THE EFFECTS OF SMALL AMOUNTS OF ANTIMONY ON THE LIQUID TO SOLID TRANSFORMATION OF HIGH PURITY ALUMINUM

Thesis for the Degree of M. S.

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Robert Austin Campbell

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THESIS

This is to certify that the

thesis entitled

The Effects of Small Amounts of Antimony on the Liquid to Solid Transformation of High Purity Aluminum.

presented by

Robert Austin Campbell

has been accepted towards fulfillment
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R. L. Sweet

Major professor

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THE EFFECTS OF SMALL AMOUNTS OF ANTIMONY ON THE LIQUID TO SOLID TRANSFORMATION OF HIGH PURITY ALUMINUM

By

Robert Austin Campbell

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INTRODUCTION

The addition of small amounts of antimony either to pure aluminum or to aluminum alloys has found little commercial use. The German alloy K-S Seewasser (3% Mn, 2-3% Mg, 0.75% Sb)[5*] contains antimony in small amounts for the purpose of preventing seawater corrosion. Results have been dubious. Corson[3] contends that the compound SbAl gives aluminum high wear resistance. There is one American patent, #1453928[3], which mentions an aluminum antimony alloy containing 1-1.5% Sb. At least seven other United States Patents mention antimony as an alloying agent for aluminum, mostly in connection with large amounts of Cu and Zn. Little basic work has been done on the aluminum-antimony system compared to the alloy systems of at least moderate commercial importance.

This investigation of the aluminum-antimony system was a continuation of the work started by Stone.[13] The diagram obtained by Stone (Fig. 7) showed evidence of error either in procedure or materials or both.

Previous equilibrium diagrams have not shown complete agreement on the region of 0 to 2% Sb. The diagrams from Corson[3] (Fig. 1), the International Critical Tables[9] (Fig. 2), and from Dowdell and associates[4] (Fig. 3) all show no solid solubility of antimony in aluminum. Some of the later work, shown in the diagrams from Mondolfo[11] (Fig. 4), Dix, Keller, and Willey[5] (Fig. 5), and the Metals Handbook[10] (Fig. 6), indicates that an eutectic exists at 1.1% antimony. The texts, which accompany these latter three diagrams, all agree that the limit of solid solubility is 0.1% antimony.

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* Numbers refer to bibliography at the end of the thesis.

The diagram by Stone[13] (Fig. 7) shows an eutectic at 0.9% Sb and a curious minimum at 0.3% Sb. There are also points at 0.1% and 0.7% which do not fall on the liquidus curve at all. The liquidus points are too scattered to give much confidence as to their accuracy. The solidus and eutectic points are similarly scattered, but it is to be expected that a solidus is more difficult to determine by thermal analysis than a liquidus.

The prime factor to be questioned in Stone's work was the purity of the aluminum used. Since the aluminum was only 99.70% pure, the addition of antimony in three of the compositions used was in lesser amounts than the impurities present. Since the antimony was free to combine with the impurities, the samples were in reality alloys of six elements rather than binary alloys.

It was decided to rework part of the equilibrium diagram using some highly refined aluminum (99.9968%) subsequently obtained. A better grade of antimony (99.83%) was also employed.

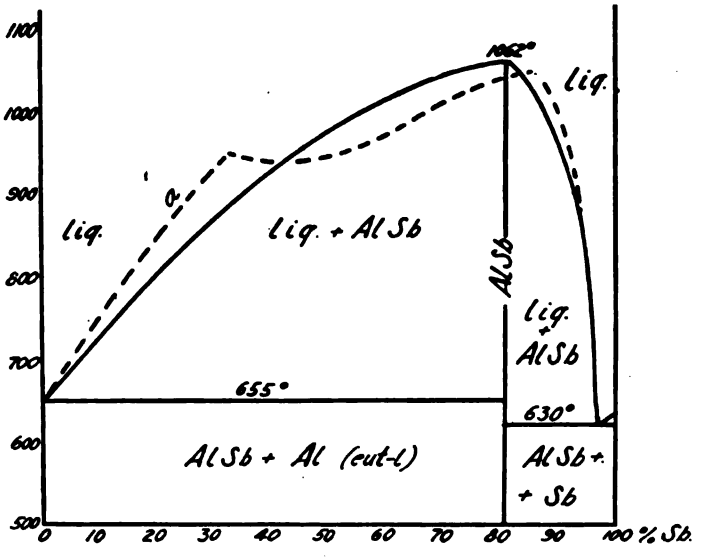


FIG. 45. Const-l diagram of Al-Sb series by Urasov.
(J. R. Ph. Ch. S., 1919, v. 51, p. 461.)

Fig. 1 Diagram from Corson[5] by Urasov

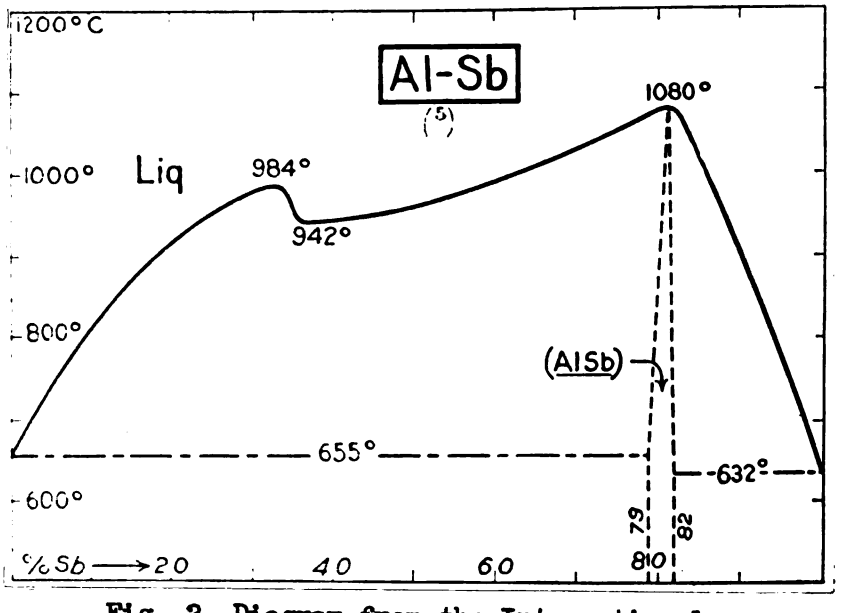


Fig. 2 Diagram from the International Critical Tables[9] by Campbell and Matthews.

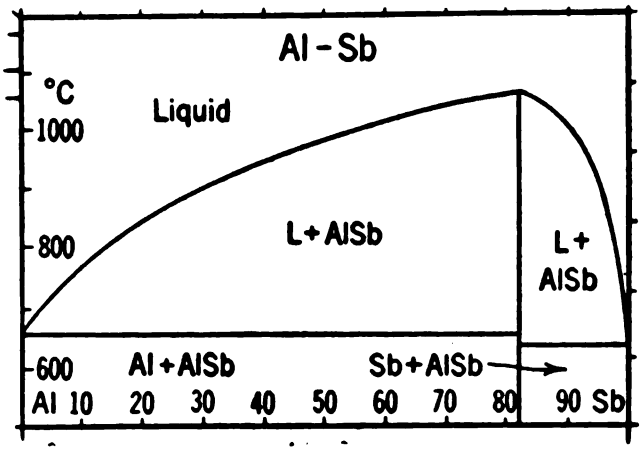


Fig. 3 Diagram from Dowdell and associates[4].

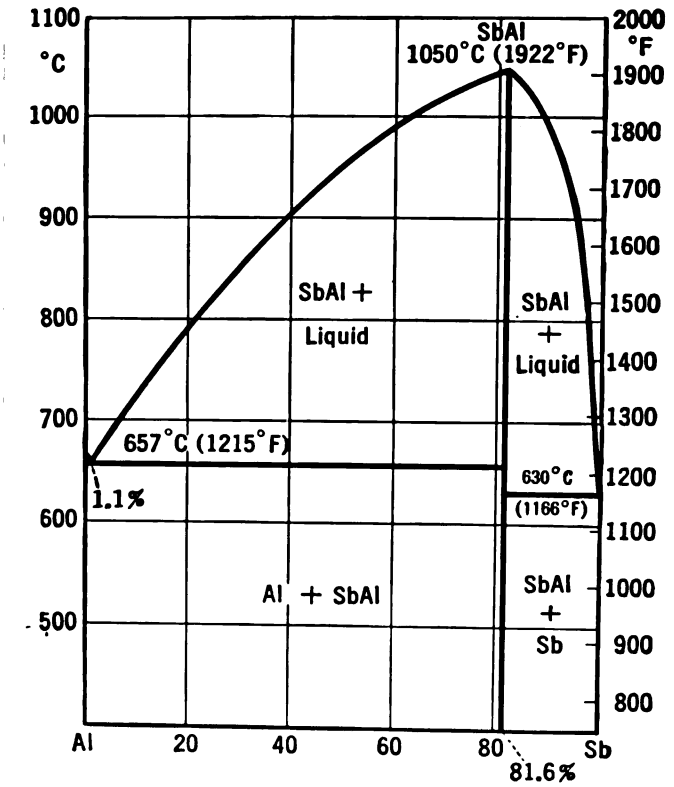


FIG. 35. System Al-Sb, equilibrium diagram.

Fig. 4 Diagram from Mondolfo[11]

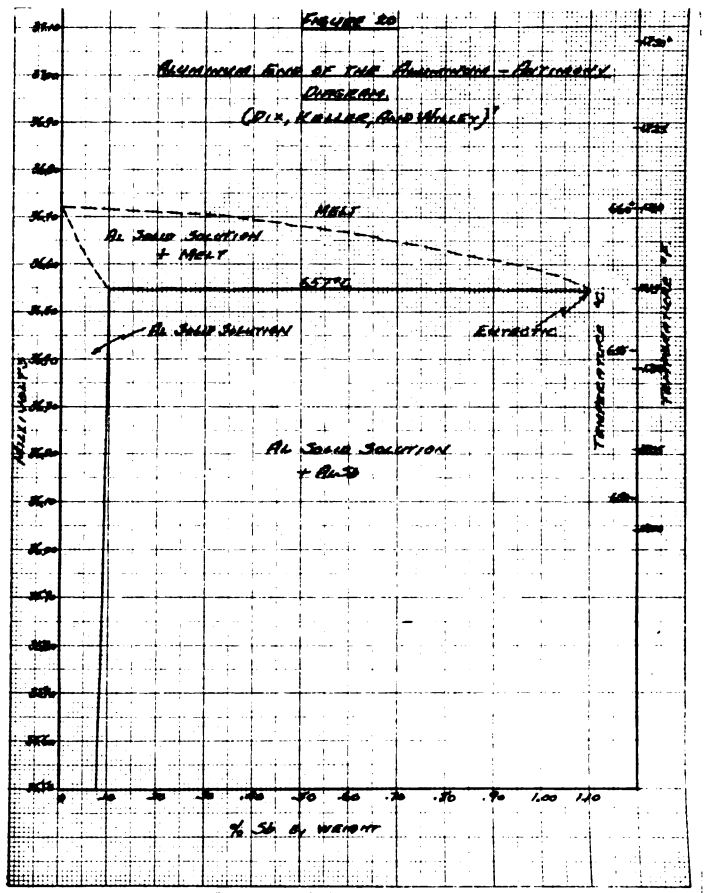


Fig. 5 Diagram from Dix and associates[5]

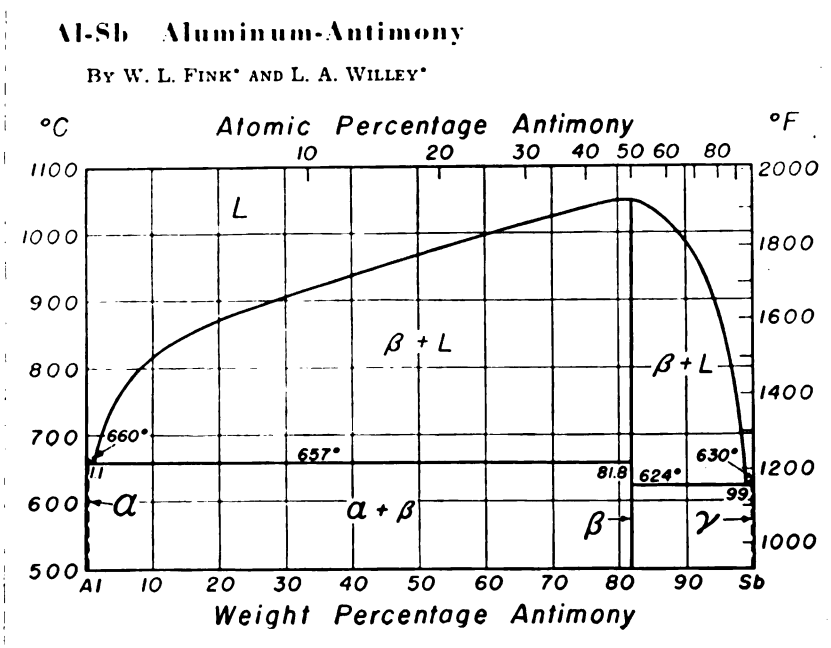


Fig. 6 Diagram from the Metals Handbook[10]

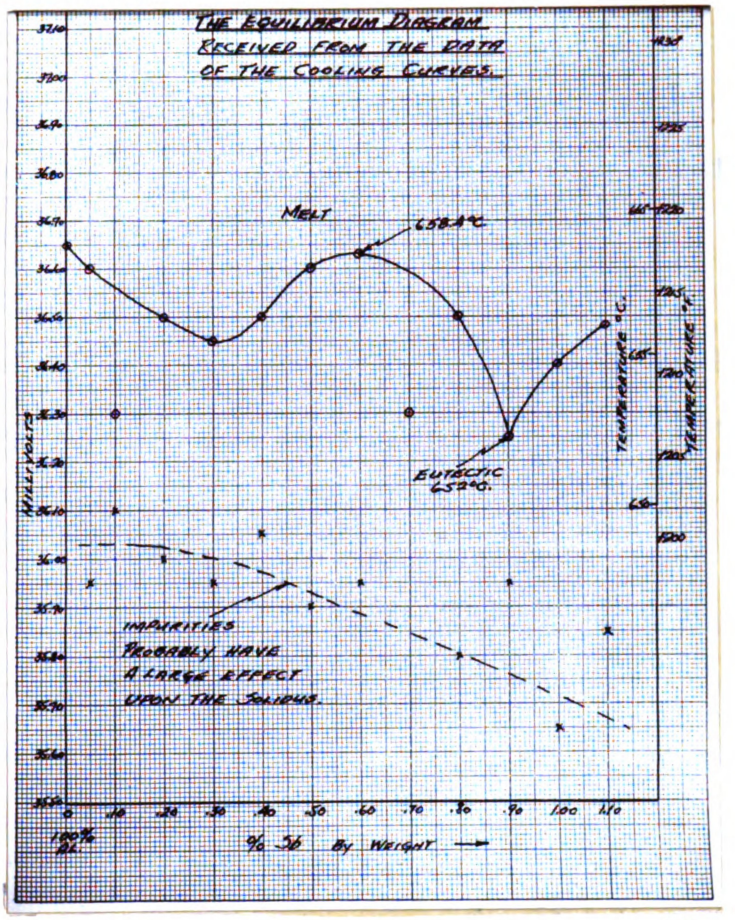


Fig. 7 The diagram according to Stone[13]

EQUILIBRIUM DIAGRAM INVESTIGATION BY THERMAL ANALYSIS

Theory

It is possible to predict to a limited extent the type of equilibrium diagram that may be expected from alloying aluminum and antimony.

