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BARIUM-TIN ALLOYS

BY

JAMES RICHARD WHANGER

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

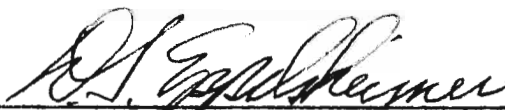
Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1949

Approved by



D. S. Eppelsheimer
Professor of
Metallurgical Engineering

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INTRODUCTION

Barium was discovered by Davy in 1808 by electrolyzing the fused mixtures of barium oxide and mercuric oxide. A mercury amalgam was obtained that gave the pure metal when the mercury was distilled away. Although barium minerals are plentiful in nature, there is no cheap method now available for the production of this metal. The present procedure is to place a mixture of barium oxide and aluminum in a metal bomb.⁽¹⁾ A vacuum is applied and the tempera-

(1) Elder, Albert L., Textbook of Chemistry, N. Y., Harper and Brothers, 1941, p. 529.

ture is raised to 1000°C. There is an equilibrium reaction, whereby barium and alumina are formed. Since barium has the higher vapor pressure, it distills and is condensed on a cold surface in an inert atmosphere.

The use of barium in the metallic state has been limited to small amounts used in bearing metals, spark-plug points, "getters" in radio tubes, and as a scavenger in the refining of copper. The chemical activity of barium is largely responsible for the limited metallurgical uses of this metal. With the exception of lead and magnesium, very little work has been done on the binary alloy systems of barium. Ray and Thompson in 1929⁽²⁾ studied barium alloys

(2) Ray, K. W., and Thompson, G., Thesis, State University of Iowa, Iowa City, Iowa. 1929.

of tin prepared by electrolysis of fused salts, but their

method was applicable to alloys of low barium content only.

The large atomic diameter of 4.48\AA (3) makes barium

(3) Goldschmidt, V. M., *Über Atomabstände in Metallen*,
Z. Physik. Chem., Vol. 133, p. 397, 1928.

an unusual element. The alloys of this type element, with those of the B family metals, form many intermetallic compounds. To discover these intermetallic compounds and note their properties will add to the knowledge available for the study of phase diagrams. Attempts are being made to formulate the underlying principles which cause alloy systems to take their particular form.(4)

(4) Hume-Rothery, W., *The Metallic State*, Oxford, 1931.

Ray and Thompson state that when they were grinding their samples in a mortar they observed flashes of light. On the basis of this and observations from similar alloy systems(5), it was thought that these alloys might have

(5) Eppelsheimer, D. S., Unpublished work on Pb-Zr.

pyrophoric possibilities.

With these thoughts in mind, the author attempted to produce alloys of barium and tin using metallic barium and barium hydride. Also, an attempt was made to study the phase diagram using thermal analysis and X-ray investigation.

REVIEW OF LITERATURE

A review of the literature reveals that little work has been done on alloys of high barium content.

Most of the work with barium alloys has been on the very low barium end of the binary systems. These alloys have been used as bearing metals. One of the most important of these alloys is Frary metal⁽¹⁾, which contains

(1) Cowan, W. A., Simpkins, L. D., and Hiers, G. O., Chem. Met. Eng. 25, 1181 (1920).

lead, barium, and calcium. This alloy was made by the electrolysis of a fused mixture of calcium chloride and barium chloride with molten lead as the cathode. The alloys contained from 0.5 per cent to 2.0 per cent barium and from .25 to 1 per cent calcium.

A barium-tin alloy of low barium content has also been made electrolytically by Charles Vickers at Columbia University.⁽²⁾

(2) Vickers, Charles, Trans., Am. Electrochem. Soc. 40, p. 15 (1921).

K. Jellinik and J. Wolff have prepared alloys of tin with barium and potassium electrolytically.⁽³⁾

(3) Jellinik, K., and Wolff, J., Zeit. Anorg. Chem., 146, p. 329 (1925)

Ray and Thompson⁽⁴⁾ used an electrolytic method to

(4) Ray and Thompson, op. cit., p. 1.

prepare barium-tin alloys up to 27 per cent barium. Their method consisted of the electrolysis of an eutectic mixture of potassium chloride and barium chloride over molten tin in a chrome plated iron crucible. The molten tin was made the cathode and a carbon electrode was extended into the salt bath to serve as the anode. On electrolysis, chlorine was given off at the anode, while barium was deposited at the cathode which became associated with the molten tin.

Thermal analysis was performed on the alloys using a chromel and nichrome thermocouple. Melting was done in pyrex test tubes under kerosene. With this technique the low barium end of the phase diagram was developed to 27 per cent barium.

A THEORETICAL STUDY
OF Ba-Sn ALLOYS

When considering a binary alloy system, the first important fact to determine is whether the alloying metal is soluble in the host metal in the solid state. The next factor is whether any intermetallic compounds are formed between the alloying metals. After these results are considered it is desirable to determine if there are any eutectics, peritectics, or monoeutectics formed and at what compositions and temperatures.

In the formation of binary alloys certain rules seem to govern the types of alloys formed. These rules, as set forth by Hume-Rothery⁽¹⁾, are as follows: 1. The concep-

(1) Hume-Rothery, W., The Structure of Metals and Alloys, The Institute of Metals Monograph No. 1, 1947, London.

tion of atomic size-factor, 2. The electrochemical factor, 3. Relative valency effect, 4. Crystal structure.

When a substitutional solid solution is formed there will be less distortion of the primary lattice if the atomic diameters of the two metals are approximately the same size. When the atomic sizes of the host and solute metals differ by less than 15 per cent, the size factor is favorable for the formation of solid solutions. If the atomic sizes exceed this limit, the solubility is restricted according to the amount the limit is exceeded.

The electrochemical effects are very powerful factors in determining solid solubility. The electrochemical factor is determined by the difference between the solvent and the solute metals in the electromotive series. Generally speaking, the greater the difference between the two metals, the greater is the tendency for the formation of stable compounds. The tendency is for metals of the same valence as the host metal to be more soluble. Also, a metal with a low valence will tend to dissolve one of higher valency more than vice versa.

The crystal structure of the two metals affects the limit of solubility. If the crystal form of the solute metal is different from that of the host metal, then only a limited solubility will be expected. The more dissimilar the crystal structure, the more limited will be the range of solid solution.

These rules now will be applied to the Ba-Sn system: The atomic diameter of barium is 4.48\AA , while the atomic diameter of tin is 3.08\AA .⁽²⁾ Considering barium as the host

(2) Goldschmidt, V. M., *Über Atomabstände in Metallen*, Z. physik. Chem., Vol. 133, p. 397, 1928.

metal, the atomic size difference is $\frac{3.08 - 4.48}{4.4} = -31.2\%$.

Considering tin as the host metal, the atomic size difference is $\frac{4.48 - 3.08}{3.08} = +45.4\%$.

Thus the atomic size factor is unfavorable for solid solutions of tin in barium or barium in tin.

When the electrochemical series of the elements is examined, barium will be found near the top of the series. Tin is found very close to hydrogen which is considered to be at the center of the series. This great difference in the electrochemical series will be reflected in the binary system by the formation of relatively stable compounds.

The normal valence of barium is two and that of tin is four. Thus, the relative valency effect is against the formation of large amounts of solid solubility. This would indicate that there would be a greater tendency for some solid solubility to occur in the barium rich portion of the system.

The room temperature crystal structure of barium is body-centered-cubic, while the room temperature structure of tin is body-centered-tetragonal. This difference in crystal structure would tend to limit any solid solutions if any were formed.

Another factor that has an influence on the alloying nature of metals is the entropy.⁽³⁾ It has been observed

(3) Whanger, J. R., The Alloying Nature of Nickel, Dissertation, Missouri School of Mines and Metallurgy, Rolla, Mo., 1948.

that metals which show complete solid solubility have entropy values very close together. This relationship is very much like the size-factor since it is a condition that must be fulfilled before complete solubility can be considered;

yet the fulfillment of this condition does not insure complete solid solubility. The entropy value for barium is 40.7, while for tin it is 12.3.⁽⁴⁾ This is a very large

(4) Kelley, K. K., Contributions to the Data on Theoretical Metallurgy, U. S. Bureau of Mines, Bulletin 350, 1932.

difference which would decrease the likelihood of any sizeable amount of solid solubility between barium and tin.

From a consideration of the factors listed above, it would appear that the system of barium-tin will consist of practically no solid solutions on the high tin side, and very little if any on the high barium side of the diagram. However, these factors indicate that there would be a strong tendency for relatively stable compounds to be formed between barium and tin.

PREPARATION OF ALLOYS

In order to produce any alloys of barium, it was known that some protection would be needed to keep the barium from reacting with the oxygen and nitrogen of the air. The first attempt to produce alloys of barium and tin was to use lump BaH_2 and tin. Chemical analysis of the materials used is shown in Table I. The BaH_2 decomposes at $675^\circ C$ into H_2 and Ba. By holding this mixture at a temperature above this value, the hydrogen was to be given off leaving the barium free to alloy with the molten tin. This charge was put into a graphite crucible under a salt bath for a cover. The salt bath was an eutectic mixture of KCl and $BaCl_2$ (45 per cent $BaCl_2$). This charge was heated in a muffle furnace to $900^\circ C$ and held at that temperature for two hours. Experiments were made using this method, but only small amounts of barium alloyed with the tin.

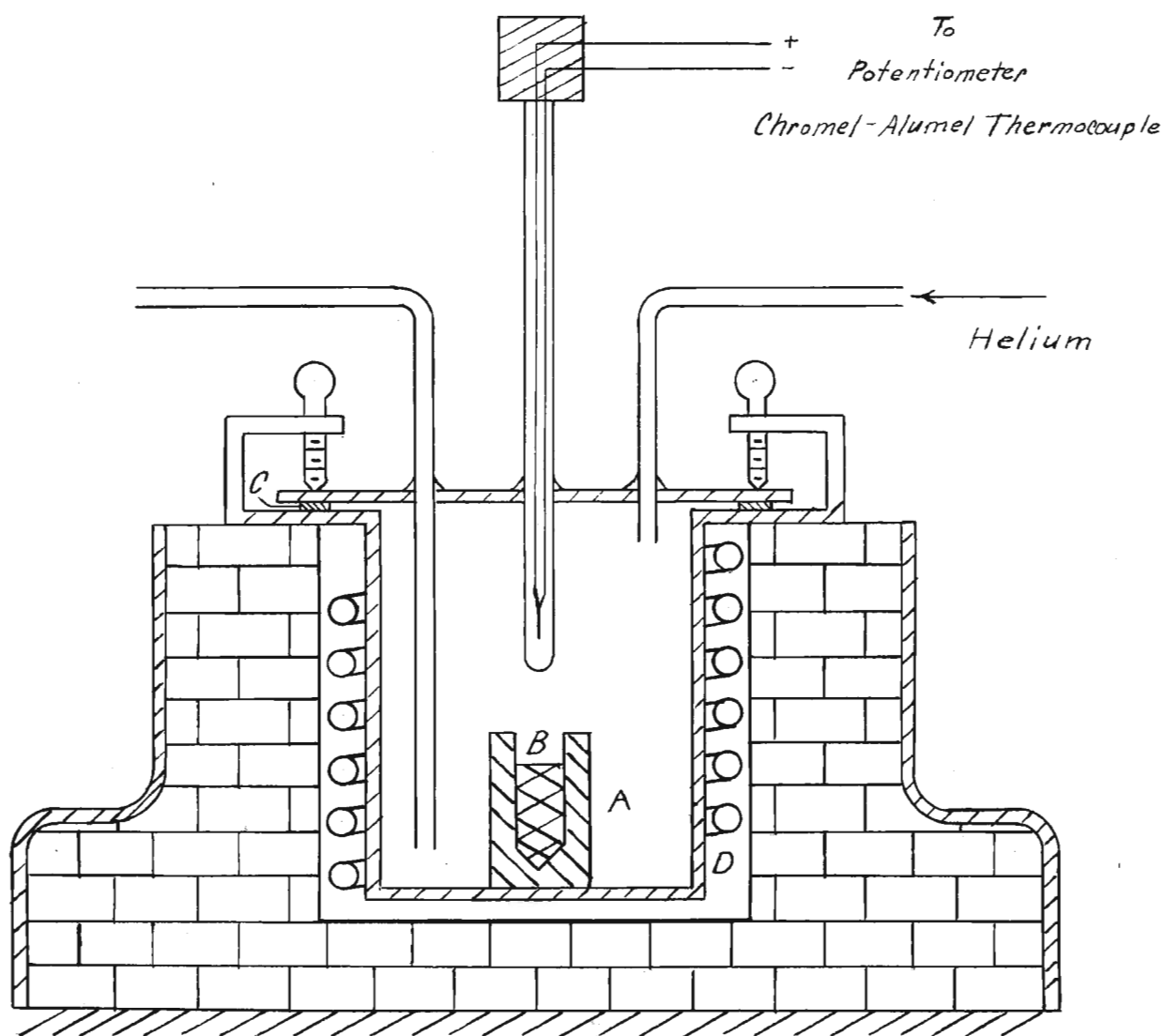
This technique was altered by using metallic barium and tin under the salt bath. While more barium alloyed with the tin (15 per cent), this method was not satisfactory because the resulting alloy still had considerably less barium in it than was added.

In order to produce alloys of a greater barium content, and to be able to put a known amount of barium into the tin without loss, a method using an inert atmosphere was devised. The laboratory setup for this method is shown in Figure 1. This gas-tight retort was heated by means of

TABLE I
CHEMICAL ANALYSIS OF MATERIAL USED

	Sn	Pb	Sb	Cu	As
Sn (Belmont Virgin Pig)	99.85				
Sn (Charles Hardy Powder)	99.80	.02	.037	.025	.02
	Ba			H ₂	
BaH ₂ (Metals Hydrides)	97.58			1.42	
Ba (King Laboratories)	99+				

FIG. 1 HELIUM ATMOSPHERE SET UP FOR
PREPARATION OF Ba-Sn ALLOYS



- A- Graphite Crucible
- B- Barium-Tin Charge
- C- Asbestos Rope
- D- Heating Element

a Lindberg pot furnace. Photographs of the retort and the complete furnace setup are included in Figures 2 and 3. The first series of alloys were made keeping a positive pressure of helium throughout the heating and cooling. In melting these charges, a temperature of 921°C was reached. The compositions of the alloys are shown in Table II. It is obvious that by this method alloys of any composition could be made, although the per cent obtained is not very satisfactory. This yield was improved by using taller crucibles and charging the barium metal in a different manner. It consisted of compressing the barium into small cylinders one and one-fourth inches in diameter, which was the same size as the hole in the carbon crucibles. These pellets were compressed by means of a hand-operated hydraulic press at 3000 pounds per square inch. These samples were melted in the same manner at a temperature of 963°C with a helium atmosphere and the results are given in Table III. These data show that the use of barium compacts prior to melting is very effective in increasing the per cent yield of the high barium alloys. Sample No. 28 was made by using BaH_2 and although the recovery is good, the alloy was quite porous and alloying was not as complete as with the samples made from metallic barium.

