

sur la

METALLURGIE DU PLUTONIUM

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THE PLUTONIUM-COPPER PHASE DIAGRAM
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Operated by
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for the
United States Atomic Energy Commission

SUMMARY

The constitution of the plutonium-copper binary alloy as determined by differential thermal analysis is presented. The system is characterized by two congruent melting compounds, PuCu_2 (m.p. $865^\circ\text{C}.$) and $\text{Pu}_4\text{Cu}_{17}$ (m.p. $954^\circ\text{C}.$); two incongruent melting compounds, PuCu_4 (m.p. $906^\circ\text{C}.$) and $\text{Pu}_2\text{Cu}_{11}$ (m.p. $926^\circ\text{C}.$); three eutectics, 96 atom per cent copper (m.p. $626^\circ\text{C}.$), 70.5 atom per cent copper (m.p. $849^\circ\text{C}.$), and 91 atom per cent copper (m.p. $881^\circ\text{C}.$); and two peritectics at 75 atom per cent (m.p. $906^\circ\text{C}.$) and 85.5 atom per cent (m.p. $926^\circ\text{C}.$). Solid solution was found above 97 atom per cent plutonium. The apparatus, the method of investigation, and the binary alloy phase diagram is discussed.

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INTRODUCTION

Ternary alloys of plutonium and copper have been proposed as possible liquid reactor fuels [1]. A complete knowledge of the binary and ternary phase diagrams for these fuels is necessary in their evaluation. Before a ternary system could be examined effectively, an investigation of the plutonium-copper binary system was required. The results of this work by Mound Laboratory are presented in this paper.

MATERIALS

The plutonium metal used in this study had an impurity content of less than 600 p.p.m. as determined by spectrochemical and photometric analyses [2]. The principle impurities were 250 p.p.m. silicon, 200 p.p.m. iron, 50 p.p.m. nickel, 40 p.p.m. manganese, 15 p.p.m. aluminum and less than 20 p.p.m. chromium.

The copper was spectrographic grade, having a purity of 99.999 per cent, and contained only minute traces of lead, nitrogen and silver [3].

APPARATUS

The phase equilibrium diagram for the plutonium-copper binary system was determined by differential thermal analysis. The studies were made with automatic control and recording equipment. A block diagram of the apparatus is shown in Figure 1.

The heating and cooling rates of a resistance furnace were controlled by a program controller. Rates of one to three degrees per minute were found most desirable.

Sealed tantalum capsules containing the alloys along with a similar reference capsule of calcined alumina are held in over-sized holes of a cylindrical Inconel block. Each capsule is centered and insulated electrically from the block by an aluminum silicate (lava) ring at the top of the capsule and by a thermocouple insulator below the thermowell. The capsule rests on the thermocouple in such a manner that the "spring" of the thermocouple wires maintains intimate contact between the thermocouple bead and the top of the thermowell.

This block assembly is enclosed in a stainless steel vacuum chamber fitted at the top with a water-cooled flange and an "O" ring seal. The apparatus is evacuated and filled with helium for each determination. Helium provides a very desirable heat transfer medium and prevents oxidation of the tantalum capsules. The complete differential thermal

analysis furnace is shown in Figure 2. A disassembled block assembly and chamber are shown in Figures 3 and 4. Chromel-alumel thermocouples mounted in porcelain thermocouple insulators, as shown in Figure 4, are brought out from each thermowell to the X-Y recorder. Before being recorded, the differential temperature is amplified twenty times by means of a direct current amplifier. A pen positioning control voltage (see Figure 1) is applied in series with the differential voltage to position the base line of the heating and cooling traces on opposite sides of the recording paper. A typical heating trace for plutonium is shown in Figure 5.

Initially the thermocouples were calibrated against aluminum and lead obtained from the National Bureau of Standards, as well as high-purity inorganic salts. It was found that the thermocouples were always reproducible within $\pm 1^{\circ}\text{C}$. The accuracy of the determinations was limited only by the accuracy ($\pm 2^{\circ}\text{C}$) with which the transition could be read from the recording paper.

Sample containers were small tantalum capsules provided with thermowells. Both a completed capsule and a sectioned sample capsule, showing the thermowell detail, appear in Figure 6. Sealed sample capsules were found to be desirable for ease of sample handling, homogenization, and the elimination of oxidation and composition changes.

ALLOY PREPARATION

The alloy preparations were made directly in the tantalum capsules employed in each determination. The samples ranged in weight from 4 to 15 grams, depending upon the composition being examined. Desired compositions were made by accurately weighing to one milligram the appropriate weights of copper and plutonium, the latter having been mechanically cleaned of oxide in a helium atmosphere. The capsules were capped and sealed by arc welding under an argon atmosphere. All other operations were performed in dry-air alpha boxes having a moisture content of two to five parts per million. By observing proper handling techniques in loading and transfers, the exterior of the capsules were free of alpha contamination.

The sealed capsules were enclosed in an evacuated quartz container, induction heated to 1200°C., and the contents were shaken vigorously for homogenization. Subsequent rapid cooling of the sample provided a fine-grained homogeneous alloy.

- 7 -

RESULTS

The complete phase equilibrium diagram for the plutonium-copper binary system is given in Figure 7 while Figure 8 shows the plutonium-rich end of the diagram in detail. The invariant equilibria and their respective temperatures are presented in Table 1.

This binary system was particularly suited to examination by differential thermal analysis because of the inherent sensitivity in metal systems and the accuracy resulting from rapid equilibrium rates. The transition temperatures, with the exception of solidus transformations resulting from the allotropic forms of plutonium, were found to be very reproducible. The data are shown in Tables 2 and 3.

Three eutectics were identified in this binary system at 6.0 atom per cent copper (626°C.), 70.5 atom per cent copper (849°C.) and 91 atom per cent copper (881°C.). The eutectics were located within ± 1 atom per cent by the intersection of the accurately established liquidus curves and their respective solidus. The absence of the eutectic arrest in the plutonium-rich end of the diagram, as indicated in Figure 8, along with reliable solidus observations established the existence of a limited solid solution. The maximum solubility of copper in epsilon-plutonium, which occurs at 626°C., is about three atom per cent. In several of the compositions between 96 and 100 per cent plutonium some thermal indication was observed for the limit of solid

solubility below the eutectic temperature. Compositions at every one-half atom per cent in this area were examined by differential thermal analysis but the thermal arrests were inconclusive. Uncertainty for the limit of solid solution below the solidus is indicated on the diagram.

