AN INVESTIGATION OF THE MANGANESE-INDIUM SYSTEM

Thesis by

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ABSTRACT

A preliminary phase-equilibria study has been made of the manganese-indium alloy system by means of thermal analysis (cooling curves) and metallographic studies (photomicrographs). Ferromagnetism has been found to exist in alloys containing up to 70 atom percent manganese and has tentatively been attributed to the compound Mn_2In. A phase diagram has been proposed, on the basis of the data obtained, in which the indium rich portion of the system consists of indium plus Mn_2In, while the manganese rich portion is made up of a manganese solid solution. Additional experiments have been outlined to further identify the nature and extent of the phases present. A new scheme of chemical analysis has been applied to the alloys with good success.

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Introduction

Following the work of Grinsted and Yost on the manganese-copper-indium alloys (1), it was deemed advisable to investigate the phase equilibria in the previously unreported manganese-indium system. Besides being of interest in itself, a thorough knowledge of this system coupled with the data from the well investigated manganese-copper and copper-indium systems (2)(3), might be profitably integrated with the results of Grinsted and Yost to give a clearer picture of the ferromagnetism observed.

The present investigation was carried out primarily by means of thermal analysis. These data were later supplimented with metallographic studies and qualitative magnetic measurements.

Thermal Analysis

Thermal analysis, in the form of cooling curves, constituted the principal source of data. The alloys were prepared by melting mixtures of the pure metals under argon in an induction furnace. The cooling curves were obtained by means of a thermocouple placed in the alloy. These cooling curves were, as a rule, continued only through the region of solidification, as the liquid-solid phase transitions were of primary interest in this preliminary investigation, and solid-solid transitions usually involve such a small heat effect and have such a slow rate that their detection and interpretation are difficult. Compositions of the alloys were determined by chemical analysis.

Apparatus: The furnace that was used was similar to that used by Van Dusen and Dahl (4) and is shown in Fig. 1. The body consisted of a 61 mm. pyrex tube about 14 inches long and open at the top. A 35 mm. side arm connected to a vacuum system and a source of inert atmosphere. The top of the furnace was closed by sealing a 3 mm. pyrex plate to it with apiezon sealing wax W.

Heating was done by means of a Westinghouse 10KW radio-frequency generator operating at a frequency of about 450 kilocycles. A work coil consisting of ten turns of 3/8 inch o.d. copper tubing was connected to its output terminals and fitted snugly around the pyrex furnace tube for a length of about six inches. The turns of the coil were spaced slightly greater near the center to obtain a more uniform field inside. Cooling water flowing through the coil kept both the copper and the pyrex tube cool. The heat was generated by the R.F. field in the outer graphite crucible (Fig. 1) and the sample, contained in the inner alumina crucible, was heated by conduction.

The thermocouple protective tube was sealed off at the lower end with packed magnesia to prevent the molten alloy from coming in direct contact with the thermocouple and as an aid in positioning the thermocouple. The alumina crucible cover and various graphite and zircon washers served several purposes. They helped insulate the sample by preventing convection currents in the argon directly above it, and protected the pyrex plate from receiving too much heat (in some preliminary runs in which the upper zircon washers were not used, the pyrex plate got so hot that the wax melted and the seal was broken). They also served as weights to hold the crucibles in place, and kept the thermocouple tube centered in the crucible (prior to this arrangement, the tube tended to float to one side of the crucible causing the loss of good thermal contact between alloy and thermocouple).

The space between the outer graphite crucible and the furnace tube was filled with 325 mesh insuloxide (zirconia powder) obtained from B.F. Wagner and Co., Pasadena. Pyrex wool was placed in the side arm to prevent the zirconia from being drawn or blown into the rest of the system. Small (1/64 inch) holes were drilled in the inner graphite crucible and in the various washers to provide a ready avenue of escape for the air during evacuation.

A Cenco Megavac forepump and an oil diffusion pump were used for evacuating the system which consisted of about six feet of 35 mm. pyrex tubing in addition to the furnace. At a point near the furnace small (7mm.) lines were run to a mercury manometer and sources of air and argon. A 12 mm. stopcock connected the pumps with the furnace. Later on in the work a line was run from a point near the furnace to a six liter flask. This flask provided a reservoir of argon to minimize pressure changes in the furnace during heating and cooling. The manometer was used chiefly for regulating pressures near one atmosphere.

"Triangle RR recrystallised alumina" crucibles were obtained from Morganite, Inc., and used for all alloy preparations. These crucibles were very dense and had walls only 3/64 inch thick. Two sizes were used: 7/8 inch o.d. by 1-5/16 inches tall (held about 40 grams of alloy), and 1-1/8 inches o.d. by 1-9/16 inches tall (held about 70 grams of alloy). Silica or graphite crucibles could not have been used as manganese reacts with silica and also forms a carbide (5). Basic oxides such as alumina or magnesia are satisfactory (6), and zirconia was also found suitable, though crucibles of the desired size and shape were difficult to obtain, and attempts to prepare them by slip-casting gave crucibles which were quite brittle and somewhat porous (7).

The most dense alundum crucibles available (alundum extraction crucibles, porosity grade RA84, dimensions 90 x 19 mm., Norton Abrasive Co.) were found to be fairly satisfactory, though the porosity caused the loss of a few percent of the manganese and indium during the preparation and cooling runs (7).

A test was made to compare the porosities of the alundum and alumina crucibles. One of each type was dried in an oven at 110°C, cooled in a desiccator and weighed. They were then placed in boiling water for an hour, removed, dried lightly with absorbent cotton and reweighed. The alundum crucible gained over 2 grams to give an increase in weight of over 14%, while the alumina crucible weighed only 0.01 gram more, or less than a 0.03% increase. While this crude measurement served only to compare the porosities, it did show that the alumina crucible was much more dense and was therefore more satisfactory for this alloy work.

The thermocouple tubes, made of alumina and some silica, were obtained from the Stupakoff Ceramic Co. The silica present did not appear to cause any trouble, possibly because it was in combination with the alumina. These tubes had an outside diameter of 4.75 mm. and a wall thickness of about 1/2 mm. All of the ceramic pieces were fired to 1000°C in a muffel furnace prior to use to remove any carbonaceous material.

It was necessary to extract the graphite crucibles and washers in a Soxhlet extractor with 6 normal nitric acid for three days and then with 6 normal hydrochloric acid for three days to remove the organic binder and other foreign material. (A very strong thicyanate test for iron was obtained on the extract.)

The pieces were then thoroughly washed in boiling water to remove the acid and dried at 150°C.

Temperature measurements were made with chromel-alumel thermocouples, the construction and calibration of which is discussed in the next section. The leads were threaded through a two-hole porcelain thermocouple insulator which fit snugly down inside of the protection tube. The wires were lead out of the furnace through two small holes at one side of the pyrex plate. These holes were sealed with Apiezon sealing wax W.

A Brown "Electronik" recording potentiometer was used to record the thermocouple emf over the temperature range 500-1150°C. A self-compensating circuit which corrected for room temperature was contained within the instrument, so that no cold junction was necessary. It was necessary, however, to have the entire circuit of chromel-alumel wire so that the effective cold junction would be on the terminal block inside the case containing the compensator. The temperature was recorded on a moving chart, resulting in automatic drawing of the cooling curves.

Below 500 and above 1150°C the emf was measured by means of a Leeds and Northrup type K potentiometer in conjunction with a calibrated Epley standard cell. The sensitivity of the galvanometer used for the null indication was such that a 10 division deflection corresponded to about 1½°C. A double-pole, double-throw switch was used to transfer from one circuit to the other.

Thermocouple Calibration: A great deal of difficulty was experienced in the use of the thermocouples, the average life of which was too short to be of value. About 30-40 thermocouples were prepared and partially or completely calibrated, only to break before sufficient data could be obtained with them.

The first thermocouples were prepared from 28 gauge chromel-alumel wire, as a sensitive couple was desired, and this size had been used successfully on a previous experiment of similar nature (7). These couples usually gave out around 1100-1200°C, however, and were of no value.

Thermocouples were next made from 26 gauge wire obtained from the Hoskins Wire Co. These had too short a life at high temperatures and the wire was very inhomogeneous. Couples made from wire taken from different portions of the spools gave emf values which differed by as much as 25°C at 1000°C.

Finally, 22 gauge Leeds and Northrup wire was used. This gave couples with a sufficiently long life that, after calibration, three to five samples could be run before they gave out. Also, after calibrating couples cut from different sections of the wire, it was found to be quite homogeneous, so that subsequent couples from the same spools did not need to be calibrated separately before use. The high temperatures employed were responsible for the failure of the thermocouples, for at these temperatures a heavier wire (8-10 gauge) should be used. A platinum-rhodium thermocouple could not be used as the Brown recorder was calibrated for chromel-alumel.

The thermocouples were prepared by twisting the cleaned ends of the two wires tightly together, heating gently, fluxing in borax, fusing in a hot flame, cooling, and then removing the excess borax. The couples were then annealed for 1-2 hours at about 1000°C by passing current through them as they hung suspended from two binding posts.

The thermocouples were calibrated at the freezing points of four to six of the following materials: copper, silver, copper-silver eutectic alloy, antimony, zinc, lead and tin. Copper, zinc, lead and tin were obtained from the National Bureau of Standards, each with a certificate giving the value of the freezing point. The silver was obtained from Wildberg Bros., Los Angeles, and was said to be 99.9995% pure. The copper-silver eutectic alloy was prepared from 16 gauge copper wire (99.9+% pure) obtained from the Malin Wire Co., and the pure silver. It contained 28.1% copper and 71.9% silver. The antimony was Baker's lump antimony, 99.83% pure. Baker and Adamson 99.98% zinc and 99.97% tin were also used. The impurities in these metals should not have lowered any of the freezing points by as much as 2°C, as the freezing point of silver may be lowered by as much as 0.1°C and that of antimony, zinc and tin by as much as 0.05°C by 0.01% of impurities (8).

The calibration runs were done in the same furnace as the alloy preparations, using, however, the Norton alundum crucibles. About 50 grams of metal was used per sample, and several determinations of each freezing point were made. The metal was brought to essentially a uniform temperature at the beginning of freezing by holding its temperature constant at about 10°C above the freezing point for several minutes, and then cooling slowly. The antimony and tin had a marked tendency to undercool before freezing, but this did not interfere with the freezing point determinations.

The calibration data for thermocouple number 22A, typical of those used, is given in Table I. The difference curve for this couple is shown in Fig. 2. The abscissa is the observed temperature and the ordinate is the correction to be added to the observed temperature to get the true temperature. The temperatures obtained in the thermal analysis, after correction according to this curve, were considered accurate to ± 3°C.

