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Properties of Plutonium Alloys

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ABSTRACT

Six elements--aluminum, gallium, germanium, silicon, thallium and indium--were found to stabilize the soft, high temperature phase (delta) of plutonium. Of these, gallium conferred complete stability down to the temperature of liquid air, and the percentage required was low enough to permit nuclear applications.

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Properties of Plutonium Alloys

When plutonium was being produced on only a small scale in the early days of its history, the metal exhibited an erratic behavior. For example, the densities of metal specimens subjected to similar treatments gave widely different densities. A density as low as 15.8 grams per cc was occasionally obtained, whereas it was known that the density of α, the phase stable at room temperature, had a density of 19.6 or more. Pure α was hard and brittle, but the low density metal was soft and malleable. It was apparent that some impurity or impurities occasionally present were stabilizing some soft, low density, high temperature form at room temperature. It was later learned that this was the δ phase and was normally stable only in the temperature range 300-470°C.

As time passed, it became necessary to develop a well stabilized δ phase alloy. Pure metal had to be pressed around 250°C in the γ field of stability, as neither α nor β metal was malleable enough. A contraction from γ to β and β to α was encountered in each pressing cooled from 250°C to room temperature. The contraction in the $\beta \rightarrow \alpha$ transformation alone was about 11% in volume. This frequently led to distortion and cracking. A δ phase alloy which would undergo no transformation on cooling thus had obvious advantages so far as fabrication was concerned. A stabilized low density alloy was also desired for certain nuclear experiments.

A search was therefore begun for one or more elements which, when alloyed with plutonium, would stabilize the δ phase at room temperature.

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It was recognized at the outset that two types of stability of the δ phase at room temperature were possible:

A - Stability in which the transformation temperatures were so altered by the alloying elements that the δ phase would be the thermodynamically stable phase at room temperature.

B - Stability in which rates of transformation were so slowed by the alloying elements that the δ phase could be super-cooled to room temperature and there be retained for weeks or even months without transforming to a phase of higher density.

It was hoped that type A stability would be found, but it was recognized that type B stability was more likely in view of the early results in which the δ phase was partially stabilized by impurities.

In the early period of the search for a stable δ phase alloy, plutonium was very scarce, and it was not possible to investigate each element independently. Instead, alloys were made which contained as many as four intentionally added alloying elements. Discrimination was used in choosing combinations of elements which would be unlikely to interfere with each other. Certain elements which were considered more promising than others were alloyed individually with plutonium. The as-cast densities were determined for all the alloys. Usually the alloys were then annealed in vacuum at 400°C, cooled rapidly, and their densities re-determined.

Alloys in which both the as-cast and annealed densities were greater than 18.0 were not considered at all promising. Alloys which had

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the ability of stabilizing the δ phase generally showed as-cast densities well below 18.0, and the annealed densities were substantially lower than the as-cast densities.

Table I reveals that six elements were found which stabilized the δ phase to some degree: aluminum, gallium, germanium, silicon, thallium, and indium. In all cases, type B stability only was observed.

Aluminum Alloys

The first element found which had a stabilizing effect on the δ phase was aluminum. Alloys from ½% aluminum* to 4% aluminum were studied. Alloys with 1½% or more aluminum could be readily stabilized as δ metal (see Fig. 1). The δ phase was stable at as low a temperature as -75°C. The metal was quite soft at room temperature and could even be hammered into a foil. These alloys showed practically no change in length on heating. The percentage change in length from room temperature is shown in the following table, and the dilatometric curves are shown in Fig. 2.

Percentage Change in Length from Room Temperature

To Various Temperatures

Temp. Range	2% Al. alloy	3% Al alloy	4% Al alloy
25° to 300°C	-.005%	+.009%	+.068%
25° to 350	-.022	+.007	+.070
25° to 400	-.055	-.050	+.070
25° to 450	-.105	-.160	+.052
25° to 550	-.242	------	-.018

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* All percentages for alloys are atomic.