First it may be stated that aluminum and antimony will form a substitutional type alloy. The other choice, the interstitial alloy, is formed only by the metalloids; hydrogen, carbon, nitrogen, or boron, alloyed with one of the transition elements.[12] The substitutional type alloy may be viewed as the lattice of one of the metals, with some of the lattice atoms replaced by atoms of the second metal. This is known as a substitutional solid solution. The extent to which the solute atoms replace at random atoms on the solvent lattice is termed solid solubility. The several factors that govern the solid solubility are the crystal structures, the atomic sizes, the alloying valences, and the electrochemical factors of the metals involved.[2]

The crystal structure of the solute must be the same as the solvent or complete solid solubility cannot be expected. Since aluminum has a face centered cubic structure and antimony has a rhombohedral structure, the factor of crystal structure is in this case unfavorable.

Where the atomic diameters of the two metals differ by 15% or less, the size factor is considered favorable for the formation of solid solution.[2] If the sizes differ by more than 8% but less than 15% the liquidus usually has a minimum, indicating a tendency toward eutectic formation. Borderline cases where the atomic size of the solute differs from the atomic size of the solvent by about 15% tend to give erratic results. As a general rule,

the greater the difference in size, the greater is the restriction on solid solubility. As the size factor becomes more unfavorable, the liquidus and solidus both become steepened, the solidus being more affected than the liquidus. This condition gives rise to wide freezing ranges. In this case the size factor is very favorable as antimony is about 1% larger than aluminum.[12]

As the valency of metals becomes more widely separated (the size factor being favorable), the solid solubility becomes more restricted. The liquidus and solidus are steepened, and the solidus is again the one most affected. In this case the valency factor is questionable since antimony exhibits valences of both three and five.

The greater the difference in electromotive potential, the greater is the tendency to restrict solid solubility. This factor tends to cause the formation of compounds, and the greater this electrochemical effect, the greater the stability of the compound. It should be noted that the electronegative degree of metals on the periodic chart increases from left to right in any period and from bottom to top in any group. The melting point of the compound is an indication of the compound stability, and in general the higher the melting point of the compound, the lower the solid solubility.[2] Several other facts follow from the melting point of the compound. As the melting point is higher, the eutectic composition is lower and the eutectic temperature is higher. From the latter two points, it follows that as the eutectic composition becomes lower, the eutectic temperature becomes higher; that is, closer to the pure solvent melting point.

Since it has been previously established that aluminum and antimony form a normal valence compound (SbAl) with a very high melting point (1050°C), it is to be expected that the solid solubility will be low and that the eutectic will be of low composition and high temperature.

Since the size factor is favorable and the valency effect probably favorable, the crystal structures and the electrochemical effect are the factors which limit solid solubility and position the eutectic.

Materials and Apparatus

The aluminum used to make up the alloys was a highly refined grade whose analysis is given in Table 1. This aluminum was supplied by the Aluminum Company of America in the form of small four section pigs. The antimony used was a good grade. The analysis is given in Table 2. The zinc used for calibrating the thermocouple was a standard laboratory grade. The analysis is given in Table 3.

A standard laboratory size electric resistance furnace and a suitable controller was used to soak the metals at high temperature. A Hoskins Electric Furnace, type FA-120, using 110v and rated at 3.27 amps was used to heat and cool the alloys during thermal analysis. A two piece refractory cover was used in conjunction with the furnace. Iron and constantan thermocouple wire of #24 B and S gauge was used to make the thermocouples. Potential readings were made with a Leeds and Northrup type K potentiometer used in conjunction with a suitable highly sensitive galvonometer and the usual light and scale apparatus. The furnace input was regulated by means of a Varitran transformer that delivers from 0 to 130v and is rated at 7.5 amps. A second Varitran was used to supply the low voltage to the bulb in the light source.

TABLE I

Aluminum Analysis (by %)

Al	99.9968
Si	0.0011
Fe	0.0006
Cu	0.0004
Mg	0.0007
Na	0.0004

TABLE II

Antimony Analysis (by %)

Assay	99.83
Fe	0.005
S	0.04
As	0.000
Pb	0.005
Cu	0.000

TABLE III

Zinc Analysis (by %)

Insol. H_2SO_4	0.005
As	0.000001
Pb	0.001
Fe	0.003

The alloys were heated in alundum crucibles 3/4" tall and 1 3/8" in outside dimension. Inside diameters ranged from 1/2" at the bottom to 1" at the top. A fairly close fitting refractory cover was made for the crucibles.

Miscellaneous equipment included a Weston standard cell, two #6 dry cells, a stop watch, a thermos jug filled with cracked ice and water used as a cold junction, A.C. meters, some animal charcoal, and some ground spectrographic grade carbon rod.

The equipment was assembled as shown in Fig. 8 and Fig. 9.

Thermocouple Calibration

Thermocouples made of any particular grades of wires give fairly consistant results from one thermocouple to the next, but when doing work of the accuracy employed in this investigation, it is necessary to calibrate the thermocouple against some known standard as small deviations usually exist due to a certain amount of unavoidable contamination of the bead.

This contamination was held at a minimum by using a special welding technique to prevent any oxidation of the metals at the bead. A small, wide mouth bottle was filled with a layer of mercury about 3/8" deep. The bottle was then filled to the top with some clean light-weight motor oil. A copper wire was inserted into the bottle so that it made contact with the mercury and was fastened rigidly to the top of the bottle. This served merely as an electrode. The ends of the thermocouple wires were twisted together and connected directly to one side of a 110v A.C. line. The other side of the line was connected thru an adjustable resistor to the copper electrode. The twisted end of the wires was then carefully

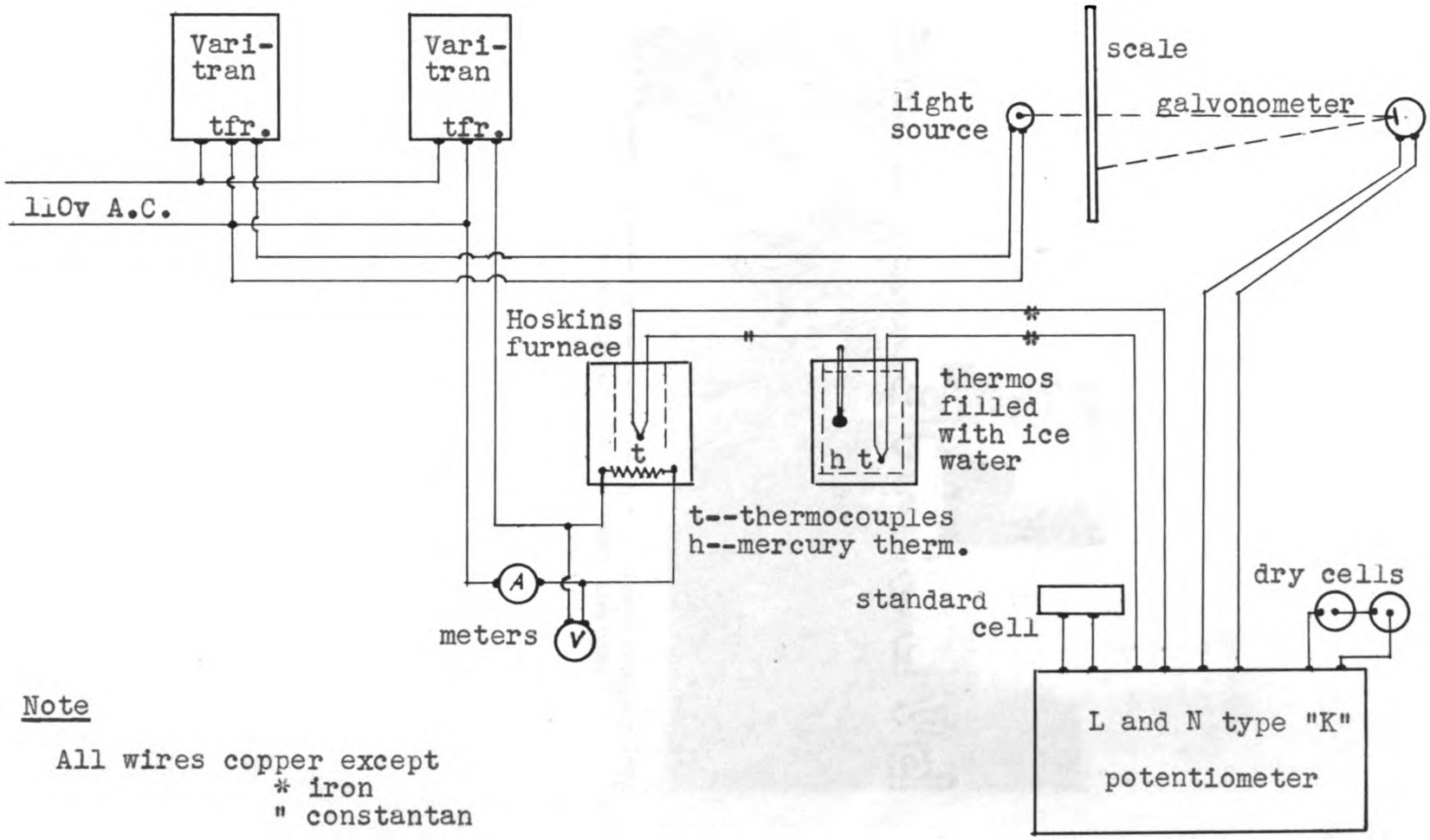


Fig. 8. Schematic Drawing of the Equipment for Thermal Analysis

Fig. 9 The equipment for thermal analysis in operating position.

lowered thru the oil toward the mercury, and removed the instant a flash appeared. The resistor had to be experimentally adjusted so that the twisted wires would weld but not melt off. Before it was used, the thermocouple was covered with a thin coating of alundum powder. The wires were insulated from one another with refractory and plastic insulators.

The high purity aluminum and some good quality zinc were used as standards. Their analyses are given in Table 1 and Table 3. The metal was heated in the Hoskins furnace. When the metal was molten, the thermocouple was inserted and the furnace was sealed with the refractory cover. The Varitran transformer was set at a predetermined point, and the furnace was allowed to cool. When the melting point range was reached, a potential reading was taken every sixty seconds.

The data was plotted on a time-temperature graph and the potential was noted adjacent to the horizontal section of the cooling curve. This potential was converted to $^{o}F.$ by means of a table[14].

The heating curves were also plotted to show the amount of hystersis present. This amounted to about 0.05% difference which was negligible.

The results of the calibration indicated that zinc gave a reading .12 mv too low while aluminum gave a reading .04 mv too high as compared to the handbook value of 36.72 mv. Since the aluminum .034 mv is equal to about $1^{o}F.$, the thermocouple read a little better than $1^{o}F.$ high. This was taken into account when plotting the final graph.

In choosing the proper voltage for heating and cooling the furnace, the values given by Stone[13] were used as a starting point and small adjustments made as needed. Stone listed 83-85 v as the heating voltage and 63-65 volts as the cooling voltage.