Materials: Electrolytic manganese, in the form of small plates, was obtained from the U.S. Bureau of Mines and from A. D. Mackay and Co. of New York. Both lots were said to have a purity of 99.9% or better. Indium of 99.97% purity was obtained in the form of small pellets from the Indium Corporation of America. The purity of the metals was checked by chemical analysis and found to be at least 99.9% in all cases.

Argon, with a reported purity of 99.8%, was obtained from the Linde Air Products Co.

Procedure: The manganese and indium were cleaned and cut up just prior to making a run. For the indium this involved removing a thin layer of oxide from the surface with dilute (1 normal) hydrochloric acid, and then cutting the pellets into very small pieces with a pocket knife. The acid wash proved

Table I

Calibration Data for Thermocouple #22A.

Material	Observed Freezing Point °C	True Freezing Point °C	Correction °C
Copper	1079	1083.0	+4
Silver	957.5	960.5	+3
Antimony	627.5	629.2	+1.75
Tin	232.5	231.9	-0.5

troublesome at first, as the pellets fused together in the dilute hydrochloric acid and had to be cut apart. This happened whenever two pellets came in contact while in the acid. To avoid washing them one at a time a tower was constructed using a 30 mm. piece of glass tubing, about four feet long, with a narrow constriction at the center. This tube stood upright in a flask of distilled water and was filled to the constriction with water. Dilute hydrochloric acid was carefully poured into the upper half of the tube, and then the indium pellets were poured into the acid. The oxide coat was removed as they fell though the acid, and the clean pellets collected in the flask of water at the bottom where they did not fuse together. The indium was dried with acetone and ether and then cut up.

The majority of the manganese was very free from oxide and was used without cleaning. Efforts to clean it proved fruitless, as manganese readily oxidizes in moist air and usually became severely tarnished after washing in acids or water or even in acetone or ether. Only clean manganese plates were chosen, therefore, and these were reduced to a powder in a diamond mortar.

At first the desired amounts of the powdered manganese and cut-up indium were weighed out to the nearest 5 milligrams before mixing and placing in the crucible, a total of 40 or 70 grams being used for each preparation. Subsequently the weighings were done to 0.1 gram on a pan balance, as analysis showed that a small amount (about 0.5%) of the manganese was being lost during the runs. The exact composition of the alloys was determined by chemical analysis after the completion of the runs.

After the crucible, containing the well mixed sample and the thermocouple tube, had been placed in the furnace, the thermocouple inserted, and the pyrex plate sealed on, the system was evacuated for several hours. This had to be done carefully at first to prevent the entrapped air from blowing the zirconia all through the system and displacing the outer graphite crucible in relation to the heating coils. It would have been extremely difficult to obtain a really good vacuum in a furnace of this type without a long period of outgassing at a high temperature, but this was impractical due to the rapid sublimation of manganese at elevated temperatures in a vacuum (9)(10). The outgassing was usually done, therefore, at 125°C (below the melting point of indium, 157°C) for about 15 minutes, though a few were outgassed at temperatures as high as 800°C. The system was then flushed with argon several times before the final filling with argon to about one atmosphere pressure.

An inert atmosphere was necessary due to the sublimation of the manganese in vacuo and its oxidation in air. Neither hydrogen nor nitrogen could be used as manganese reacts with each (11). The argon was available and proved satisfactory.

The sample was heated to about the melting point of manganese (1242°C) for a few minutes and then held at 1200-1225°C for an hour or more. No significant segregation should have taken place during the time between the melting of the indium and the dissolution of the manganese in the melt, as the densities of the two metals are very similar; 7.3 for indium and 7.2 for manganese (12). The finely powdered manganese dissolved satisfactorily in the melt at 1200-1225°C as shown by subsequent microscopic examination of the alloy. The manganese-rich alloys were heated to 1260-1270°C for a short time before the anneal at 1200-1225°C.

The samples cooled too rapidly in the argon atmosphere to give good cooling curves, but by reducing the power output of the R.F. generator it was possible to control the cooling rate within narrow limits. The rate of cooling was usually maintained at 10-15°C per minute. Several curves were run for each alloy until the thermal arrests on two or three successive curves, run at different cooling rates, agreed to within 1-2°C. The temperature was maintained at about 1200°C for 30 minutes or so between runs. After the last run, the sample was heated to 1200-1225°C and allowed to cool rapidly (power off) to prevent excess segregation. Line voltage fluctuations did not cause any trouble, and there was no harmful effect on the thermocouple by the R. F. field as it was shielded by the graphite crucibles and by the sample itself.

During a run the thermocouple emf was read on the potentiometer down to 1150°C, then switched to the Brown recorder where the cooling curve was automatically drawn down to 500°C, and then back to the potentiometer circuit. Simultaneous readings of the potentiometer and a stopwatch were recorded every 15 seconds, which was often enough to easily determine the position and duration of the breaks on the cooling curves.

Data obtained: The cooling curves are shown in Figs. 3 through 8, arranged in order of increasing manganese content so that the similarities and progressive changes among the alloys are more readily observable. The abscissas run from right to left as this is the manner in which the curves were drawn by the Brown recorder. The others were plotted this way for uniformity. Above 1150 and below 500°C the ordinates are in millivolts, elsewhere in degrees centigrade.

The significance of these curves is discussed in the section on results, so only a few general comments will be made here. It will be noted that many of the curves (e.g., A19, Fig. 4 and A18, Fig. 5) show two arrests, corresponding to the formation of two solid phases, and indicating the locations of the liquidus and solidus. Curves such as A5, Fig. 4 and the upper half of A15, Fig. 7 are also characteristic of the solidification of one excess constituent followed by the freezing of an eutectic mixture. The type of break at 1185°C on A14, Fig. 8 indicates formation of a solid solution.

Flat (isothermal) arrests are apparent on the lower portion of each of the first twelve curves as well as at 873°C on A18, Fig. 5, 1004°C on A15, Fig. 7, and elsewhere. If the solid which is being formed has the same composition as the liquid, solidification takes place at a constant temperature and the rate of cooling is zero. This is the case in the freezing of a pure metal, compound or eutectic mixture, or in a peritectic reaction. If the composition of the solid which is being formed differs from that of the liquid phase, however, the temperature will still fall during the freezing, but at a slower rate. When the temperature is reached at which the liquid has the same composition as the solid being formed, the remaining liquid solidifies isothermally. Examples of non-isothermal breaks of this type include the arrest at 744°C on A4, Fig. 3, and the one at 1009° on A10, Fig. 6. A break of this last type may have so little slope, i.e., the entire process may take place during such a small temperature interval, that the break appears isothermal. Such is the case for the above mentioned arrest at 873°C on A18, Fig. 5, as will be pointed out in the section on results.

It is interesting to note that the average temperature of the lowest arrest on the first fifteen curves was at 157.5°C (to the nearest 0.5°C), and the average diviation from this value was only 0.5°C. Also, the length of this break was proportional to the composition, decreasing with increasing manganese content.

The temperatures (corrected) of the various thermal arrests on the cooling curves are summarized in Table II. Some other small breaks, besides those listed, were occasionally observed. In the preparation of this table all of the arrests on all of the cooling curves were considered. Many appeared on only one of several curves for a particular alloy, while others were so slight as to be doubtful. A break at about 660°C was observed on the cooling curves of nearly every alloy, and was probably due to a thermal change in some part of the furnace other than the sample itself. A careful, systematic study was made of

Table II

Temperatures of Thermal Arrests

(Degrees Centigrade)

Alloy	Breaks			
4	157.0	744		
5	156.5	830		
6	158.0	866		
7	157.5	880		
10	157.0	876	946	1009
11	157.0	885	1004	1029
12	156.5	662		
13			1005	1129
14		1039	1079	1185
15	157.0	883	1004	1087
16	157.5	871	922	948
17		1015	1042	1155
18	158.0	873		
19	157.5	840		
20	158.0	793		
21	157.5	873	941	1037
22	157.5	602		
23	158.5	877	997	1051

all these arrests, and only the ones that are believed to be fairly definite have been included in Table II, though no large breaks were omitted.

Physical characteristics: The hardness of the alloys increased rapidly with the manganese content. Alloys containing up to 15% manganese* could be cut with a knife, while alloys A13, A17 and A14 (77.2, 84.4 and 90.7% manganese, respectively) were hard enough to scratch glass, A14 being the hardest. As the same glass could not be scratched with pure metallic manganese, it appears that the addition of a few percent of indium to manganese causes a large increase in hardness.

The alloys containing up to about 35% manganese had no appreciable amount of external oxidation, but those of greater manganese content had significant amounts of a black-green oxide film on the upper, exposed surface. The insides of the specimens were silver-colored, becoming more shiney as the manganese content increased. Alloy A7 (37.9% manganese), when broken, had a beautiful, fibrous structure with long crystals lying parallel to each other in groups, adjacent groups being at right angles to each other. This made the sample appear to be made up of groups of metallic stairsteps stacked at right angles.

The indium rich alloys adhered very tightly to the alumina crucibles, and it was necessary to break the crucibles in order to remove the samples. The high manganese alloys, however,

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*Unless otherwise stated, compositions are in weight percent.

were removed by merely inverting the crucibles.

Magnetic properties are discussed under Ferromagnetism.

Chemical Analysis

Both manganese and indium were lost during the heating and cooling of the alloys so that it was necessary to chemically analyze all of the samples to insure homogeneity and to determine their exact composition. Some metal, principally manganese, was lost by absorption into the crucibles, the crucible walls appearing greyish after a run. Hot acid washes seemed to remove most of the visable metal indicating that it was merely surface adsorption, but subsequent firing to 1000°C. in air turned the crucible walls brown, probably due to more deeply absorbed manganese which was oxidized. The alloys containing a large percentage of indium wet the alumina crucibles and were difficult to remove; some indium adhering very firmly to the upper walls. Manganese, which sublimes rapidly at high temperatures in vacuo (9) might also have been lost during the outgassing. (An electric field has been found to greatly increase this rate of vaporization around 800 - 900°C (13).) Indium has a vapor pressure of 9.38×10^{-2} mm. at 1075°C (14) and that of manganese is 7.60×10^{-2} mm. at 1388°C (15) so that evaporation losses during the runs should be negligible.

The component metals were very pure at the start and the only impurity which was likely to be introduced was a small amount of oxide from residual air in the apparatus. The large surface of graphite near the alloy probably prevented the formation of any oxides of indium (the alloys containing less than 35% manganese appeared free of any oxide), but manganese oxides would be formed by direct reaction with residual oxygen as well as by reduction of carbon dioxide and, above 400°C (16), carbon monoxide. Most of the alloys containing more than 35% manganese had a blackish-green surface layer of oxide, most likely MnO_2 (black) and MnO (green), but as it could easily be removed mechanically or by washing in acid, and the rest of the alloy appeared clean and metallic, only manganese was determined directly, the indium content being obtained by defference. It was desirable to omit the indium analysis as no reliable volumetric method for its determination is know (7) and the gravimetric method (17) is tedious and time consuming.