The pyrophoric nature of the barium-tin system was definitely established as the alloys No. 16 and No. 19 gave off white sparks when scratched with a knife blade. When scraped with a hack saw blade showers of hot sparks

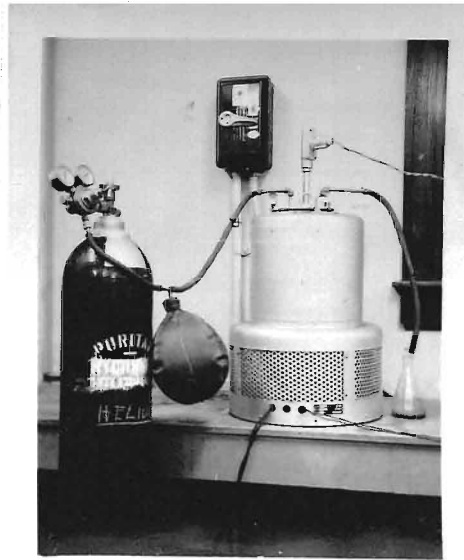


Figure 2. Helium Atmosphere Furnace
Set up for Operation

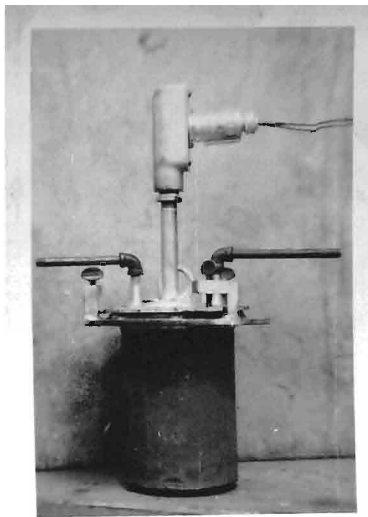


Figure 3. Closeup of Retort Used in
Furnace

TABLE II
 DATA FOR HELIUM ATMOSPHERE PREPARATION
 OF Ba-Sn ALLOYS

Melting Data				Results			
Sample No.	GmBa	GmSn	%Ba	Total Weight	Weight of Resulting Alloy	%Obtained	%Ba
16	24	9	73	33	11	33	72.2
18	11	20	35	31	Boiled over	0	
19	21	4.5	82	25.5	8.25	32	74.8
20	8.1	21.9	27	30	17	56	12.9
21	4	26	13.5	30	29	96.5	13

TABLE III
 DATA FOR HELIUM ATMOSPHERE PREPARATION
 of Ba-Sn ALLOYS USING COMPRESSED BARIUM PELLETS

Sample No.	Melting Data			Results			
	GmBa	GmSn	%Ba	Total Weight	Weight of Resulting Alloy	%Obtained	%Ba
17	18	13	58	31	24.5	82	30.1
24	27.5	31.5	47	5.9	34.5	59	33.4
23	31.7	6.5	83	38.2	28.5	75	75.5
25	18	35	34	53	18	34	39.3
26	31	31	50	62	37	60	44.0
27 _A	32	28	53	60	42	83	69.5
27 _B	32	28	53	60	8	83	95.2
28	22	33	40	55	54	98	39.4

were given off. Sample No. 27 showed some very interesting properties. There was segregation and the top part of the alloy had the best sparking characteristics of any of the alloys. This is the sample known as No. 27_A.

The bottom part of this alloy (No. 27_B) sparked only a little. However, in this portion there were two small cavities filled with perfect crystals. These resembled drusy cavities. The crystals were cubic and corroded very rapidly. Figure 4 was a perfect cube, but the time needed to focus the camera was enough to allow the crystal to crack by corrosion. Figure 5 shows a section relatively free from oxidation, while Figure 6 pictures the cube in Figure 5 with greater magnification.

These cubes in Alloy No. 27_B may have been caused from one of three things: (1) pure barium (body-centered-cubic system), (2) a solid solution of a small amount of tin in barium, or (3) an intermetallic compound of tin and barium. The composition as shown in Table III rules out the third possibility. The crystals were so small that it was impossible to take only the cube for analysis. Therefore, the cubes could be 100 per cent barium in a ground mass of barium tin alloy. This does not rule out the second possibility, and the fact that the material was hard would tend to substantiate the presence of an alloy because barium is very soft and ductile.

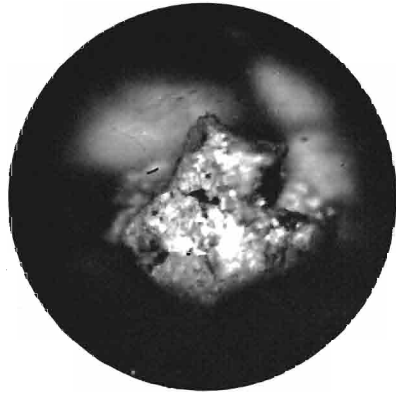


Figure 4

40X

Photograph of a segregated cube cracked
by oxidation.



Figure 5

40X

Segregated cubes relatively free from oxidation.

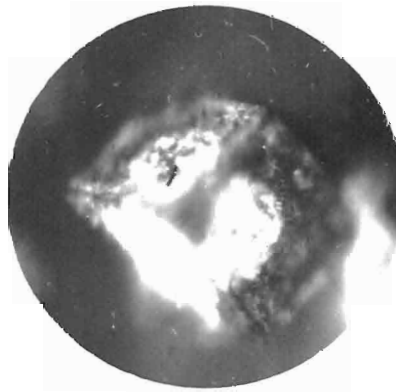


Figure 6

100X

Single cube from Figure 5 with greater magnification.

THERMAL ANALYSIS

In an effort to use thermal analysis on the barium-tin alloys, several methods were tried before a satisfactory technique was devised. The first was to put a few drops of kerosene over the alloy in a quartz tube and rely on the evaporation to furnish an inert atmosphere of hydrocarbons. With high barium alloys this was not enough protection. Next, a salt bath (eutectic mixture of BaCl_2 and KCl) was tried, but the alloy oxidized before the salt melted. A combination of these two methods was tried and still the high barium alloys oxidized instead of melting.

A new method was devised, whereby the metal was protected during the heating stage, as well as while it was molten. This system is shown in Figure 7. It will be noticed that a differential thermocouple was employed. For a metal with a relatively high melting point, barium has a small heat exchange when the molten metal solidifies. For this reason the differential thermocouple was constructed.(1)

(1) U. S. Bureau of Standards, Pyrometric Practice, Technologic Paper No. 170, p. 202, 1921.

The data from a typical cooling curve are included in Table IV along with that from a differential thermal analysis. A normal cooling curve is plotted in Figure 8 from this data. Figure 9 shows the differential cooling curve for the same sample. The ultimate refinement in thermal

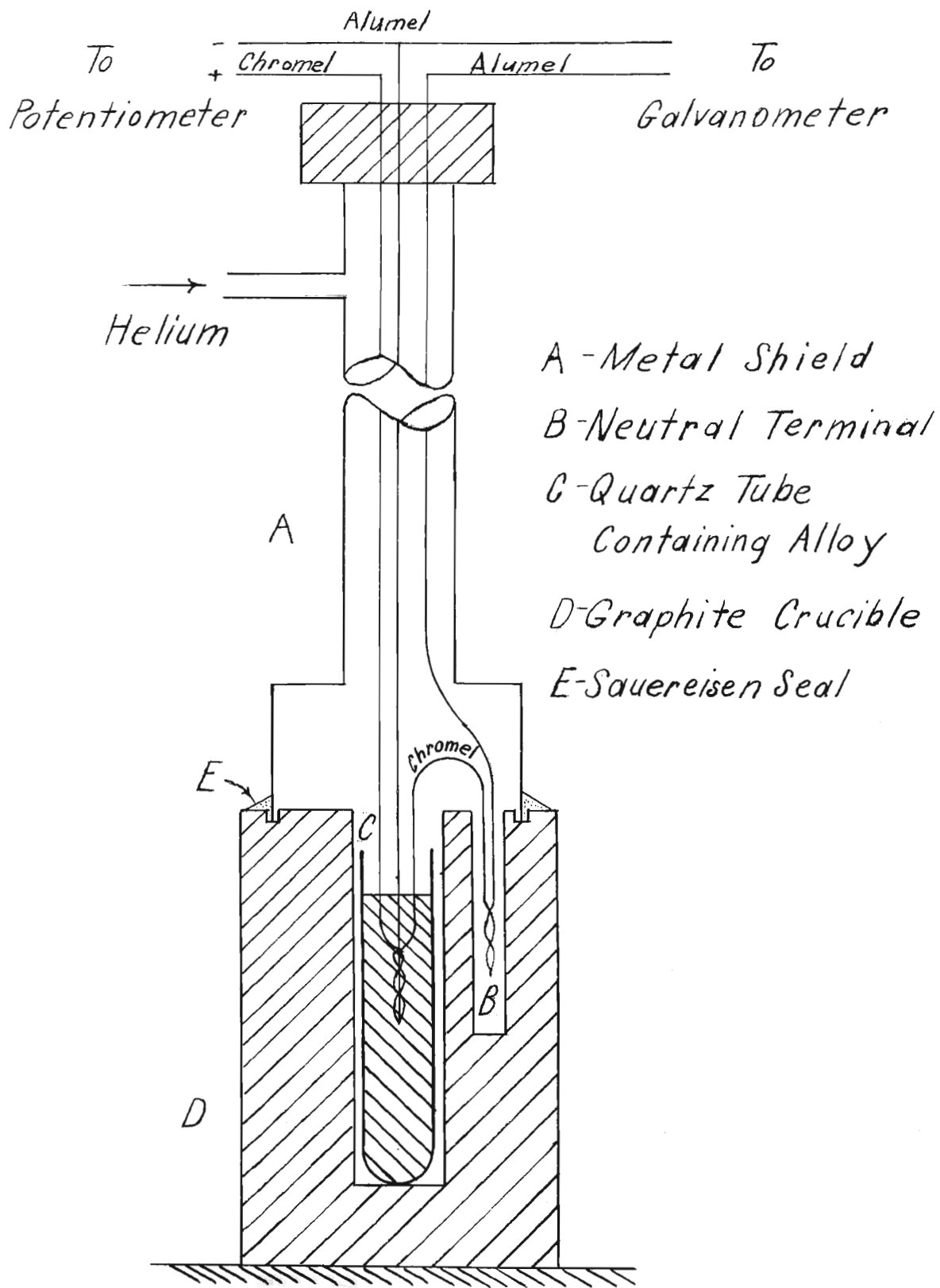
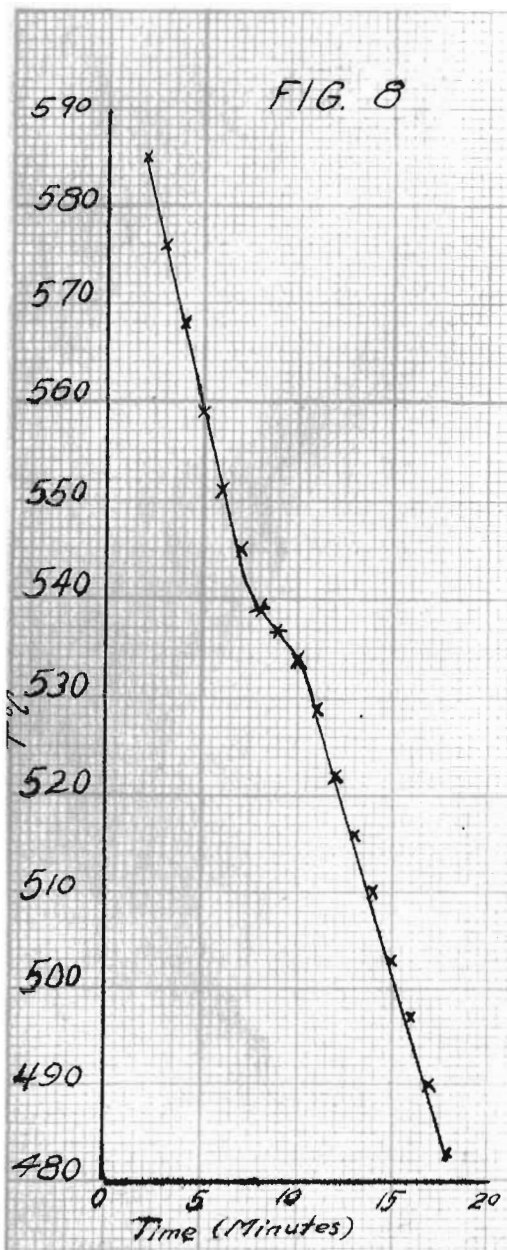


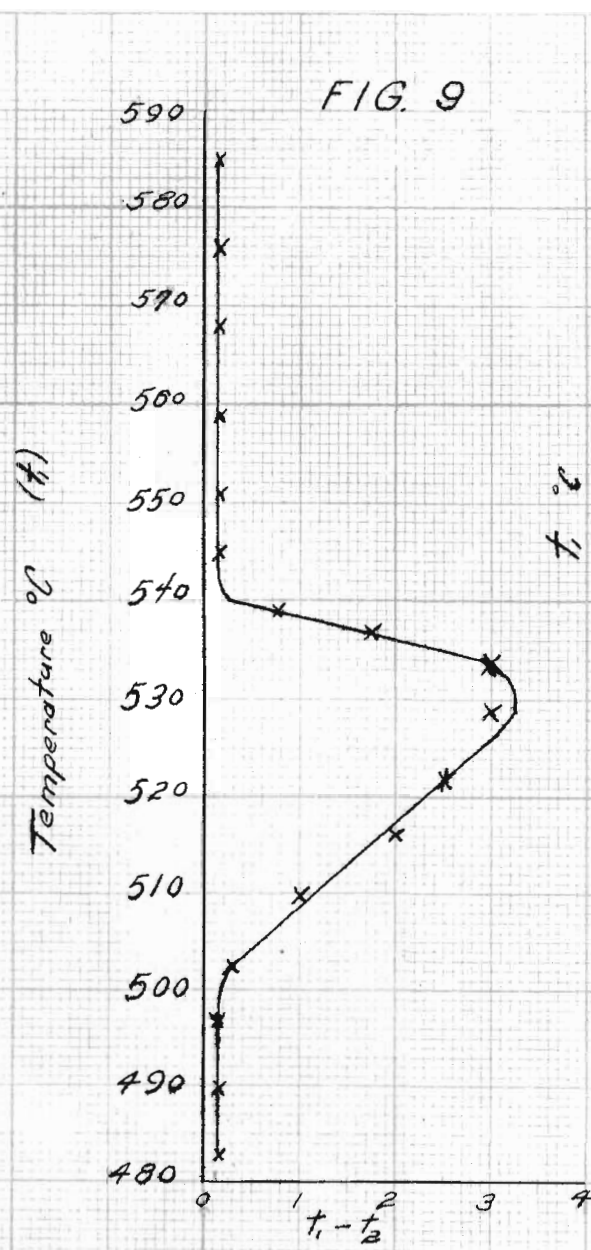
FIG 7 METHOD FOR THERMAL ANALYSIS
 OF HIGH BARIUM ALLOYS