DATA FOR THERMOCOUPLE CALIBRATION

TABLE #4 DATA FOR THE TRANSFORMATION CURVE OF ALUMINUM

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	37.82	23"	36.65	0"	35.97
1"	37.69	24"	36.64	1"	36.19
2"	37.56	25"	36.63	2"	36.43
3"	37.49	26"	36.63	3"	36.61
4"	37.38	27"	36.62	4"	36.63
5"	37.28	28"	36.62	5"	36.63
6"	37.18	29"	36.61	6"	36.63
7"	37.07	30"	36.61	7"	36.63
8"	36.98	31"	36.61	8"	36.64
9"	36.89	32"	36.60	9"	36.64
10"	36.80	33"	36.60	10"	36.67
11"	36.69	34"	36.60	11"	36.75
12"	36.75	35"	36.60	12"	36.87
13"	36.74	36"	36.60	13"	36.97
14"	36.75	37"	36.58	14"	37.06
15"	36.74	38"	36.57	15"	37.14
16"	36.73	39"	36.57	16"	37.22
17"	36.71	40"	36.55	17"	37.28
18"	36.70	41"	36.51	18"	37.34
19"	36.69	42"	36.47	19"	37.37
20"	36.68	43"	36.24	20"	37.40
21"	36.67	44"	35.91	21"	37.83
22"	36.66			22"	38.43

TABLE #5 DATA FOR THE TRANSFORMATION CURVE OF ZINC

Cooling		Heating	
Time	Mv	Time	Mv
0"	24.03	0"	22.00
1"	23.81	1"	22.12
2"	23.61	2"	22.23
3"	23.42	3"	22.34
4"	23.25	4"	22.46
5"	23.11	5"	22.57
6"	23.01	6"	22.69
7"	22.94	7"	22.76
8"	22.87	8"	22.78
9"	22.83	9"	22.79
10"	22.79	10"	22.79
11"	22.79	11"	22.80
12"	22.79	12"	22.80
13"	22.79	13"	22.80
14"	22.79	14"	22.80
15"	22.79	15"	22.80
16"	22.79	16"	22.80
17"	22.79	17"	22.80
18"	22.79	18"	22.80
19"	22.79	19"	22.85
20"	22.79	20"	22.94
21"	22.72	21"	23.01
22"	22.61	22"	23.09
23"	22.50	23"	23.15
24"	22.15	24"	23.21
25"	21.85	25"	23.27
		26"	23.32
		27"	23.38
		28"	23.42
		29"	23.48
		30"	23.52
		31"	23.57
		32"	23.62
		33"	23.68
		34"	23.78
		35"	23.97

Figure 10

Aluminum
Calibration Cooling Curve

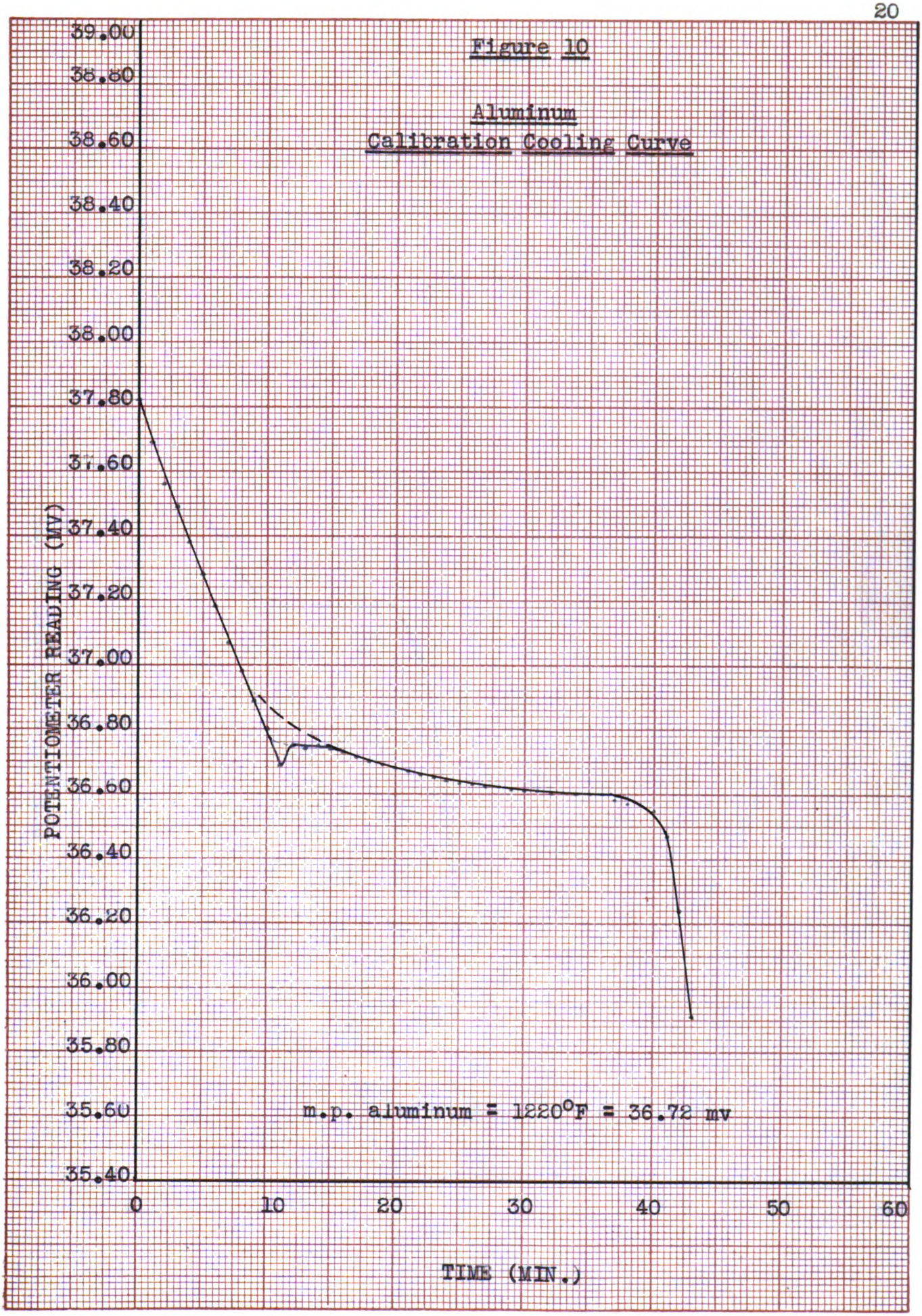
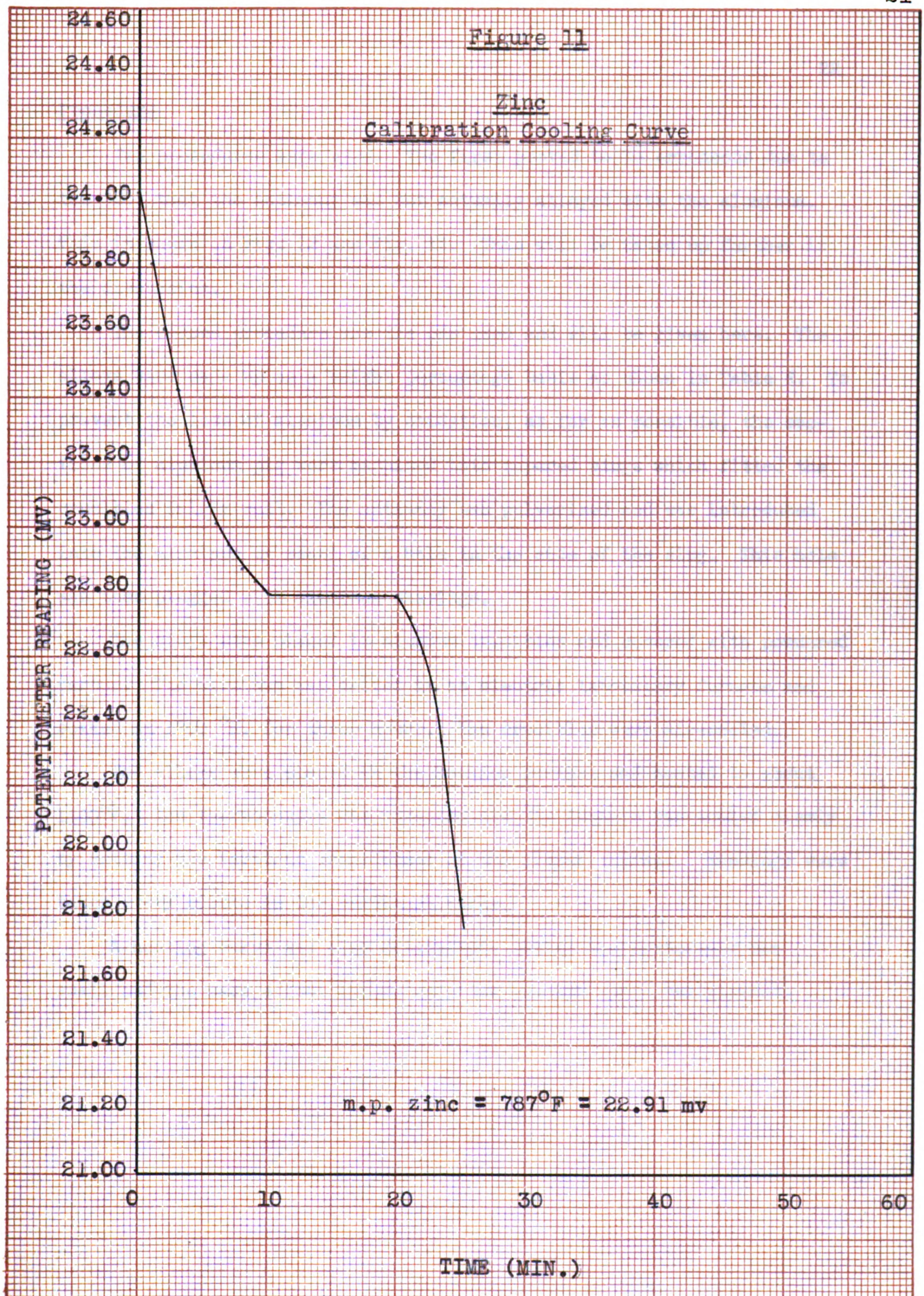


Figure 11

Zinc
Calibration Cooling Curve



Procedure

Two procedures were used. The first proved to be erroneous due to the fact that the antimony was not actually alloyed with the aluminum. This is shown in Fig. 12 and Fig. 13. This will be taken up further in the discussion.

The second procedure was the one used and will be given here. The alloys were made up on a weight percentage basis as shown in Table 6. To prevent the loss of aluminum by oxidation, as far as possible, the sections of aluminum pig were machined into tapered slugs which fitted the crucibles fairly well. The antimony was pulverized and was introduced into the aluminum by means of a hole in the side of the slug. This hole was then plugged with aluminum shavings.

The slugs were placed in alundum crucibles and covered with powdered carbon. The aluminum was melted in an electric laboratory furnace and soaked at 1700 ^{o}F. for three hours. The crucibles were air-cooled.

The alloys were placed in the Hoskins furnace and heated to about 1400^{o}F. The thermocouple was inserted and the furnace was cooled slowly by setting the Varitran transformer at the proper voltage. Readings were taken every minute in the pertinent range.

A heating curve was also determined, but as the hysteresis was small and the mass effect large, only the cooling curve was plotted.

TABLE #6

Alloy Analysis (by weight)

% Sb	Wt. Al (grams)	Wt. Sb (grams)
0.05	36.326	0.019
0.15	39.513	0.059
0.80	35.709	0.237
1.10	37.495	0.417
1.40	36.667	0.520

Fig. 12 Antimony 0.4% showing free antimony (black). 1.5X. Etch 1% NaOH. Original thermal analysis sample cooled from 1500°F.

Fig. 13 Antimony 0.4% showing free antimony (black). 2X. Etch 1% NaOH. Held at 1500°F. for 1 hour. Air cooled.

TABULATED DATA

TABLE #7 THERMAL ANALYSIS DATA FOR THE TRANSFORMATION OF 0.05% ANTIMONY IN ALUMINUM

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	39.01	25"	36.64	0"	35.03
1"	38.86	26"	36.63	1"	35.30
2"	38.71	27"	36.62	2"	35.54
3"	38.56	28"	36.61	3"	35.77
4"	38.42	29"	36.60	4"	35.04
5"	38.27	30"	36.60	5"	35.24
6"	38.15	31"	36.59	6"	35.44
7"	37.98	32"	36.59	7"	35.52
8"	37.83	33"	36.59	8"	35.55
9"	37.71	34"	36.59	9"	35.58
10"	37.58	35"	36.59	10"	35.59
11"	37.45	36"	36.60	11"	35.59
12"	37.31	37"	36.59	12"	35.60
13"	37.20	38"	36.60	13"	35.60
14"	37.07	39"	36.59	14"	35.60
15"	36.95	40"	36.58	15"	35.67
16"	36.84	41"	36.56	16"	35.78
17"	36.80	42"	36.54	17"	35.90
18"	36.77	43"	36.49	18"	35.98
19"	36.74	44"	36.47	19"	37.08
20"	36.71	45"	36.41	20"	37.17
21"	36.70	46"	36.25	21"	37.26
22"	36.69	47"	35.85	22"	37.34
23"	36.67	48"	35.57	23"	37.25
24"	36.65			24"	37.27
				25"	37.31
				26"	37.83
				27"	38.33
				28"	38.77
				29"	39.11
				30"	39.46

TABLE #8 THERMAL ANALYSIS DATA FOR THE TRANSFORMATION OF 0.15% ANTIMONY IN ALUMINUM

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	39.02	31"	36.70	0"	35.11
1"	38.90	32"	36.68	1"	35.32
2"	38.78	33"	36.67	2"	35.55
3"	38.67	34"	36.66	3"	35.77
4"	38.56	35"	36.65	4"	35.92
5"	38.45	36"	36.64	5"	36.13
6"	38.34	37"	36.63	6"	36.28
7"	38.23	38"	36.62	7"	36.41
8"	38.14	39"	36.61	8"	36.45
9"	38.04	40"	36.60	9"	36.45
10"	37.94	41"	36.59	10"	36.48
11"	37.84	42"	36.59	11"	36.49
12"	37.74	43"	36.58	12"	36.49
13"	37.64	44"	36.57	13"	36.52
14"	37.54	45"	36.57	14"	36.52
15"	37.46	46"	36.56	15"	36.53
16"	37.37	47"	36.56	16"	36.57
17"	37.27	48"	36.56	17"	36.64
18"	37.19	49"	36.55	18"	36.69
19"	37.08	50"	36.54	19"	36.77
20"	37.00	51"	36.54	20"	36.82
21"	36.92	52"	36.52	21"	36.91
22"	36.85	53"	36.51	22"	36.97
23"	36.83	54"	36.49	23"	37.04
24"	36.81	55"	36.45	24"	37.12
25"	36.79	56"	36.42	25"	37.19
26"	36.77	57"	36.37	26"	37.27
27"	36.75	58"	36.33	27"	37.35
28"	36.74	59"	36.27	28"	37.43
29"	36.72	60"	35.99	29"	37.50
30"	36.71			30"	37.56

TABLE #9 THERMAL ANALYSIS DATA FOR THE TRANSFORMATION OF 0.8% ANTIMONY IN ALUMINUM.