The equilibrium diagram shows the temperatures of the solid phase transformations occurring in the plutonium-rich side of the diagram. Most of the thermal arrests are extensions of the transformation temperatures for the six phases found in pure plutonium metal. The transition temperatures indicated, as well as those shown for pure plutonium, were those obtained at heating rates of two and three degrees per minute. True equilibrium temperatures could be determined by special differential thermal analysis and equilibration techniques which have been employed at this Laboratory with pure plutonium. The alpha to beta, beta to gamma, and gamma to delta transition temperatures, over the range of 0 to 60 atom per cent copper, are not only slightly higher than those found in pure plutonium but show an erratic behavior. This may be due to the sluggish transformation rates induced by an added "impurity", in this instance copper [4]. The opposite is apparently true of the delta to delta prime and delta prime to epsilon transformations in which a depressed transition is observed. All of these solid state arrests for plutonium were detected to 55 atom per cent copper.

Additional thermal arrests have been found at 120° and 350°C. for all compositions from one through 50 atom per cent copper. The weak arrest at 120°C. just preceding the alpha to beta transformation was also observed at about 114°C. in pure plutonium metal. The other transition has been observed during the first heating determination on pure plutonium but was absent from subsequent runs. To date no attempt has been made to characterize these two arrests.

The liquidus curve to the left of the compound PuCu_2 is of interest due to its unusual concave appearance. As the compositions are moved from left to right, beginning at about ten atom per cent copper, the liquidus transition rapidly grows in magnitude, due to the large amount of PuCu_2 melting over a narrow temperature range. However, above 35 atom per cent copper two peaks appear in the differential trace, the first peak resulting from a change in slope of the liquidus and the second from the liquidus itself.

Four intermetallic compounds, congruently melting PuCu_2 and $\text{Pu}_4\text{Cu}_{17}$ and incongruently melting PuCu_4 and $\text{Pu}_2\text{Cu}_{11}$ were found in this binary system. All are located in the copper-rich end of the diagram. The locations of the compounds to within plus or minus one atom per cent were ascertained by thorough analyses of the thermal data. Congruent compounds exhibited only a melting point; incongruent compounds, a peritectic transition and a liquidus. Compositions within

one atom per cent of a compound showed the appropriate eutectic and peritectic transitions whose magnitude met quantitative requirements. The compound location was further substantiated by semi-quantitative measurement of peritectic transformations in compositions to either side of the compound. The stoichiometric compositions of these compounds were determined on the basis of the empirical formulas with the smallest whole numbers which fit the data most closely. The method is sufficiently sensitive in this metal system to permit compound location within $\pm 1/4$ atom per cent. However, structure determinations by x-ray techniques are expected in future investigations.

A compound melting congruently at 865°C . and located at 66.7 atom per cent copper was assigned the formula PuCu_2 . The compound was found to melt sharply, and no thermal changes were observed either below or above the melting point. No solubility of copper in PuCu_2 was detected from determinations immediately adjacent to the compound.

The compound PuCu_4 , melting incongruently at 906°C ., exhibited a well-defined peritectic at 75 atom per cent copper as determined from heating curve data. For compositions immediately to the left of PuCu_4 , a non-equilibrium phase transition was detected in the cooling curves just below the peritectic temperature. The inherent sluggishness

of the peritectic reaction may create a non-equilibrium condition suitable for the formation of another phase. There is an absence of the phase in heating determinations, and it can be eliminated in the cooling curve by equilibrating the compositions at a temperature slightly below the peritectic.

A compound, assigned the empirical formula $\text{Pu}_2\text{Cu}_{11}$, melts incongruently at 926°C ., giving rise to a peritectic at 85.5 atom per cent copper. This compound, which exists at less than one atom per cent from the point where the peritectic intersects the liquidus, was located chiefly from quantitative measurements of the peritectic transition and was further substantiated by the absence of the eutectic arrest for all compositions to the left of the compound. Due to the peritectic sluggishness during cooling, for both PuCu_4 and $\text{Pu}_2\text{Cu}_{11}$, it was generally necessary to equilibrate the samples in order to obtain arrests from heating curves which could be evaluated quantitatively.

Selected compositions between the two compounds PuCu_4 and $\text{Pu}_2\text{Cu}_{11}$ were examined for a congruently melting compound. A determination at 80.77 atom per cent copper exhibited only a melting point of 954°C ., and was assigned the empirical formula $\text{Pu}_4\text{Cu}_{17}$. The possibility that the compound may be $\text{Pu}_5\text{Cu}_{21}$ also exists since the two compounds differ in composition only by 0.2 atom per cent. Compositions less than

one atom per cent to either side of this compound, as shown in Figure 7, yield their respective peritectic reactions, indicating that this congruently melting compound must have a composition lying between 80 (PuCu_4) and 81.7 atom per cent.

In the area between the $\text{Pu}_4\text{Cu}_{17}$ and the eutectic at 91 atom per cent copper both the peritectic and liquidus transitions were subject to supercooling. Throughout the diagram reliable data was achieved from heating curves.

These intermetallic compounds, particularly $\text{Pu}_4\text{Cu}_{17}$, show an appreciable increase in hardness over that of copper or plutonium. The range of hardness on the Vickers scale for $\text{Pu}_4\text{Cu}_{17}$ was 425 to 454 compared with 373 to 413 for PuCu_4 and 317-319 for PuCu_2 . The hardness of pure copper ranges from 89.2 to 98.5.

DISCUSSION

As reported in other investigations of various plutonium alloys, compound identification by x-ray techniques has met with considerable difficulty [5,6,7]. The intermetallic compounds often exhibit poorly defined or unresolved powder patterns after special handling and extensive annealing. According to metallographic and diffraction evidence obtained at Los Alamos Scientific Laboratory, three compounds, PuCu, PuCu₃ and PuCu₇ exist in this system, but the compositions indicated were uncertain [6]. No diagram or melting points were presented. A limited report by U.S.S.R. investigators indicate the existence of three other compounds, PuCu₂, PuCu₄, and PuCu₆ [7]. Both literature references in which metallography and x-ray diffraction were used extensively, list unsolved powder patterns for all compounds reported. The present investigation confirms two of the reported compounds, PuCu₂ and PuCu₄. However, the melting point of these compounds was found to be lower than that reported by the Russian investigators. A thorough search by differential thermal analysis was made for the other reported compounds, PuCu, PuCu₃, PuCu₆ and PuCu₇, but no thermal data was observed that could suggest their existence. Two new compounds, Pu₂Cu₁₁ melting incongruently, and Pu₄Cu₁₇ melting congruently, were shown to exist.