TABLE IV
TYPICAL COOLING DATA

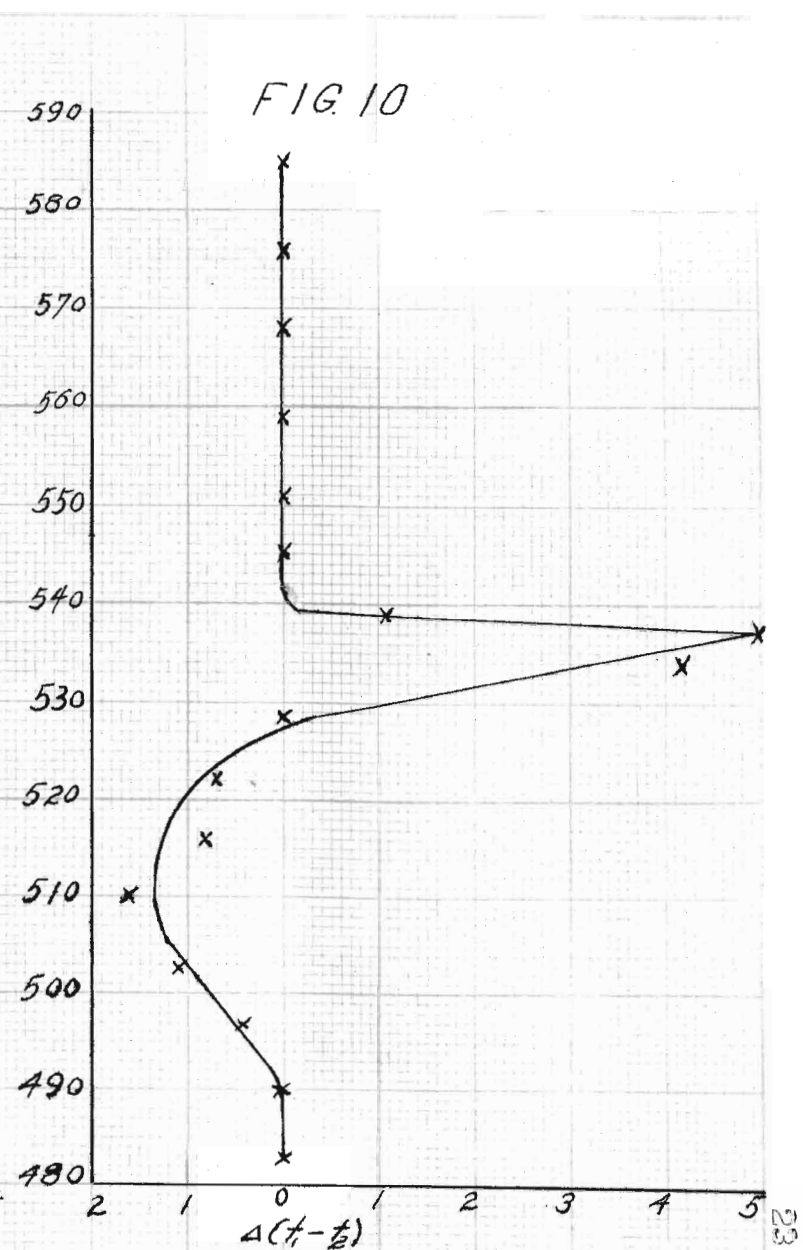
Time	T_1 °C	(Galvanometer Deflection) $T_1 - T_2$	ΔT_1	$\Delta (T_1 - T_2)$	$\frac{\Delta (T_1 - T_2)}{\Delta T_1}$
1	595	1 8			
2	585	1 8	10	0	0
3	576	1 8	9	0	0
4	568	1 8	8	0	0
5	559	1 8	9	0	0
6	551	1 8	8	0	0
7	545	1 8	6	0	0
8	539	3 4	6	5 8	.104
9	537	1 3 4	2	1	.500
10	534	3	3	1 1 4	.416
11	529	3	5	0	0
12	522	2 1 2	7	-1 2	-.071
13	516	2	6	-1 2	-.083
14	510	1	6	-1	-.167
15	503	1 4	7	-3 4	-.107
16	497	1 8	6	-1 4	-.041
17	490	1 8	7	0	0
18	483	1 8	7	0	0
19	447	1 8	6	0	0
20	471	1 8	6	0	0



Cooling Curve



Differential Cooling Curve



Derived Differential Cooling Curve

analysis is the derived differential curve⁽²⁾ shown in

(2) Burgess, G. K., Bureau of Standards Scientific Papers, No. 99, 1908.

Figure 10. This curve was drawn from the same data as the differential curve, but it has employed the good points of the other two methods. The derived differential cooling curve is essentially a plot of the change of slope of the differential curve versus temperature. Thus, if T_1 is the temperature of the material being investigated and T_2 the temperature of the neutral body, the derived differential is the graph of $\Delta(T_1 - T_2) / \Delta T_1$ versus T_1 . The advantages of this method are the amplification of transformations and the smoothing out of other irregularities.

The equipment shown in Figure 7 consists of a standardized chromel-alumel thermocouple, a Leeds and Northrup Portable Precision Potentiometer, and a Fisher low resistance d'Arsonval galvanometer. With this setup several runs were attempted using pre-alloyed samples. The one-sixteenth inch lumps of alloy were placed in the quartz tube and the system was flushed out with helium. The metal shield was sealed to the graphite crucible with sauer-eisen, and an inert atmosphere was maintained. The charge was heated in the Lindberg pot furnace to 1000°C, and an attempt was made to obtain cooling data. These runs were unsuccessful because the alloys oxidized and

sintered instead of melting. The pre-alloyed samples had formed oxides and perhaps adsorbed some gas before the melt was attempted. The only alternative was to produce the alloys in contact with the thermocouple while in an inert atmosphere, and obtain the thermal data by cooling this melt.

This was accomplished by mixing powdered tin and powdered BaH_2 in the desired ratio and pouring them into the quartz tube. The shield was then sealed to the graphite crucible and helium introduced as before. When this was attempted it was noticed that during heating the temperature of the neutral junction surpassed that of the working junction. This was due to the rapid heating from the coils of the furnace first striking the outside of the crucible where the neutral junction was located. However, at about $900^\circ C$ the temperature inside the quartz tube surpassed that of the neutral body even though the neutral body was closer to the source of heat. This was due to heat being evolved during the formation of intermetallic compounds inside the quartz tube. The samples were held at 1050° to $1100^\circ C$ until the two junctions reached equilibrium. This meant that the formation of intermetallic compounds was complete. The thermal data was then obtained during the cooling of these alloys.

The barium-tin diagram was examined by Ray and Thompson⁽³⁾ up to 27 per cent barium. In general their work

(3) Ray and Thompson, op. cit., p. 1.

was assumed to be correct by this investigator. Several check runs were made to confirm the more important parts of the low barium portion of the diagram. The incongruent melting point of BaSn_5 was found to be $422 \pm 1^\circ\text{C}$ which was in agreement with the results of Ray and Thompson. However, with very low barium concentrations the separation of tin came at 226°C instead of at 232°C , which is the melting point of pure tin. This would suggest the possibility of an eutectic at an extremely low barium content.

With higher barium alloys the strongest heat exchange came at $537 \pm 3^\circ\text{C}$, as shown in Figures 11, 12, and 13. This would be the solidus line for the portion of the diagram covered by these alloys with an eutectic at about 34 per cent barium. This solidus line ceased to exist when the cooling curve was obtained for the 45 per cent barium alloy shown in Figure 14. Here the solidus came in quite distinctly at a temperature of $640 \pm 8^\circ\text{C}$.

The forty atomic per cent alloy would present a likelihood for an intermetallic compound. Forty atomic per cent came to 43.4 weight per cent, so this alloy was the next one to be tested. The cooling curve for this specimen is shown in Figure 15. It is of the type that is characteristic for pure elements or compounds. In this case it is thought to be the intermetallic compound Ba_2Sn_3 .

With barium compositions above 43 per cent, the solidus appeared to be at 640°C . This held true until the cooling curve of the 55 per cent barium alloy was obtained as

shown in Figure 17. With this specimen the solidus at 640° no longer appeared, but in its place was a solidus at $910 \pm 10^{\circ}\text{C}$. The reasoning used above was applied here and the appearance of an intermetallic compound was suspected at the fifty atomic per cent composition, which would conform to 53.6 weight per cent barium. When a run was made on an alloy of this Ba-Sn ratio, the straight line shown in Figure 18 was obtained. This would indicate that the intermetallic compound BaSn could be present, but the melting point would be at a temperature above that obtainable with the equipment available.

An attempt was made to determine how far the solidus of 910°C extended. Here the data began to be quite erratic. Figures 19 and 20 show the results of cooling curves for these very high barium alloys. A solidus at about 700°C shows up throughout this range. The 65 per cent barium cooling curve shows the first evidence of solidification at 880°C , and this appears to be the liquidus. The solidus line of 910°C must stop before this barium content is reached. This may be an indication of the presence of another intermetallic compound Ba_3Sn_2 since the composition of this compound would place it between the compositions where the 910°C solidus line appeared to end.

From a survey of these data, the potential phase diagram of barium-tin was extended to a higher barium content, as shown in Figure 21.

FIG. 11 ALLOY 30 DERIVED
DIFFERENTIAL COOLING CURVE
(32% Ba)

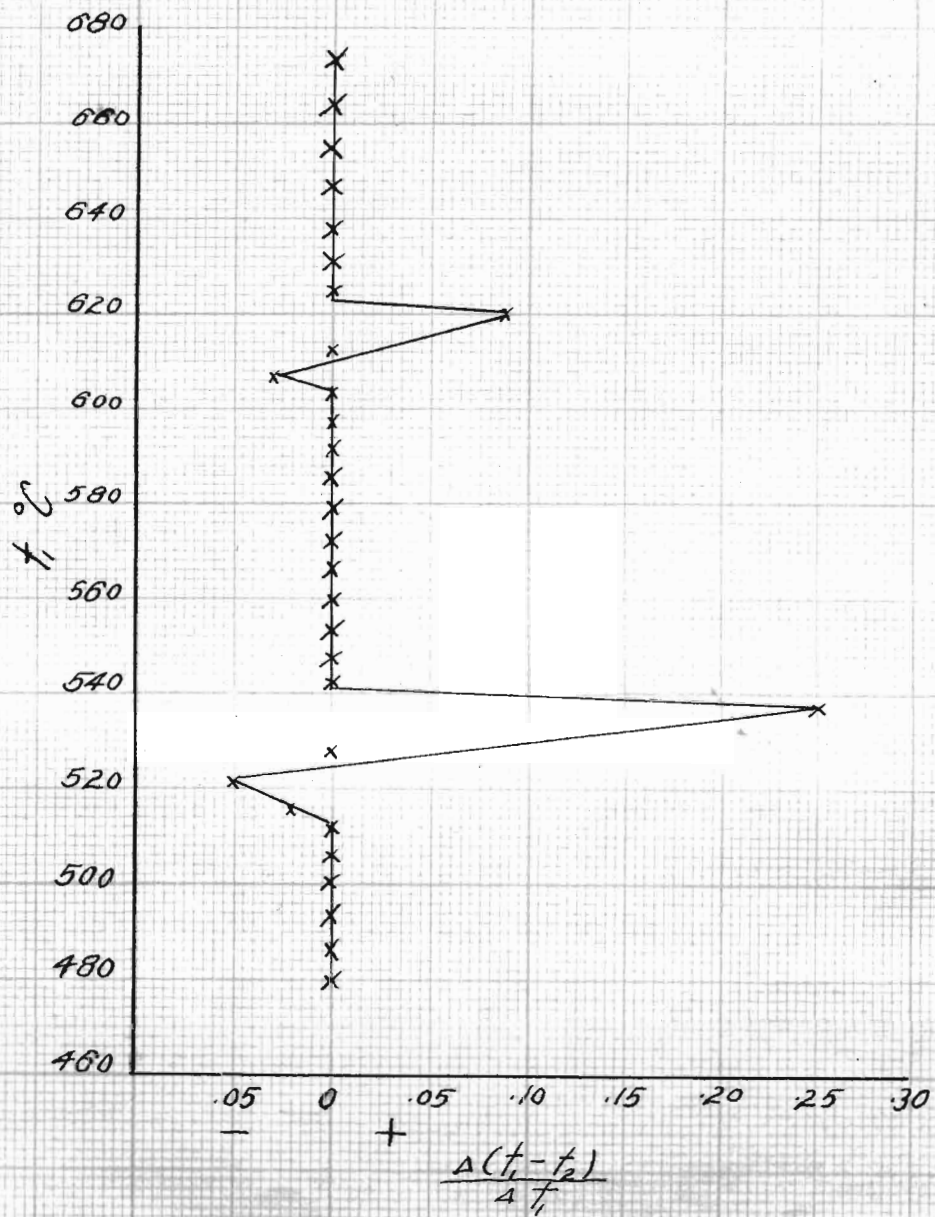
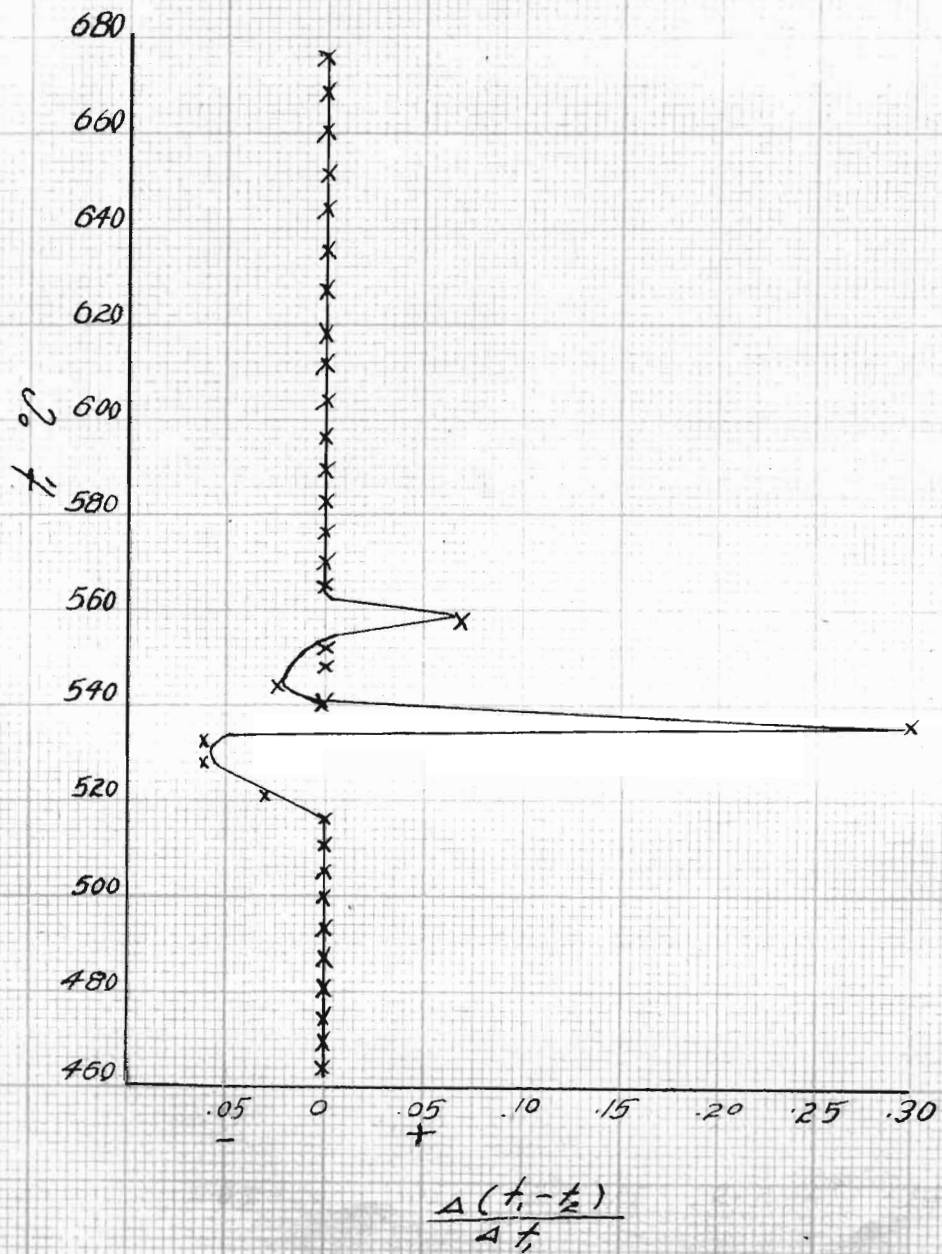