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	38.58	27"	36.70	0"	36.19
1"	38.44	28"	36.69	1"	36.47
2"	38.32	29"	36.67	2"	36.55
3"	38.19	30"	36.66	3"	36.55
4"	38.08	31"	36.65	4"	36.55
5"	37.96	32"	36.64	5"	36.55
6"	37.84	33"	36.63	6"	36.59
7"	37.74	34"	36.62	7"	36.63
8"	37.62	35"	36.61	8"	36.71
9"	37.51	36"	36.60	9"	36.83
10"	37.41	37"	36.59	10"	36.96
11"	37.30	38"	36.58	11"	37.11
12"	37.21	39"	36.56	12"	37.25
13"	37.12	40"	36.56	13"	37.39
14"	37.00	41"	36.55	14"	37.52
15"	36.94	42"	36.55	15"	37.63
16"	36.89	43"	36.54	16"	37.76
17"	36.86	44"	36.54	17"	37.89
18"	36.83	45"	36.54	18"	38.27
19"	36.82	46"	36.54		
20"	36.80	47"	36.54		
21"	36.79	48"	36.54		
22"	36.76	49"	36.54		
23"	36.75	50"	36.52		
24"	36.74	51"	36.51		
25"	36.72	52"	36.48		
26"	36.71	53"	36.11		

TABLE 10 THERMAL ANALYSIS DATA FOR THE TRANSFORMATION OF 1.1% ANTIMONY IN ALUMINUM

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	38.61	31"	36.60	0"	35.98
1"	38.51	32"	36.59	1"	36.33
2"	38.41	33"	36.57	2"	36.33
3"	38.30	34"	36.56	3"	36.42
4"	38.21	35"	36.55	4"	36.45
5"	38.12	36"	36.54	5"	36.45
6"	38.03	37"	36.53	6"	36.45
7"	37.93	38"	36.52	7"	36.45
8"	37.86	39"	36.51	8"	36.46
9"	37.75	40"	36.50	9"	36.46
10"	37.67	41"	36.50	10"	36.47
11"	37.59	42"	36.50	11"	36.49
12"	37.49	43"	36.49	12"	36.56
13"	37.42	44"	36.49	13"	36.65
14"	37.32	45"	36.48	14"	36.73
15"	37.24	46"	36.47	15"	36.82
16"	37.15	47"	36.47	16"	36.91
17"	37.08	48"	36.46	17"	36.99
18"	37.01	49"	36.46	18"	37.05
19"	36.93	50"	36.45	19"	37.13
20"	36.85	51"	36.45	20"	37.19
21"	36.77	52"	36.44	21"	37.25
22"	36.70	53"	36.44	22"	37.31
23"	36.64	54"	36.44	23"	37.39
24"	36.65	55"	36.43	24"	37.58
25"	36.68	56"	36.42	25"	38.02
26"	36.67	57"	36.41		
27"	36.66	58"	36.39		
28"	36.63	59"	36.38		
29"	36.63	60"	36.36		
30"	36.61				

TABLE #11 THERMAL ANALYSIS DATA FOR THE TRANSFORMATION OF 1.4% ANTIMONY IN ALUMINUM

Cooling				Heating	
Time	Mv	Time	Mv	Time	Mv
0"	39.04	31"	36.64	0"	35.50
1"	38.89	32"	36.64	1"	35.65
2"	38.74	33"	36.62	2"	35.80
3"	38.61	34"	36.61	3"	35.93
4"	38.48	35"	36.60	4"	36.06
5"	38.36	36"	36.59	5"	36.21
6"	38.24	37"	36.58	6"	36.34
7"	38.13	38"	36.57	7"	36.46
8"	38.03	39"	36.56	8"	36.49
9"	37.92	40"	36.55	9"	36.50
10"	37.82	41"	36.52	10"	36.50
11"	37.70	42"	36.54	11"	36.50
12"	37.59	43"	36.52	12"	36.50
13"	37.50	44"	36.50	13"	36.50
14"	37.39	45"	36.50	14"	36.51
15"	37.29	46"	36.49	15"	36.51
16"	37.22	47"	36.49	16"	36.51
17"	37.12	48"	36.48	17"	36.54
18"	37.01	49"	36.49	18"	36.59
19"	36.93	50"	36.49	19"	36.66
20"	36.84	51"	36.48	20"	36.72
21"	36.81	52"	36.48	21"	36.78
22"	36.78	53"	36.48	22"	36.84
23"	36.76	54"	36.47	23"	36.90
24"	36.74	55"	36.45	24"	36.94
25"	36.73	56"	36.42	25"	37.00
26"	36.72	57"	36.39	26"	37.04
27"	36.69	58"	36.36	27"	37.09
28"	36.69	59"	36.30	28"	37.15
29"	36.67	60"	35.99	29"	37.19
30"	36.66			30"	37.23