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TABLE I

Densities of Alloys

Sample No.	Nominal Composition in atomic %	Densities: As Cast	Densities: After 400°C Anneal	Densities: After Holding in Ice Water
5857J-1	1% Gallium	16.67	calc. 15.80	
5857J-2	"	16.98	" 15.80	
5857P-1	2% Gallium	16.23	15.82	
5857P-2	"	16.27	15.79	
5764L-1	3% Gallium	15.93	15.75	
5764L-2	"	16.01	15.66	
7057B-1	3½% Gallium	15.92	calc. 15.70	
5057B-2	"	15.89	" 15.70	
7083A-1	4% Gallium	15.77	calc. 15.70	
7083A-2	"	15.74	" 15.70	
5557K	1% Si, Ge, Sn, Pb	16.47	16.32	17.00
5498.2AlA	½% Aluminum	17.58	17.25	17.45
5498 AlA	1% Aluminum	16.92	16.76	16.90
5536F	1½% Aluminum	16.55	16.05	16.30
5783D	1½% Aluminum	16.72	----	
5783E	1½% Aluminum	16.74	15.74	
5536E	2% Aluminum	16.01	15.80	15.98
5664G	"	16.47	15.60	
5664E	3% Aluminum	16.18	15.57	
5664C	4% Aluminum	15.93	15.59	
5596K	1% Silicon	16.82	16.63	
5664L	2.2% Silicon	16.94	15.73	
5664H	3.3% Silicon	15.79	15.49	
5664J	4% Silicon	15.89	15.44	
5764H-1	1/3% Al, 1½% Si	16.48	15.65	
5764H-2	"	16.89	15.81	
5789G	½% Al, 1% Si	16.06	15.77	
5789H	"	16.18	15.84	
5764J-1	3/4% Al, 1% Si	16.94	15.87	
5764J-2	"	16.75	15.85	
5764E-1	2% Germanium	17.85	calc. 17.80	
5764E-2	"	17.89	----	
7170E-1	3% Thallium	17.06	----	
7170E-2	"	17.16	16.64	
5857T	3% Indium	16.80	calc. 16.80	

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TABLE I, contd.

Densities of Alloys

		Densities		
Sample No.	Nominal Composition in atomic %	As Cast	After 400°C Anneal	After Holding in Ice Water
5415-25A	1% Uranium	18.65	18.46	
5857-R1	4% Uranium	19.37	----	
5857-R2	"	19.35	----	
5857-L1	8% Uranium	19.10	----	
5857-L2	"	19.06	----	
5764-N1	15% Uranium	18.0	----	
5764-N2	"	17.95	17.99	
5857-N1	25% Uranium	18.07	----	
5857-N2	"	18.07	----	
5437-MnA	1% Manganese	18.46	18.69	
5465-Co,Ni	1% Co, 1% Ni	18.12	18.40	
5465-Ti,V	1% Ti, V, Cr, Mo, Zr	18.73	18.67	
5465-FeA	1% Fe	18.38	18.44	
5529-A	1% Li	18.42	18.84	
5529-D	1% Ru, Rh, Pd	18.55	18.61	
5529-F	1% Pt, Ir	18.93	18.95	
5557-F	1% C	19.12	19.11	19.11
5557-G	1% Th	19.28	19.24	19.28
5557-I	1% Mg, Zn, Cd	18.74	18.76	18.92
5596-E	1% Cu, Ag, Au	18.88	18.82	18.75
5596-G	1% La, Ce, W	18.81	18.76	18.86
5596-I	1% Ta	19.21	19.06	
5415-3BeO	Be	19.16	----	