As long as indium was not being determined as a check, it was desirable to have a very reliable method of analysis for the manganese. The method used by Grinsted (7) for determining manganese in copper-manganese-indium alloys was investigated using accurately made up mixtures of pure indium and manganese as "standards". In this procedure a 200-800 milligram sample was dissolved in 20 ml. of 16 normal HNO_3, heated to boiling and $KClO_3$ added until the vigorous reaction ceased. The solution was boiled a few minutes to expel all the ClO_2, diluted with 30 ml. of water and filtered through an asbestos filter, the precipitate being washed several times with hot water until the filtrate was free of acid. The precipitate was redissolved in a solution of 10 ml. of 6 normal HCl and 3 grams of KI in 40 ml. of water and the iodine liberated according to the reaction

$$MnO_2 + 3I^- + 4H^+ = 2H_2O + Mn^{++} + I_3^-$$

titrated with standard 0.1 normal $Na_2S_2O_3$ solution to a starch end-point.

Several difficulties were incountered in the analysis: the precipitate of MnO_2 was tricky to handle and dissolved very slowly in the acid-KI solution (up to 24 hours was required in some cases), and the results were neither precise nor accurate. Refinements in the technique were invoked with only partial success; the average of ten determinations on known samples was 0.5% low with a precision of ±1.5%. Swift feels that this method is not good to better than 1% (18), and Grinsted states that his results for manganese were probably low by about one percent, but since most of his alloys contained less than 30% manganese the error would usually be less than 0.3% and he decided to accept this accuracy. The specimens in this work contained up to 91% manganese and a more accurate and reliable method was required. Also, with a highly precise method it is fairly easy to test the alloys for inhomogeneities by analyzing samples from different regions of each specimen.

Lingane and Karplus (19) investigated the potentiometric titration of manganous ion with permanganate ion in neutral pyrophosphate solution and got exceptionally good results on several different alloys containing various amounts of manganese. The dipositive manganese is oxidized and the permanganate reduced to the pyrophosphate complex of the tripositive state:

$$4Mn^{++} + MnO_4^- + 8H^+ + 15H_2P_2O_7^= = 5Mn(H_2P_2O_7)_3^{\equiv} + 4H_2O.$$

This method was adopted to the analysis of the manganese-indium alloys and the following procedure used: A weighed sample containing about 600 milligrams of manganese was dissolved in 20 ml. of 16 normal HNO_3, diluted with 40 ml. of water and the solution boiled thoroughly to expel most of the NO_2, the remainder being removed by adding about 1/2 gram of urea. This was an important operation as oxides of nitrogen interfere and cause high results. The solution was now the delicate pink color characteristic of dipositive manganese. It was cooled and accurately diluted to 200 ml., from which 50 ml. aliquots were taken for analysis. These aliquots were added to 300 ml. of freshly prepared 0.3 molar (saturated) sodium pyrophosphate solution and the pH adjusted to 6.5 with dilute H_2SO_4. The titration with standard 0.02 molar $KMnO_4$ solution was done in a beaker using a motor driven glass stirrer and a bright platinum indicator electrode in conjunction with a calomel reference electrode. The voltages were read on a Beckman Model G pH Meter which was also used in adjusting the pH. The potential change, $\Delta E/\Delta V$, was 100-200 millivolts/0.1 ml. and virtually independent of the amount of manganese titrated, the volume of the solution and the concentration of the permanganate solution (just before use the permanganate was diluted 4 to 1 and 10 to 1 for some of the low manganese-alloys to avoid taking an unnecessarily small sample). A blank was run on each new batch of pyrophosphate solution, but was negligible except when using the extremely dilute permanganate solution. A typical titration curve is shown in Fig. 9.

Aluminum precipitates at this pH and had been found to interfere with the titration due to co-precipitation of the manganese (19). The indium, however, evidently complexed with the pyrophosphate as no precipitate was formed. Manganese, when present in large amounts, formed a white precipitate which dissolved as the titration proceeded and did not interfere.

The average of six determinations on known samples containing 10, 50 and 100% manganese of purity 99.9+% was $99.9_2 \pm .0_6$% for the purity of the manganese. This method of analysis was subsequently used on all of the alloys; samples being taken from different sections of the 40 to 70 gram specimens in order to test for homogeneity. The results of these analyses, including the uncertainties due to inhomogeneity, are given in Table III.

All volumetric glassware used in this work was carefully calibrated as were the weights which were used. Standard solutions were checked against primary standards at frequent intervals. Reagent grade chemicals were used throughout. The results of the analyses are probably accurate to 0.1%, as the method is limited only be the accuracy of the volumetric measurements.

Table III.

Chemical Composition of Alloys

Alloy	Weight-Percent Manganese	Weight-Percent Indium	Atom-Percent Manganese	Atom-Percent Indium	Uncertainty due to inhomogeneity*
4	9.6	90.4	18.1	81.9	±0.2
5	19.3	80.7	33.4	66.6	±1.0
6	29.6	70.4	46.8	53.2	±1.2
7	37.9	62.1	56.0	44.0	±0.8
10	48.9	51.1	66.6	33.4	±0.2
11	59.4	40.6	75.4	24.6	±0.6
12	4.6	95.4	9.2	90.8	±0.4
13	77.2	22.8	87.6	12.4	±0.2
14	90.7	9.3	95.3	4.7	±0.4
15	69.6	30.4	82.7	17.3	±0.1
16	43.4	56.6	61.6	38.4	±0.2
17	84.4	15.6	91.9	8.1	±0.0
18	32.2	67.8	49.8	50.2	±0.0
19	23.9	76.1	39.7	60.3	±0.2
20	15.2	84.8	27.3	72.7	±0.5
21	53.2	46.8	70.3	29.7	±0.1
22	3.1	96.9	6.2	93.8	±1.7
23	64.5	35.5	79.1	20.9	±0.2

* weight-percent

Metallographic Studies

Microscopic examination of most of the alloys was made both visually and photographically in an attempt to correlate the thermal data with the number and types of phases present at various temperatures. The final cooling of the alloys was done rapidly from a high temperature (about 1225°C) in order to keep segregation to a minimum. This cooling took about two hours, however, so that the specimens did not necessarily represent equilibrium conditions, due to lack of time for stabalization of the phases. In order to develop and preserve the equilibrium structures present at higher temperatures, the alloys were annealed and then quenched.

Two or three small pieces of the sample to be annealed were placed in a quartz tube (2 to 3 inches long and about 1/4 inch i.d.) which was closed off at one end. The open end was attached to a vacuum line and the tube alternately evacuated and filled with high purity helium 20 to 30 times, then sealed off at a previously prepared neck while under about 3/4 atmosphere pressure of helium.

The annealing was done in a "Hevi Duty", resistance type furnace with a large heat capacity. A lavite box and lid (interior dimensions 2 by 3 inches and walls about 3/4 inch thick) was placed inside the furnace and a chromel-alumel thermocouple, previously calibrated against a National Bureau of Standards platinum-10% platinum-rhodium thermocouple, introduced into the box through a small hole in the rear, the insulated leads extending out the rear of the furnace to a cold junction and a Wheelco model 330 potentiometer. A larger chromel-alumel thermocouple, placed inside the furnace but outside the lavite box, was connected to a Wheelco Capacilog (recording-controlling potentiometer) which controlled the heating circuit of the furnace. After the furnace had been brought to the desired temperature, the quartz tube containing the samples was placed in the lavite box. Since the control thermocouple was outside the lavite box of large heat capacity, and the Wheelco Capacilog responded to small changes in temperature (2 to 3°C), the temperature of the sample, as read from the calibrated thermocouple, fluctuated less than one degree during the anneal.

At the end of the anneal period the quartz tube was quickly removed from the lavite box, plunged into a large volume of water and broken with one blow from a hammer. This procedure caused the samples to be quenched in less than three seconds (probably about one second, as the thickwalled, poorly conducting quartz should have insulated the samples from the time they left the furnace until they came in contact with the water). A film of oxide usually appeared on the specimens after the quench (samples A10 and A23 were the exceptions), and was removed by washing in dilute hydrochloric acid.

Not all of the specimens were annealed. The solidus for the indium rich alloys (less than 40 weight percent manganese) was at 157.5°C and so far below the liquidus that a high temperature anneal was impractical. Also, this portion of the phase diagram was fairly clear from thermal data alone. (This is discussed in greater detail in a later section.)

The temperatures and durations of the anneals for the various alloys are given in Table IV. Samples A10 and A11 appeared to have been largely molten at the annealing temperature, as pieces of quartz were imbedded in them and they had lost their original shape. Sample A17 looked as though a small portion had melted and run out.

Photomicrographs were taken of all the alloys that were annealed and quenched and of many that were not. Those containing less than 30 weight percent manganese were too soft for the polishing procedure (described below) and hence could not be photographed.

The specimens to be photographed were mounted in lucite using a Buehler mounting-press with a 1¼ inch mold. As many of the alloys had a thermal arrest at 157-8°C, the usual temperature of 150°C employed when mounting in lucite was deemed too high. It was found that satisfactory mounts could be obtained at 110°C, and this was the maximum temperature used for this purpose. The usual pressure of 3000 pounds per square inch was also too high for some of the alloys which were crumbly, and a lower pressure (1500 pounds per square inch) was successfully used.

The polishing was done successively on 1/0, 2/0, 3/0, and 4/0 emery polishing paper and finished on a cloth-covered wheel using first levigated alumina and distilled water and finally rouge and distilled water.

Table IV.

Temperature and Duration of Anneal

Alloy	Temperature (^{o}C)	Time (hrs.)
A10*	850	69
A11	950	18½
A13	880	15
A14	990	20
A15	820	65
A16	820	65
A17	990	20
A21	820	65
A23	950	20

* Annealed in vacuo.

A definite structure, visable to the unaided eye, was usually apparent at this time, due primarily to a very soft phase which was removed to an appreciable depth during the polishing. The surfaces of some of the alloys (low manganese content) tended to smear, and some (high manganese content) polished to a high luster. While electrolytic polishing would probably have caused less disturbance of the metal, it was not tried, since satisfactory results seemed to be obtained by the above procedure.

The structure was further developed by etching for a few seconds with two percent nital (a two percent solution of nitric acid in methyl alcohol). This proved satisfactory in all cases except alloy A17, which stained badly. Successful etching of this alloy was finally accomplished in a one percent nital solution.

The photomicrographs, Figs. 10 to 17 inclusive, were taken on a Bausch and Lomb Metallograph (model ILS) using a carbon arc light source, a green filter and kodak 5 by 7 inch metallographic plates. Kodak Azo paper was used for printing, the grade used in each case being that which brought out the most detail in the final picture.

The significance of the photomicrographs, in relation to the phase equilibria, is discussed in a subsequent section. At this point, however, it is interesting to examine some of the characteristics of the various alloys as shown in the pictures.