Figure 14

0.05% Antimony Alloy
Cooling Curve

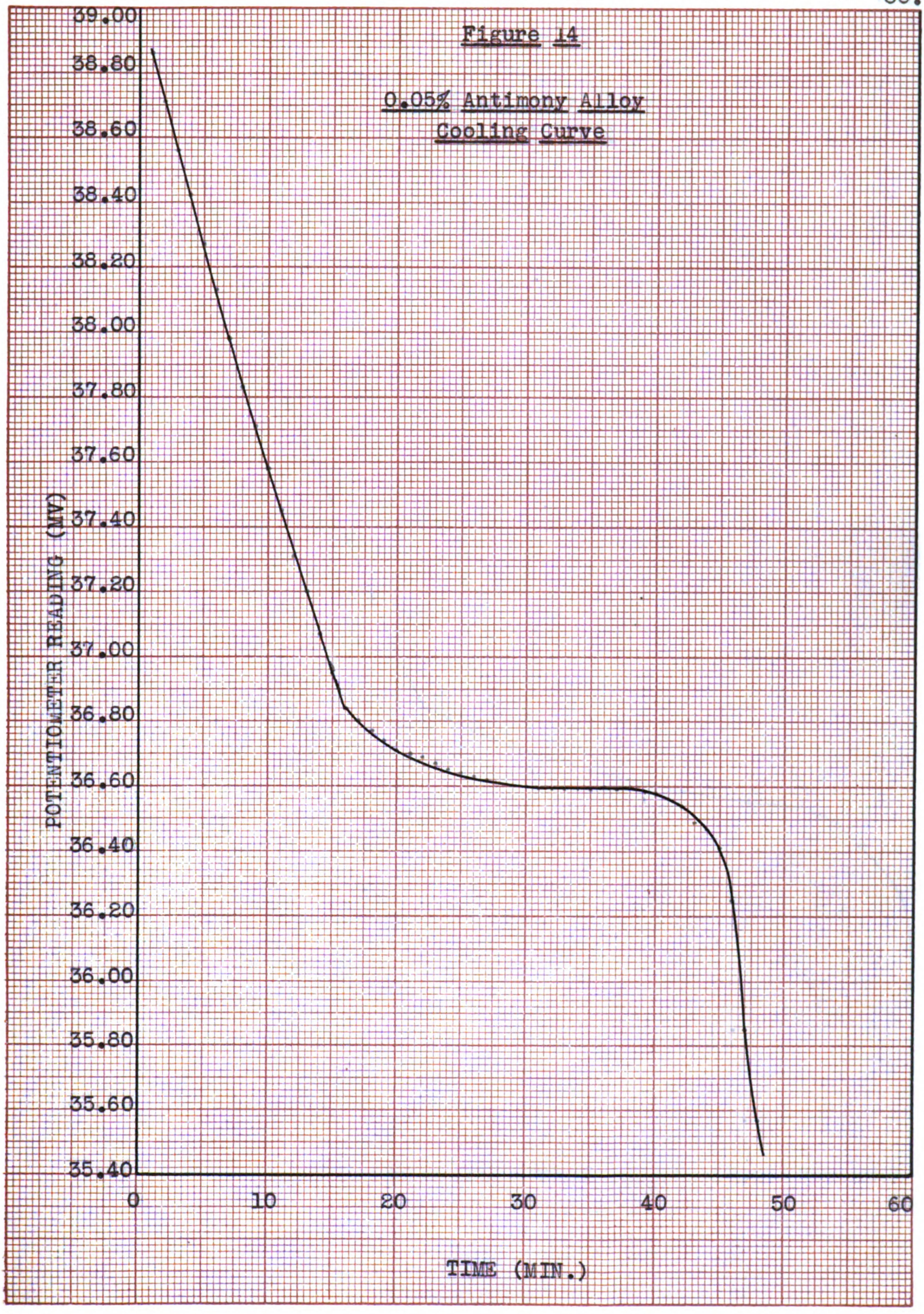


Figure 15

0.15% Antimony Alloy
Cooling Curve

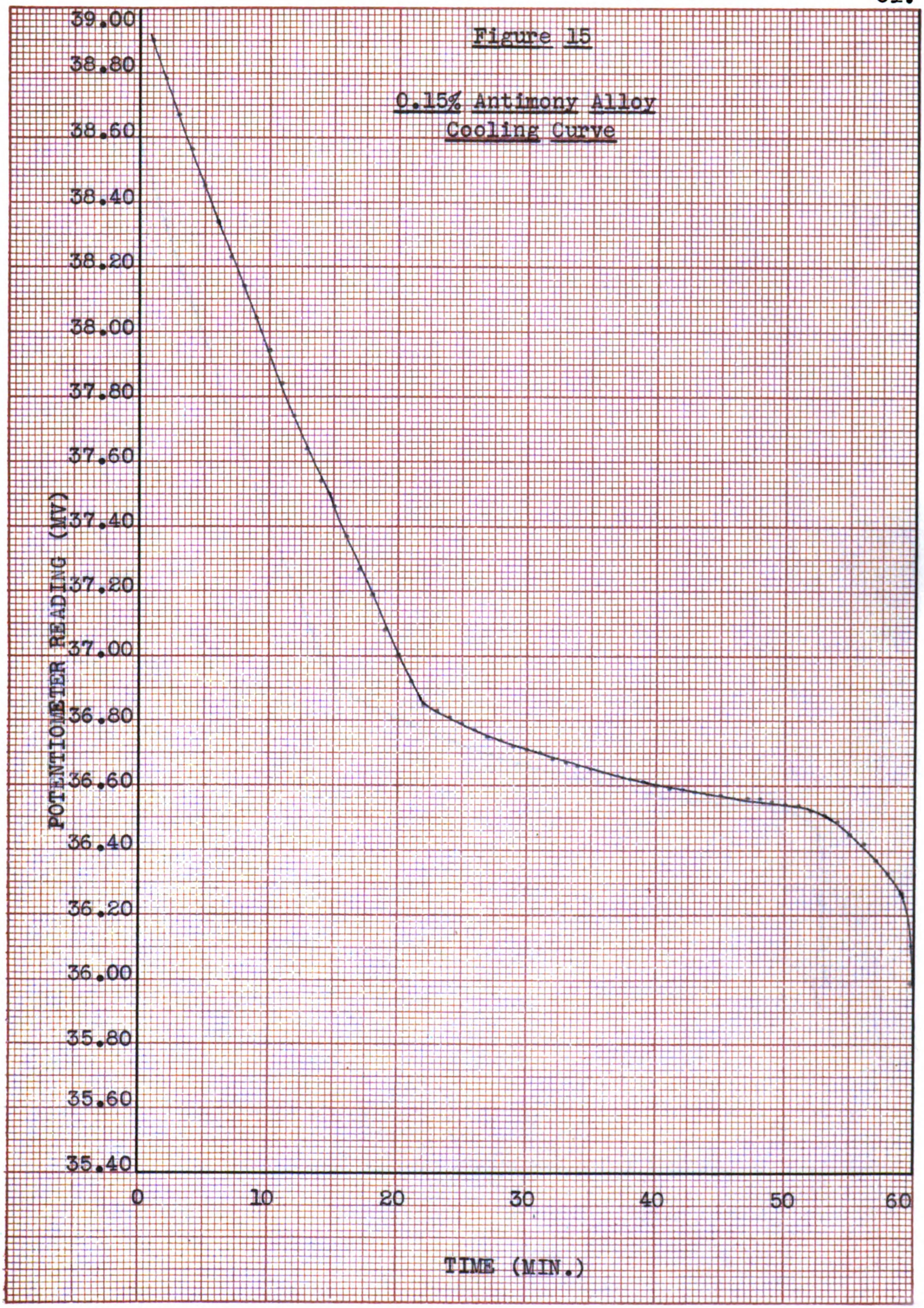


Figure 16

0.8% Antimony Alloy
Cooling Curve

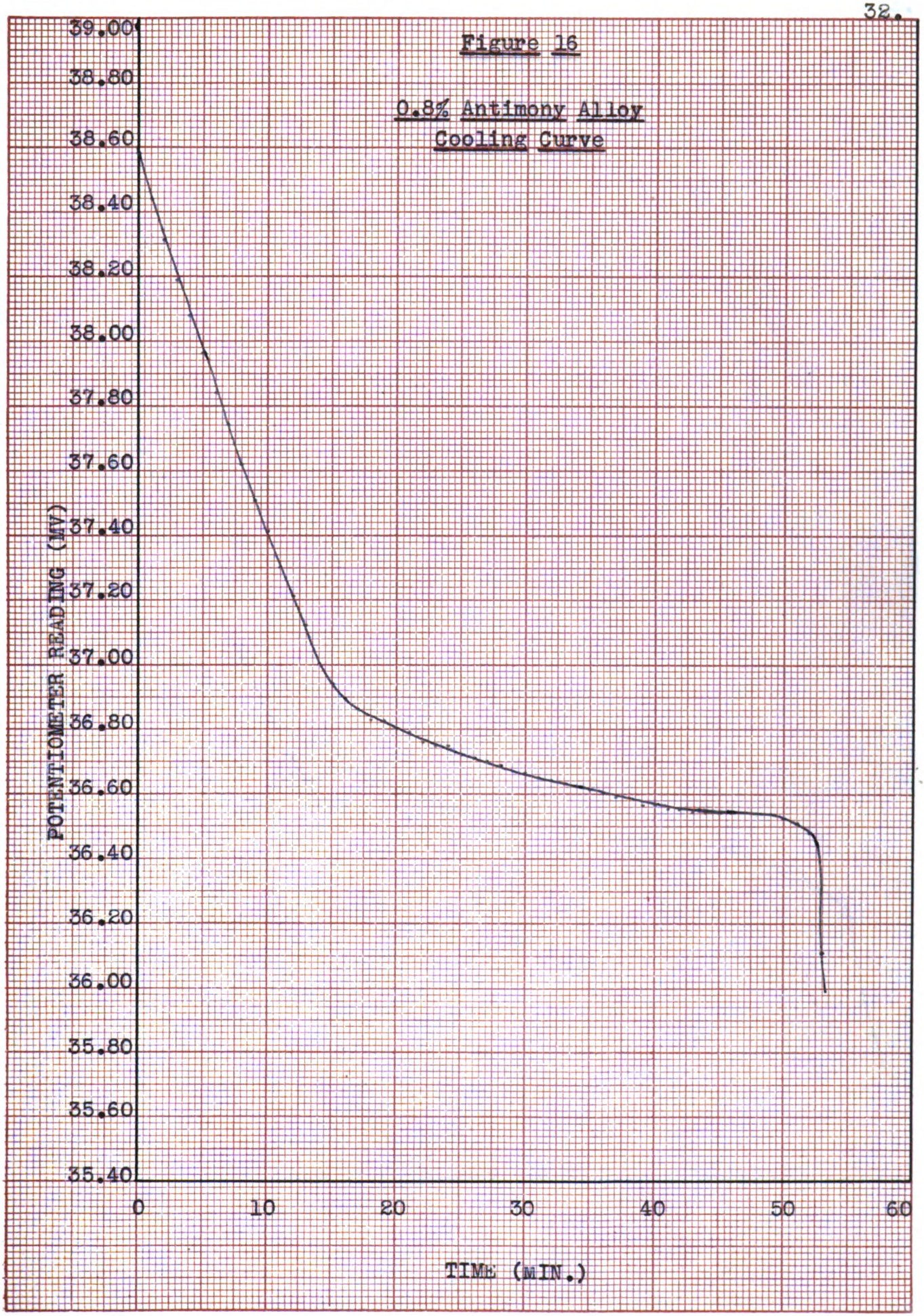


Figure 17

1.1% Antimony Alloy
Cooling Curve

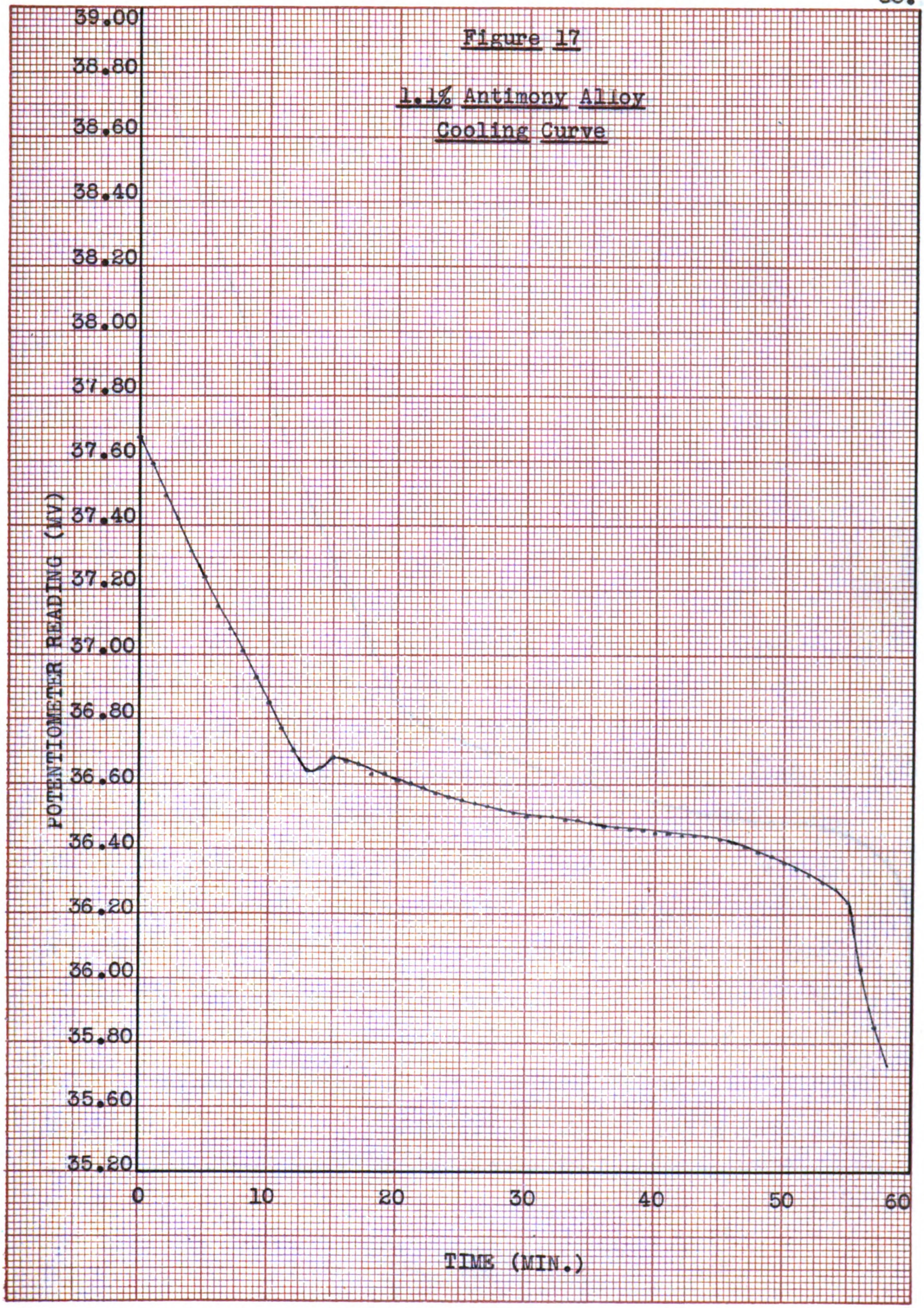
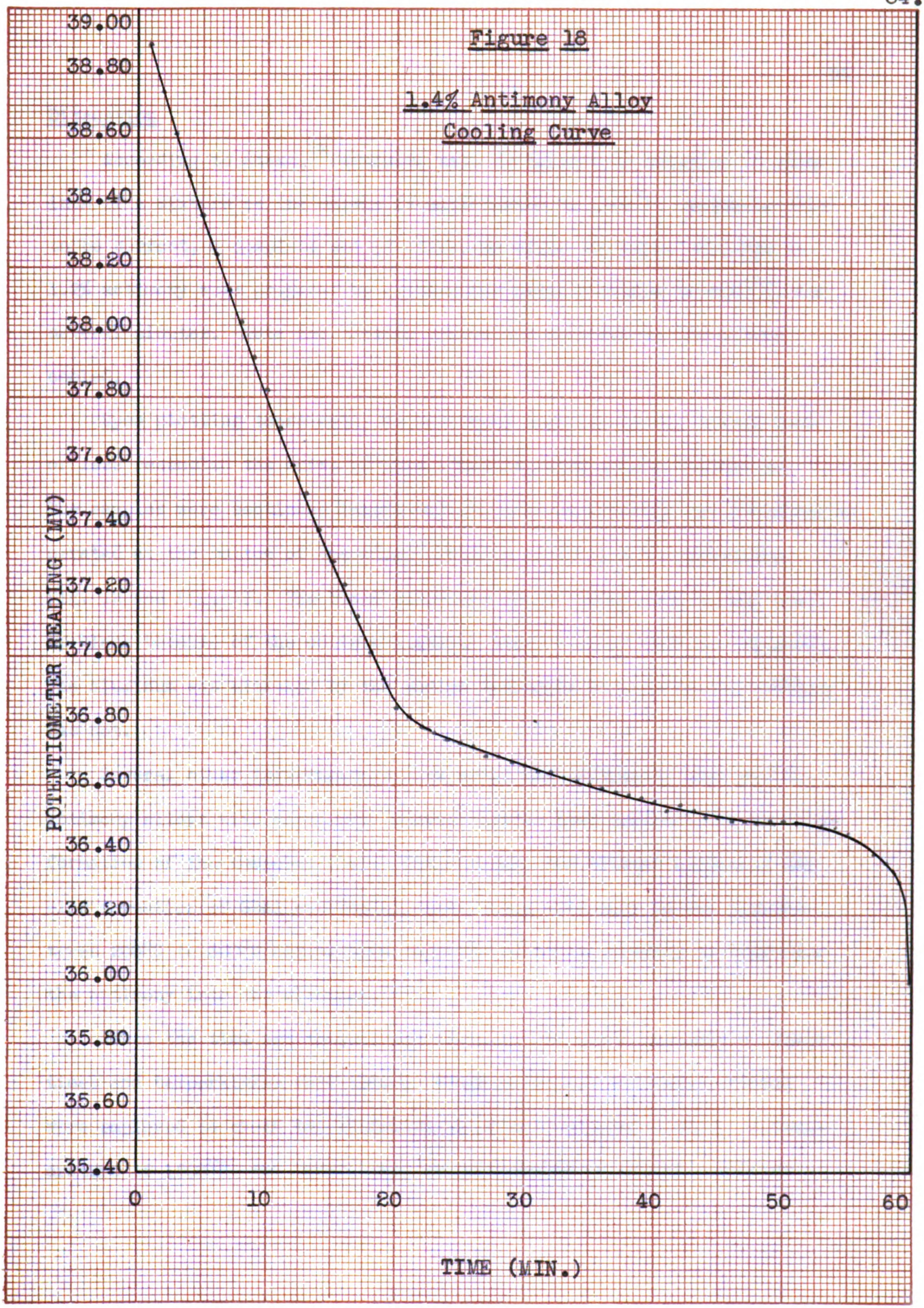


Figure 18

1.4% Antimony Alloy
Cooling Curve



Discussion

According to Stone,[13] antimony will be taken into solution in aluminum if a mixture of the metals is superheated to 1500°F. Assuming this to be correct, a complete set of alloys covering the range of 0.05% to 1.2% antimony were prepared by heating the metal mixtures to 1500°F. for several minutes. Data for cooling curves was recorded as the alloys cooled.

Upon plotting these data, it was found that all of the curves more or less resembled the curve of pure aluminum, with slight variations. The samples were sectioned longitudinally and the antimony was found agglomerated at the bottom of the slug. This is shown in the macrographs Fig. 12 and Fig. 13. The black areas are the antimony areas; they show up black because of the oblique lighting used to photograph the samples. The aluminum was attacked by the sodium hydroxide etch while the antimony was not.

Several other investigators have noted the difficulty with which antimony alloys with aluminum. Corson[3] states that Urazov noted the slow formation of the compound SbAl. Dix, Keller, and Willey[5] mentioned the slow formation of SbAl and stated that it was necessary to use temperatures 200°C to 300°C higher than would be normally expected to introduce the antimony into the aluminum.

Since the time and temperature used did not alloy the metals, other times and temperatures were tried. Rough polishing and heavy etching were employed to check the distribution of the compound (SbAl). A temperature of 1500°F. was tried, but the time needed to assure a uniform

distribution of compound was too long. It took roughly twenty hours at temperature. At 2000°F. the alloy formed in twenty to twenty-five minutes. But it was feared that too much aluminum and antimony would be lost by oxidation at this temperature. The alloy appeared to form homogeneously in three hours at 1700°F. so this temperature and time combination were employed thereafter.

Various means of mixing the metals to aid alloying were tried. Stirring with a refractory insulator was tried, as was pouring from one crucible to another. But, due to the small size of the crucibles and the small amounts of metals being used, these processes were quite unsatisfactory. If large amounts of metals are used, these techniques should be quite satisfactory. Dix, Keller, and Willey[5] advocate stirring the melt.

Several attempts were made to protect the aluminum from oxidation. Molten anhydrous sodium tetraborate was tried, but the alundum crucibles readily absorbed the liquid. This method would probably be satisfactory if carbon crucibles were used. It was attempted to melt the metals in an atmosphere of nitrogen and of carbon dioxide. The exact difficulty was not ascertained, but white fumes were given off by the antimony in both cases. According to Anderson,[1] nitrogen combines with molten aluminum. Also, carbon dioxide breaks down at about 800°C. and oxidizes aluminum. It was further stated that hydrogen is harmful to aluminum as it is highly soluble in the molten metal. In a private conversation, Dr. Fink of the Aluminum Company of America said that aluminum could be melted bright in a highly purified atmosphere of one of the inert gases such as helium or argon. Dr. Fink said further that if chemical analysis was subsequently made, then it was not necessary to protect the aluminum, as loss due to

oxidation was small. It was obvious to the author that the powdered carbon used to cover the samples did not prevent oxidation, but it was felt that the carbon formed a good heat seal for the exposed metal surface during thermal analysis.

The cooling curves derived from the data obtained according to the final procedure are shown in Fig. 14 thru Fig. 18. The liquidus points were taken as the point where the graph first showed a break on cooling.

The solidus points were taken at the point of the best horizontal section of the curve. If the solid solubility is taken as 0.1% Sb, then the 0.05% Sb curve shows the error apparent in determining a solidus from a cooling curve. Fink[7] states that the solidus point on a cooling curve is very apt to be in error as the first crystals formed do not attain equilibrium with the last liquid to freeze. This would be particularly true in a case where the diffusion rates are as slow as they are with aluminum and antimony. Fink further asserts that the solidus is best determined from the heating curve of a homogeneous solid specimen. According to Dix and associates[5], it takes in the range of hundreds of hours to form a homogeneous solid specimen of aluminum-antimony alloy. Such a procedure was beyond the scope of this investigation. The critical points obtained from the cooling curves are given in Table 12. The plot of these points on a time-temperature graph is shown in Fig. 19. No attempt was made to draw a curve thru these points as there are several discrepancies apparent. The liquidus points of the alloys are all at a higher temperature than the melting point of pure aluminum. Also, the eutectic cooling curve should resemble the curve for a pure metal in that there should be only one transformation point. The curve for the 1.1%

antimony alloy shows a curve similar to the 0.8% and 1.4% antimony alloy curves. There are several possibilities for error in determining the liquidus points. First, the eutectic may not have been taken back into the solution entirely at the temperature of 1400°F. for a half hour used to melt the alloys for thermal analysis. This would be more of a possibility in the alloys of higher antimony content. Second, due to the small temperature differential between solidus and liquidus, a very small mass effect could easily cover up the true critical points. More will be said about these two possibilities later. Thermocouple contamination and changes in the standard cell voltage due to temperature variation are other possibilities.