FIG. 12 ALLOY 31 DERIVED

DIFFERENTIAL COOLING CURVE
(35.6% Ba)



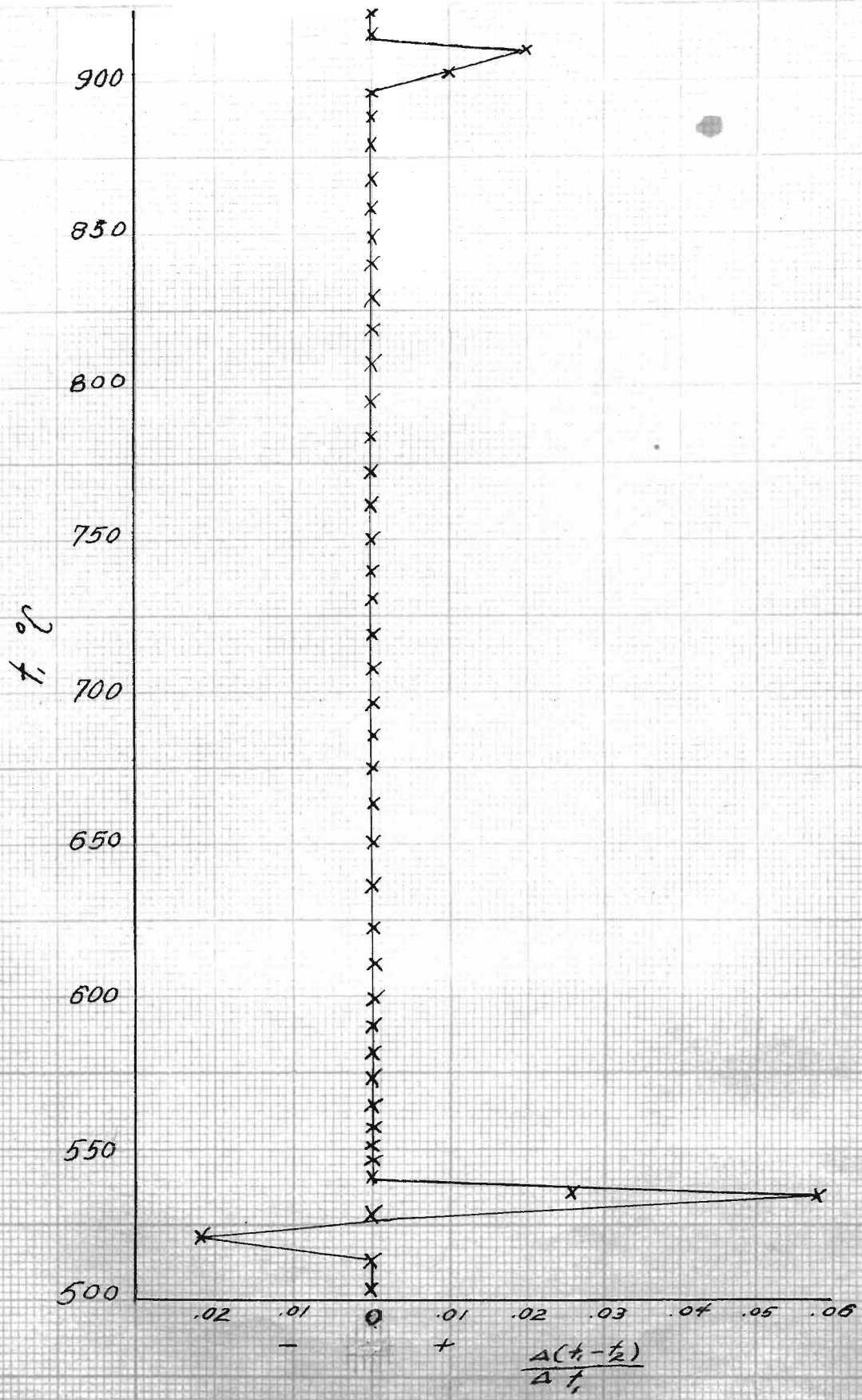


FIG.13 ALLOY 32 DERIVED
DIFFERENTIAL COOLING CURVE (39% Ba)

FIG. 14 ALLOY 33 DERIVED
DIFFERENTIAL COOLING CURVE
(46% B α)

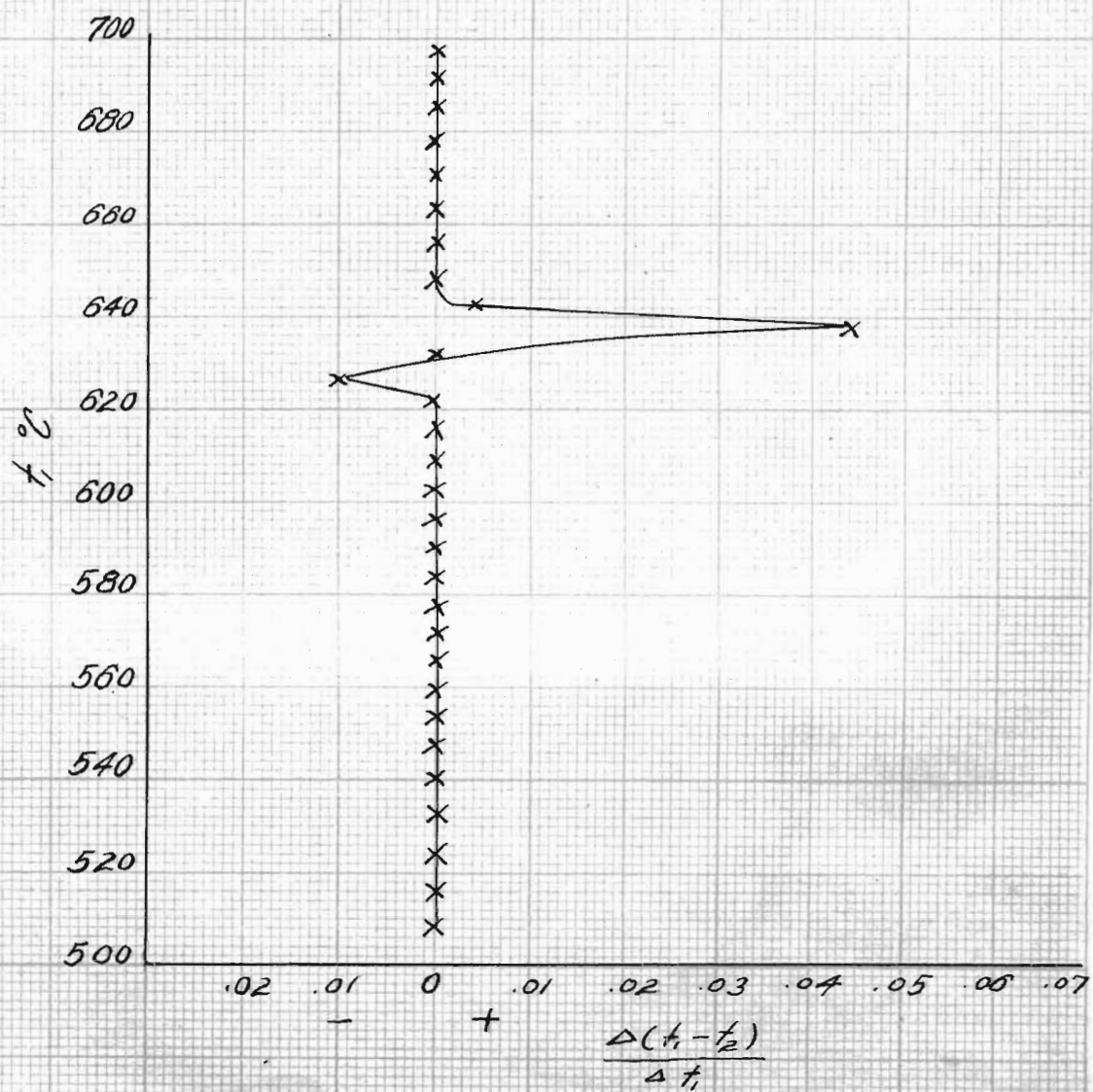


FIG. 15 ALLOY 34 DERIVED
DIFFERENTIAL COOLING CURVE
(43% B α)

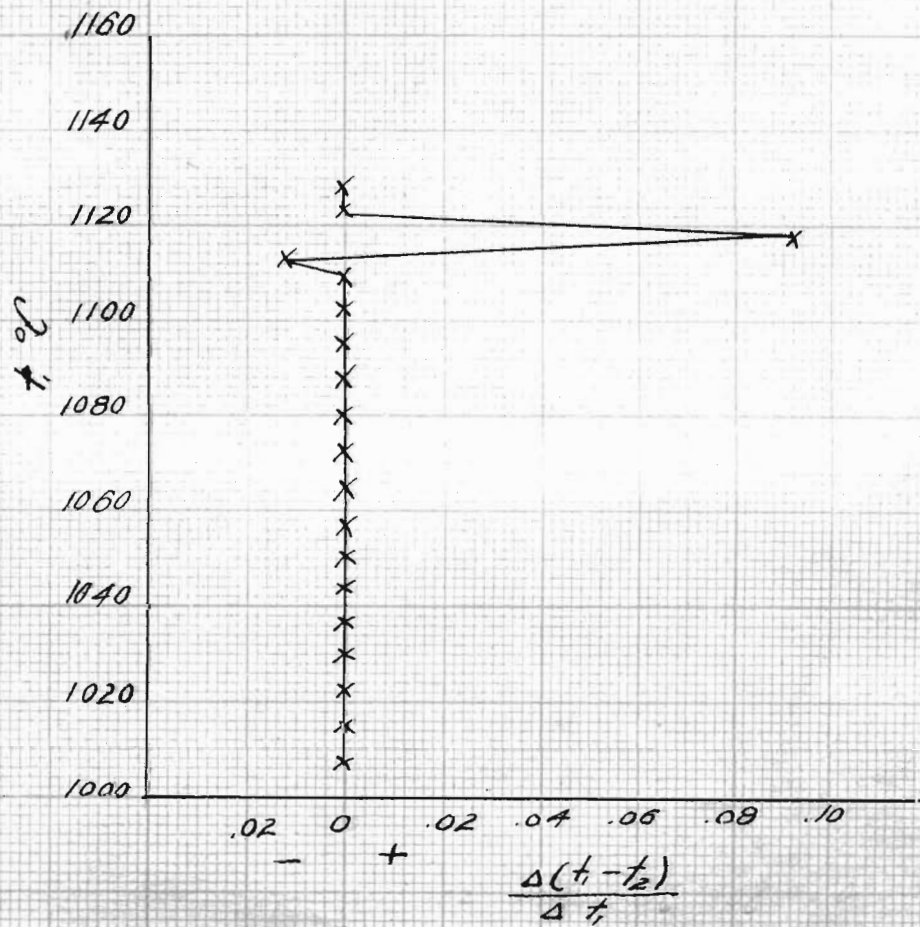


FIG. 16 ALLOY 35 DERIVED
DIFFERENTIAL COOLING CURVE
(49% Ba)

