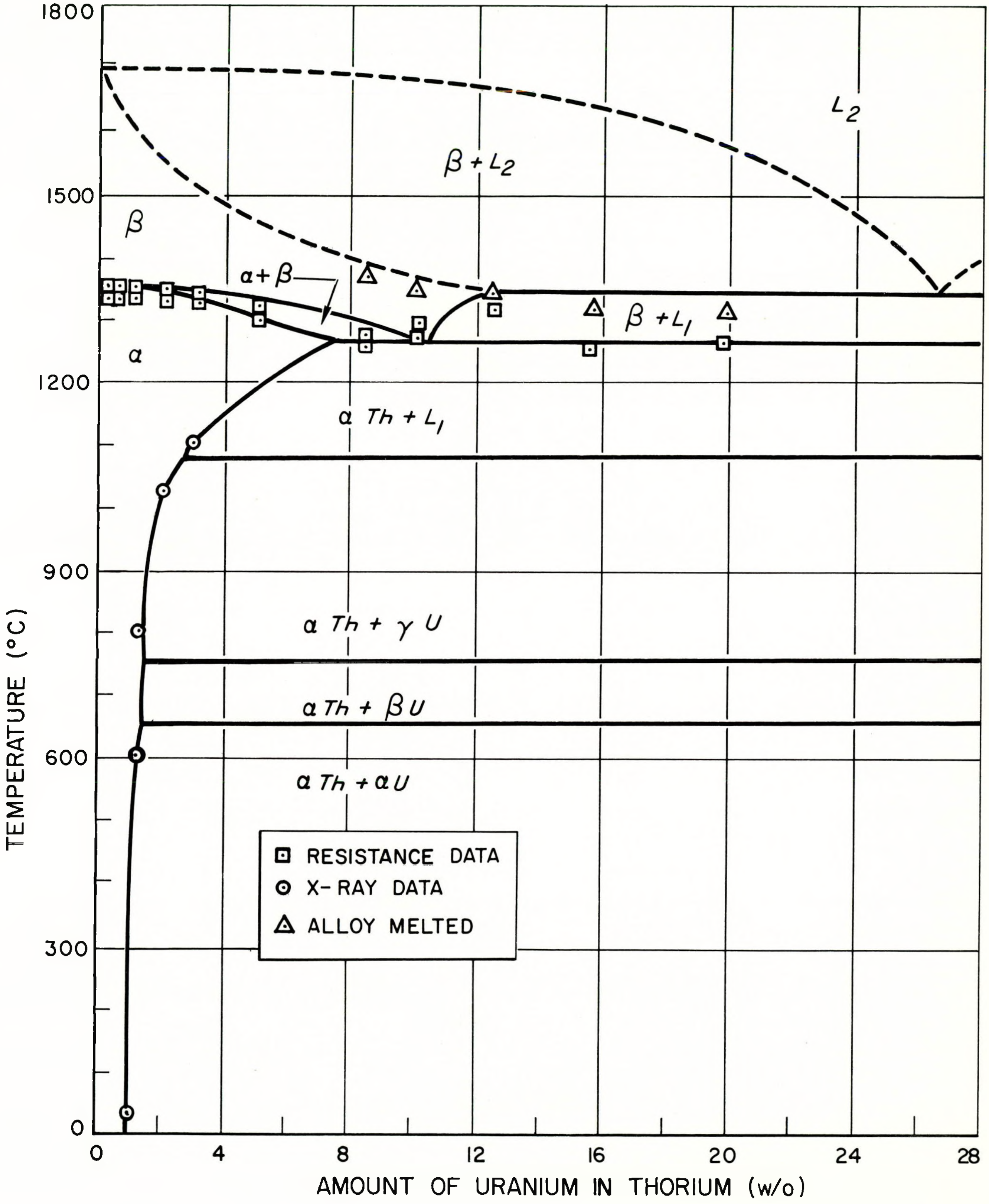


Fig. 11. Partial Thorium-Uranium Phase Diagram

The transformation temperatures of all of the alloys are shown in Table III; the increase in contamination of the commercial-quality thorium as compared to the crystal-bar thorium is reflected in higher temperatures of transformation.