TABLE #12

DATA FOR EQUILIBRIUM DIAGRAM

Sb %	Critical Point on Cooling Curve (mv)	Corrected* Liquidus (mv)
0.00	36.76	36.72
0.05	36.83	36.79
0.15	36.84	36.80
0.80	36.90	36.86
1.10	36.80	36.76
1.40	36.83	36.79

Sb %	Critical Point on Cooling Curve (mv)	Corrected Solidus (mv)
0.00	----	----
0.05	36.59	36.55
0.15	36.56	36.52
0.80	36.54	36.50
1.10	36.44	36.40
1.40	36.49	36.45

*As noted in the thermocouple calibration, correction of -.04 mv must be added to the experimental data.

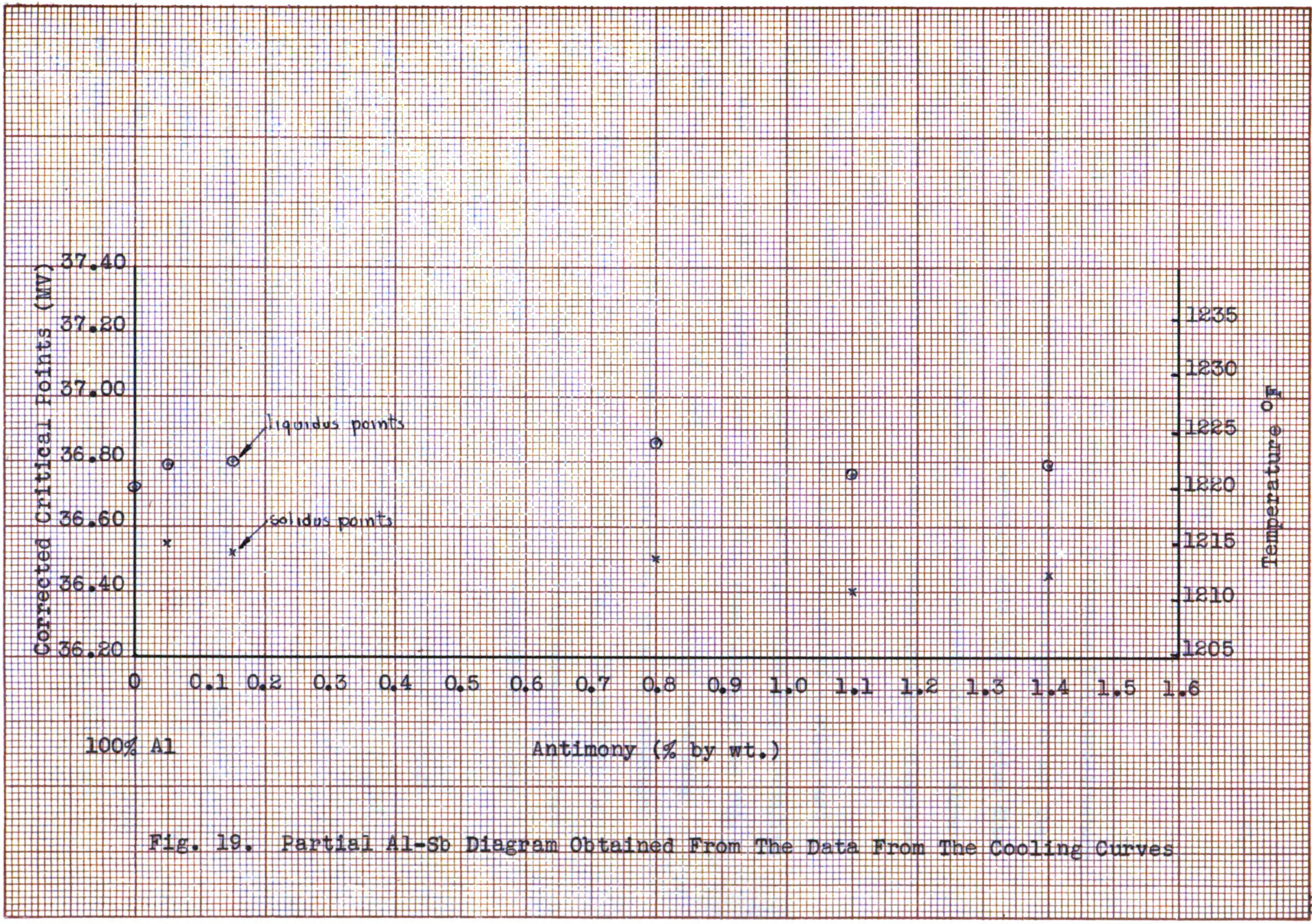


Fig. 19. Partial Al-Sb Diagram Obtained From The Data From The Cooling Curves

MICROSTRUCTURE

Introduction

It was felt that it would be desirable to examine the microstructure of the thermal analysis specimens in order to observe whether or not the microstructure of the specimens would correlate with the equilibrium diagram obtained. It was deemed desirable to show the grain size and structure of the pure aluminum, and the components present and their distribution in the alloy specimens.

Dix and associates[5] found that the microstructure of a chill cast alloy containing 0.1% antimony showed fine particles which they identified as SbAl. Subsequent to various heat treatments, examination showed this alloy to have particles of SbAl out of solution. An alloy containing 1.04% antimony exhibited a hypoeutectic structure. An alloy containing 1.14% antimony showed a few particles of primary SbAl. The authors further stated that it was impossible to prepare an alloy showing a uniform eutectic structure and that in all cases primary compound and primary aluminum occurred in the same field.

It was known before hand that polishing a metal as soft as high purity aluminum requires special techniques. Many different techniques were tried and are reported herein.

Polishing and Etching Procedures

The polishing procedure was divided into four stages; namely, rough grinding, emery paper grinding, rough polishing, and final polishing.

The rough grinding was done on a medium grade grinding wheel. Care was taken to use the wheel only as long as was necessary to remove saw

marks, to use moderate pressure, and to frequently cool the specimen in cold water.

The emery paper grinding was done on a series of six papers. These were numbers 180, 280, 400, 0, 2/0, and 3/0. The latter are listed in the order of descending grain size, which was the order used. The specimens were first ground on the plain papers, but the resulting surface was dark and scuffed. Several lubricants were tried including chalk, which worked fairly well but was very dirty, and a solution of paraffin in acetone, which did not work at all because the acetone dissolved the binder in the emery paper. A method was finally discovered that gave very clean, bright surfaces with a minimum of flow. This method consisted of coating the papers with paraffin by drawing a bar of paraffin across the surface several times. Less pressure was used to apply the paraffin as the grade of the paper became finer.

The rough polishing was a difficult stage. Several techniques were tried. The specimens were polished using suspensions of #320 and #500 abrasive on billard cloth*. The resulting surfaces were badly smeared and dragged out. A wax wheel was used with #500 abrasive, and the surfaces were again badly smeared. As suggested by Mondolfo[11], a suspension of #600 abrasive was continuously dripped on a wheel covered with Kitten-ear cloth. The specimens were polished on this wheel at medium speed. The resulting surfaces were fairly well polished without undue smearing, but the polishing time was quite long and the hard constituents were badly dragged out. This technique was tried with #320 abrasive and the surfaces were quite badly smeared. While not entirely satisfactory,

* All cloths, Adolph Buehler, Ltd.

the best results were obtained by using a small amount of light lubricating oil on a used canvas #320 wheel and later on billiard cloth. This method gave a bright surface in a short time at a moderate polishing wheel speed. Further experimentation showed that the best results were obtained by using oil and abrasive quite liberally on a broken-in microcloth.. There was still some pitting and drag-out, but with care these defects could be reduced to a minimum.

The final polishing was also difficult and no really satisfactory method was found. Some of the methods tried are listed below. All final polishing was done on a special slow speed wheel.

1. Alumina on billiard cloth wet wheel. Smearing.
2. Alumina on selvyt cloth wet wheel. Smearing.
3. Chrome green* on silk. Bad scratches and smearing.
4. Micropolish* on microcloth moist wheel. Scratches.
5. Micropolish on kitten-ear wet wheel. Scratches.
6. Micropolish on billiard cloth moist wheel. Scratches.
7. MgO on kitten-ear moist wheel. Scratches and corrosion.
8. MgO calcined[11] at 1650°F. for 3 hours and passed thru a 120X sieve, on kitten-ear moist wheel. Scratches and corrosion.
9. Relevigated alumina dripping continuously on a partly broken-in billiard cloth. Fairly good surface produced.
10. Alumina on a fairly dry billiard cloth oil wheel. Fairly good but some scratches.

From these attempts it was decided that the best method tried was that of continuously dripping relevigated alumina on a partly broken-in billiard cloth. However, these methods are for the most part very sensitive to small changes of pressure on the specimen and to the amount of moisture, oil, and abrasive on the cloth.

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* Adolph Buehler, Ltd.

To recapitulate, the best polishing procedure found consists of the collowing steps:

1. Rough grinding
2. Paraffin coated emery papers number 180, 280, 400, 0, 2/0, 3/0.
3. #320 oil wheel
4. Relevigated alumina dripping on slow speed wheel.

Etching was difficult because of the small amount of surface flow that remained from polishing. The etch either did not reveal the microstructure, or it left a dirty, over-etched surface. Hydrofloric acid (1%) and sodium hydroxide (1%, 5%, and 10%) were tried. Immersion in the 5% NaOH at 160°F. gave the most satisfactory results.

Specimens were taken from the thermal analysis ingots and were prepared for microscopic examination by the above method. A specimen of pure aluminum was also prepared.

Discussion

The polishing job on the specimens from which the photomicrographs were made was far from perfect. There is evident in the pictures some pitting and an excessive amount of drag-out of the compound. The pure aluminum specimen was unavoidably over-etched, due to small amounts of surface flow that could not be eliminated.

The 0.05% antimony specimen (Fig. 21) shows no evidence of eutectic. This substantiates the presence of some solid solubility. The 0.15% specimen (Fig. 22) shows a small amount of eutectic in the grain boundaries, surrounding the grains of solid solution. The amount of eutectic shown in the 0.8% specimen (Fig. 23) does not seem sufficient for a composition so close to the eutectic. The 1.1% specimen (Fig. 24) shows the compound quite evenly distributed in the matrix, but there was in some sections not

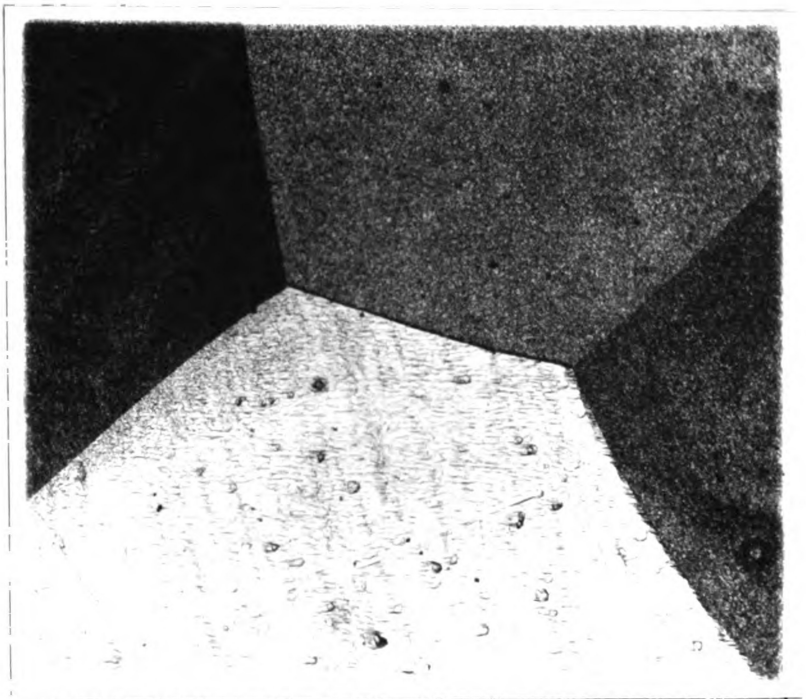


Fig. 20 High purity aluminum. Etchant, 5% NaOH at 160°F. 75X.

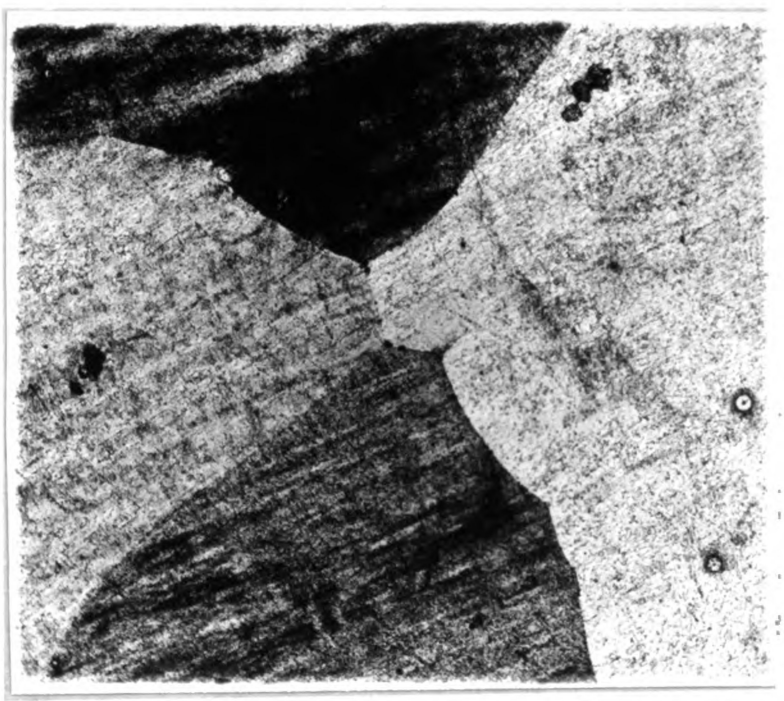


Fig. 21 0.05% antimony in aluminum. Etchant, 5% NaOH at 160°F. 75X.