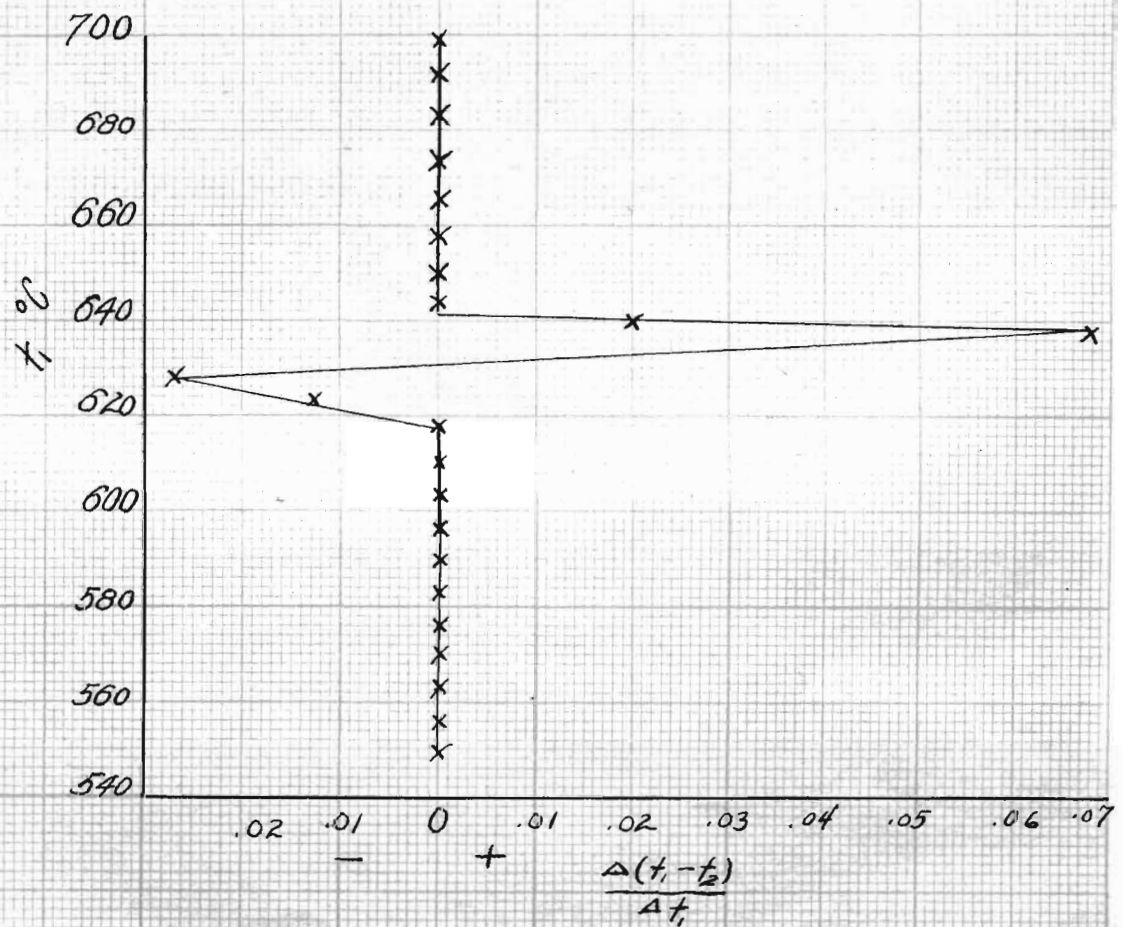


FIG. 17 ALLOY 36 DERIVED
DIFFERENTIAL COOLING CURVE
(57% Ba)

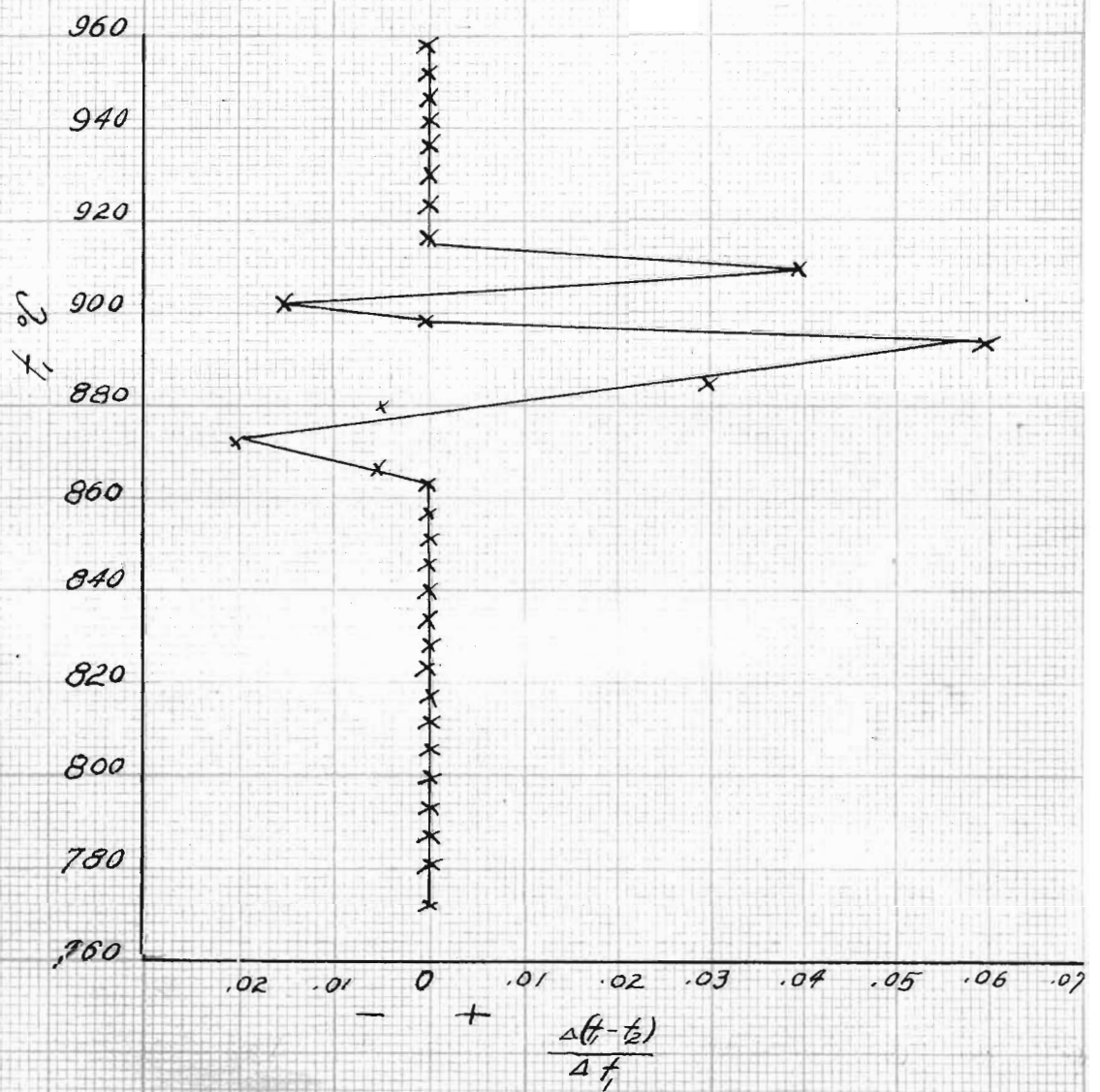


FIG. 18 ALLOY 37 DERIVED
DIFFERENTIAL COOLING CURVE
(52.3% Ba)

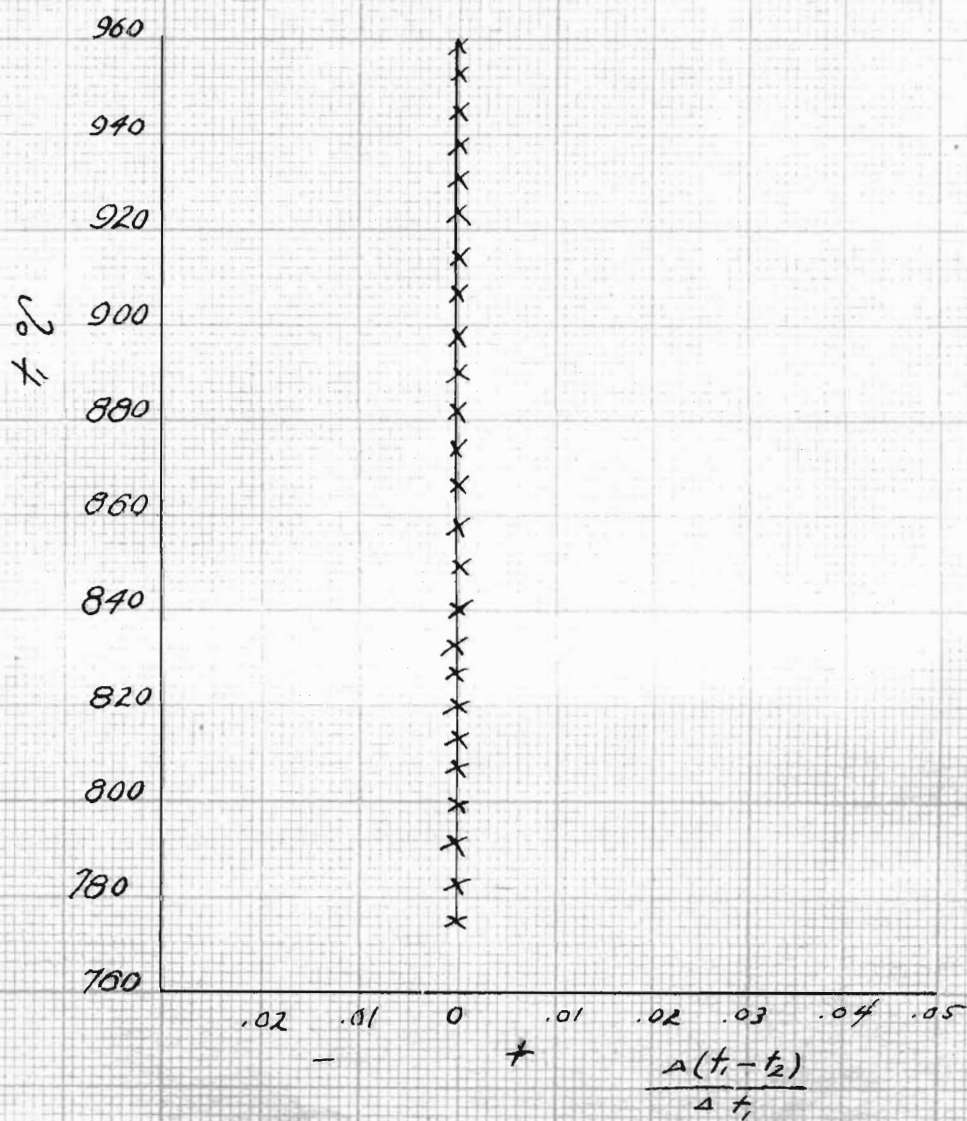


FIG. 20 ALLOY 40 DERIVED
DIFFERENTIAL COOLING CURVE
(82% Ba)