The photomicrographs in Figs. 10 and 11 show two phases and indicate that dissociation took place during the cooling to room temperature. Slowly cooled (unannealed) alloys usually show this dissociation, since equilibrium with respect to structual rearrangements has not been obtained and frozen in. This is especially evident in A10 and A18, Fig. 10. In this latter picture the inhomogeneity is readily apparent in the discontinuous (light colored) phase where the color varies from the edge to the center, indicating a probable concentration gradient.

Alloys A17 and A14, Fig. 12, are single phase and show no large amount of grain growth. No undissolved manganese is visable in any of the photomicrographs, hence it must have all combined with the indium in the formation of the alloy as previously concluded. Dendritic structure is very evident in A11 and A23, Fig. 11.

Alloys A16AQ and A10AQ*, Fig. 13, are two phase, the matrix being the softer phase. Hardness measurements were made on A10AQ using a Tukon hardness tester. The discontinuous phase had a D.P.H. (diamond point hardness) number of 440. This is quite hard, since annealed copper is around 200 and pure manganese about 360 (20). The matrix had a hardness of only 8, while that of pure indium was about 4. But the difference between 8 and 4 on the D.P.H. scale is within the limits of error, since hardness measurements in this range are very difficult.

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*The letters "AQ" following an alloy number indicate an annealed and quenched specimen.

It looks as though a third phase were present in the photomicrograph of A10AQ at 500X, Fig. 13, but those small globules were found to have the same hardness numbers as the larger pieces of the same color.

Alloys A21AQ and A11AQ, Fig. 14, and A23AQ and A15AQ, Fig. 15, were also two phase. The precipitation of the matrix in A11AQ and A23AQ is very apparent in the photographs at 500X, indicating that this phase was probably liquid at the annealing temperature. All of the specimens up to A13AQ (77% manganese) probably had one liquid phase at the annealing temperature, since the cooling curve for each of them had an arrest at about 157.5°C. Annealing for subsequent quenching and microscopic examination is commonly done at a temperature just under the solidus, but in the present case the solidus temperature was so low in comparison to the liquidus temperature that little diffusion and rearrangement of the high temperature phase would have taken place under these conditions. It was decided, therefore, to attempt annealing at temperatures near the liquidus, and, consequently, one phase was liquid at the time of quenching and precipitated as fine particles. This is shown very clearly in the two photomicrographs mentioned above, as well as in that of A16AQ, 250X, Fig. 13, and A11AQ, 100X, Fig. 14.

Beautiful grain boundaries are apparent in the photomicrographs of alloys A17AQ and A14AQ, Figs. 16 and 17. A small precipitation product can be seen in the boundaries on A14AQ at 750X.

The dark spots in the discontinuous phase in the various pictures (e.g., A11AQ, Fig. 14, A13AQ, Fig. 16, and A14AQ, Fig. 17) are holes. This is especially apparent in A11AQ at 100X.

Ferromagnetism

Of the approximately twenty-five alloys that were prepared, over half were (accidentally) found to be ferromagnetic. The existance of ferromagnetism in this system was suggested by Hames and Eppelsheimer (21), but no data were given. In the present investigation, qualitative magnetic measurements were made with a small alnico magnet, and the intensity of magnetization found to increase fairly regularly from 3 to about 50 weight percent manganese, and then to die out completely. Alloy A21, containing 53.2% manganese, is strongly ferromagnetic, while the next one, A11, containing 59.4% manganese, is unaffected by the magnet, as are the subsequent alloys of increasing manganese content.

The same range of ferromagnetism holds for the annealed and quenched specimens. Alloys A10, 16 and 21 are ferromagnetic after quenching while alloys A11, 13, 14, 15 and 17 are not. (See Table IV for time and temperature of anneal and Table III for composition.)

Figure 18 shows the relative strengths of attraction to the magnet for the various alloys, the strengths being arbitrarily divided into five groups, viz.,0) no action, 1) tilt (the specimen, when carefully balanced, will lean toward the magnet), 2) roll (the specimen will roll along a smooth surface toward the magnet, 3) lift (the specimen may be lifted with the magnet and 4) jump (the specimen actually jumps up to the magnet). While this is a rough grouping, it gives a good picture of the gradation in magnetic intensity with manganese content.

The significance of these measurements, in relation to the phase equilibria, is discussed in a later section.

Results

The primary purpose of this investigation, as stated in the introduction, was to determine the locations of the phase boundaries in the manganese-indium system. The results of the thermal analysis were the primary source of data for this preliminary interpretation. The ferromagnetic measurements proved very valuable in helping to establish the extent and composition of the indium-rich portion of the phase diagram, while the metallographic studies were useful for confirming assumptions based on the cooling curves.

The temperatures of the thermal arrests on the cooling curves (Table II) are plotted against the composition of the alloys in Fig. 19. The phase boundaries indicated in this proposed phase diagram are of two general types, viz., fairly certain (represented by the solid lines), and uncertain (represented by the broken lines). The discussion of this diagram will be considered by regions to begin with, and then as a unit.

<u>0-56 atom % Mn</u>: The cooling curves in this range had two arrests. There was a sloping one which appeared at 602°C for alloy A22 (6.2 atom % Mn) and increased in size and temperature up to 880°C for A7 (56.0 atom % Mn), and an isothermal arrest at 157.5 ±1°C for each of the nine alloys in this region. The size of this second arrest was dependent on the manganese content, and in Fig. 20 the length of this arrest, in minutes per gram of alloy, is plotted against percent manganese, showing the regularity with which the strength of the arrest diminished

with increasing manganese content.

The temperature of this second arrest also identifies the second phase, namely indium. The accepted value for the freezing point of indium seems to be 156.4°C (12) (20), though a recent investigator reports 157.2 ±0.8°C (21a). While the freeqing point of pure indium was not determined in the present investigation, the value of 157.5°C is believed to be sufficiently close to identify the phase as indium. Also, the hardness test on alloy A10AQ, previously described, showed the softer of the two phases present to have a hardness number essentially the same as pure indium. If the value for this series of arrests had been lower than 156.4°C, an eutectic mixture would have been suspected, but the present evidence points to indium freezing out of each of the alloys at 157.5 ±1°C. The shape of the arrests indicate that it is a pure material rather than solid solution.

This region is evidently monotectic, that is, an eutectic range in which the eutectic mixture (in this case indium) contains an infinitely small amount of one component. If a liquid whose composition lies between 0 and 56 atom % manganese is slowly cooled, there will first be a break at the liquidus corresponding to the freezing out of a solid component, this freezing continuing until all of the manganese has been used up, at which time the pure indium remaining freezes at 157.5°C. The extrapolation of the liquidus to the freezing point of indium is probably a very good assumption, the solubility of manganese in indium undoubtedly being zero. No alloy containing less than 6 atom % (3 weight %) manganese was prepared because the break at 602°C on A22 was just barely perceptible.

The flat, almost isothermal nature of the upper arrests on alloys A19, A6, A18 and A7 is easily explained by the low slope of the liquidus in this range. There is a large change in the composition of the melt during freezing over a very small temperature range, giving rise to these pseudo-isothermal arrests, as explained in a previous section.

The alloys in this region were ferromagnetic, the intensity of magnetization increasing with the manganese content (Fig. 18). This would indicate a two phase system, or possibly a solid solution, in which one component (the manganese rich one) was ferromagnetic. When viewed with the results of the thermal analysis it appears to be the former, i.e., a compound between manganese and indium which is ferromagnetic.

No specimens in this region were annealed and quenched for microscopic work due to the low temperature of the solidus and the high indium content. Photomicrographs of A18 and A7 (49.8 and 56.0 atom % Mn), unannealed, indicate a two phase system in which the softer (dark colored) phase seems to constitute less than half of the alloy.

<u>60-71 atom % Mn</u>: This is the most difficult region of the phase diagram to interpret. The break at 157°C continued with diminishing strength and the liquidus appeared to level off at about 873°C. But there were two additional high temperature

arrests on the cooling curves of these three alloys (A16, A10 and A21). The strength of the uppermost arrest increased with increasing manganese content while the flatter one below it appeared strongest for the center alloy, A10, (66.6 atom % Mn).

The data suggest one, or possibly two, peritectic reactions in this region. The phase diagram shows one possibility: a peritectic reaction peaking at the compound Mn_2In. There is quite a bit of evidence to support the existance of this compound. The aforementioned breaks were strongest at this composition and their shape was nearly isothermal. Also, the ferromagnetism was strongest in this region and could have been due to this compound, the diminishing intensity with decreasing manganese content being due to the decreasing amount of Mn_2In in the alloys. This proposal seems to leave the breaks at 873°C unaccounted for, but they were very small and could have easily been caused by segregation in the alloys during cooling. The liquidus rises rapidly to 1037°C (alloy A21) at 70.3 atom % manganese.

The photomicrographs of the unannealed samples (A16 and A10, Fig. 10, and A21, Fig. 11) show two, or possibly three, phases. A16 and A21 appear very similar. The pictures of the same alloys annealed between 800 and 850°C (A16AQ and A10AQ, Fig. 13, and A21AQ, Fig. 14) show very similar structure and in each case just two phases. A10AQ should show one phase (Mn_2In) predominately as it was almost exactly this composition, but some of the manganese appeared to have reacted with the silica of the quartz annealing tube (darkening of the quartz) so that the quenched alloy probably contained less that 66.6 atom % manganese. (The alloys were chemically analyzed after the cooling curve runs, but not after annealing and quenching.)

70-100 atom % Mn: The arrest at 157°C continued with diminishing strength until it disappeared at about 83 atom % manganese. The manner in which the phase diagram has been interpreted does not account for these last four breaks at this temperature, except by saying they are due to segregation in the alloy. But this seems unlikely in regard to the regular manner in which the strength of the breaks decreased with increasing manganese content (Fig. 20).

The liquidus falls regularly from the melting point of manganese, 1242°C (6), to about 1000°C around 73 atom % manganese. The characteristics of the arrests along this liquidus, previously discussed, indicate the formation of a solid solution, and the other data seem to support this conclusion. The photomicrographs of A17 and A14 (91.9 and 95.3 atom % Mn), Fig. 12, show them to be single phase. Photomicrographs of the same alloys after annealing at 990°C indicate a single phase also, while A13 (87.6 atom % Mn) is two phase before annealing (Fig. 12) but appears as a single phase afterwards (Fig. 16). The photomicrograph of A14AQ at 750X (Fig. 17) shows what appears to be a precipitate in the grain boundaries. The alloy was brought to equilibrium at the annealing temperature as evidenced by the nearly 120° angles at the corners of the grains, and on quenching the precipitate could either have formed at a lower temperature as a result of minor segregation, or it could be another phase of the manganese solid solution. The data indicate a compound, or intermediate phase of some type, around 70 atom % manganese. As sample A21 (70.3 atom % Mn) is the last ferromagnetic alloy, the compound probably lies just to the right of it, and Mn_5In_2 (71.4 atom % Mn) represents the most likely compound agreeing with the most data. Thus if the ferromagnetism is due to Mn_2In, as proposed, the intensity of magnetization would fall off on either side of this composition, reaching zero at pure indium on the left and at Mn_5In on the right. This agrees with the measurements made (Fig. 18).