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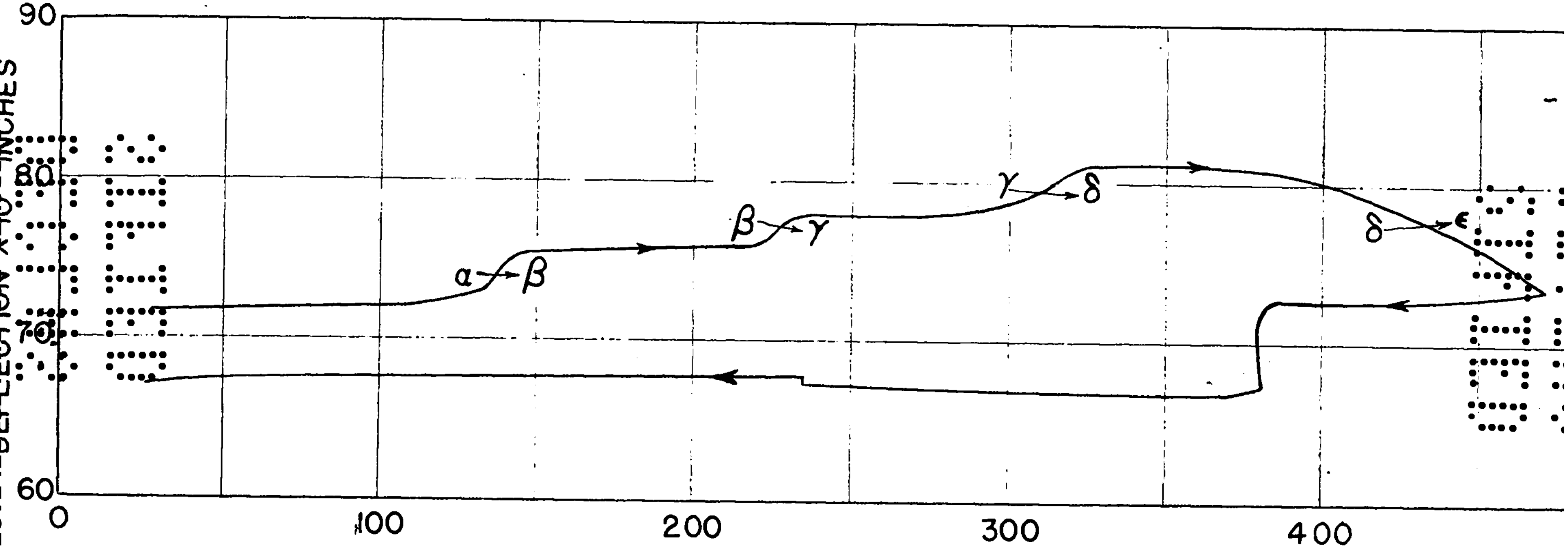