TABLE III

TRANSFORMATION TEMPERATURES OF THORIUM ALLOYS FOUND BY RESISTANCE MEASUREMENTS

Amount of U in Commercial-Purity Th (w/o)	Transformation Temperature (°C)		Amount of U in High-Purity Th (w/o)	Transformation Temperature (°C)	
	Beginning	End		Beginning	End
0.0	1365 ± 10	1370 ± 10	0.0	1330 ± 10	1335 ± 10
1.07	1350 ± 10	1360 ± 10	0.29	1330 ± 10	1340 ± 10
3.17	1317 ± 10	1327 ± 10	0.56	1330 ± 10	1340 ± 10
5.46	1317 ± 10	1327 ± 10	1.06	1330 ± 10	1340 ± 10
8.90	1291 ± 10	1300 ± 10	2.08	1330 ± 10	1340 ± 10
10.46	1315 ± 10	1330 ± 10	3.14	1315 ± 10	1330 ± 10
-	-	-	5.28	1295 ± 10	1315 ± 10
-	-	-	8.43	1265 ± 10	1270 ± 10
-	-	-	10.6	1270 ± 10	1280 ± 10
-	-	-	12.4	1310 ± 10	*
-	-	-	15.4	1265 ± 10	*
-	-	-	19.9	1270 ± 10	*

*Melted before end of transformation was reached

E. THERMAL CONDUCTIVITY

The thermal conductivity (C_t) of the alloys was calculated from the resistivity data using the Weidemann-Franz relation:

$$C_t = \pi^2 k^2 T \rho / 3e^2 \quad ;$$

where

k = Boltzman's constant (1.38 x 10^{-6} erg/°K),

T = absolute temperature (°K),

ρ = resistivity (ohm-cm),

e = charge on the electron (4.802 x 10^{-10} esu).

Since an absolute measure of the resistance is not available, the calculated thermal conductivity values were normalized to an average thermal conductivity for the alloy at 100° C. The calculated values agree well with the average measured conductivities of thorium and uranium to 600° C, the highest temperature at which conductivity data were found for thorium. The calculated values are plotted in Fig. 12.

F. X-RAY LATTICE PARAMETER MEASUREMENTS

Lattice parameters were measured by X-ray diffraction. The sample was a 3/8-inch diameter, 1/8-inch long disc which was attached to a rotating specimen mount. Preliminary tests indicated that rotating the specimen in the plane of the X-rayed face resulted in more precise measurements. Unfiltered X-rays from a copper target were used. A geiger tube mounted on a goniometer head was connected to a strip-chart recorder which recorded the intensity of the diffracted X-rays. The 531, 600, 620, 640, and 711 lines were used and were extrapolated against $\cos^2 \theta$ after the method of Bradley and Jaye.[6] Duplicate tests were performed on many of the samples. The maximum variation in line position was 0.01 degrees θ. The samples for a given heat treatment were vacuum sealed in a quartz tube. They were heated to a temperature of 1100° C or higher, held at 1100° C for one hour, and allowed to cool at 10° C per hour to the temperature from which they were quenched. The actual temperature of the sample at time of quench was not measured. However, the transfer of samples from the furnace to the water was about 1 second. The effects of contamination from the quartz tube were checked by the repeated heating and quenching of the same sample from 1100° C. No lattice parameter changes were noted. A significant increase in the lattice parameter was caused by polishing. Therefore, all of the data presented were taken from samples