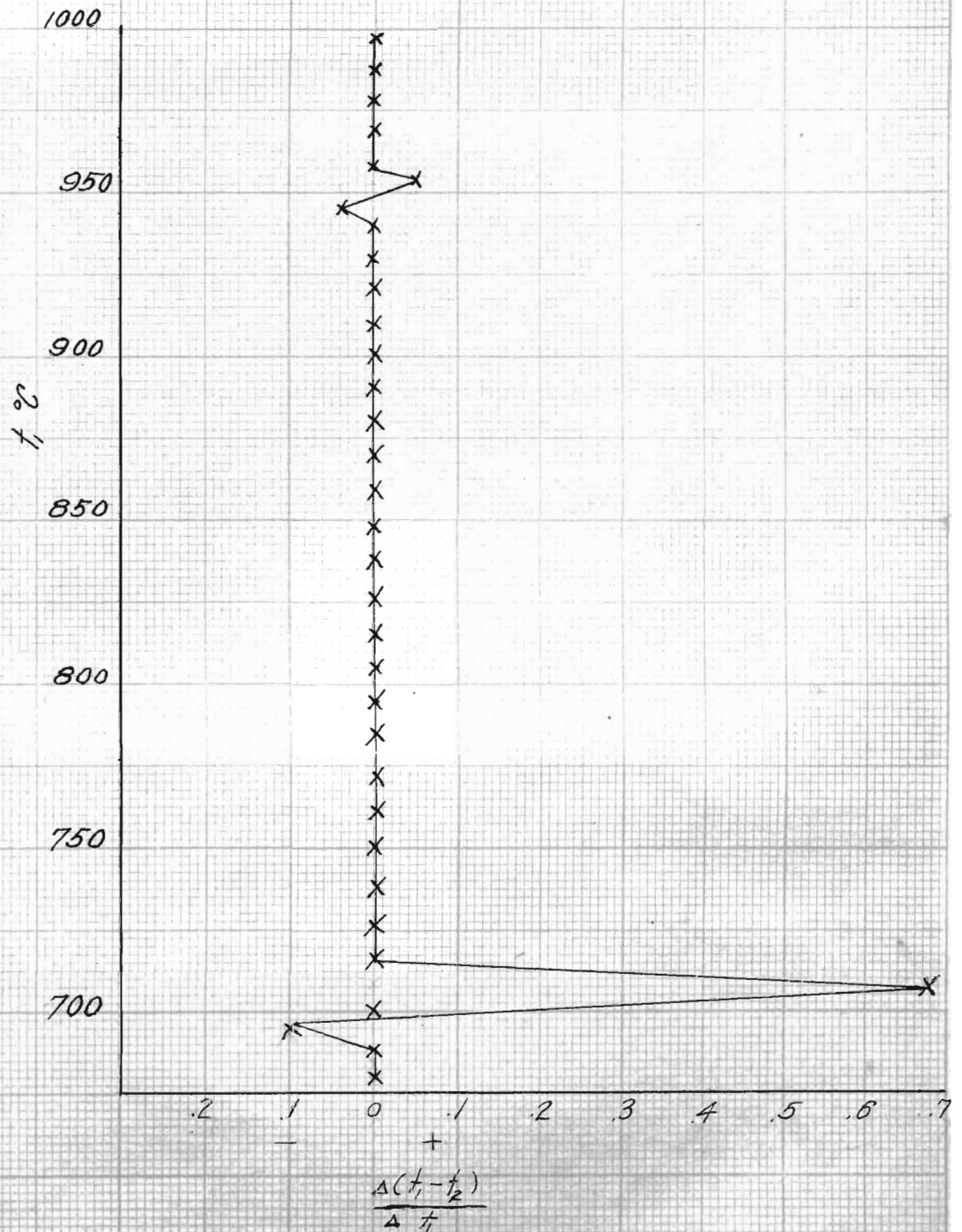


FIG. 21 POTENTIAL PHASE DIAGRAM FOR Ba-Sn

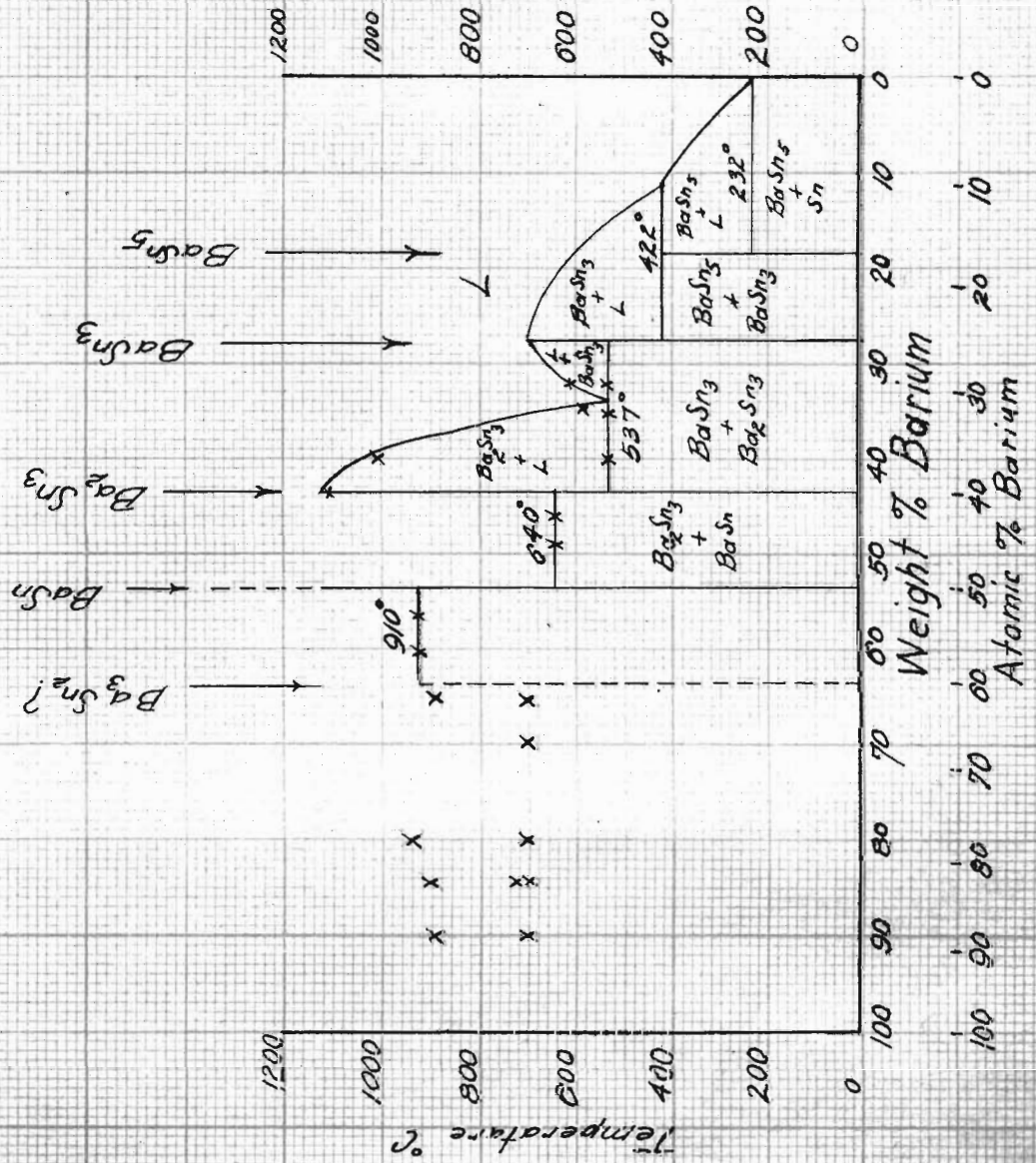


TABLE V
A LIST OF INTERMETALLIC COMPOUNDS
REVEALED BY THERMAL ANALYSIS

Formula	Wt%Ba	Melting Point
Ba ₂ Sn ₃	43.4	1120°C ?
BaSn	53.6	Above 1130°C

METALLOGRAPHY

The use of metallography as a tool in the examination of barium-tin alloys is limited to the low barium alloys. Specimens with a high barium content were acted upon by the atmosphere to such an extent that they appeared black under the microscope. Figure 22 shows a low barium alloy in the as cast condition, while Figure 23 is an annealed low barium alloy. These samples were etched with distilled water for thirty seconds. The intermetallic compound (BaSn_5) etched dark, while the tin remained unetched and white. Figure 24 shows a mixture of intermetallic compounds (BaSn_3 and Ba_2Sn_3), while the high barium alloy in Figure 25 is so badly over-etched that nothing is distinguishable. These specimens were etched by allowing them to be exposed to the atmosphere during the polishing operation. After a fifteen minute period of exposure, these samples were pitted deeply due to the rapid oxidation of barium.



Figure 22

100X

Barium-Tin alloy, 13 wt. %Ba, as cast,
ten sec. etch in cold water. $BaSn_5$ in
matrix of tin.

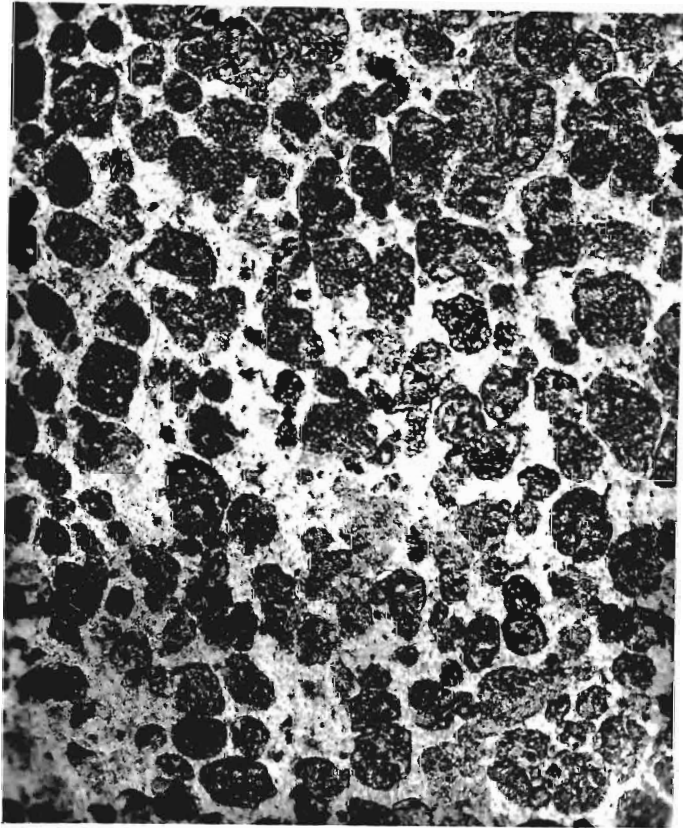


Figure 23

150X

Barium-Tin alloy, 13 wt. %Ba, as annealed at 200°C for 24 hrs. Etched ten sec. in cold water. BaSn₅ (black) in a matrix of unetched tin.

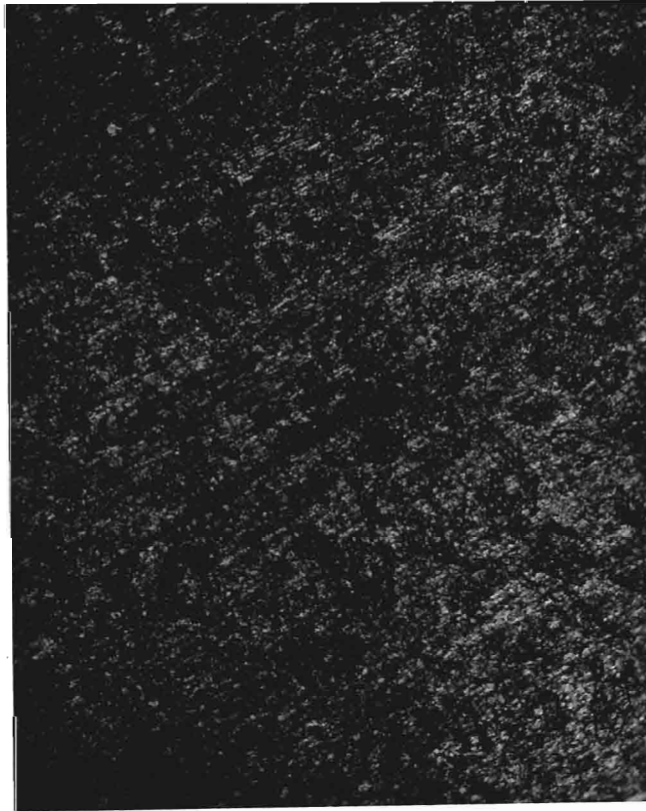


Figure 24

150X

Barium-Tin alloy, 30.1 wt. %Ba, as annealed at 500°C for 24 hrs. Etched by exposure to the atmosphere during polishing. Very dark Ba_2Sn_3 in a matrix of dark $BaSn_3$.



Figure 25

100X

Barium-Tin alloy, 57 wt. %Ba. Badly overetched by exposure to the atmosphere during the polishing operation.

CHEMICAL ANALYSIS

The method of chemical analysis used was the gravimetric determination of barium.⁽¹⁾ A .2000 gram sample

(1) Scott, W. W., Standard Methods of Chemical Analysis, Vol. I, 1939, p. 127.

of the alloy was weighed and transferred to a 600cc beaker. The sample dissolved in 300cc of cold distilled water. This solution was heated to boiling in order to facilitate decomposition of the barium-tin compounds. The solution was cooled and neutralized with concentrated hydrochloric acid. One cc excess of the acid was added and the liquid was decanted through a fine filter paper. The residue was washed, using water with a drop of hydrochloric acid. The filtrate was heated to boiling and 1-20 sulfuric acid was added, drop by drop, with constant stirring. In order to have the sulfuric acid in slight excess, 35cc were added.

The solution was boiled and digested for four hours. It was cooled and the supernatant liquid was decanted through a fine filter paper. The precipitate was washed three times with water containing a drop or two of hydrochloric acid. The residue was then transferred quantitatively to the filter paper. The filter paper and precipitate were dried and ashed in a porcelain crucible which had been previously ignited to constant weight at 850°C. The crucible and contents were heated to 850°C until a constant weight was obtained. From the weight of the barium sulfate

obtained, the amount of barium in the original sample was calculated as follows:

$$\text{Weight BaSO}_4 \times \frac{\text{Ba}}{\text{BaSO}_4} = \text{Weight of barium in original sample.}$$

At first metallic mercury was put into the distilled water before adding the barium-tin alloy. The mercury amalgamated with the tin and barium, but the barium amalgam was unstable in the presence of water. It was thought that this would be necessary to break up the barium-tin intermetallic compounds so all of the barium could go into solution. However, it was found that this step was unnecessary because the barium in the alloys above 30 per cent barium reacted quite vigorously and completely with the water. The results of these analyses are included in Table VI.

TABLE VI
RESULTS OF CHEMICAL ANALYSIS

Sample No.	Weight % Ba
16	72.2
17	30.1
19	74.8
20	12.9
21	13.0
23	75.5
24	33.4
25	39.3
26	44.0
27 _A	69.5
27 _B	95.2
28	39.4
30	32.1
31	35.6
32	39.0
33	46.1
34	43.0
35	49.2
36	57.0
37	52.3
38	63.8
39	87.3
40	81.7

X-RAY ANALYSIS

The X-ray work was done on a North American Phillips X-ray spectrometer with a copper target and a nickel filter. The samples were sealed in an evacuated pyrex tube and annealed for twenty-four hours at 150 to 200°C below the melting point of the alloy. The alloy was ground to approximately 200 mesh in an agate mortar under oil. The high barium samples reacted with collodion, so they were pressed into plastic sample holders as the relatively dry powder. Trouble was encountered here in getting a smooth surface that could be placed in the X-ray beam. Even when this was accomplished the powder oxidized rapidly, thus swelling and spalling off during X-ray exposure.

As a result of these difficulties, the X-ray data was not conclusive enough to make any predictions as to the phase diagram. However, when an attempt was made to correlate the X-ray results with the thermal analysis, the two methods were in agreement.

Thermal analysis showed the presence of an intermetallic compound Ba_2Sn_3 at 43.3 weight per cent barium. There were diffraction lines in the phase fields where this phase was thought to exist, and these lines were most intense at 43.3 weight per cent barium. These d/n values are listed in Table VIII.

The presence of another intermetallic compound, $BaSn$, was suspected at 53.4 weight per cent barium. The X-ray data showed several lines in the composition range where

this phase would be present. These lines were more intense at approximately the composition where BaSn would appear on the phase diagram. These values are also listed in Table VIII.

There were enough lines assigned to the Ba₂Sn₃ phase for an attempt to be made to determine the crystal structure of this intermetallic compound. The method used was a graphical determination developed by Hull and Davey.(1)

-
- (1) Hull, A. W., and Davey, W. P., Graphical Determination of Hexagonal and Tetragonal Structures from X-Ray Data, Physical Review 17, pp. 549-570. (1921)
-

These workers published charts whereby the distance between planes in an unknown crystal are compared to the calculated values possible in several crystal systems. When an exact match is found between the chart and the interplanar spacing of the unknown, then the crystal belongs to the system and subdivision marked on the chart, and the correct axial ratio is given on the ordinate. If an exact match is found for the pattern it should be verified by computing the density of the specimen in the following manner:

$$\rho = n \frac{M \times 1.649 \times 10^{-24}}{c(d \times 10^{-8})^3}$$

Where:

ρ is the density

M is the molecular weight

d is the interplanar spacing (distance between the 100 planes in the crystal). If the line corresponding to these planes is missing,

then twice the distance of the second order line must be used.

n is the number of atoms in the unit cube

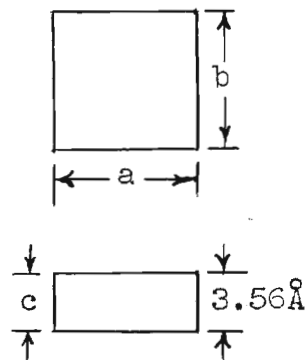
c is the axial ratio (one for the cubic system)

This procedure was followed and an exact match was possible in only two places. (1) In the body-centered-tetragonal system with an axial ratio of $c = .34$ and (2) in the face centered tetragonal system where $c = .24$. The density of this pure phase was measured in kerosene and found to be $5.5 \pm .10$. The two possible solutions were checked in the following manner:

For the body-centered-tetragonal $c = .34$

only the second order 001 line was present. The value was $1.78\text{\AA} \times 2 = 3.56\text{\AA}$.