TEMPERATURE – °C

FIG I

DILATOMETRIC CURVE, 1.5% ALUMINUM ALLOY

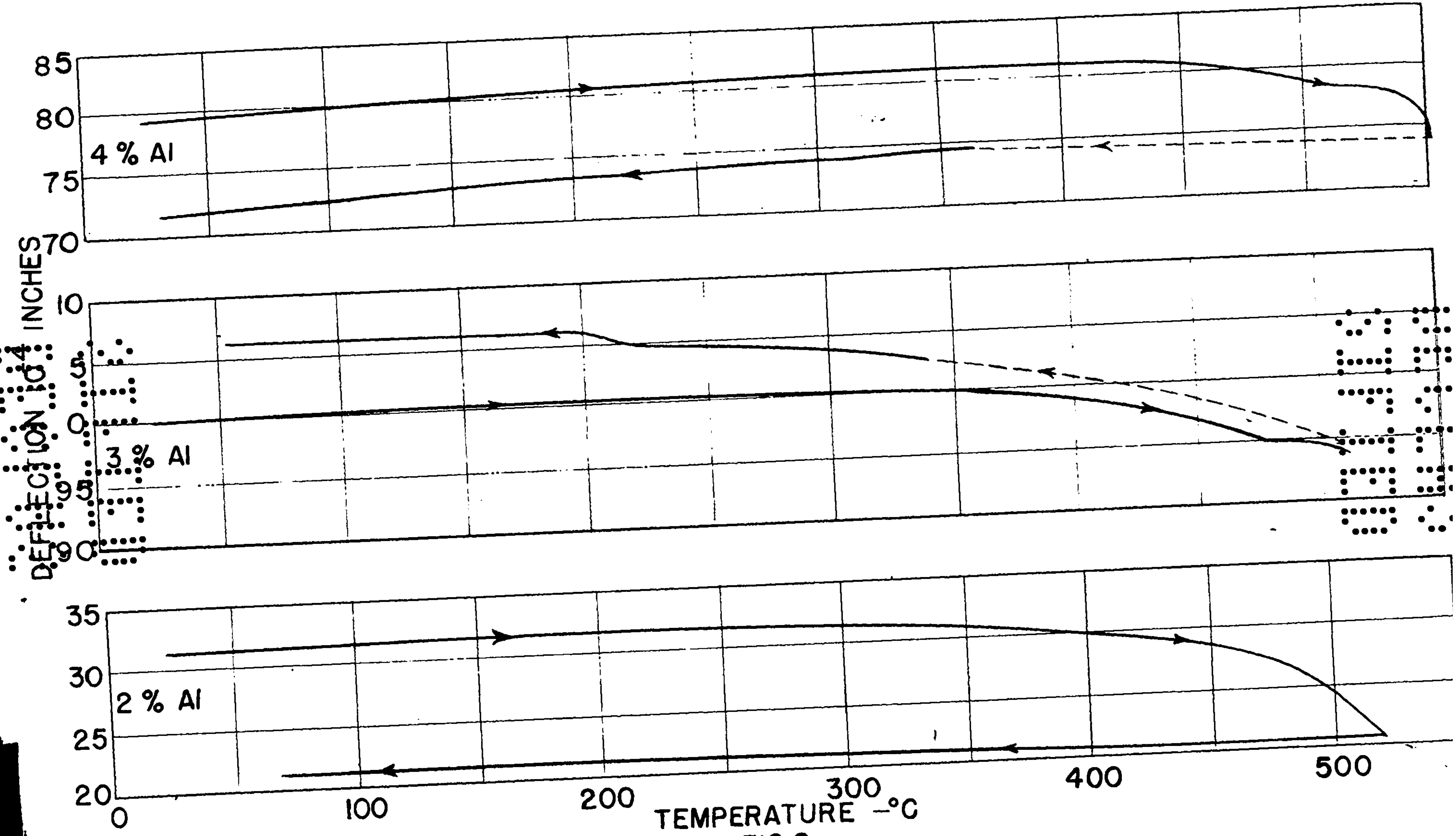

FIG 2

DILATOMETRIC CURVES, 2%, 3%, & 4% ALUMINUM ALLOYS

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This is probably the smallest linear expansion for such a large temperature range ever observed for a metal.

On annealing the 1% aluminum alloy gave a density of about 16.8 instead of 15.7 to 15.8, the density of the δ phase. This density suggests that the δ phase on cooling transforms to γ or a mixture of γ and β. Dilatometric studies have conclusively shown that this is an erroneous explanation. In the case of this alloy and of all other partially stabilized alloys, the results have been identical. The presence of small inflections in dilatometric curves at the transformation temperatures of α, β, and γ indicates that a certain fraction of δ phase has been stabilized and the remainder has transformed all the way to α, so that a partially stabilized alloy at room temperature is composed primarily of the δ and α phases. However, in some cases when such a partially stabilized alloy is heated into the β field and held for some time, the β formed from the α is stabilized so that when the alloy is then cooled to room temperature, it consists of the δ and β phases with substantially no α or γ.

A partially stabilized alloy, such as a 1% aluminum alloy, shows the $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \delta$ transformations on heating in a dilatometer. The transformations occur at about the same temperatures as for pure metal.

The only thing very unusual about them is that the $\gamma \rightarrow \delta$ transformation appears to be more sluggish as it takes place over a wider temperature range. The true equilibrium temperatures of the

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transformations have not been determined for these alloys. The dilatometer data indicate, however, that they have not been radically shifted by the alloying contents. This indicates that only type B stability is involved in these alloys.

After much work had been done on aluminum alloys, the tolerance on aluminum content for other reasons was set at about 0.75% aluminum, which eliminated these alloys from further consideration as 1½% aluminum was needed to stabilize δ.

Silicon Alloys

Alloy 5557K which contained 1% each of Si, Ge, Sn, and Pb gave an as-cast density of 16.47 and an annealed density of 16.32. It was apparent that one or more of the four elements was partially stabilizing the δ phase. Silicon and germanium were later alloyed individually with plutonium, and both turned out to be effective. The silicon was the more effective of the two. Tin and lead have not been tried as yet.

Four alloys from 1 to 4% silicon were investigated. Alloys of 2% or more suppressed the transformation of δ to α to room temperature, and consequently these alloys looked very good for a while as the tolerance for silicon was twice as great as for aluminum. However, when the stability of the alloys below room temperature was investigated, it was found that they partially transformed to α between 20°C and 10°C (see Fig. 8).