The solvus line indicated in the diagram is indefinite to ± 10 atom % at higher temperatures and only a guess at lower temperatures. Its slope is so great that it can not be detected by ordinary thermal analysis.

The solidus is uncertain from 87.5 to 100 atom % manganese. There is probably a phase transition in the manganese giving rise to the extra arrest on each of the last two cooling curves, as the arrest, while quite small in each case, was larger for sample A14 (95.3 atom % Mn).

Summary and additional comments: The proposed, tentative phase diagram, when viewed as a whole, satisfies most of the data. There are, of course, several cooling curve arrests unaccounted for and some regions of uncertainty, but there are just insufficient data to identify all of the phases and their boundaries with a large degree of certainty. Five alloys were prepared in the ranges 55-75 atom % manganese, but it is now apparent that many more must be prepared before a reasonably accurate interpretation of this region will be possible. The compound Mn_2In is fairly certain, though the maximum temperature at which it first appears might be somewhat in doubt, and the compound Mn_5In_2 is less certain, being used primarily to represent an intermediate phase whose composition might be somewhat variable. The percent manganese-formula conversion data compiled in Table V are an aid when examining the phase diagram for possible compounds.

The ferromagnetism observed is extremely interesting. Bozorth has pointed out (22) that there are now known about fifteen binary systems, containing no ferromagnetic elements, which show ferromagnetism. Of these binary systems, both components are metals in seven cases (Mn-As, Mn-Sb, Mn-Pt, Mn-Bi, Mn-Sn, Cr-Pt and Cr-As). The manganese-indium system described here provides a new additional case. Systems which might be analogous to the present one are manganese-tin, in which the compounds MnSn, Mn_2Sn and Mn_4Sn are ferromagnetic (23), and manganese-antimony, in which MnSb and Mn_2Sb are said to be magnetic compounds (24).

While pure, metallic manganese is not ferromagnetic even at the temperature of solid hydrogen, $14^{\circ}K$ (25), Slater has shown that ferromagnetism is to be expected when the manganese atoms are arranged in a space lattice with a certain interatomic distance, and that their separation in the Heusler alloys is equal to this distance, whereas in pure manganese the separation is too small (26).

Table V.

Percent Manganese - Formula Conversion

Atom-percent Manganese	Weight-percent Manganese	Formula
87.50	77.01	Mn_7In
85.71	74.17	Mn_6In
83.33	70.53	Mn_5In
80.00	65.69	Mn_4In
77.78	62.62	Mn_7In_2
75.00	58.95	Mn_3In
71.43	54.48	Mn_5In_2
70.00	52.76	Mn_7In_3
66.67	48.91	Mn_2In
63.64	45.58	Mn_7In_4
62.50	44.37	Mn_5In_3
60.00	41.79	Mn_3In_2
58.33	40.12	Mn_7In_5
57.14	38.96	Mn_4In_3
55.56	37.43	Mn_5In_4
54.55	36.48	Mn_6In_5
53.85	35.83	Mn_7In_6
50.00	32.37	$MnIn$
46.15	29.09	Mn_6In_7
45.45	28.51	Mn_5In_6
44.44	27.69	Mn_4In_5
42.86	26.42	Mn_3In_4
41.67	25.48	Mn_5In_7
40.00	24.19	Mn_2In_3
37.50	22.31	Mn_3In_5
36.36	21.48	Mn_4In_7
33.33	19.31	$MnIn_2$
30.00	17.02	Mn_3In_7
28.57	16.07	Mn_2In_5
25.00	13.76	$MnIn_3$
22.22	12.03	Mn_2In_7
20.00	10.69	$MnIn_4$
16.67	8.74	$MnIn_5$
14.29	7.39	$MnIn_6$
12.50	6.40	$MnIn_7$

Proposed Studies

As is usually the case following the preliminary investigation of a phase system, more work is needed to definitely establish the phase boundaries. Investigations along the following lines should provide the necessary data.

A) More thermal analysis is needed in the manganese rich postion of the system. New alloys may have to be prepared every percent or so over some of this region.

B) Additional photomicrographs of annealed and quenched alloys in this same region would be useful.

C) Since the solubility of manganese in indium cannot be accurately checked by thermal analysis, due to the smallness of the arrest on the cooling curve below 6 atom % manganese, some alloys might be prepared using radioactive manganese. Autoradiomicrographs could then be made to determine how the manganese was distributed in the alloy.

D) X-ray data, to determine the natureand structure of the phases, would be extremely valuable in identifying phase transitions and indefinite boundaries such as the solvus.

E) Experiments to determine the variation of Curie point and Bohr magneton with composition would undoubtedly aid in explaining the ferromagnetism.

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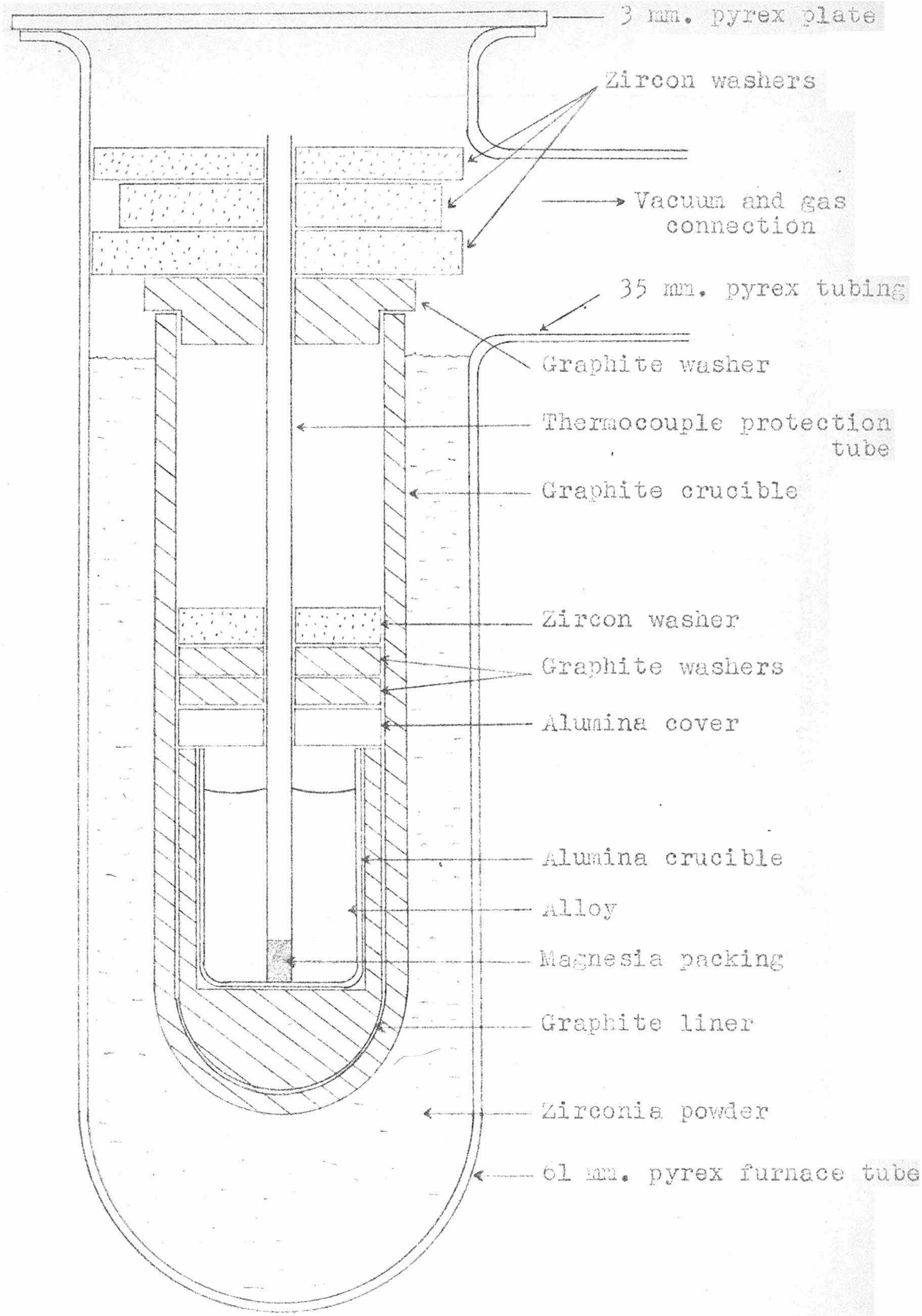


Fig. 1. Furnace.

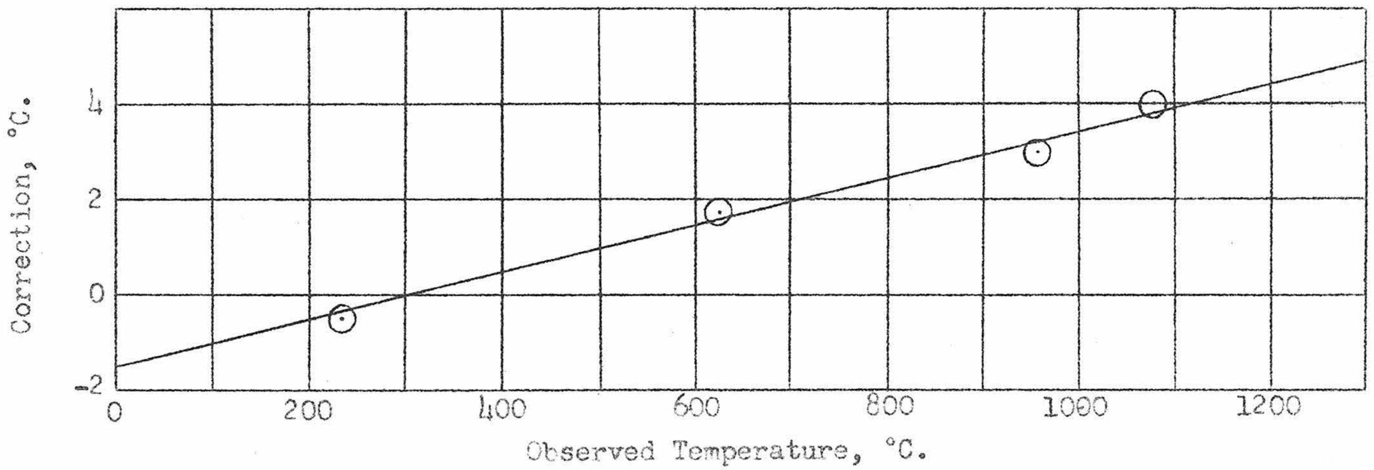


Fig. 2. Difference Curve for Thermocouple #22A.