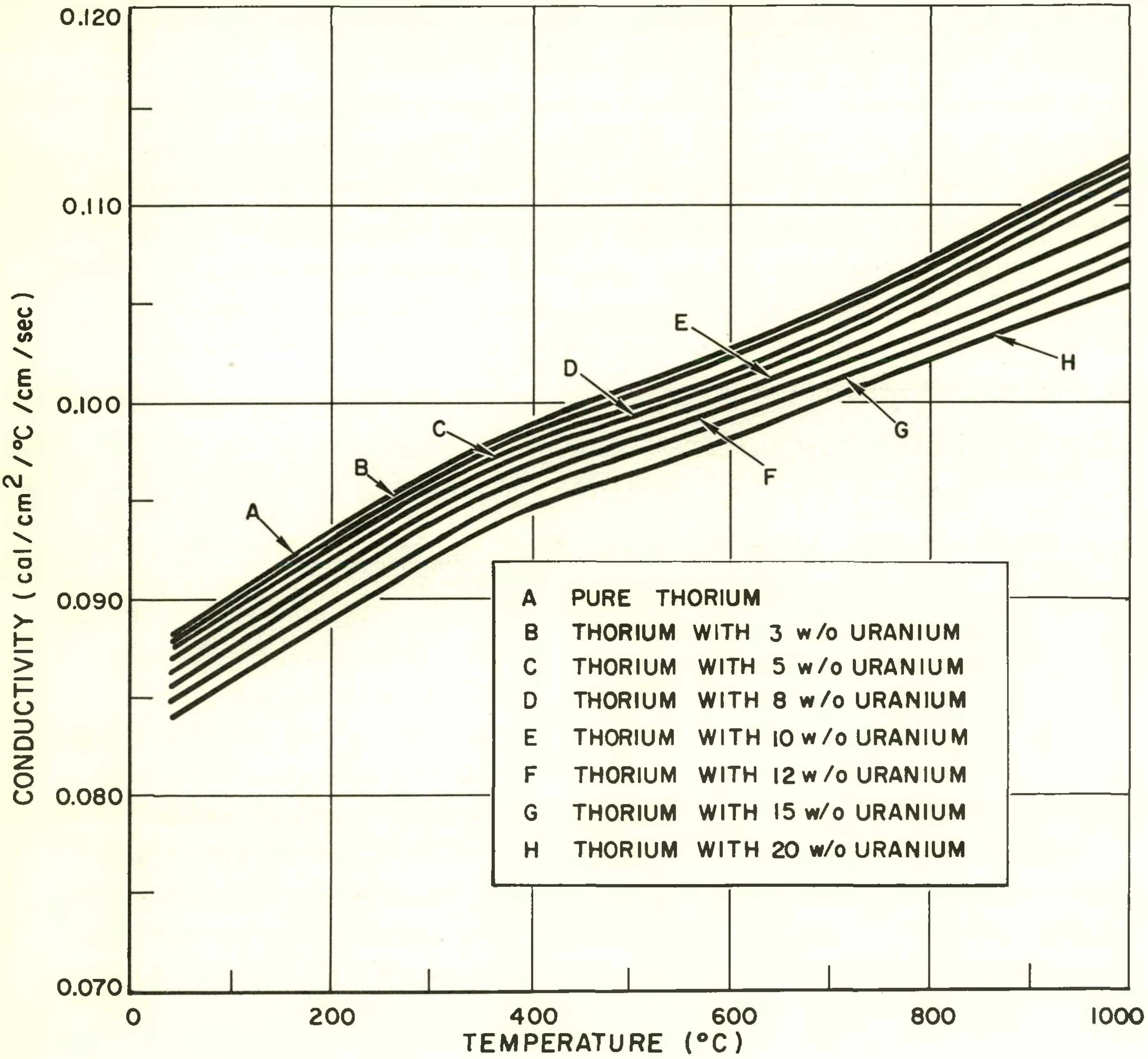


Fig. 12. Thermal Conductivity of Thorium-Uranium Alloys

which were etched without polishing after their respective heat treatments. This procedure was found to give reproducible lattice parameters.