Combination Aluminum and Silicon Alloys

Combination aluminum and silicon alloys were tried in the hope that one might be found which would be within the composition tolerance

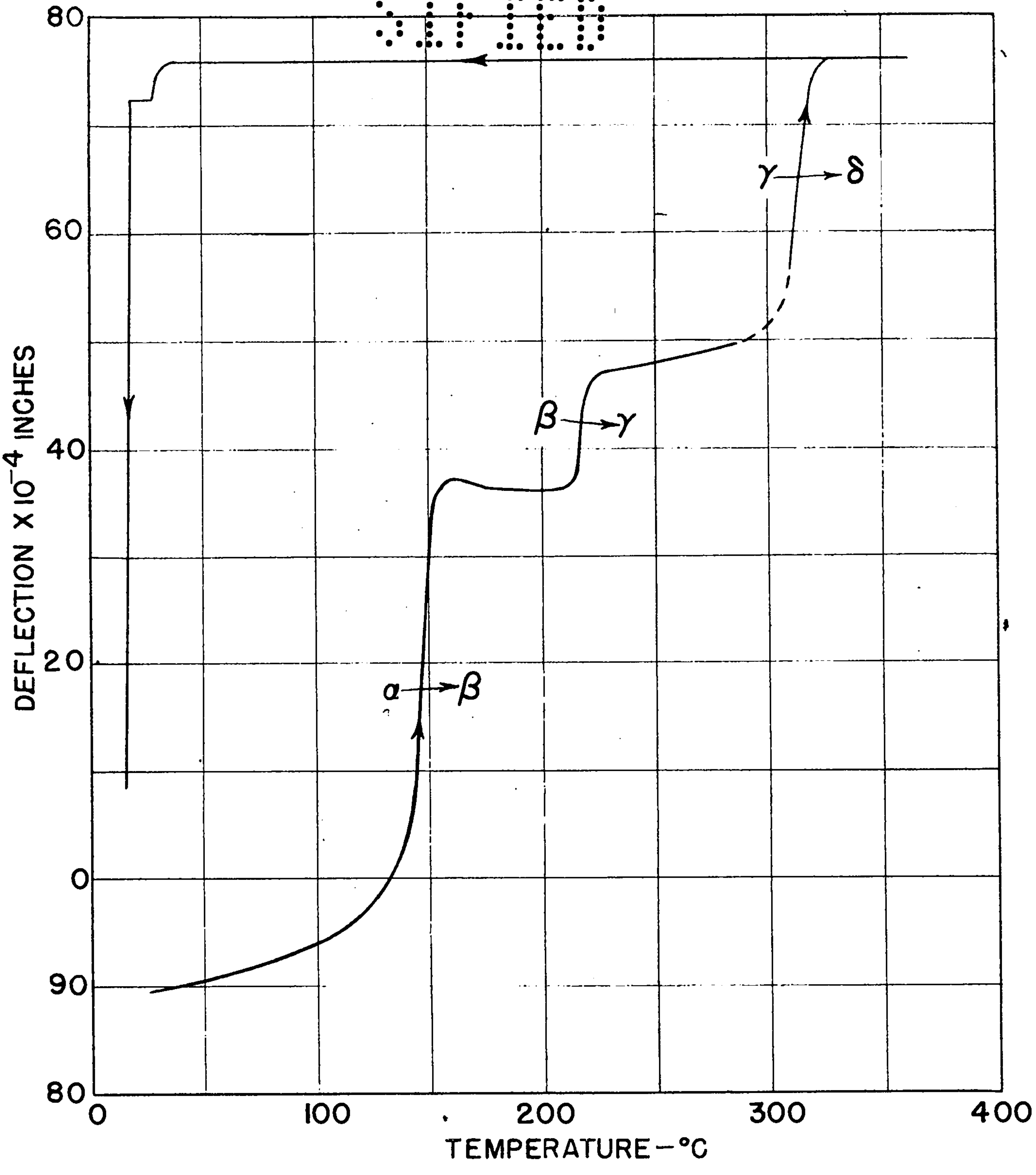

FIG 3
DILATOMETRIC CURVE, 2.2 % SILICON ALLOY

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limits and yet be as stable as the 1½% aluminum alloy.

The alloys tried were 1/3% Al, 1½% Si; ½% Al, 1% Si; and 3/4% Al, 1% Si. These three alloys behaved alike. The δ phase was stabilized down to room temperature, but in none of them was the δ phase stable down to -75°C. They all transformed between -20°C and -60°C depending on the length of anneal and on the rate of cooling.