The three eutectics found in the present investigation confirm, in general, the eutectic locations given by

Bochvar [7]. Eutectic temperatures were in good agreement except at 70 atom per cent copper.

A very limited solubility of three atom per cent copper in plutonium was observed. This restricted solubility in epsilon-plutonium is to be expected in view of the unfavorable size factor. Lack of solubility of copper in the other allotropic forms of plutonium is not unexpected, due to their complex structures [6]. As shown in the iron-plutonium diagram, iron, which possesses nearly the same atomic radius as copper, shows a similar degree of solubility in epsilon-plutonium [5]. No solid solution was detected in other areas of the plutonium-copper system in which compositions within one atom per cent of each compound exhibited the appropriate eutectic or peritectic transitions.

TABLE 1

INVARIANT EQUILIBRIA IN THE SYSTEM Pu-Cu

Composition		Temperature*	Type of Invariant Point
Atom Per Cent Pu	Atom Per Cent Cu		
94.0	6.0	626	Eutectic Pu + PuCu ₂
33.3	66.7	865	Congruent m.p. of PuCu ₂
29.5	70.5	849	Eutectic PuCu ₂ + PuCu ₄
25.0	75.0	905	Peritectic Point
19.2	80.8	906	Incongruent m.p. of PuCu ₄
20.0	80.0	954	Congruent m.p. of Pu ₄ Cu ₁₇
16.7	83.3	926	Incongruent m.p. of Pu ₂ Cu ₁₁
14.5	85.5	926	Peritectic Point
9.0	91.0	881	Eutectic Pu ₂ Cu ₁₁ + Cu

* Accuracy $\pm 3^{\circ}\text{C}$.

TABLE 2

DIFFERENTIAL THERMAL ANALYSIS OF Pu-Cu SYSTEM

Composition Atom Per Cent		Transitions, °C.			
<u>Pu</u>	<u>Cu</u>	<u>Eutectic</u>	<u>Peritectic</u>	<u>Liquidus</u>	<u>Solidus</u>
99.0	1.0	--	--	640	636
98.0	2.0	--	--	639	630
97.0	3.0	--	--	635	627
96.0	4.0	626	--	633	--
94.0	6.0	625	--	626	--
92.5	7.5	626	--	660	--
91.0	9.0	625	--	687	--
85.0	15.0	626	--	708	--
80.0	20.0	625	--	716	--
75.0	25.0	626	--	722	--
70.0	30.0	626	--	734	--
65.0	35.0	626	--	742	--
60.0	40.0	626	--	756	--
55.0	45.0	627	--	769	--
50.0	50.0	624	--	787	--
45.0	55.0	625	--	819	--
40.0	60.0	626	--	841	--
37.0	63.0	620	--	855	--
34.0	66.0	--	--	865	--
33.0	67.0	847	--	864	--
31.5	68.5	849	--	862	--

TABLE 2 (Continued)

Composition Atom Per Cent		Transitions, °C.			
<u>Pu</u>	<u>Cu</u>	<u>Eutectic</u>	<u>Peritectic</u>	<u>Liquidus</u>	<u>Solidus</u>
29.0	71.0	849	--	854	--
27.5	72.5	849	--	891	--
25.0	75.0	849	--	906	--
24.0	76.0	849	908	926	--
22.0	78.0	854	906	948	--
21.0	79.0	850	907	951	--
20.0	80.0	854	906	952	--
19.2	80.8	--	--	954	--
18.2	81.8	--	928	954	--
16.7	83.3	--	926	952	--
16.0	84.0	--	928	951	--
15.39	84.61	--	926	941	--
14.5	85.5	881	--	926	--
12.0	88.0	881	--	916	--
8.0	92.0	880	--	916	--
5.0	95.0	881	--	1002	--

TABLE 3
SOLID PHASE TRANSITIONS

Composition Atom Per Cent		Transitions, °C.						
<u>Pu</u>	<u>Cu</u>	<u>Other</u>	<u>α-β</u>	<u>β-γ</u>	<u>γ-δ</u>	<u>Other</u>	<u>δ-δ'</u>	<u>δ'-ϵ</u>
99.0	1.0	118	134	218	317	358	439	453
98.0	2.0	121	129	229	321	350	447	454
97.0	3.0	124	132	216	319	360	445	457
96.0	4.0	124	134	222	321	365	450	457
94.0	6.0	124	130	227	322	346	447	453
92.5	7.5	122	132	222	319	358	448	452
91.0	9.0	122	132	226	336	353	450	457
85.0	15.0	120	128	230	327	351	448	457
80.0	20.0	122	128	232	325	350	447	454
75.0	25.0	110	122	234	324	355	448	457
70.0	30.0	116	124	220	322	338	450	458
65.0	35.0	122	128	222	331	346	452	462
60.0	40.0	122	128	222	329	353	450	462
55.0	45.0	118	126	222	324	348	448	459
50.0	50.0	116	122	212	324	--	448	457
45.0	55.0	--	122	222	326	--	445	457
40.0	60.0	--	122	--	324	--	--	455
37.0	63.0	--	122	--	--	--	--	455