Figure 13 represents the various series of alloys quenched from elevated temperatures and X-rayed at room temperature. The lattice parameters of unalloyed thorium are believed to vary because of impurities. The parameter of the slowly-cooled thorium sample agrees well with other data.[5] The point at which the lattice parameter becomes constant is assumed to indicate a solid solution of thorium saturated with uranium. These saturation points are plotted as circles on the phase diagram, Fig. 11.

IV. GENERAL DISCUSSION

An original objective was to use the mechanical properties of the thorium-uranium alloys to investigate the phase diagram; however, neither hardness or strength gave well defined limits of solid solubility. One explanation is that the effects of a fine uranium-rich precipitate in the matrix, plus other impurities, mask any solid solution hardening effect.

The metallography of the alloys indicates that the uranium-rich phase agglomerates with increasing temperature; furthermore, this agglomeration is enhanced with increasing uranium content. A critical factor is believed to be the amount of agglomerate occuring in the grain boundaries; this agglomerate may have a direct bearing on the radiation stability of the alloys. Of course, the significance of the agglomerate at the grain boundaries can only be found from high temperature irradiation tests of alloys with varying uranium content.

The lines in the phase diagram representing the monotectic, eutectic, liquidus, and uranium transformations are from the previous work of Carlson[7] with temperature modifications as suggested by Wilson et al.[3] The existence of a $\beta + L_1$ region fits the transformation points as found by resistivity. Because the newly proposed region is narrow, it may have avoided detection during previous studies.