These alloys might have proven satisfactory, but at about the same time the 3% gallium alloy was developed and proved to be much better.

Germanium Alloys

Only one germanium alloy was tried, a 2% alloy. It was not very good. The δ phase began to transform at about 100°C after annealing and ended up with the same as the as-cast density.

It is possible that a germanium alloy could have been found which would have been satisfactory, as the tolerance was higher than for silicon. However, it seemed unlikely considering the relatively high density after annealing.

Gallium Alloys

Gallium alloys looked good right from the first test. The as-cast densities were particularly good. Whereas it took 4% aluminum, which was way over tolerance for aluminum, to bring the as-cast density of its alloys down to 16.0, it took only 3% gallium, which, on the other hand, was way under its tolerance. Also, even 1% gallium stabilized the δ phase to below room temperature. This alloy transformed at -20°C.

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Alloys with 2% or more gallium did not transform even after being held at -75°C for three days (Fig. 4).

The expansion coefficient of the δ phase did not appear to be greatly influenced by the gallium content as shown in the following table.

Alloy	Expansion Coefficient x 10^{-6} (δ phase)	Average Value of Exp. Coeff. x 10^{-6} 25 to 400°C
1% Ga	.9 in/in/°C	.9
2% Ga	-9.0	-9.0
3% Ga	1.4, 2.0, 4.0	2.5
3½% Ga	3.2, .9	2.0
4% Ga	4.0, 2.0	3.0

These values were determined in the range from room temperature to 400°C. The apparent expansion coefficient of the δ phase for pure metal in the range 350 to 450°C is -20×10^{-6}.

The δ phase was stabilized in gallium alloys by annealing at 410°C for 16 hours. After such a treatment, the alloys were stable at any temperature down to -75°C, excepting the 1% gallium alloy which began to transform at about -20°C. The 2% and 3% gallium alloys were found to be stable in liquid nitrogen at -195°C. The others were not tested at this extremely low temperature.

A δ phase alloy once stabilized was partially converted to a higher density form by the application of extreme pressures; usually greater than 100,000 psi at room temperature or at dry ice temperatures. Once an alloy was partially converted to α by pressure, it could usually be further converted to α by extended low temperature treatments, preferably liquid nitrogen.