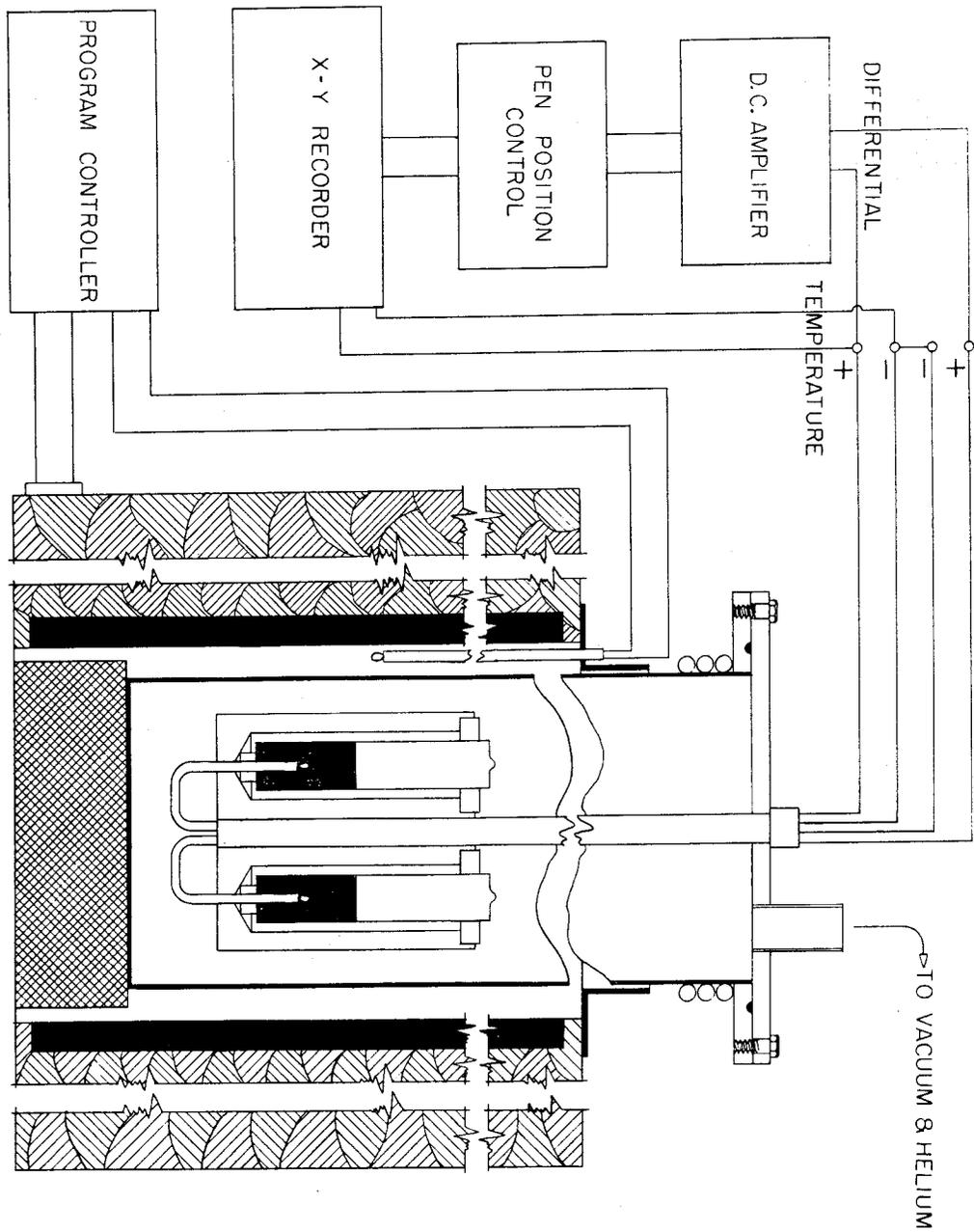
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Interaction between Plutonium and Other Metals in
Connection with Their Arrangement in Mendeleev's
Periodic Table.

Second United Nations International Conference on
Peaceful Uses of Atomic Energy. July 7, 1958.