This is the height of a tetragonal prism where $a = b$ and $\frac{c}{a} = .34$.



Therefore, $a = \frac{c}{.34} = \frac{3.56}{.34} = 10.48$.

Solving for the density

$$\rho = n \frac{\text{Ba}_2\text{Sn}_3 \times 1.649 \times 10^{-24}}{c(d \times 10^{-8})^3}$$

$$\rho = 2 \frac{631 \times 1.649 \times 10^{-24}}{.34(10.48 \times 10^{-8})^3}$$

$$\rho = 5.30$$

For the face-centered-tetragonal $c/a = .24$

again the second order 001 line was $1.78 \times 2 = 3.56\text{\AA}$

where $a = b$ and $\frac{c}{a} = .24$

Therefore, $a = \frac{3.56}{.24} = 14.8\text{\AA}$

Solving for the density

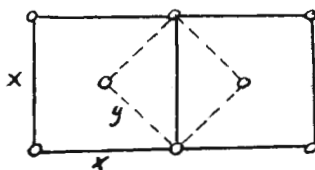
$$\rho = 4 \frac{631 \times 1.649 \times 10^{-24}}{.24(14.8 \times 10^{-8})^3}$$

$$\rho = 5.36$$

From the above it appears that either the BCT with an axial ratio of .34, or the FCT with an axial ratio of .24 could be the crystal structure for Ba_2Sn_3 . However, it may be shown that the face-centered-tetragonal lattice could be considered in two ways.

The solid lines below represent the FCT lattice:

$a_x = 14.8$, $c = 3.56$, and the axial ratio = .24. The broken lines represent the BCT lattice.



$$x^2 = 2y^2 \quad x = \sqrt{2}y$$

$$y = x \frac{1}{\sqrt{2}}$$

Substituting a_x for x and a_y for y

$$a_y = a_x \frac{1}{\sqrt{2}} = 14.8 \frac{1}{\sqrt{2}} = 10.48\text{\AA}$$

This is the same value obtained from the Hull-Davey charts, which shows that it is the same lattice being considered in two ways.

TABLE VII
 X-RAY DATA
 (CuK α RADIATION)

Tin#		BaO##		BaH ₂ #	
d	I	d	I	d	I
1.10	.1	1.06	.05	1.10	.2
1.20	.5	1.13	.15	1.11	.3
1.29	.4	1.23	.25	1.44	.5
1.30	.4	1.26	.2	1.51	.4
1.44	.7	1.38	.1	1.68	1.0
1.46	.3	1.59	.2	1.73	.5
1.48	.6	1.66	.5	1.81	.2
1.65	.2	1.95	.8	1.82	.1
2.01	.8	2.75	.9	2.06	.9
2.06	.6	3.20	1.0	2.14	.5
2.78	1.0			2.33	.8
2.89	.9			2.46	.5
				2.71	.8
				2.91	.7
				2.99	.7
				3.03	.6

Author's Values

ASTM Values

TABLE VIII
d-VALUES ASSIGNED TO SPECIFIC PHASES

PHASE							PURE PHASE	
#17	#24	#31	#34	#33	#36	#38	d	I
<u>Ba₂Sn₃</u>								
		1.79	1.78	1.79			1.78	.4
1.85	1.85	1.85	1.85	1.86			1.85	.5
2.12	2.12	2.12	2.12	2.12			2.12	.4
	2.28	2.30	2.28	2.30			2.28	1.0
2.58		2.57	2.56		2.54		2.56	.6
			2.93	2.93			2.93	.7
		3.44	3.42	3.42			3.42	.8
<u>BaSn</u>								
			1.34	1.35	1.37	1.37	1.37	.8
			1.60		1.58	1.56	1.57	.8
				1.88	1.88	1.88	1.88	1.0

TABLE IX
X-RAY DATA FOR BARIUM-TIN ALLOYS

Alloy #17, 30% Ba			Alloy #24, 33% Ba		
d	I	due to	d	I	due to
1.22	.5	Sn	1.09	.3	Sn
1.29	.4	Sn	1.22	.7	Sn
1.30	.5	Sn	1.29	.6	Sn
1.44	.8	Sn	1.30	.8	Sn
1.45	.5	Sn	1.43	.9	Sn
1.48	.9	Sn	1.45	.7	Sn
1.65	.6	Sn	1.48	1.0	Sn
1.84	.15	Ba ₂ Sn ₃	1.65	.8	Sn
1.94	.1	BaO	1.85	.2	Ba ₂ Sn ₃
2.00	2.5	Sn	1.94	.2	BaO
2.05	1.6	Sn	1.99	3.0	Sn
2.14	.1	C	2.03	2.0	Sn
2.42	.15	BaSn ₃	2.13	.15	Ba ₂ Sn ₃
2.51	.2	BaSn ₃	2.28	.4	Ba ₂ Sn ₃
2.58	.2	Ba ₂ Sn ₃	2.34	.2	?
2.77	3.0	Sn	2.39	.3	BaSn ₃
2.88	3.8	Sn	2.75	4.0	Sn
3.13	.25	BaSn ₃	2.86	4.5	Sn
3.34	.2	C	3.09	.2	BaSn ₃
			3.30	.7	C
			3.42	.3	Ba ₂ Sn ₃

TABLE IX, Cont'd

Alloy #31, 36% Ba			Alloy #34, 48% Ba		
d	I	due to	d	I	due to
1.20	.4	Sn	1.10	.15	Sn
1.24	.2	BaO	1.20	.3	Sn
1.29	.1	Sn	1.24	.2	BaO
1.30	.2	Sn	1.26	.3	BaO
1.32	.3	?	1.29	.3	Sn
1.43	.4	Sn	1.30	.2	Sn
1.44	.2	Sn	1.32	.1	?
1.47	.4	Sn	1.34	.1	BaSn
1.61	.2	BaO	1.43	.4	Sn
1.66	.4	Sn	1.45	.2	Sn
1.68	.2	BaO	1.48	.4	Sn
1.79	.25	Ba ₂ Sn ₃	1.60	.15	BaSn
1.85	.2	Ba ₂ Sn ₃	1.62	.4	BaO
1.94	.25	BaO	1.65	.35	Sn
2.00	1.0	Sn	1.68	.35	BaO
2.03	.5	Sn	1.72	.4	BaH ₂
2.12	.2	Ba ₂ Sn ₃	1.78	.4	Ba ₂ Sn ₃
2.16	.3	BaH ₂	1.81	.2	BaH ₂
2.30	.7	Ba ₂ Sn ₃	1.85	.5	Ba ₂ Sn ₃
2.39	.6	BaH ₂	1.93	.45	BaO
2.57	.5	Ba ₂ Sn ₃	1.99	1.2	Sn
2.76	1.0	Sn	2.03	.8	Sn
2.89	1.0	Sn	2.12	.4	Ba ₂ Sn ₃
3.11	.3	BaSn ₃	2.28	1.3	Ba ₂ Sn ₃
3.17	.15	BaO	2.36	1.2	BaH ₂
3.29	.25	BaO	2.56	.9	Ba ₂ Sn ₃
3.44	.4	Ba ₂ Sn ₃	2.74	1.2	Sn
			2.84	1.9	Sn
			2.93	1.2	Ba ₂ Sn ₃
			3.11	.3	BaH ₂
			3.24	1.1	BaO
			3.42	1.3	Ba ₂ Sn ₃

TABLE IX, Cont'd

Alloy #33, 46% Ba			Alloy #36, 57% Ba		
d	I	due to	d	I	due to
1.20	.2	Sn	1.09	.1	Sn
1.24	.1	BaO	1.10	.2	BaH ₂
1.26	.2	BaO	1.12	.5	Ba ₃ Sn ₂
1.30	.2	Sn	1.19	.2	?
1.35	.2	BaSn	1.20	.6	Sn
1.41	.2	Sn	1.23	.45	BaO
1.43	.3	Sn	1.26	.45	BaO
1.48	.1	Sn	1.28	.4	Sn
1.61	.1	BaO	1.30	.5	Sn
1.63	.1	BaO	1.31	.1	?
1.65	.1	Sn	1.37	.2	BaSn
1.68	.35	BaO	1.43	.65	Sn
1.79	.45	Ba ₂ Sn ₃	1.45	.5	Sn
1.86	.1	Ba ₂ Sn ₃	1.47	.65	Sn
1.88	.2	BaSn	1.50	.4	Ba ₃ Sn ₂
1.93	.2	BaO	1.54	.1	?
1.95	.1	BaO	1.58	.2	BaSn
2.00	.8	Sn	1.65	1.0	Sn
2.04	.3	Sn	1.72	.2	BaH ₂
2.12	.1	Ba ₂ Sn ₃	1.88	.25	BaSn
2.14	.25	BaH ₂	1.92	.5	BaO
2.30	.9	Ba ₂ Sn ₃	1.98	.3	Sn
2.37	.5	BaH ₂	2.03	.5	Sn
2.76	.7	Sn	2.05	.5	BaH ₂
2.88	1.2	Sn	2.27	.5	BaH ₂
2.93	.3	Ba ₂ Sn ₃	2.34	.4	BaH ₂
3.18	.1	BaO	2.54	.2	Ba ₂ Sn ₃
3.27	.3	?	2.74	.2	BaO
3.42	.65	Ba ₂ Sn ₃	2.79	.2	Sn
			2.88	.1	Sn

TABLE IX, Cont'd

Alloy #38, 64% Ba

d	I	due to
1.09	.1	Sn
1.10	.2	BaH ₂
1.12	.5	Ba ₃ Sn ₂
1.16	.2	?
1.20	.4	Sn
1.23	.3	BaO
1.26	.4	BaO
1.28	.3	Sn
1.30	.4	Sn
1.37	.1	BaSn
1.43	.6	Sn
1.45	.5	Sn
1.47	.65	Sn
1.50	.3	Ba ₃ Sn ₂
1.52	.1	Ba ₃ Sn ₂
1.56	.1	BaSn
1.60	.1	BaO
1.64	.8	Sn
1.68	.15	BaO
1.73	.35	BaH ₂
1.88	.2	BaSn
1.93	.5	BaO
1.99	1.7	Sn
2.03	.6	Sn
2.12	.25	?
2.15	.3	?
2.27	.8	BaH ₂
2.36	.8	BaH ₂
2.76	1.5	Sn
2.86	2.0	Sn
3.03	.2	BaH ₂
3.09	.35	BaO

CONCLUSIONS

1. Ba-Sn alloys of any composition can be prepared by using BaH_2 or metallic barium and tin if an inert atmosphere is maintained during heating and cooling.
2. The thermal diagram was constructed over the range from 27 per cent to 43 per cent barium with the solidus extending to 65 per cent barium.
3. Two intermetallic compounds, Ba_2Sn_3 and $BaSn$, were formed and the presence of Ba_3Sn_2 was suspected.
4. The crystal structure of Ba_2Sn_3 is believed to be face-centered-tetragonal with an axial ratio of .24.
5. An eutectic was found to exist at about 34 weight per cent barium.
6. Pyrophoric alloys do exist in the Ba-Sn binary system with a maximum intensity near 70 atomic per cent barium.

SUMMARY

A number of barium-tin alloys of high barium content were produced using metallic barium and barium hydride. Barium hydride is much easier to handle, but the alloys produced are of a more porous nature.

The predictions made from the theoretical study were apparently correct, since it appears that the phase diagram consists of a series of relatively stable intermetallic compounds. Two of these compounds, Ba_2Sn_3 and $BaSn$, were discovered. By means of X-ray diffraction the crystal structure of Ba_2Sn_3 appears to be face-centered-tetragonal with an axial ratio of .24.

The equilibrium system was studied using thermal analysis, and the diagram was extended from 27 per cent Ba to 44 per cent Ba.

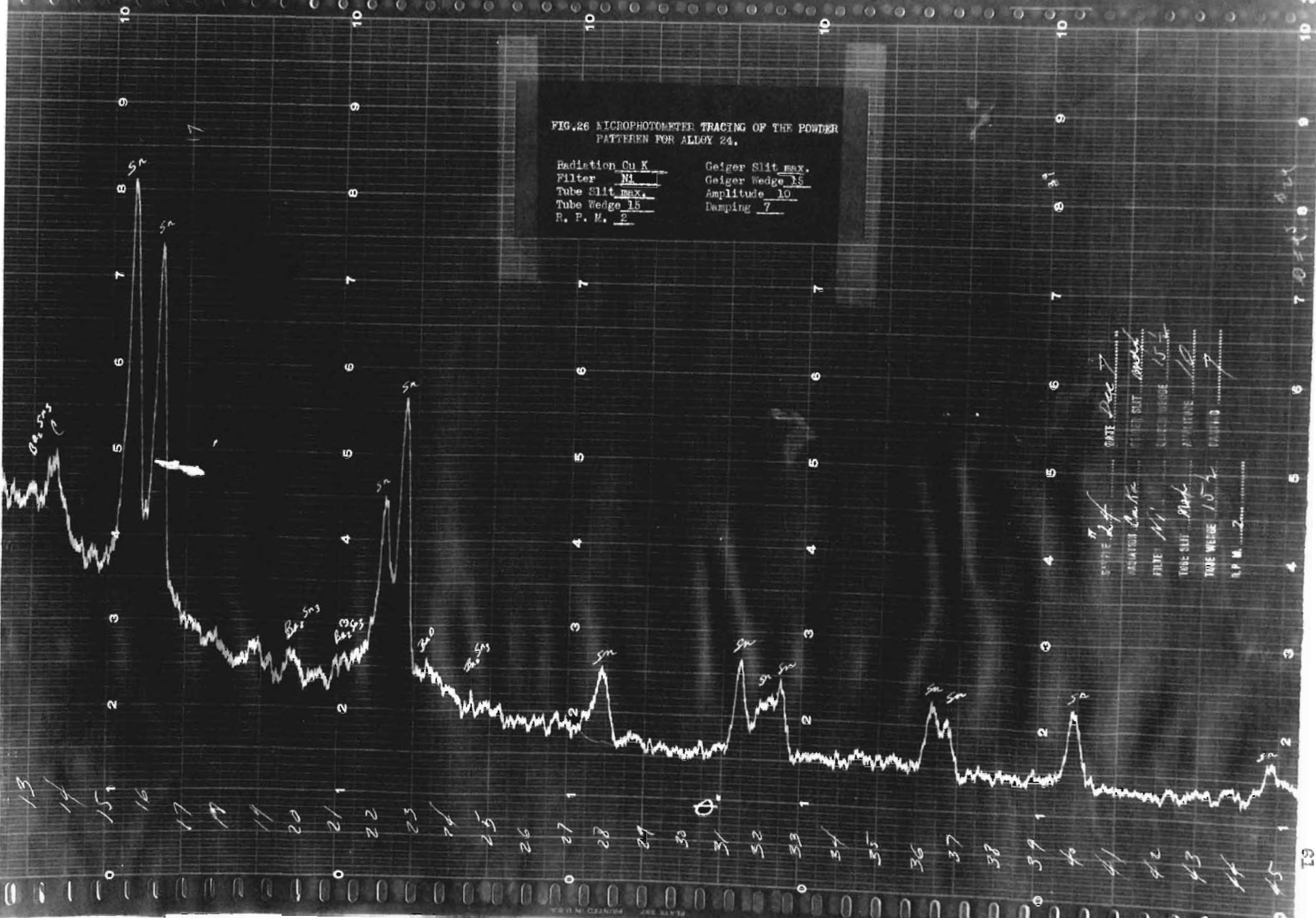
Alloys that are pyrophoric were found to exist in the Ba-Sn binary system, but the rapid oxidation of these alloys would tend to limit the commercial exploitation of this phenomenon.