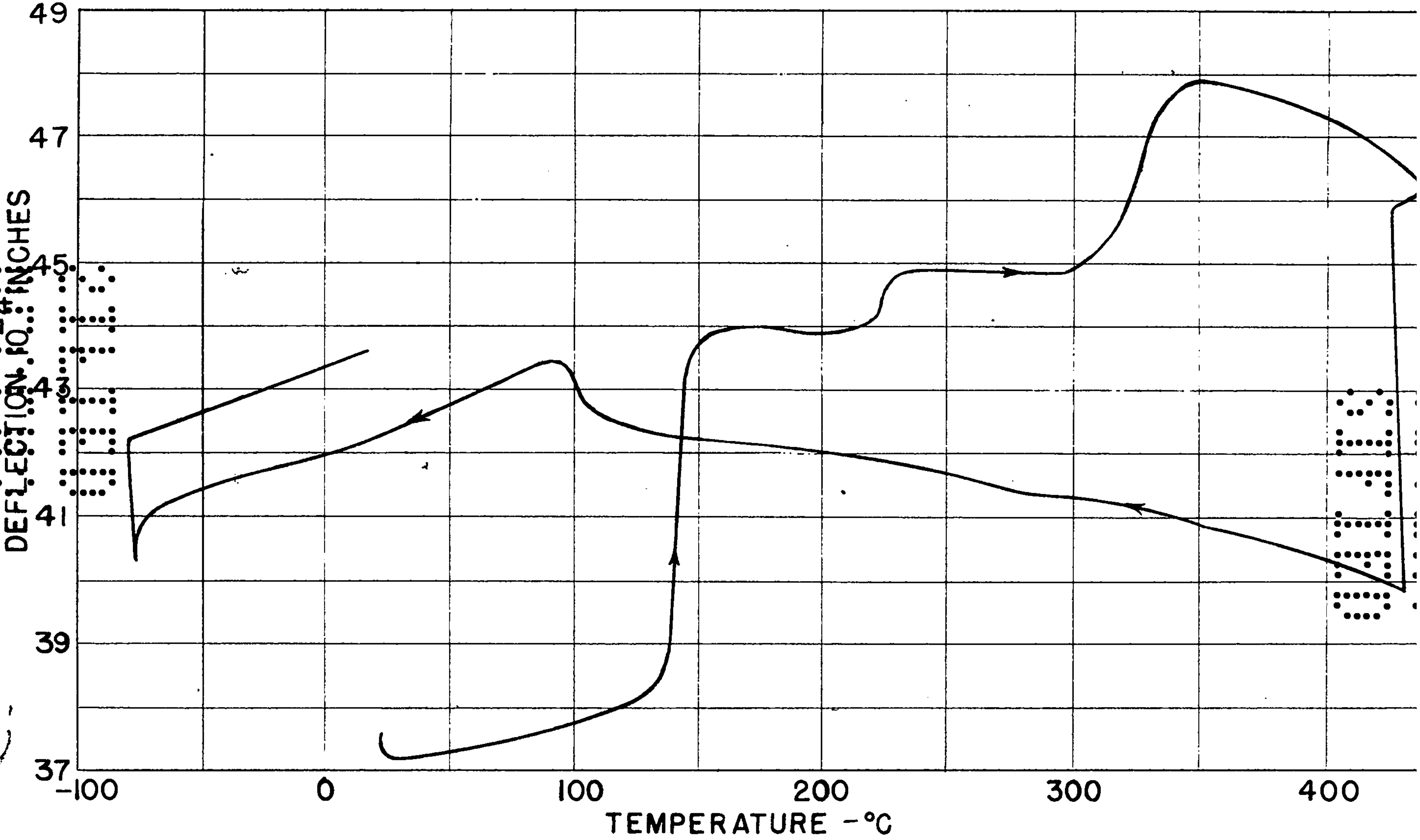

FIG 4

DILATOMETRIC CURVE, 2% GALLIUM ALLOY

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A series of tests on 18 samples of the 3½% gallium alloy was conducted to establish the stability of this alloy. A complete description of methods and results is given in Appendix I.

Indium and Thallium Alloys

Inasmuch as gallium suppressed the transformation of the δ phase to α, it was felt that the other members of its family, indium and thallium, might also, so they were tried out. Both were found to be effective but neither proved to be as good as gallium.

Uranium Alloys

Uranium was tried out in much higher concentrations than the other elements, for had it proved effective, U^{235} could have been used as the alloying metal. Consequently there would have been no inert material added.

In the case of uranium, a very definite shift in the transformation temperatures occurred. This is shown in the following table for pure metal, 4% U alloy, and 8% U alloy.

Transformations	Pure Metal	4% U Alloy	8% U Alloy
$\alpha \rightarrow \beta$	127-147°C	122-160°C	120-154°C
$\beta \rightarrow \gamma$	218-228	271-292	286-298
$\gamma \rightarrow \delta$	302-338	465-480	495- ?
$\delta \rightarrow \epsilon$	470-496	?	?

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The 15% U and 25% U alloys showed only one transformation at 280-330°C and 295-350°C respectively. It was not clear which transformation this was, but it appeared to be the $\beta \rightarrow \gamma$. In any event, the higher temperature phase was readily supercooled to room temperature.

One rather remarkable fact relative to the transformations in uranium alloys was that where the $\gamma \rightarrow \delta$ reaction occurred it was reversible with practically no hysteresis.

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Appendix I

STABILITY TESTS ON GALLIUM ALLOYS OF PLUTONIUM

A series of tests was conducted on 18 samples of 3% Ga content to determine the range of density stability of the alloy.

A comprehensive outline of the various tests and their results as to density will be seen in Table I.

The only significant changes in density, of the order of 0.2 g/cc, were accomplished by applying high pressures of 100,000 to 200,000 pounds per square inch at temperatures of 24°C to -50°C. It is peculiar that two of the six samples, all supposedly identical, subjected to high pressure, did not change in density by 0.2 g/cc until pressed at 200,000 pounds per square inch at -50°C, while the other four specimens changed in density by 0.2 g/cc under less severe conditions.

The important result of the tests is found in the unchanging densities of those samples given liquid air treatment, a 48 hour test at -180°C. One must believe, for all practical purposes, that this alloy is in a well-stabilized delta form.