D.T.A. APPARATUS
FIGURE 1

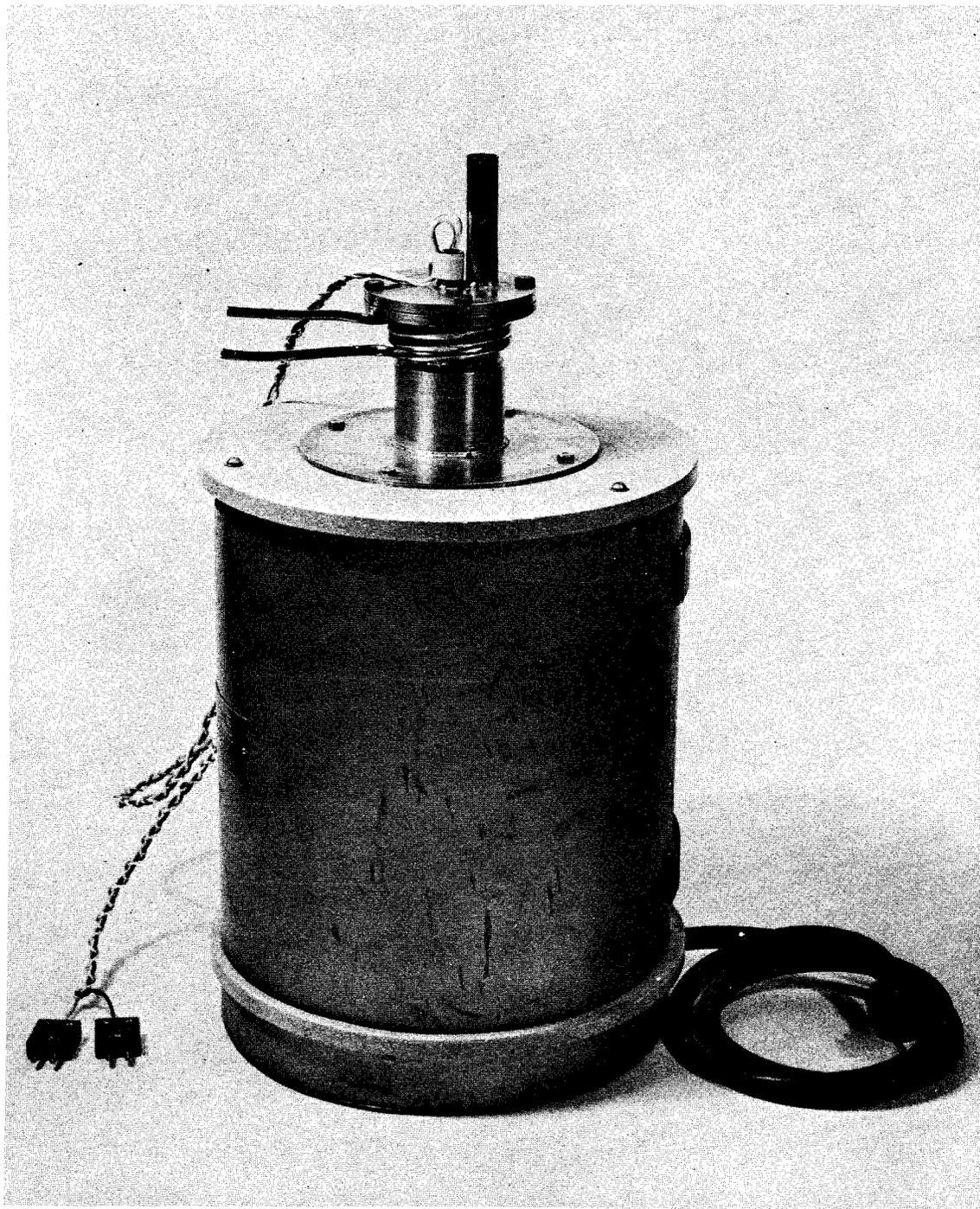


Figure 2 - FURNACE ASSEMBLY

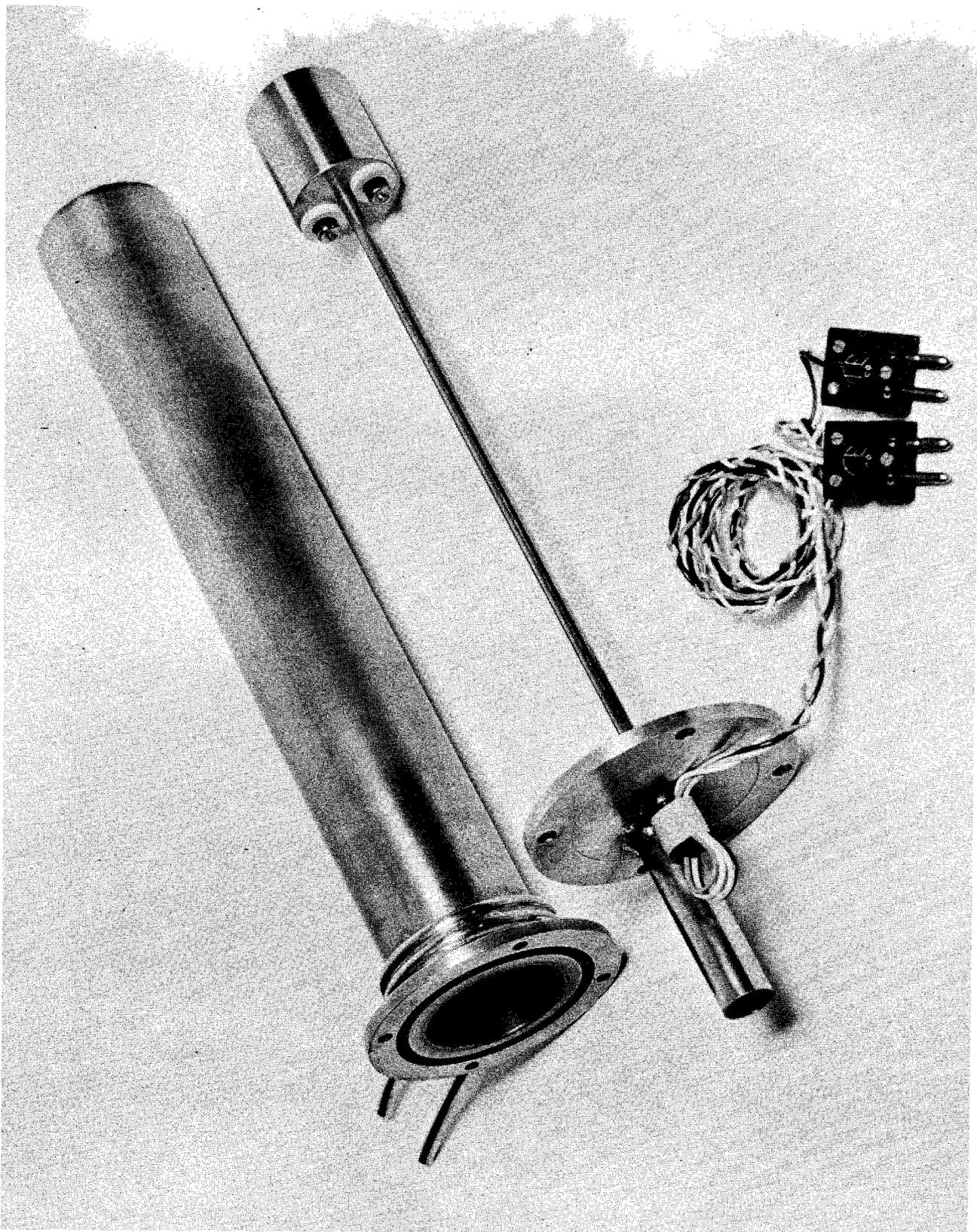