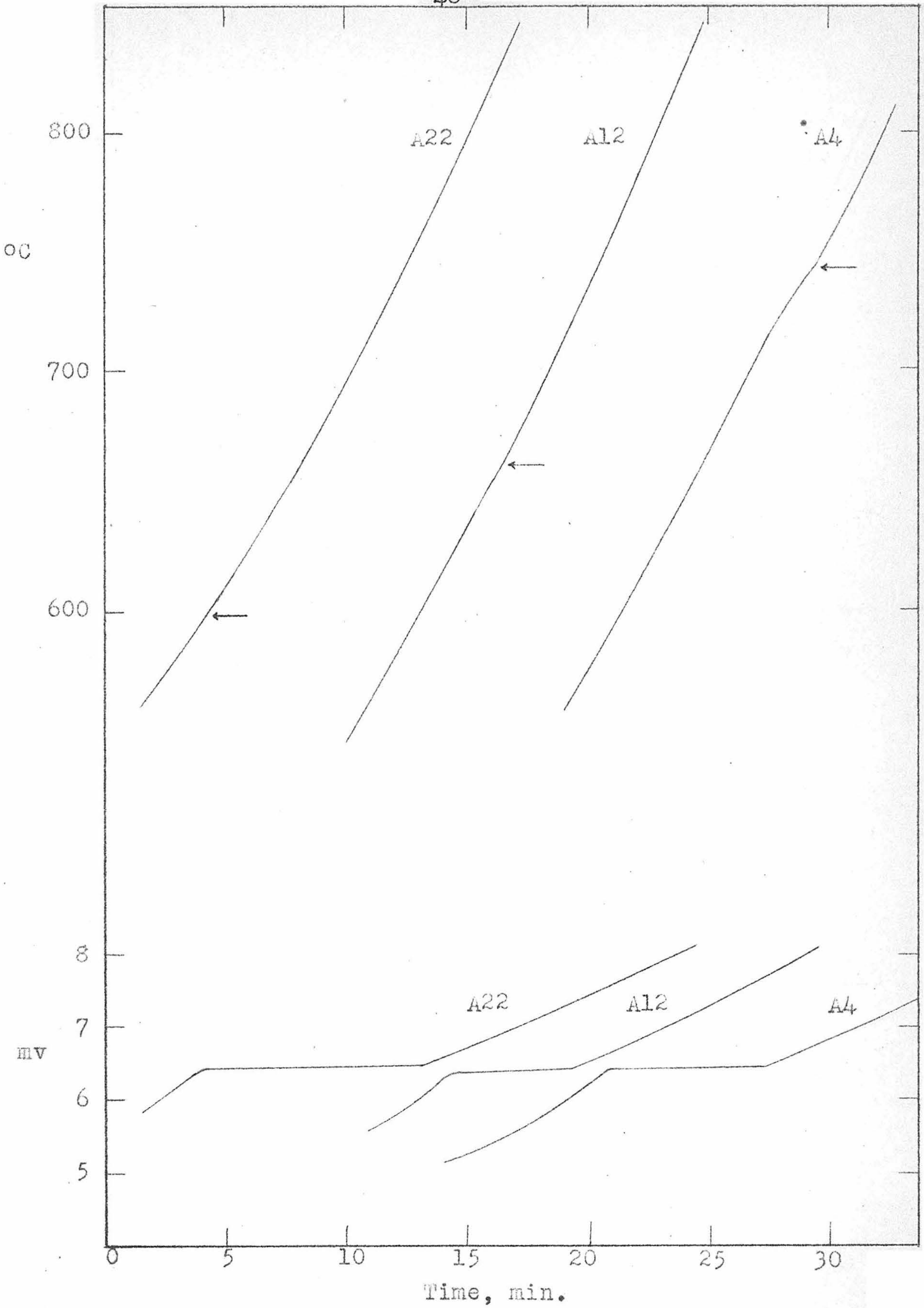


Fig. 3. Cooling Curves.

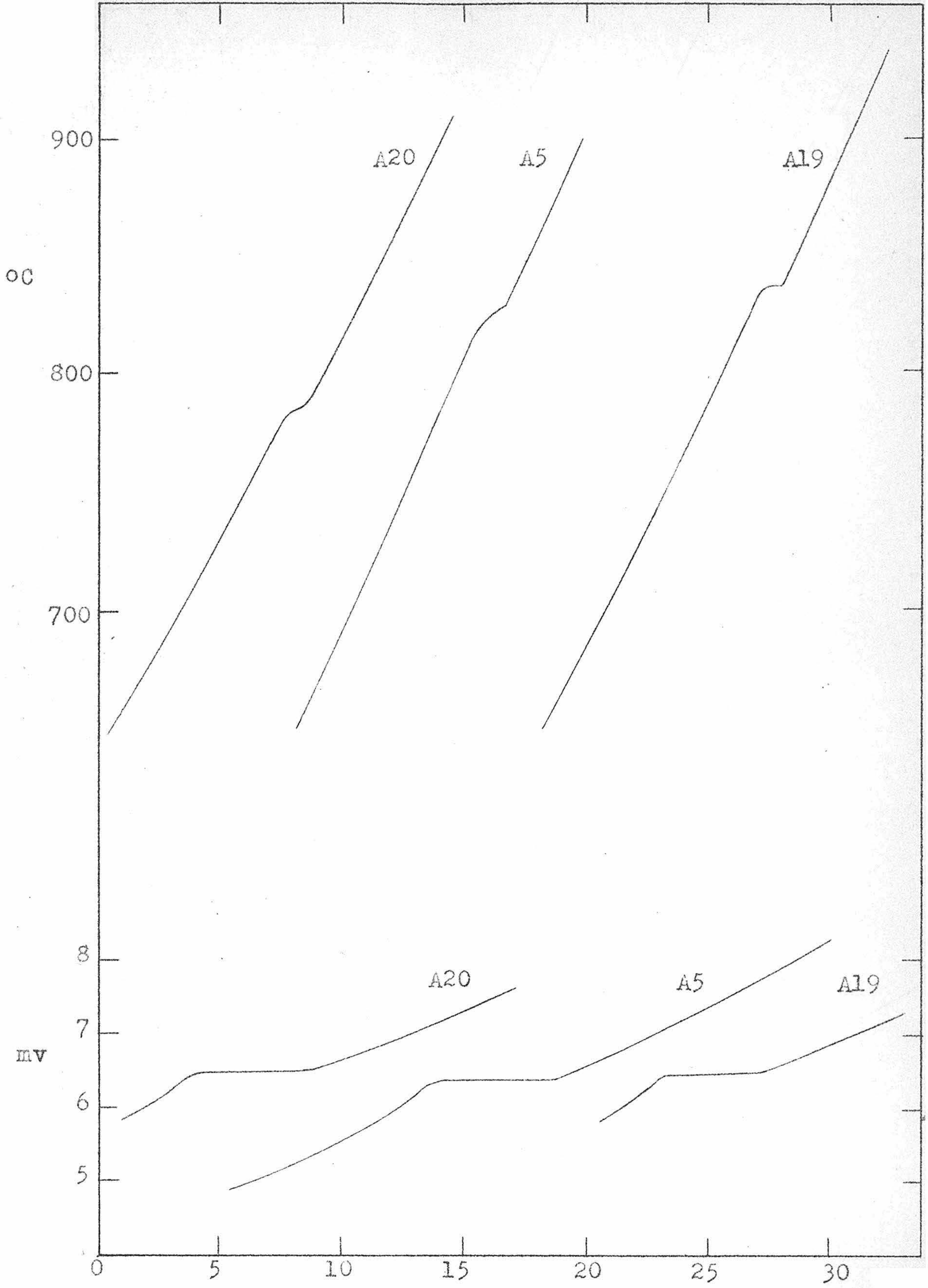


Fig. 4. Cooling Curves.

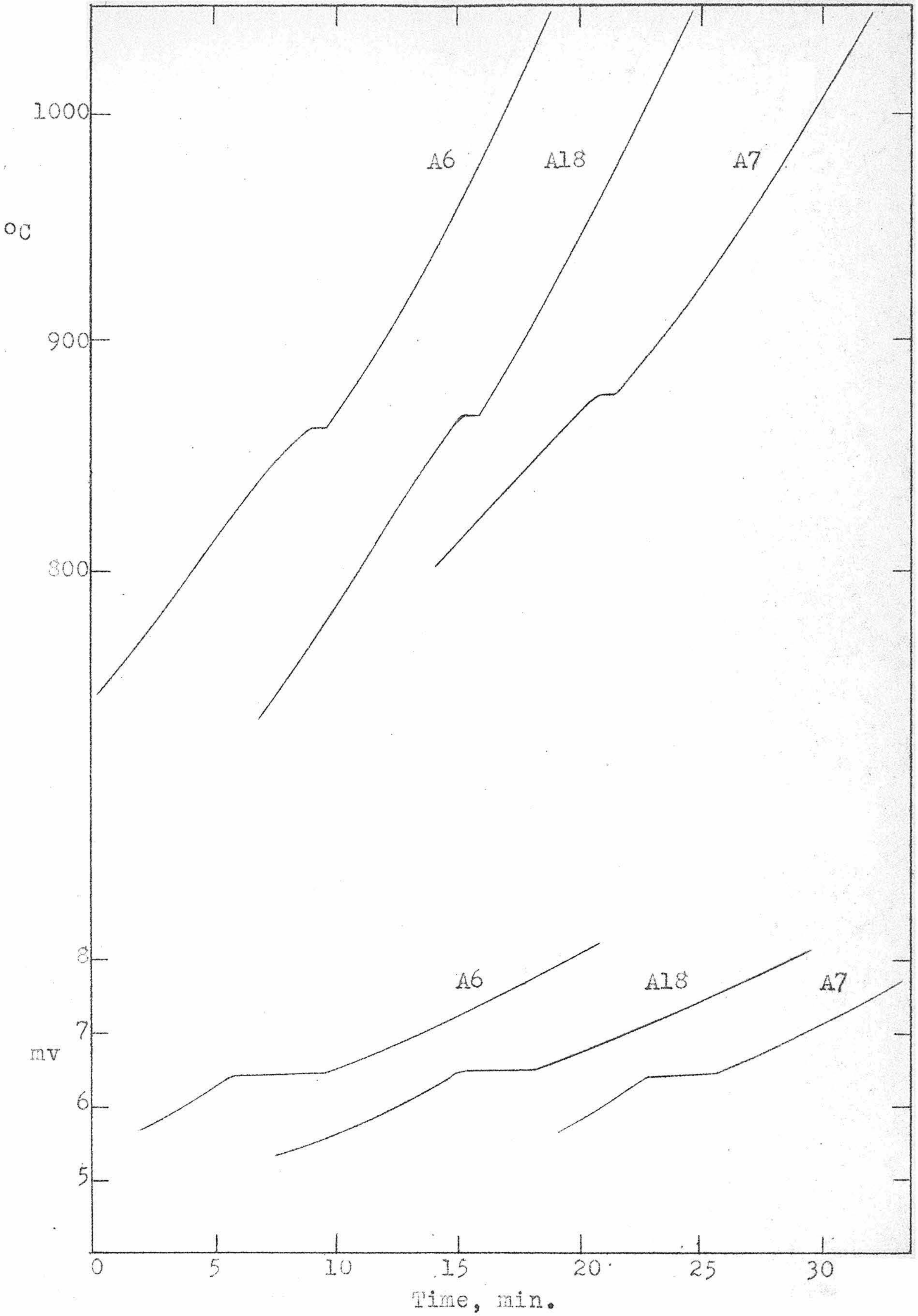


Fig. 5. Cooling Curves.