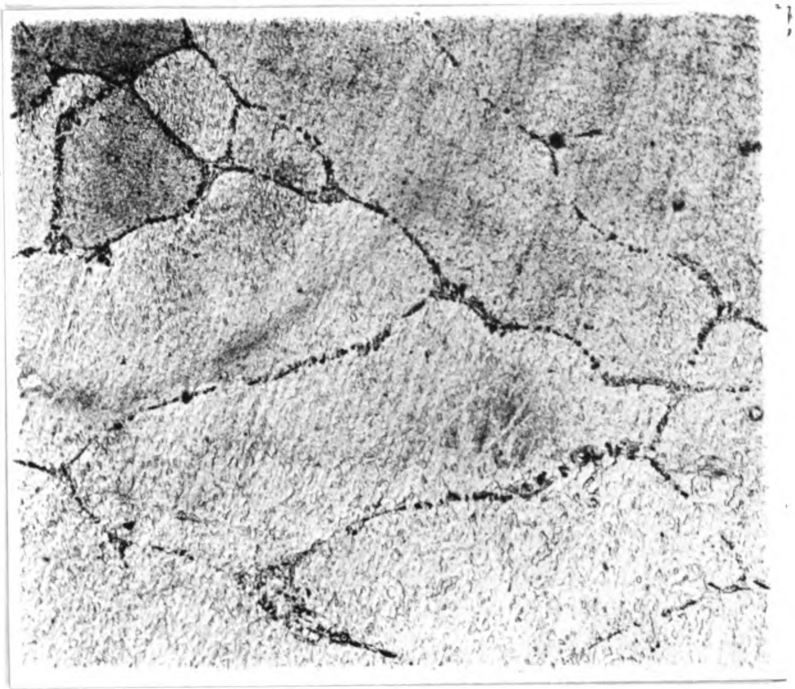


Fig. 22 0.15% antimony in aluminum. Etchant, 5% NaOH at 160°F. 75X.

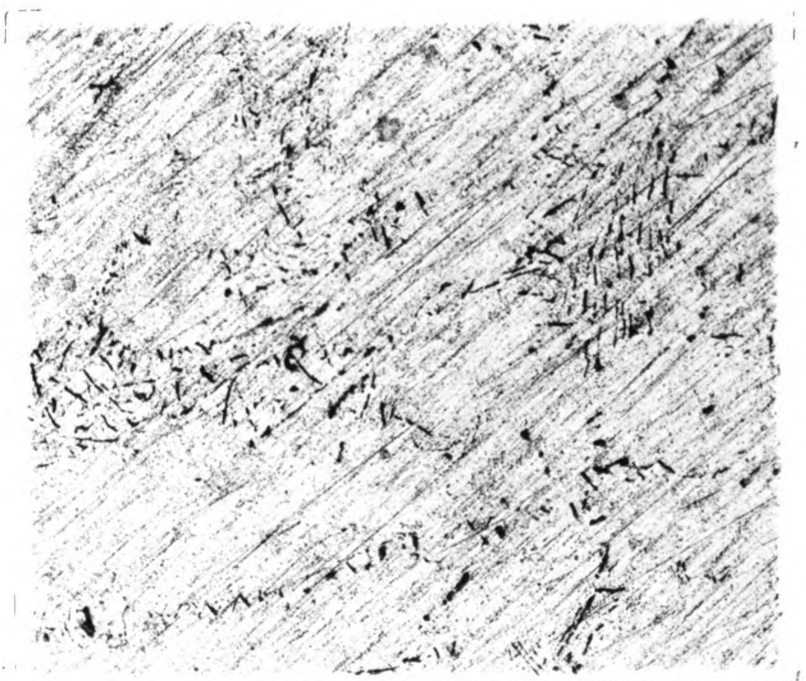


Fig. 23 0.8% antimony in aluminum. Etchant, 5% NaOH at 160°F. 75X.

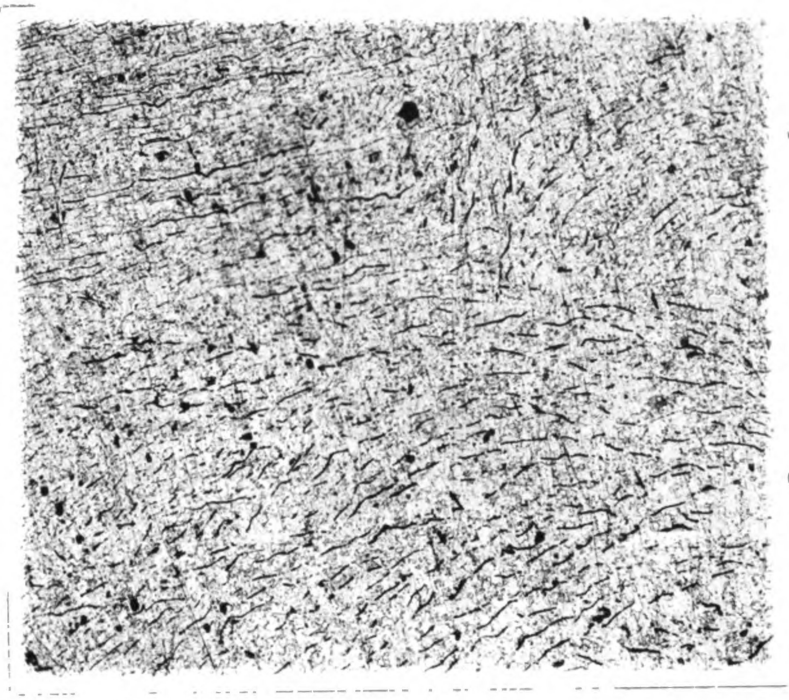


Fig. 24 1.1% antimony in aluminum. Etchant, 5% NaOH at 160°F. 75X.

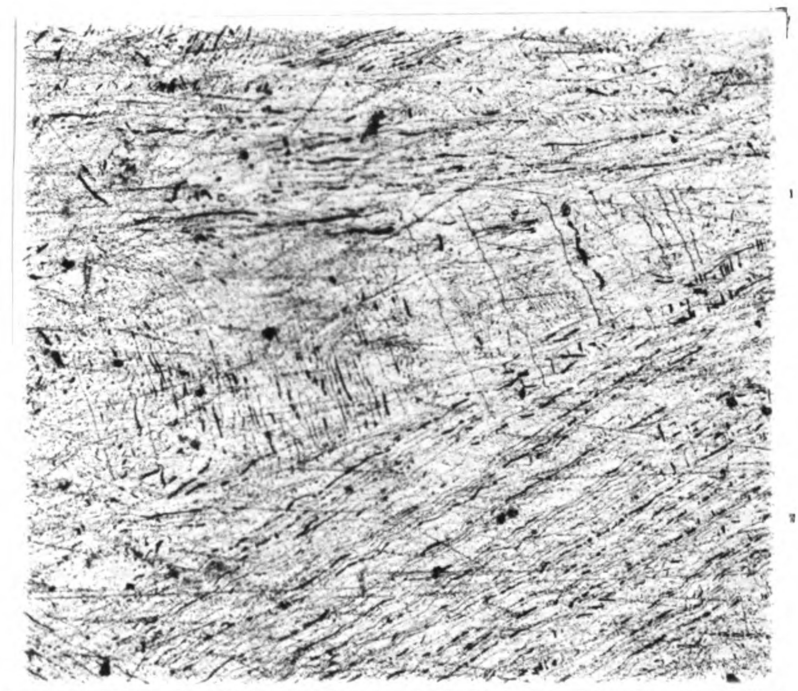


Fig. 25 1.4% antimony in aluminum. Etchant, 5% NaOH at 160°F. 75X.

shown excess solid solution. If 1.1% antimony is the eutectic composition, then the 1.4% antimony specimen should show at least a small amount of primary compound. In the photomicrograph (Fig. 25) none is evident. It is possible that the sample was not perfectly homogeneous and that elsewhere in the sample primary compound may have existed.

CONCLUSIONS AND RECOMMENDATIONS

The critical points derived from the thermal analysis work in this investigation do not correlate with any of those of the published diagrams. The discrepencies may be due to the size of the samples used or to non-uniform furnace conditions as indicated in the appendix. The rate of diffusion of small percentages of antimony in aluminum is very slow at temperatures near the melting point of aluminum. This fact plus the small temperature differential between solidus and liquidus makes the determination of the diagram by thermal analysis difficult.

The microscopic examination of the specimens verifies the limit of solid solubility at about 0.1%. The approximate composition of the eutectic could not be determined from the microstructures.

It is recommended that the 0 to 1.5% antimony portion of the diagram be reworked using samples weighing 10 to 12 grams, and that after homogenizing, the cooling curve runs be made directly from 1700°F. If possible a differentially controlled furnace should be employed.

APPENDIX

Effect of Sample Size

As noted in the discussion of the thermal analysis cooling curves, there was a discrepancy between the liquidus points obtained and those expected in view of previous diagrams. In an effort to determine whether or not this had been caused by using too large a sample, three different weights of pure aluminum were melted and the cooling curve data were taken. The weights of the three samples ran were 43.17g., 16.1g., and 14.g.,

The curve for the 43.17g. sample (Fig. 26) shows a break above the expected temperature and finally a horizontal at the temperature where the melting point of aluminum should fall assuming a small thermocouple loss. This curve is not too unlike the curves obtained for the alloys.

The 16.1g. sample curve (Fig. 27) has an altogether different shape before the horizontal. With the exception of a small amount of supercooling, the curve shows a sharp break at the melting point. The curve for the 14.g. sample (Fig. 28) shows a similar curve. It has a slower cooling rate and consequently a smaller amount of super cooling.

Another possibility to be considered here is that the smaller samples may have been less affected by furnace nonuniformity. This should be checked before drawing any definite conclusion as to the effect of sample size.

TABLE #13 DATA FOR THE TRANSFORMATION CURVE OF ALUMINUM. WEIGHT OF SAMPLE, 43.17g.

Cooling				Heating			
Time	Mv	Time	Mv	Time	Mv	Time	Mv
0"	38.77	31"	36.75	0"	35.11	24"	36.93
1"	38.65	32"	36.75	1"	35.36	25"	36.99
2"	38.54	33"	36.73	2"	35.60	26"	37.04
3"	38.42	34"	36.73	3"	35.78	27"	37.09
4"	38.33	35"	36.72	4"	35.95	28"	37.14
5"	38.22	36"	36.71	5"	36.10	29"	37.17
6"	38.11	37"	36.71	6"	36.25	30"	37.21
7"	38.03	38"	36.71	7"	36.40	31"	37.25
8"	37.92	39"	36.70	8"	36.55	32"	37.20
9"	37.82	40"	36.70	9"	36.64	33"	37.34
10"	37.72	41"	36.69	10"	36.67	34"	37.36
11"	37.63	42"	36.69	11"	36.67	35"	37.40
12"	37.56	43"	36.69	12"	36.68	36"	37.41
13"	37.45	44"	36.69	13"	36.68	37"	37.42
14"	37.36	45"	36.69	14"	36.68	38"	37.46
15"	37.27	46"	36.69	15"	36.68	39"	37.52
16"	37.16	47"	36.69	16"	36.68	40"	37.93
17"	37.06	48"	36.68	17"	36.68	41"	38.25
18"	36.96	49"	36.67	18"	36.68	42"	38.53
19"	36.86	50"	36.65	19"	36.68	43"	38.75
20"	36.84	51"	36.61	20"	36.73		
21"	36.84	52"	36.57	21"	36.77		
22"	36.84	53"	36.52	22"	36.81		
23"	36.84	54"	36.44	23"	36.83		
24"	36.83	55"	35.98				
25"	36.83	56"	35.74				
26"	36.81	57"	35.55				
27"	36.80	58"	35.36				
28"	36.78	59"	35.20				
29"	36.77	60"	35.07				
30"	36.76						

TABLE #14 DATA FOR THE TRANSFORMATION CURVE OF ALUMINUM. WEIGHT OF SAMPLE, 16.1g.

Cooling				Heating			
Time	Mv	Time	Mv	Time	Mv	Time	Mv
0"	38.97	.5"	----	0"	35.08	.5"	35.20
1"	38.61	1.5"	----	1"	35.31	1.5"	-----
2"	38.29	2.5"	----	2"	35.50	2.5"	35.61
3"	37.98	3.5"	37.82	3"	35.73	3.5"	35.82
4"	37.66	4.5"	37.53	4"	35.94	4.5"	35.00
5"	37.37	5.5"	37.23	5"	36.13	5.5"	36.23
6"	37.09	6.5"	37.97	6"	36.34	6.5"	36.44
7"	36.84	7.5"	36.72	7"	36.53	7.5"	36.64
8"	36.68	8.5"	36.67	8"	36.69	8.5"	36.69
9"	36.66	9.5"	36.66	9"	36.69	9.5"	36.69
10"	36.66	10.5"	36.67	10"	36.69	10.5"	36.69
11"	36.67	11.5"	36.67	11"	36.69	11.5"	36.69
12"	36.68	12.5"	36.68	12"	36.69	12.5"	36.69
13"	36.68	13.5"	36.69	13"	36.69	13.5"	36.69
14"	36.69	14.5"	36.69	14"	36.69	14.5"	36.69
15"	36.69	15.5"	36.69	15"	36.69	15.5"	36.69
16"	36.69	16.5"	36.69	16"	36.69	16.5"	36.69
17"	36.69	17.5"	36.69	17"	36.71	17.5"	36.71
18"	36.69	18.5"	36.69	18"	36.71	18.5"	36.74
19"	36.69	19.5"	36.69	19"	36.77	19.5"	36.79
20"	36.69	20.5"	36.69	20"	36.82	20.5"	36.86
21"	36.65	21.5"	36.33	21"	36.88	21.5"	36.92
22"	35.93	22.5"	35.53	22"	36.95	22.5"	36.00
23"	35.25	23.5"	34.97	23"	37.04	23.5"	37.10
				24"	37.24	24.5"	37.68
				25"	37.97	25.5"	37.21
				26"	38.43	26.5"	38.64
				27"	38.84	27.5"	39.01
				28"	39.19		

TABLE #15 DATA FOR THE TRANSFORMATION CURVE OF ALUMINUM. WEIGHT OF SAMPLE, 14.g.