Figure 3 - DISASSEMBLED BLOCK ASSEMBLY AND CHAMBER

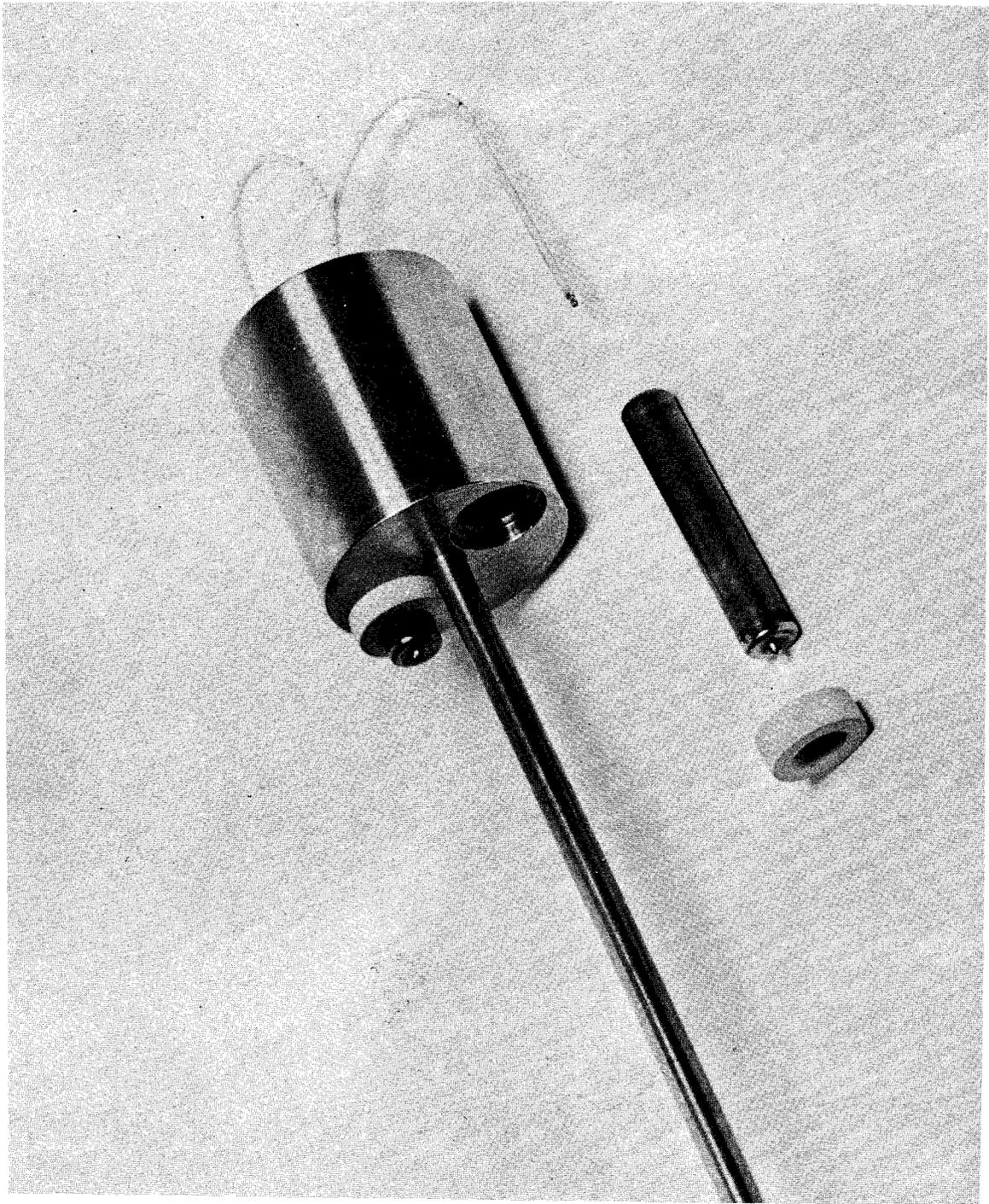
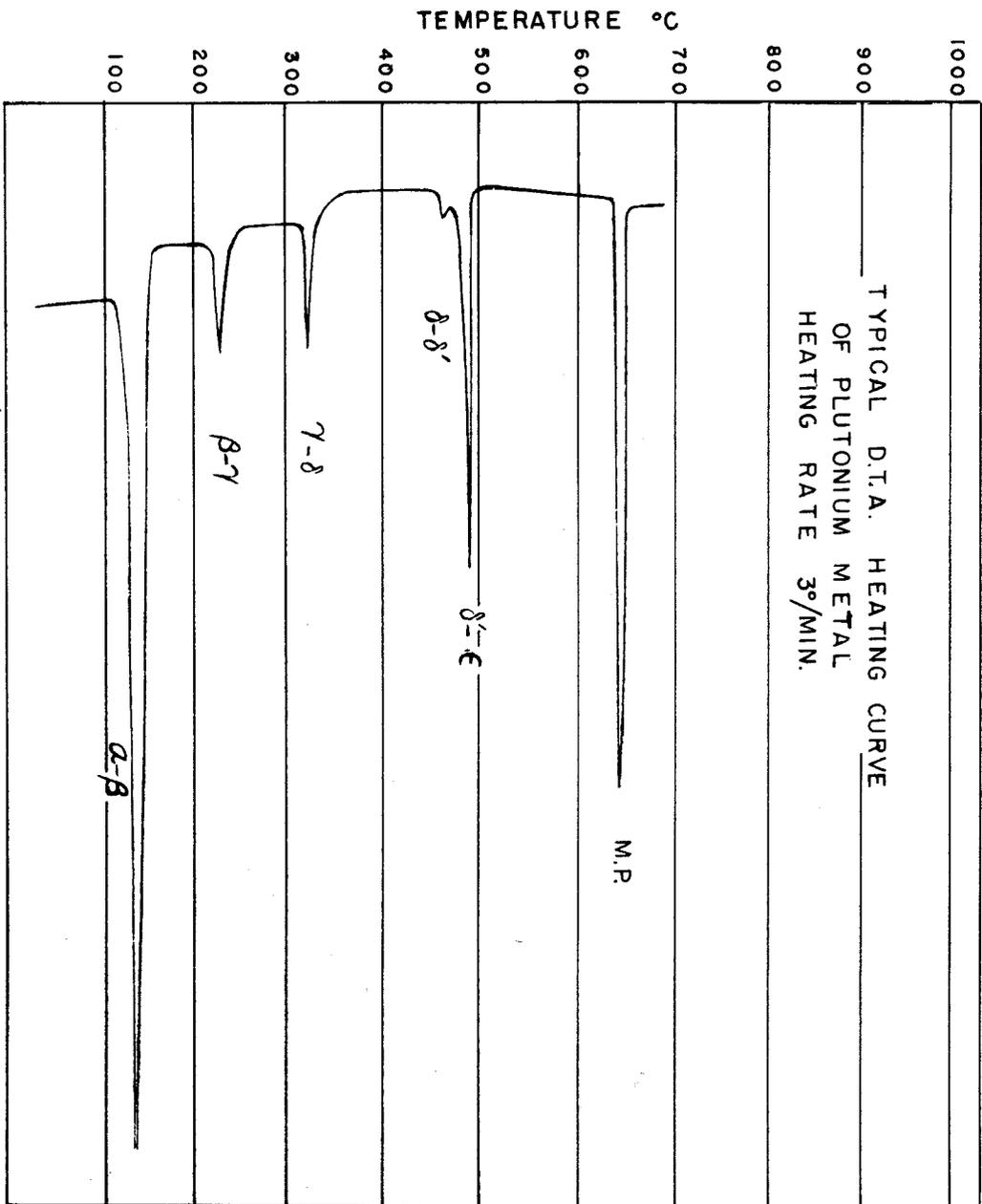