APPENDIX

FIG. 26 MICROPHOTOMETER TRACING OF THE POWDER PATTERN FOR ALLOY 24.

Radiation Cu K
 Filter Ni
 Tube Slit max.
 Tube Wedge 15
 R. P. M. 2

Geiger Slit max.
 Geiger Wedge 15
 Amplitude 10
 Damping 7



DATE Dec 7
 OPERATOR Chas
 FILTER SLIT max
 TUBE SLIT max
 TUBE WEDGE 15
 GEIGER SLIT max
 GEIGER WEDGE 15
 AMPLITUDE 10
 DAMPING 7
 R. P. M. 2

FIG. 27 MICROPHOTOMETER TRACING OF THE POWDER PATTERN FOR ALLOY S1

Radiation	Cu K	Geiger Slit	max.
Filter	NI	Geiger Wedge	16
Tube Slit	max.	Amplitude	10
Tube Wedge	16	Damping	10
E. P. N.	2		

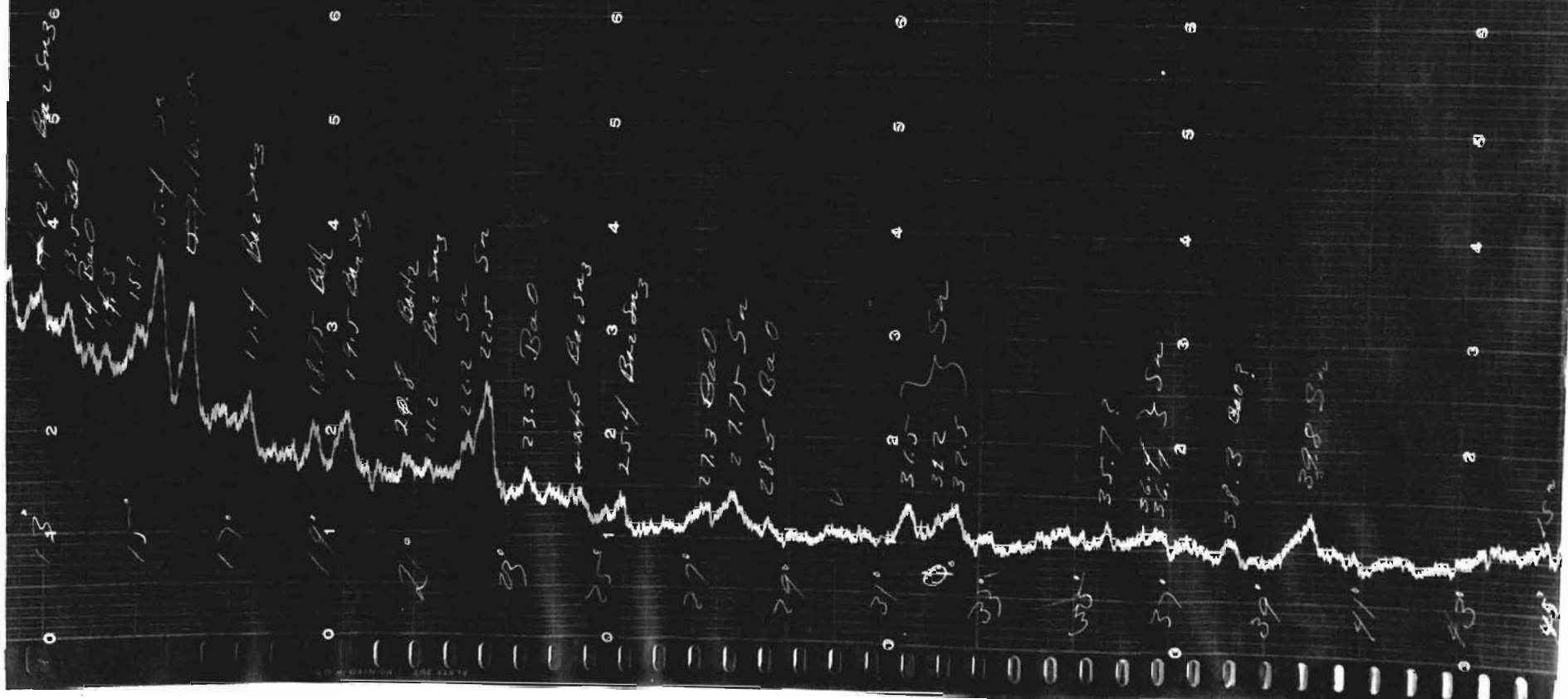


FIG. 28 MICROPHOTOMETER TRACING OF THE POWDER PATTERN FOR ALLOY 34

Radiation	Cu K	Geiger Slit	Med.
Filter	Ni	Geiger Wedge	15
Tube Slit	Max.	Amplitude	10
Tube Wedge	16	Damping	10
S. P. M.	2		

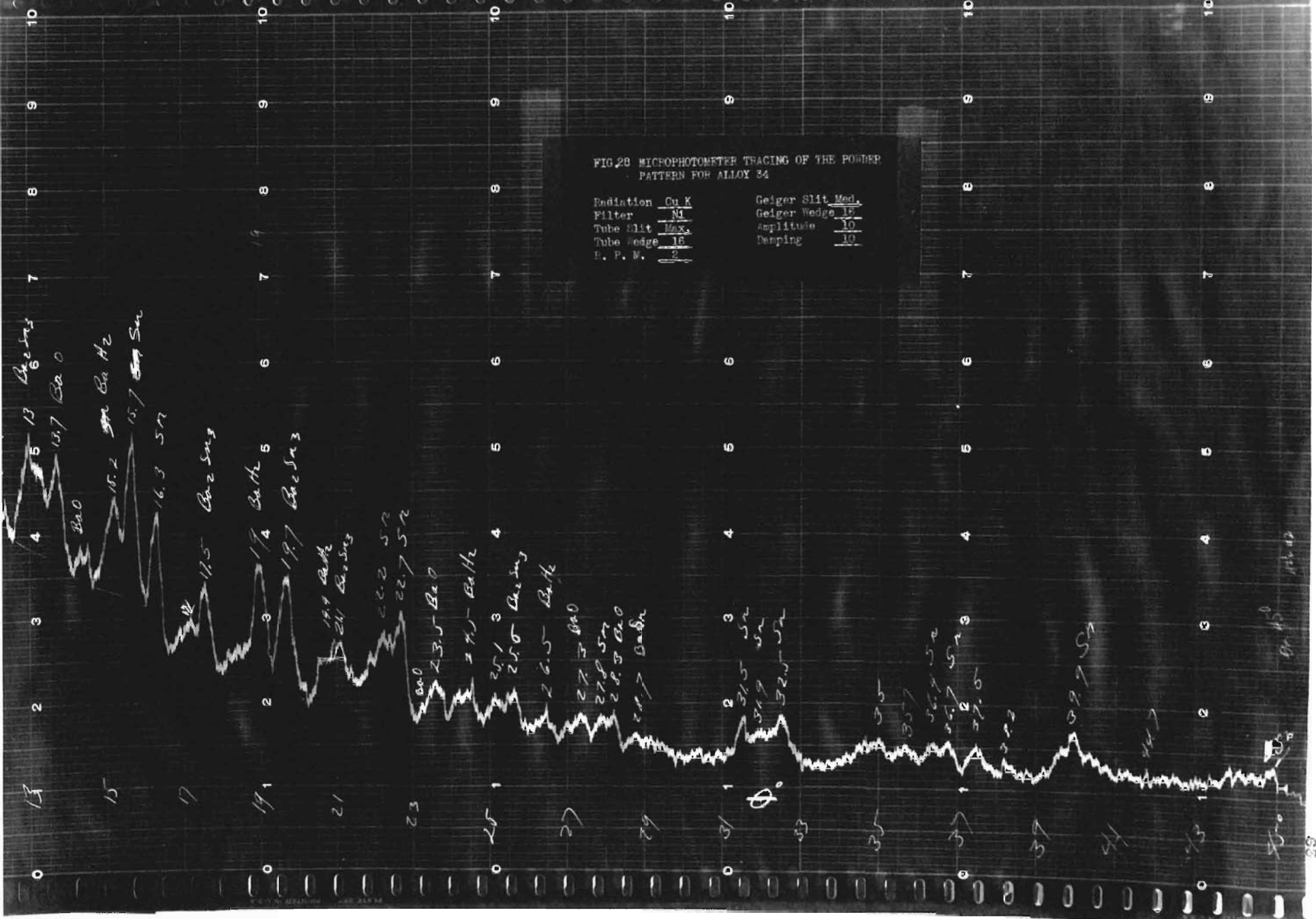
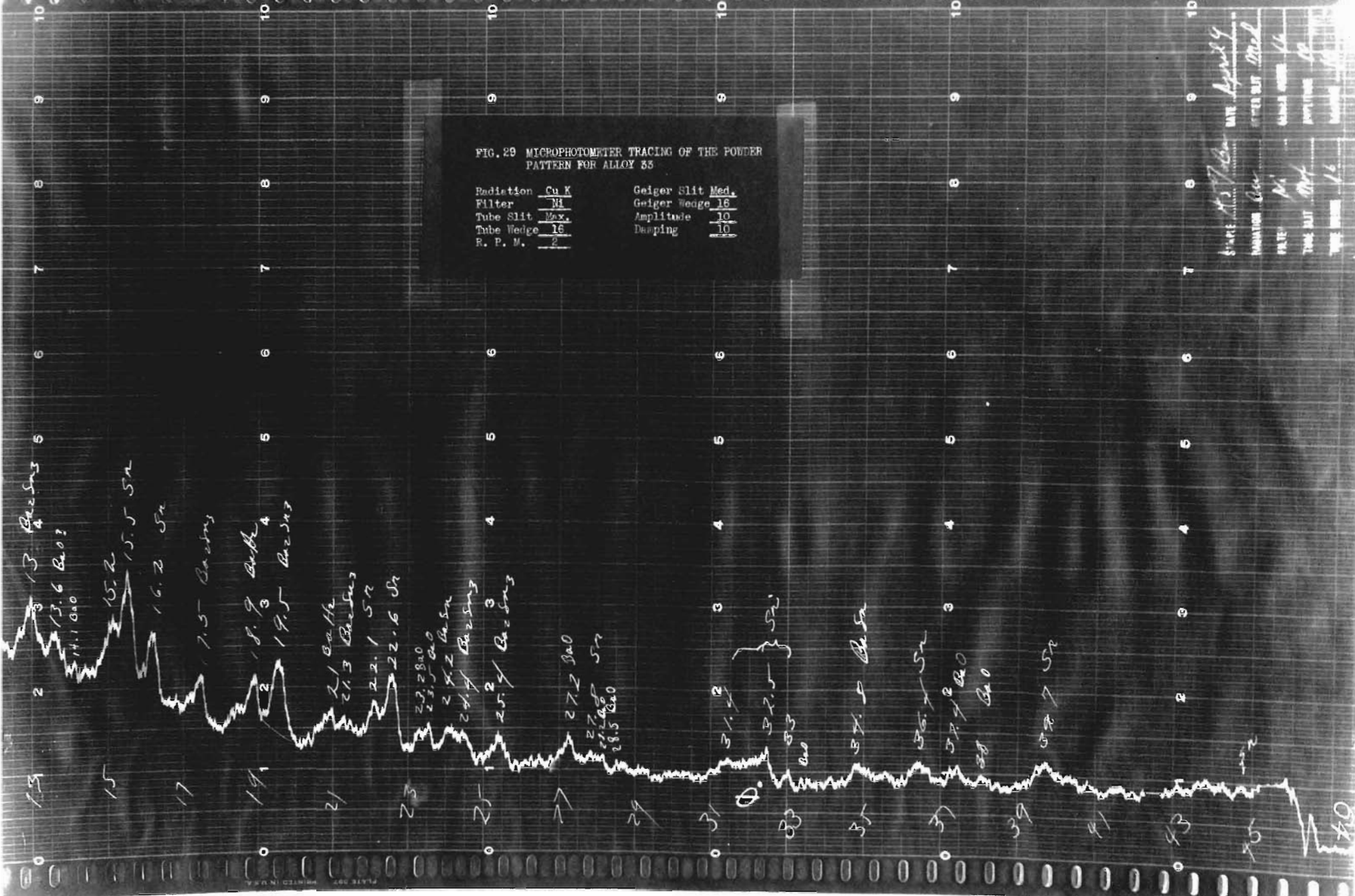


FIG. 29 MICROPHOTOMETER TRACING OF THE POWDER PATTERN FOR ALLOY 35

Radiation	<u>Cu K</u>	Geiger Slit	<u>Med.</u>
Filter	<u>M</u>	Geiger Wedge	<u>18</u>
Tube Slit	<u>Max.</u>	Amplitude	<u>10</u>
Tube Wedge	<u>16</u>	Drumming	<u>10</u>
R. P. M.	<u>2</u>		

DATE 4-27-48 MAT. Alloy 35
 OPERATOR W. J. ... OPER. SLIT Med
 FILTER M TUBE WEDGE 16
 TUBE SLIT Max AMPLITUDE 10
 DRUMMING 10 R.P.M. 2



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