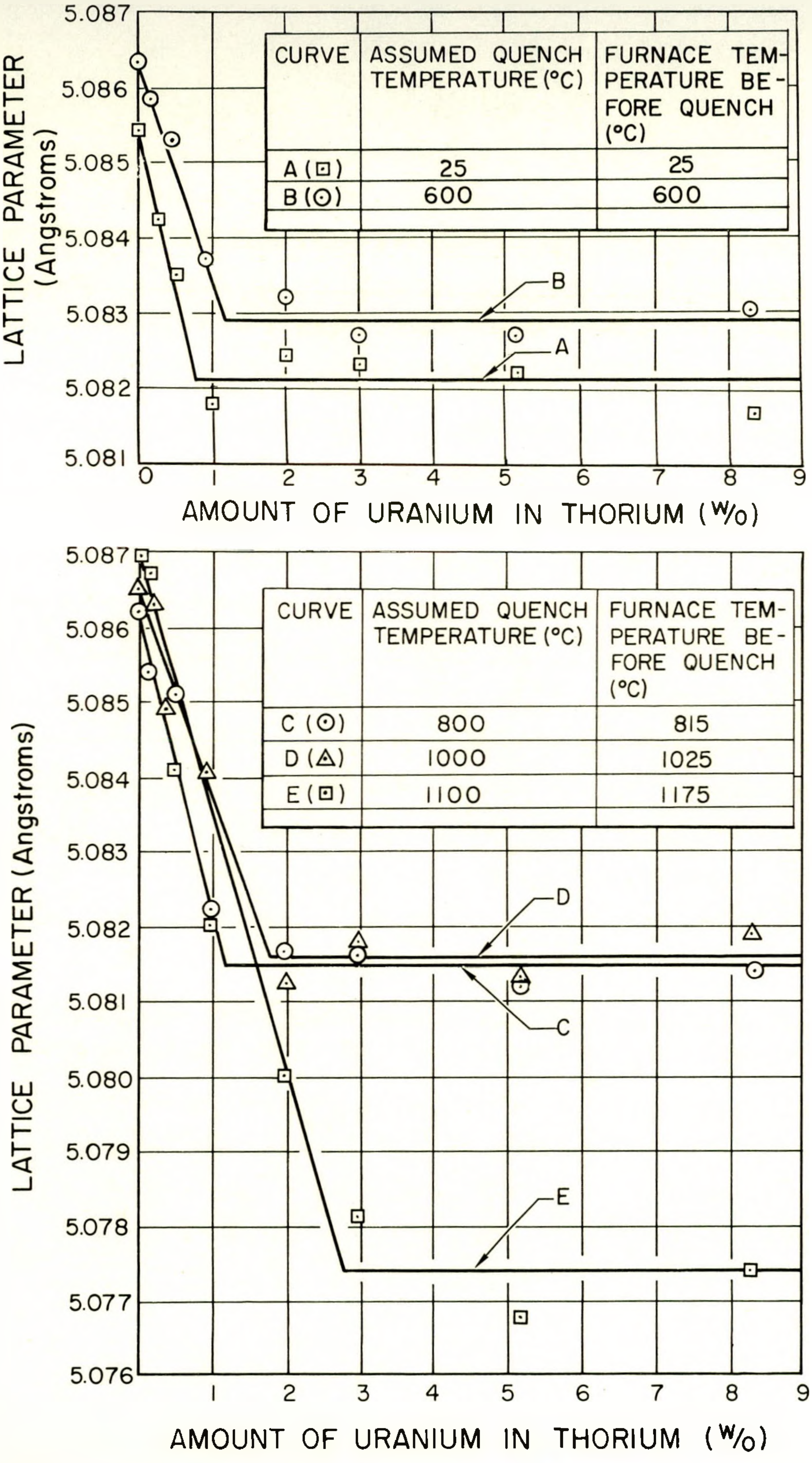


Fig. 13. Room-Temperature Lattice Parameters of Heat-Treated, Thorium-Uranium Alloys

V. CONCLUSIONS

The conclusions of this investigation are as follows:

1) Resistivity and lattice-parameter data produce a reasonable phase diagram. The diagram indicates that: (a) uranium is found to cause a slight decrease in the phase transformation of thorium, (b) uranium is found to have a solubility in thorium of less than 1 w/o at room temperature, which increases to about 3 w/o at 1100° C, and (c) resistivity data indicates that a $\beta + L_1$ region exists.

2) Metallography indicates that a uranium-rich phase occurs as a fine precipitate, evenly dispersed throughout the matrix in arc-melted alloys. This precipitate coalesces when annealed and part of the uranium-rich phase is deposited in the grain boundaries. The resultant alloy has a small part of its grain-boundary length so affected.

3) The addition of 3 or more w/o uranium strengthens thorium approximately 50 per cent when tested at 500° C; considerable strengthening was also noted during tests at room temperature.

4) The variations of the strength and hardness with uranium content in the alloys studied, apparently do not correlate with the limits of solid solubility.

REFERENCES

1. P. Chiotti, "High-Temperature Crystal Structure of Thorium," Electrochem. Soc. <u>101</u>, (11), 567 (November 1954)
2. W. D. Manly, <u>et al.</u>, "Metallurgy of Thorium and Thorium Alloys," ORNL-1090 (AEC Classified Report), December 7, 1951
3. W. B. Wilson, A. E. Austin, and C. M. Schwartz, "The Solid Solubility of Uranium in Thorium and the Allotropic Transformation of Thorium-Uranium Alloys," BMI-1111, July 12, 1956
4. W. J. James and M. E. Straumarus, "Lattice Parameter and Coefficient of Thermal Expansion of Thorium," Acta Cryst. <u>9</u>, 376 (1956)
5. H. W. Deem and R. A. Winn, "The Electrical Resistance of Thorium Through the Allotropic Transformation," BMI-1052, November 18, 1955
6. A. J. Bradley and H. H. Jay, "A Method for Deducing Accurate Values of the Lattice Spacing From X-ray Powder Photographs Taken by the Debye-Scherrer Method," Proc. Phys. Soc. (London) <u>44</u>, 563 (1932)
7. O. N. Carlson, "Some Studies on the Uranium-Thorium Zirconium Ternary Alloy System," AECD-3673, September, 1953