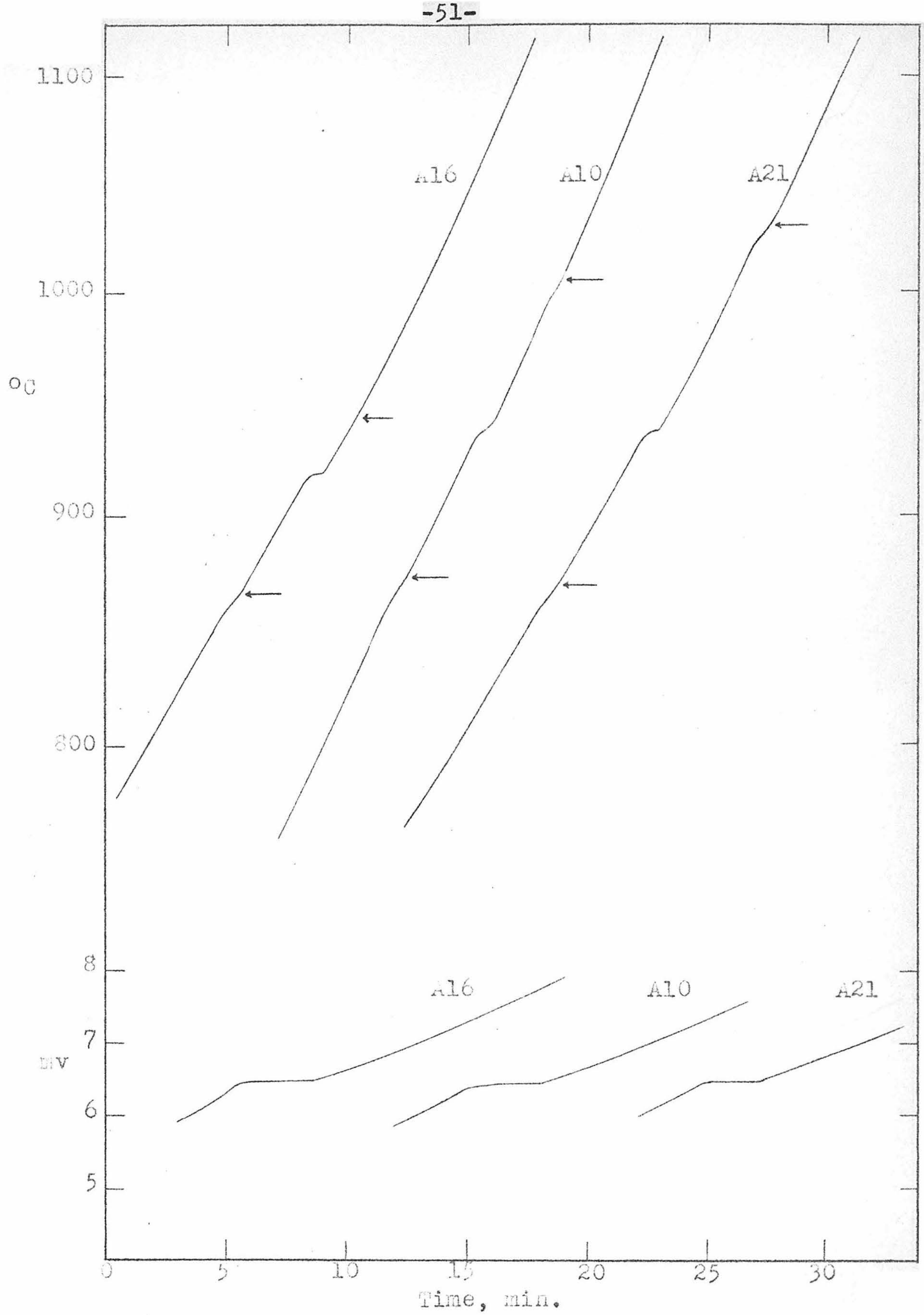


Fig. 6. Cooling Curves.

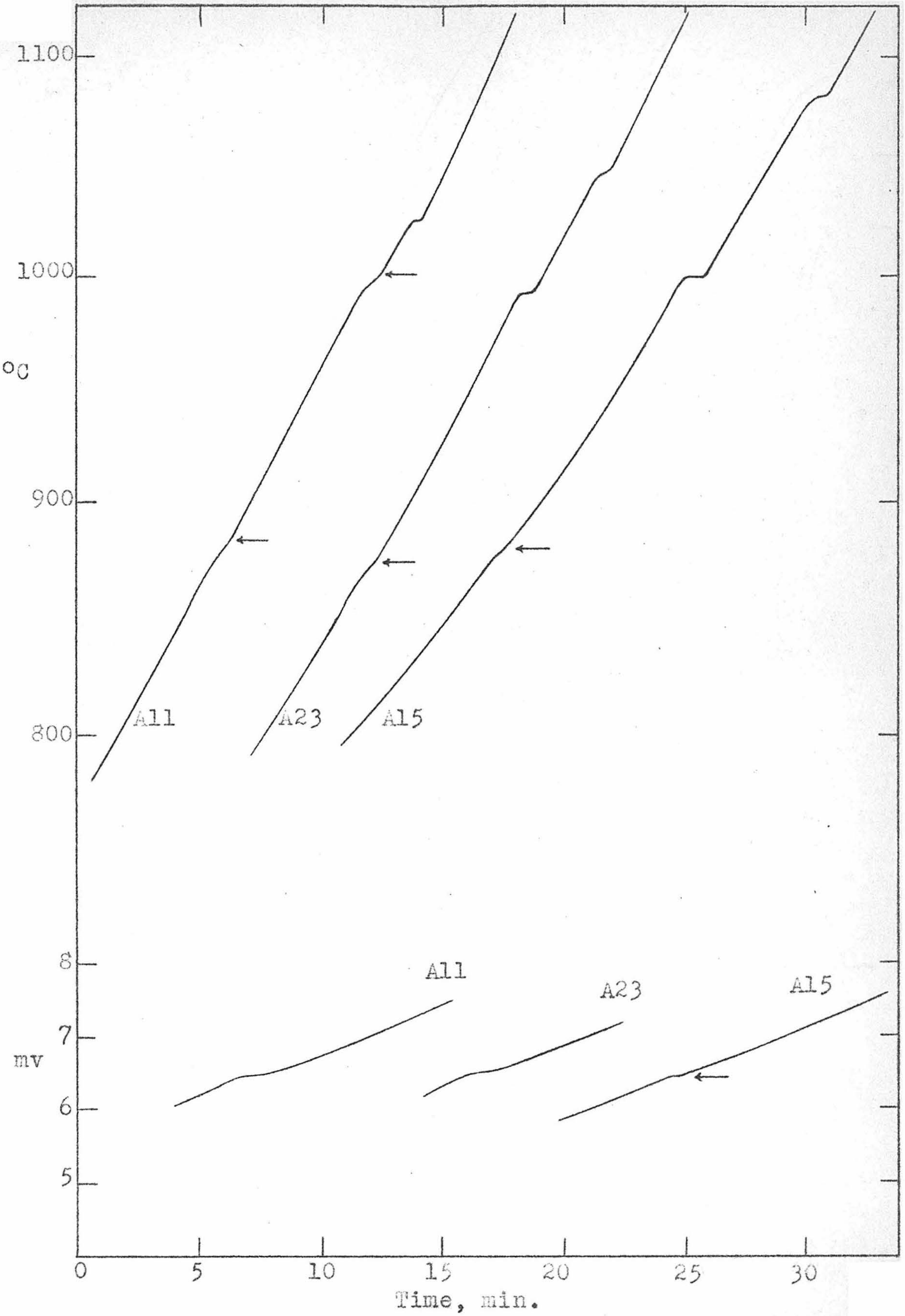


Fig. 7. Cooling Curves.