Figure 4 - BLOCK ASSEMBLY



DIFFERENTIAL
FIGURE 8

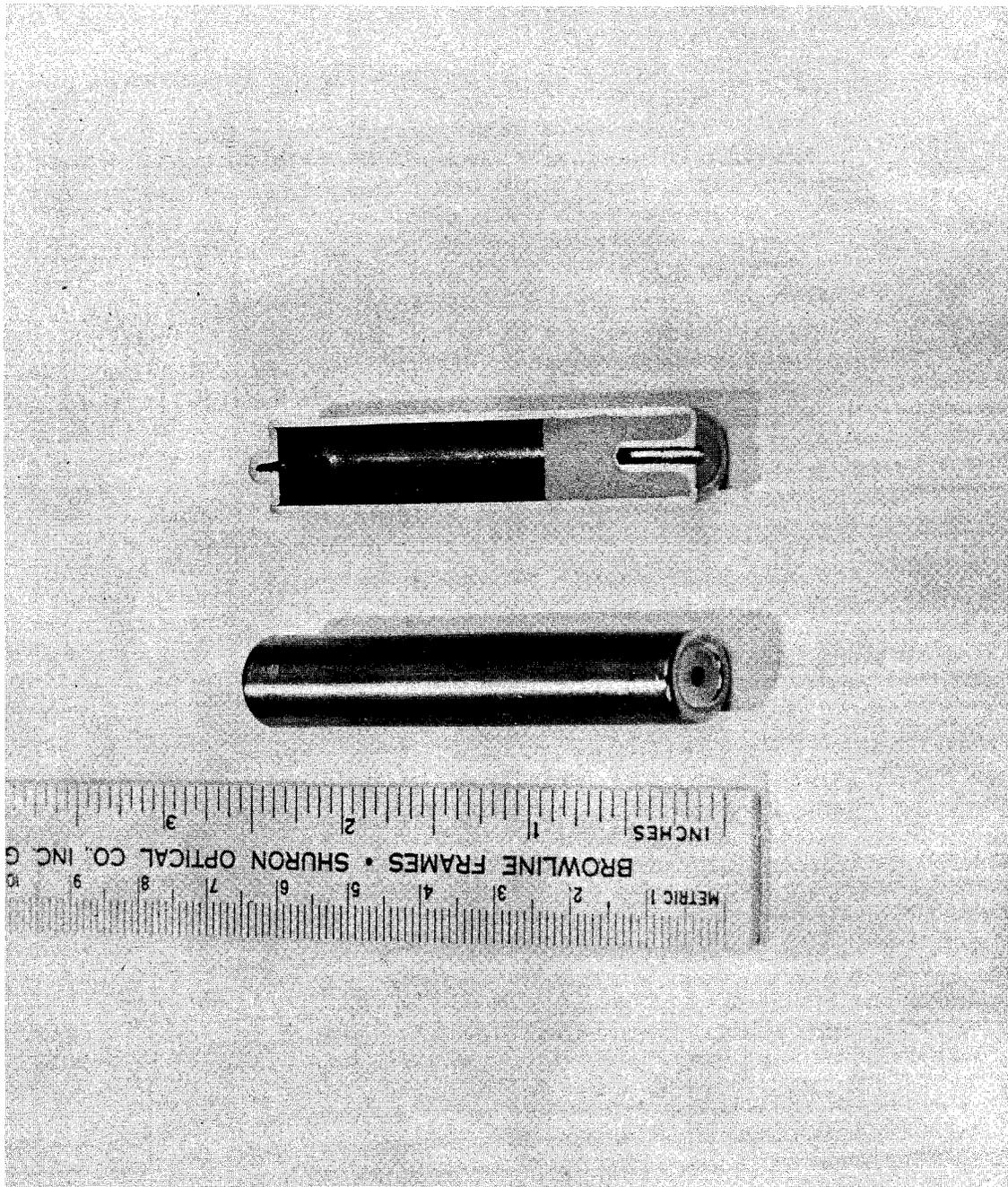


Figure 6 - TANTALUM DIFFERENTIAL THERMAL ANALYSIS CAPSULES

PROPOSED PLUTONIUM - COPPER BINARY DIAGRAM

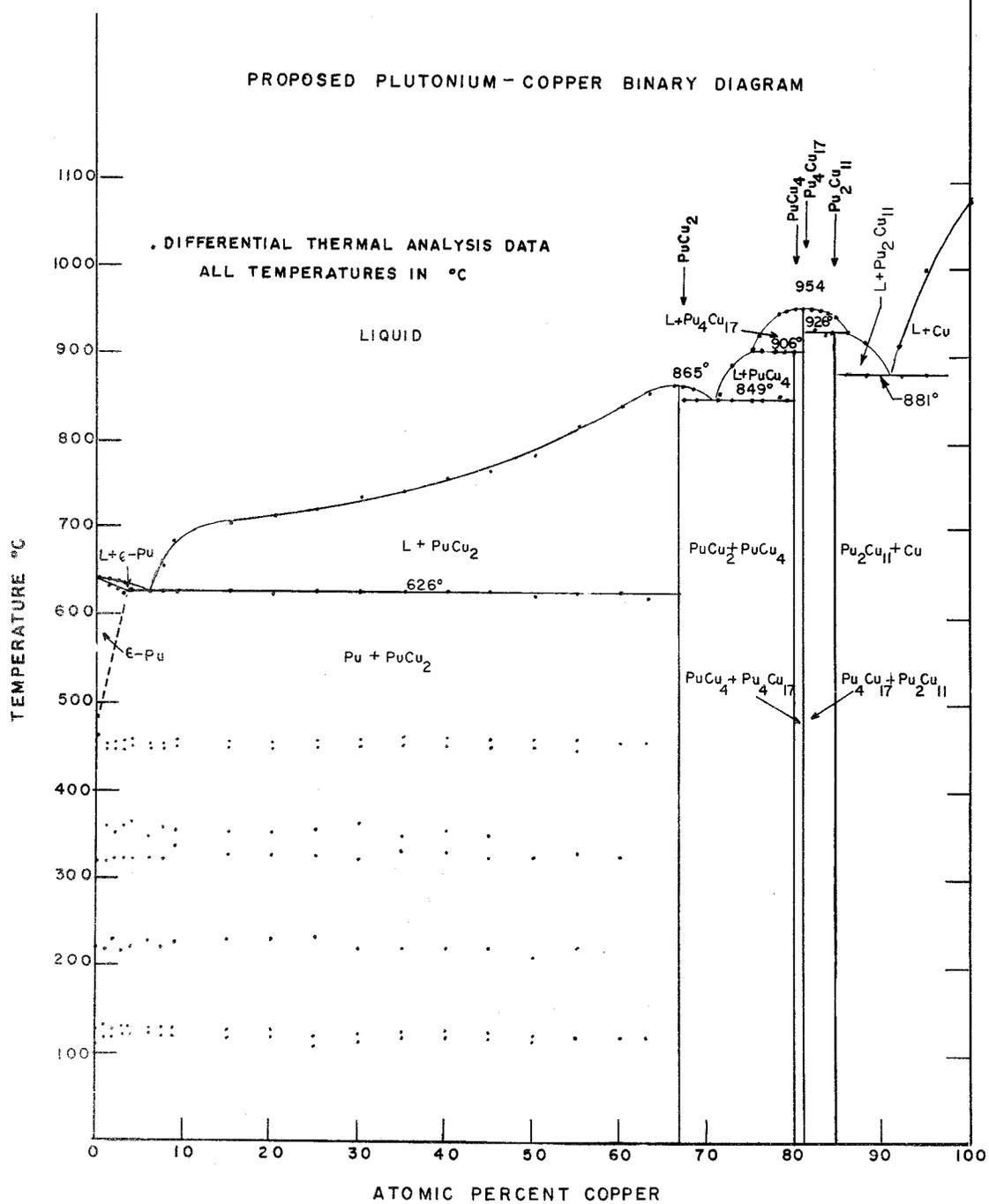


FIGURE 7

SOLID SOLUTION SECTION
Pu-Cu BINARY

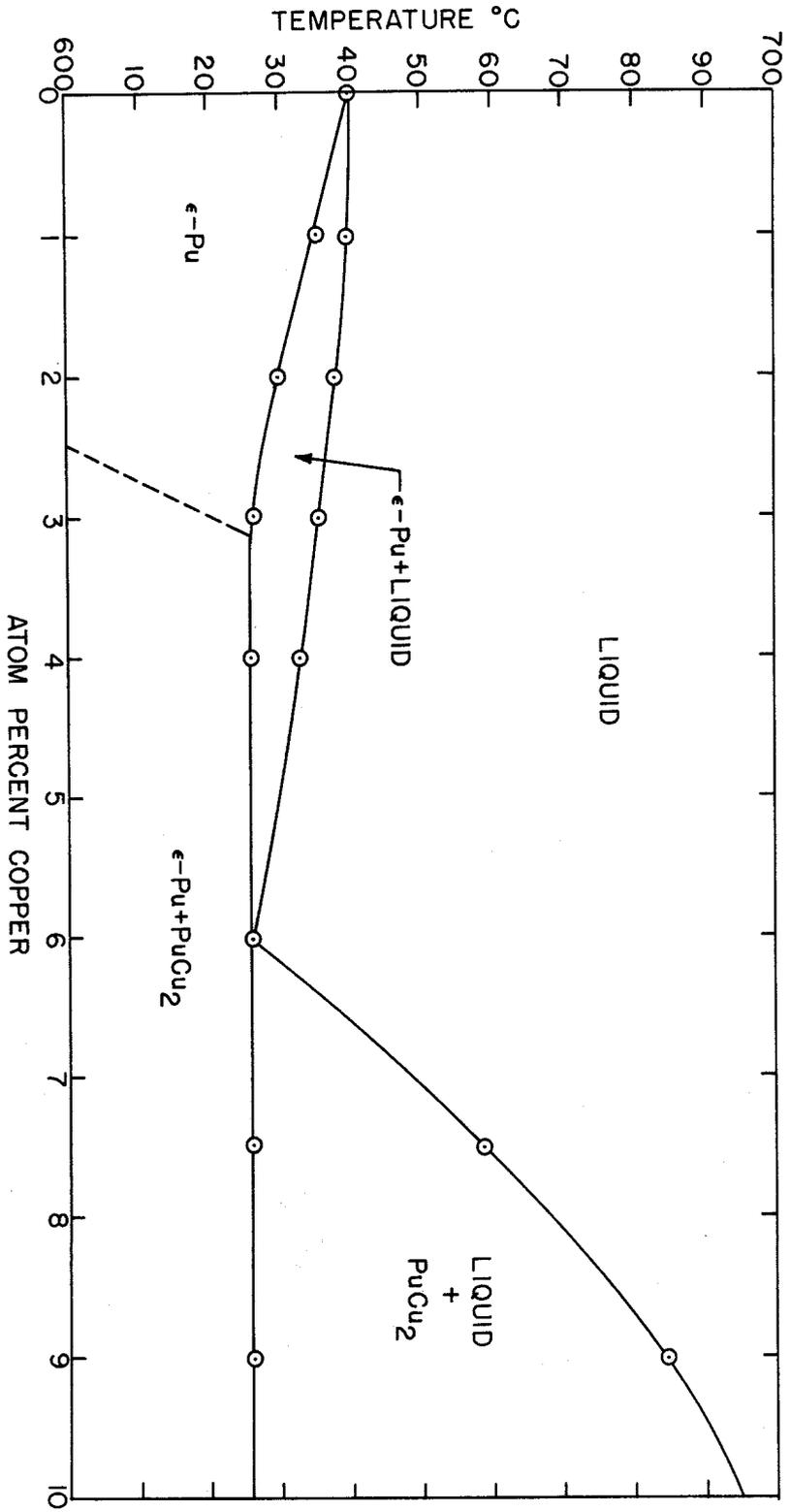


FIGURE 8

THE PLUTONIUM-COPPER PHASE DIAGRAM

The values in Table I, page 15, are to be corrected to the following:

Table I

INVARIANT EQUILIBRIA IN THE SYSTEM Pu-Cu

Composition Atom Per Cent		Temperatures* °C	Type of Invariant Point
Pu	Cu		
94.0	6.0	626	Eutectic Pu + PuCu ₂
33.3	66.7	865	Congruent m.p. of PuCu ₂
29.5	70.5	849	Eutectic PuCu ₂ + PuCu ₄
25.0	75.0	906	Peritectic Point
20.0	80.0	906	Incongruent m.p. of PuCu ₄
19.0	81.0	954	Congruent m.p. of Pu ₄ Cu ₁₇
15.4	84.6	926	Incongruent m.p. of Pu ₂ Cu ₁₁
14.5	85.5	926	Peritectic Point
9.0	91.0	881	Eutectic Pu ₂ Cu ₁₁ + Cu

* Accuracy $\pm 3^{\circ}\text{C}$.