For the high temperature annealing, the samples were sealed in evacuated glass tubes which, in turn, were enclosed in appropriate metal containers. These were placed in small controlled temperature resistance furnaces and drying ovens. For the 410°C anneal, the metal container consisted merely of a single copper cylinder closed at both ends with copper discs with a step fit, holding one glass tube at a time. For the 70°C and 100°C anneals, the metal containers were aluminum cy-

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lindrical boxes 4" in diameter. The bottoms of these boxes were 3½" thick and were drilled to accommodate four glass tubes simultaneously. A thermocouple well was drilled into these aluminum boxes, and the temperature inside was continuously controlled.

For the low temperature anneals, the specimens were placed in glass bottles covered with screw caps and sealed in paraffin. One set was maintained at 0°C by placing the bottles in a Dewar flask filled with cracked ice, and the others were held at -50°C in a Dewar flask filled with dry ice.

All the specimens were from 21 to 26 grams each, and each was stamped with its individual number. If, during the course of the test, any sample appeared to accumulate too excessive a coating of oxide, it was removed electrolytically.

All densities were determined by immersion in bromobenzene.

Since the plutonium samples were thermally active, a temperature-density chart for bromobenzene was made by weighing a plumb bob of known volume in the liquid at various temperatures. The density of each plutonium sample was then calculated for the temperature of the liquid at the time the weight of the immersed sample was recorded.

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TABLE II

Sample No.	As Cast *	17 hr. 410°C	17 hr. 450°C	10,000 psi, 24°C	100,000 psi, 24°C	17 hr. 450°C	4 hr. liq. air -180°C	136,000 psi, 24°C	48 hr. liq. air -180°C	48 hr. -50°C to 70°C cyclic	136,000 psi, dry ice -50°C	200,000 psi, dry ice -50°C	48 hr. -50°C to 70°C cyclic
7063-B #1	15.88	15.71	Metal sent to recovery after melting in die										
2	16.13	15.74		15.79		15.77	Held at 70°C for 40 days--no change						
3	15.87	15.68		15.79		15.76	Held at 100°C for 36 days--no change						
4	15.90	15.72		15.73		15.74	Held at 0°C for 27 days, 250°C for 2 days--no change						
5	15.83	15.66		15.72		15.70	Held at -50°C for 37 days--no change						
6	15.86	15.72		15.83		15.73				15.73			
7092-A #7	15.81	15.72		15.72		15.73	Held at 24°C for 32 days--no change						
8	15.83		15.75	15.74		15.75	Held at 70°C for 40 days--no change						
9	15.82	15.75		15.75		15.75	Held at 100°C for 40 days--no change						
10	15.78	[illegible]	15.74	15.74		15.74	Held at 0°C for 27 days, 300°C for 2 days--no change						
11	15.99	15.75		15.77		15.76	Held at -50°C for 37 days--no change						
12	15.88		15.76	15.77		15.76	Held at 150°C for 17 hours--no change						
13	15.80		15.76	15.75	15.75		15.75	15.77	15.76		15.81	16.02	Held at 24°C for 25 days--no ch.
14	15.84		15.71	15.72	15.84		15.85	16.03	Held at 100°C for 37 days--no change				
15	15.84		15.70	15.70	15.71		15.71	15.77	15.77		15.93	Held at -50°C for [illegible] days --no change	
16	15.77		15.66	15.74	15.92		15.94	Held at 70°C for 40 days--no change					
17	15.82		15.65	15.67	15.72		15.71	15.75	15.76		15.84	15.97	15.95
18	16.01		15.73	15.76	15.93		15.93	Held at 0°C for 75 days--no change					

7063-B - 71/2% Ga alloy
Analysis!! Ca - 10,000 ppm
Si - <200
Li - ND<1.2
Be - ND<0.12
Na - ≤10
Mg - 3
Al - 25
K - ND<49
Ca - 4

7092-A - 3% Ca alloy
Analysis!! B - 0.7 ppm
Li - ND<0.85
Be - ND<0.17
Na - 8.5
Mg - 6.8
Al - 13.6
K - ND< 17.0
Co - 5.1
Ba - ND<1.7
La - ND<1.7
Ce - ND<170.0
Mo - ND<20.0
Ga - 10,000

[redacted]

*All figures are densities in g/cc, accuracy within 0.05 g/cc.

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