Cooling				Heating			
Time	Mv	Time	Mv	Time	Mv	Time	Mv
0"	38.95	.5"	38.83	0"	35.19	.5"	35.38
1"	38.72	1.5"	38.59	1"	35.51	1.5"	35.69
2"	38.51	2.5"	38.39	2"	35.81	2.5"	35.94
3"	38.28	3.5"	38.18	3"	36.08	3.5"	36.22
4"	38.08	4.5"	38.98	4"	36.36	4.5"	36.44
5"	37.88	5.5"	37.77	5"	36.51	5.5"	36.55
6"	37.68	6.5"	37.58	6"	36.57	6.5"	36.59
7"	37.49	7.5"	37.40	7"	36.61	7.5"	36.63
8"	37.30	8.5"	37.21	8"	36.63	8.5"	36.64
9"	37.12	9.5"	37.03	9"	36.65	9.5"	36.66
10"	36.93	10.5"	36.84	10"	36.67	10.5"	36.67
11"	36.77	11.5"	36.68	11"	36.68	11.5"	36.68
12"	36.68	12.5"	36.69	12"	36.68	12.5"	36.69
13"	36.69	13.5"	36.69	13"	36.69	13.5"	36.69
14"	36.69	14.5"	36.70	14"	36.70	14.5"	36.70
15"	36.70	15.5"	36.70	15"	36.71	15.5"	36.72
16"	36.70	16.5"	36.70	16"	36.73	16.5"	36.74
17"	36.70	17.5"	36.69	17"	36.77	16.5"	36.80
18"	36.69	18.5"	36.69	18"	37.08	18.5"	37.89
19"	36.69	19.5"	36.69	19"	38.43	19.5"	38.81
20"	36.69	20.5"	36.69	20"	39.23		
21"	36.69	21.5"	36.69				
22"	36.69	22.5"	36.68				
23"	36.68	23.5"	36.67				
24"	36.67	24.5"	36.67				
25"	36.66	25.5"	36.66				
26"	36.65	26.5"	36.65				
27"	36.63	27.5"	36.63				
28"	36.61	28.5"	36.60				
29"	36.58	29.5"	36.56				
30"	36.53	30.5"	36.46				
31"	36.29	31.5"	36.08				
32"	35.76	32.5"	36.50				
33"	35.25	33.5"	35.04				

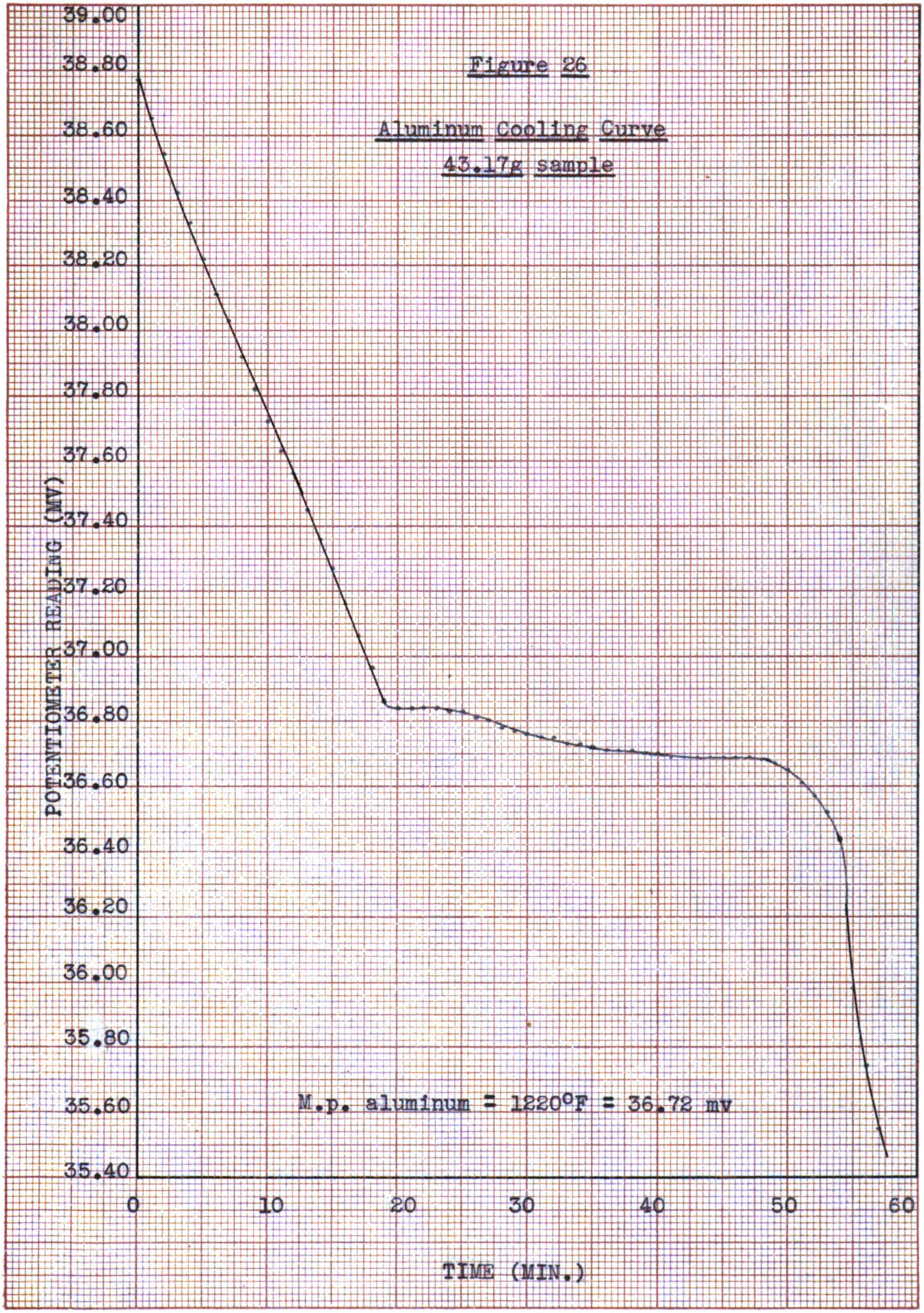


Figure 26
Aluminum Cooling Curve
43.17g sample
POTENTIOMETER READING (MV)
39.00
38.80
38.60
38.40
38.20
38.00
37.80
37.60
37.40
37.20
37.00
36.80
36.60
36.40
36.20
36.00
35.80
35.60
35.40
M.p. aluminum = 1220°F = 36.72 mv
0
10
20
30
40
50
60
TIME (MIN.)

Figure 27

Aluminum Cooling Curve

16.1g sample

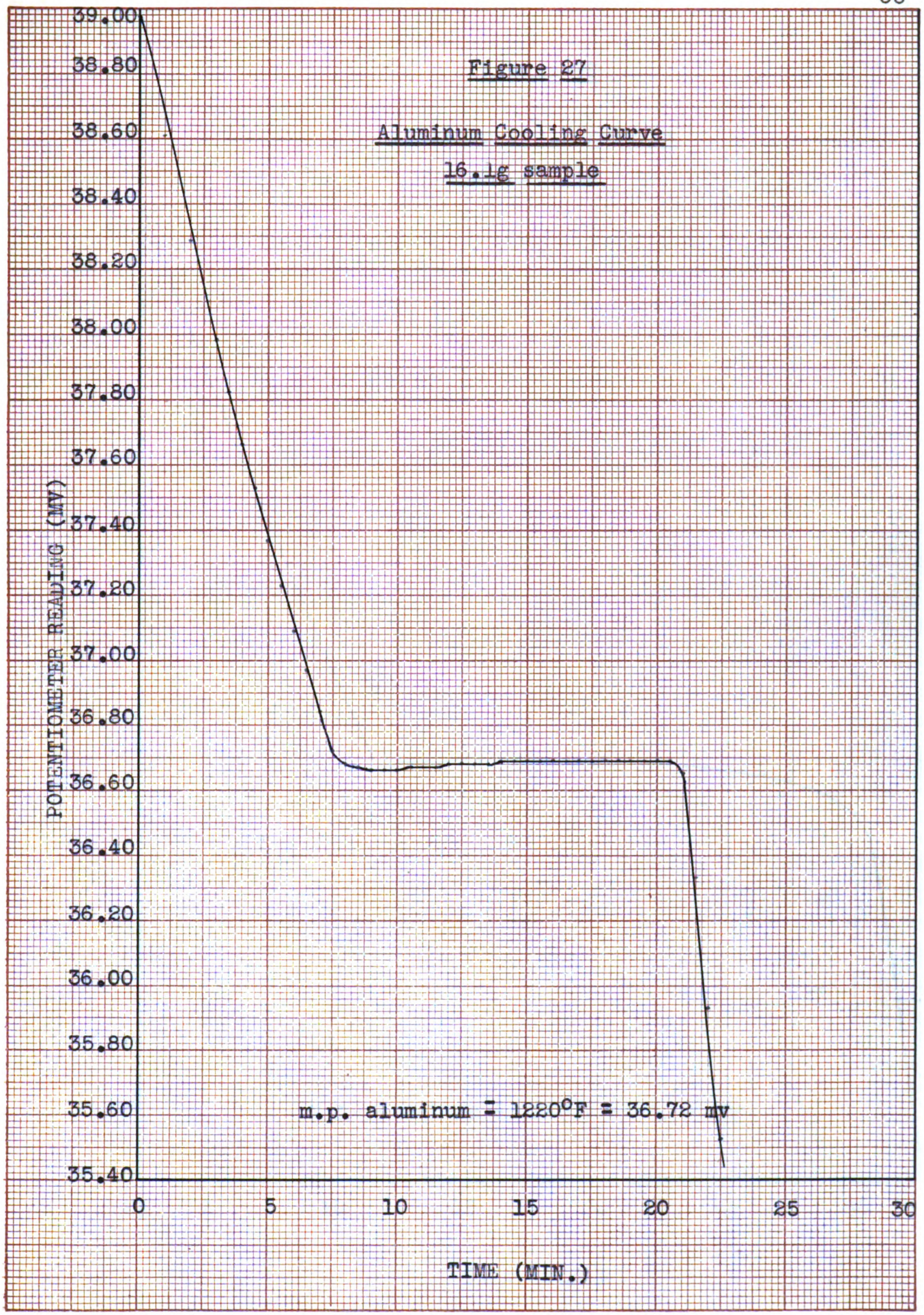
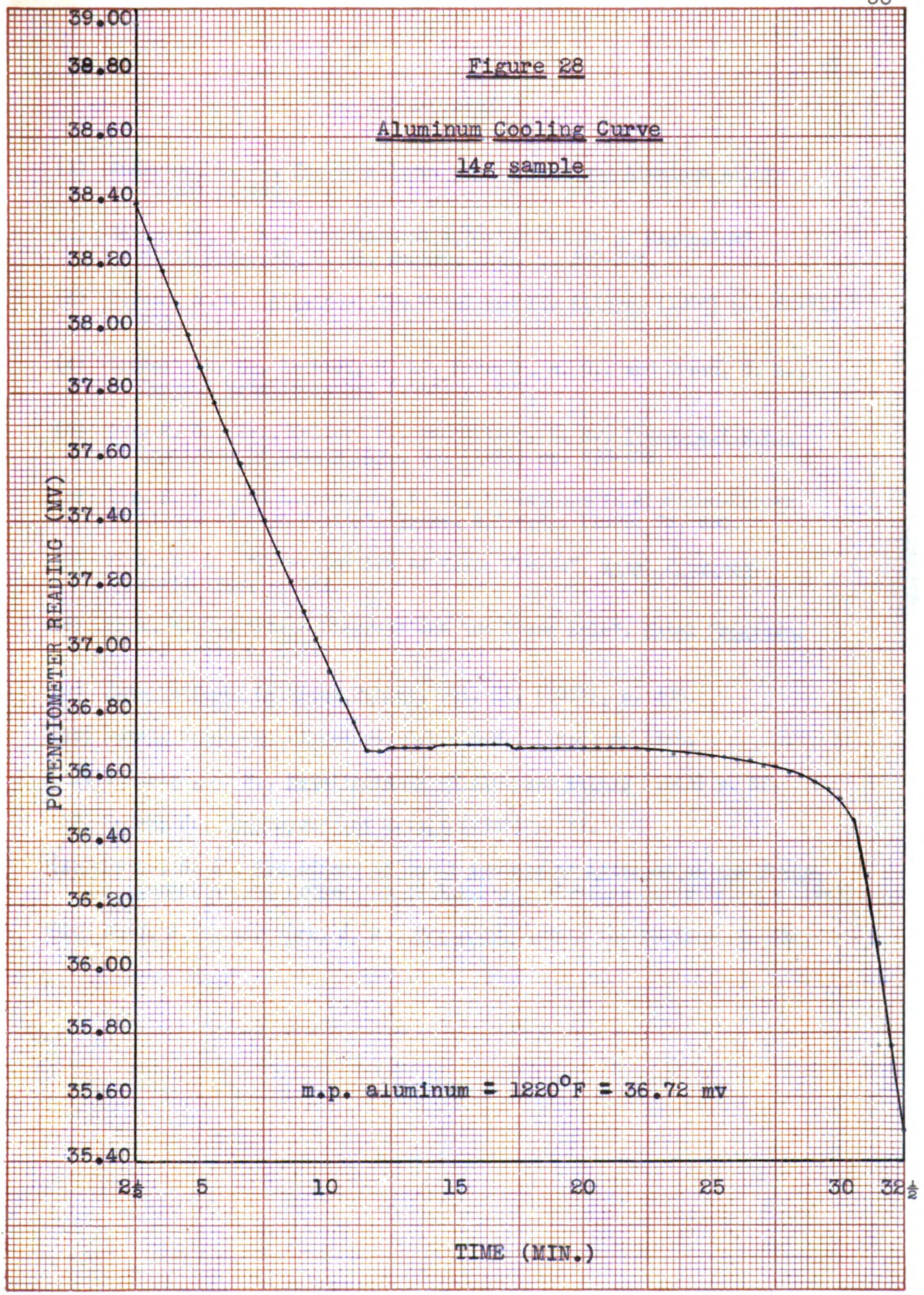


Figure 28

Aluminum Cooling Curve

14g sample



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