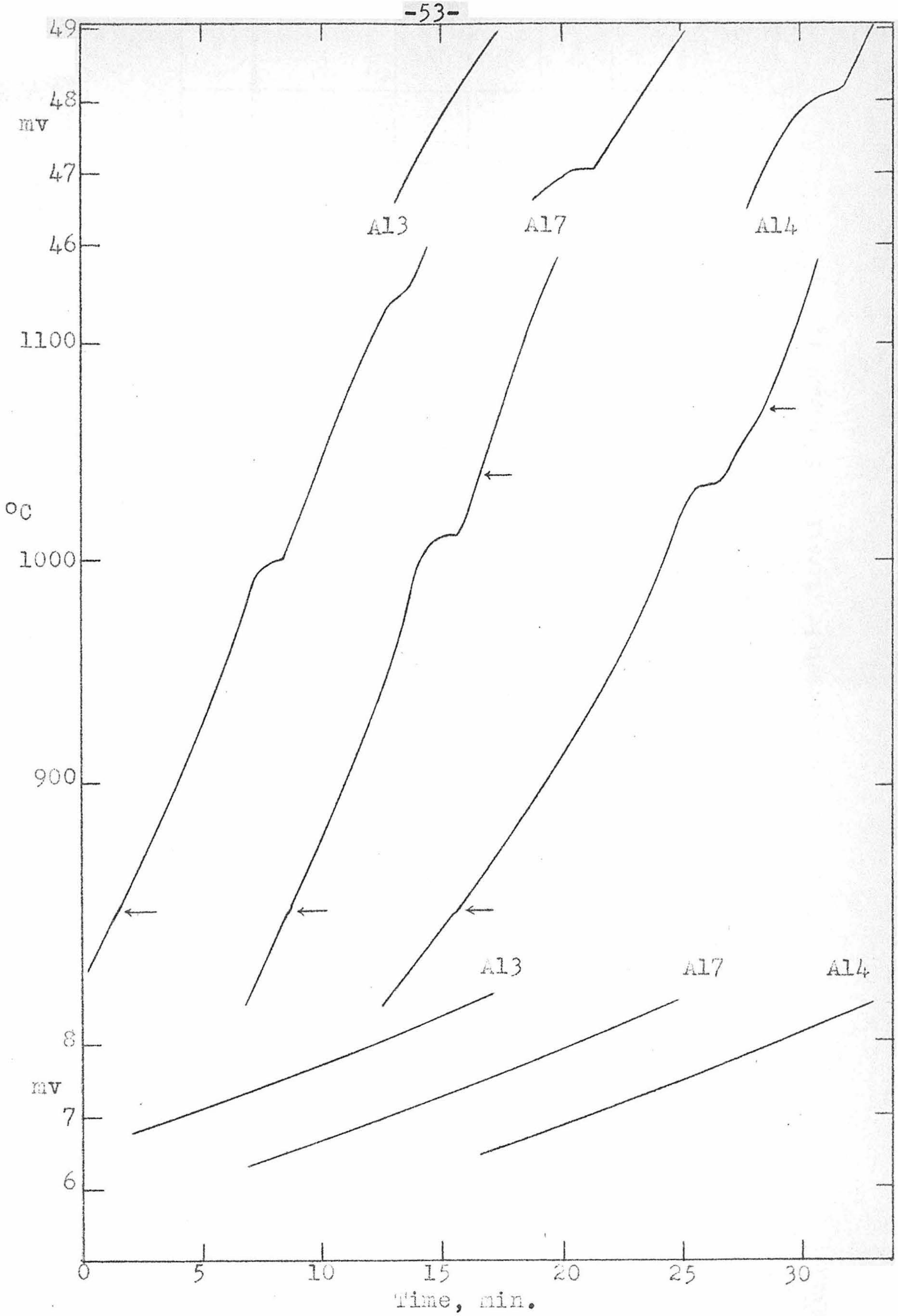


Fig. 8. Cooling Curves.

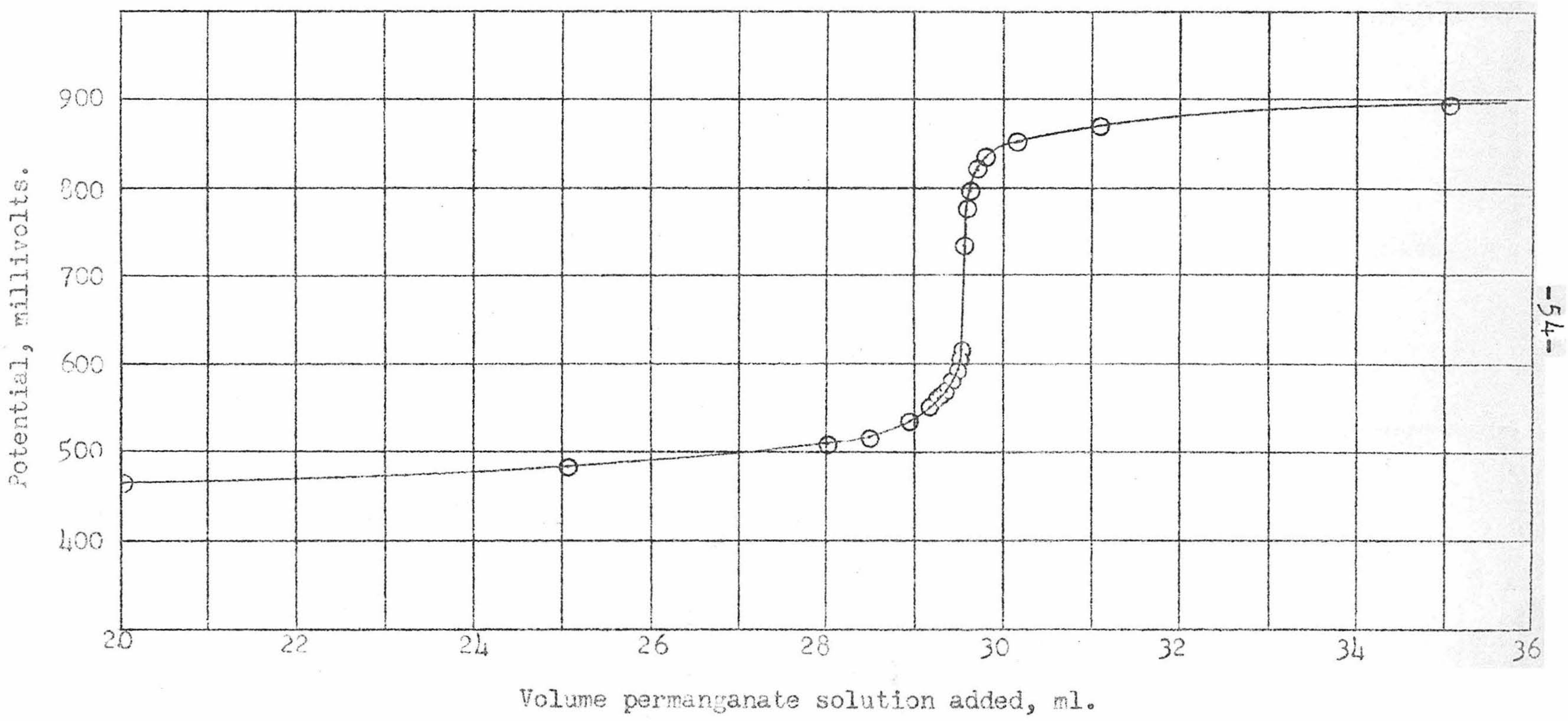
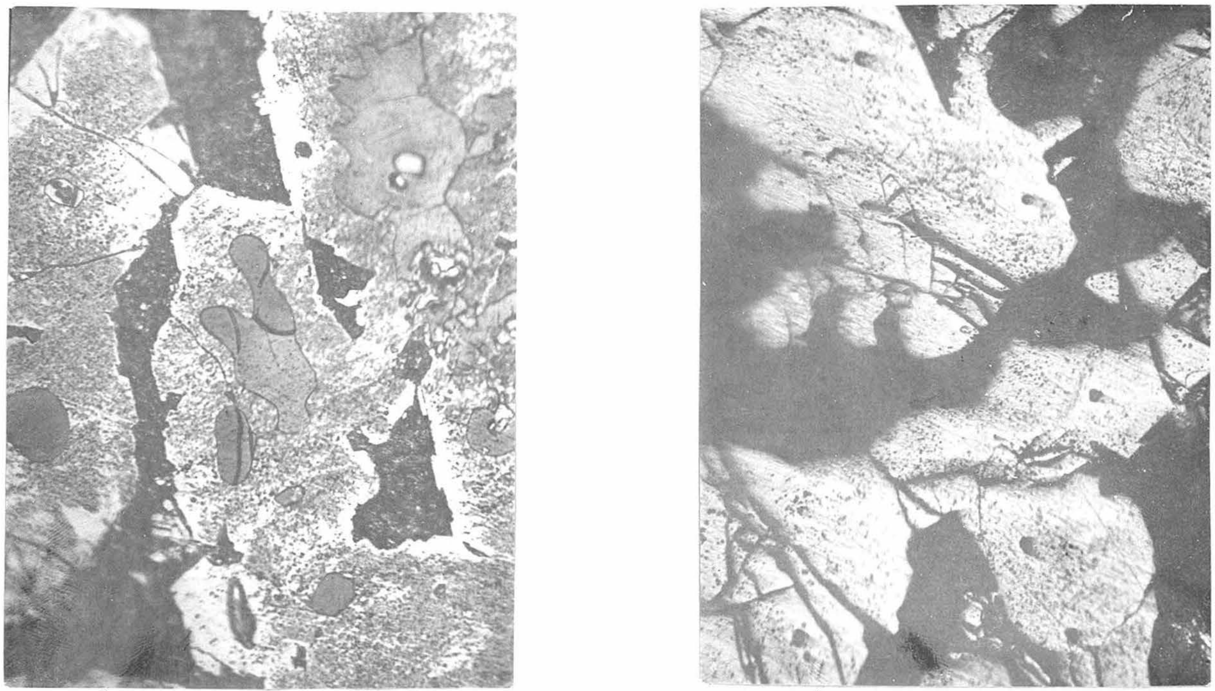
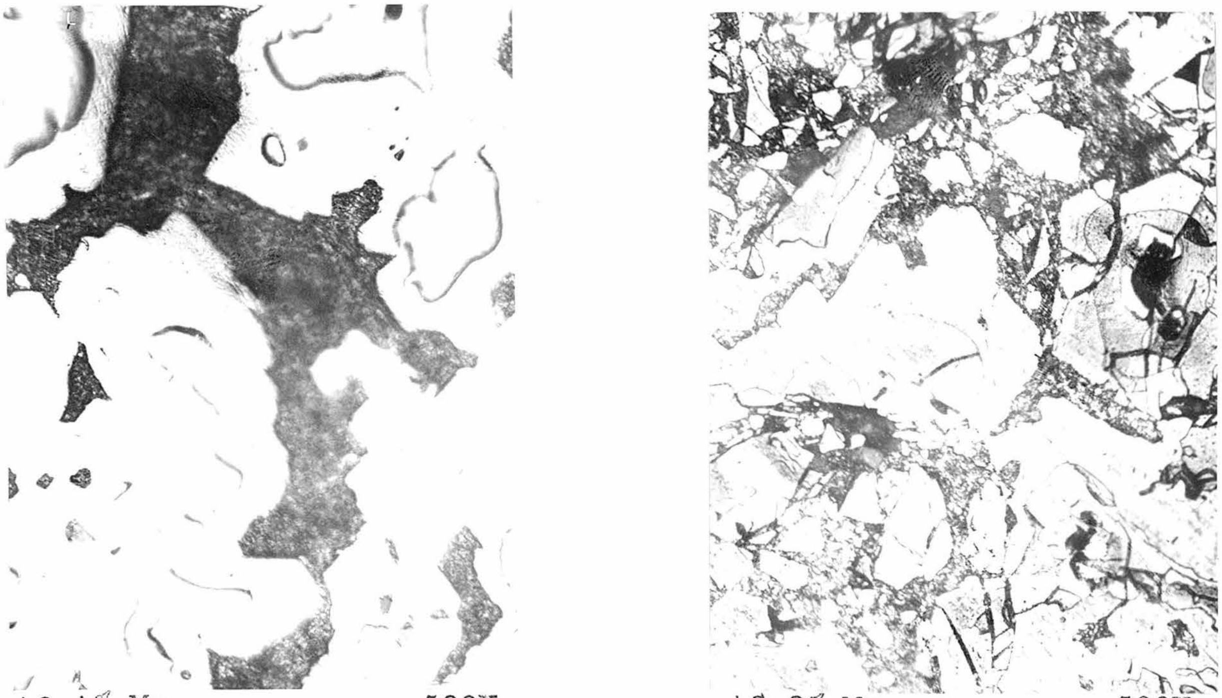


Fig. 9. Potentiometric Titration of Manganese.



32.2% Mn 500X
A18

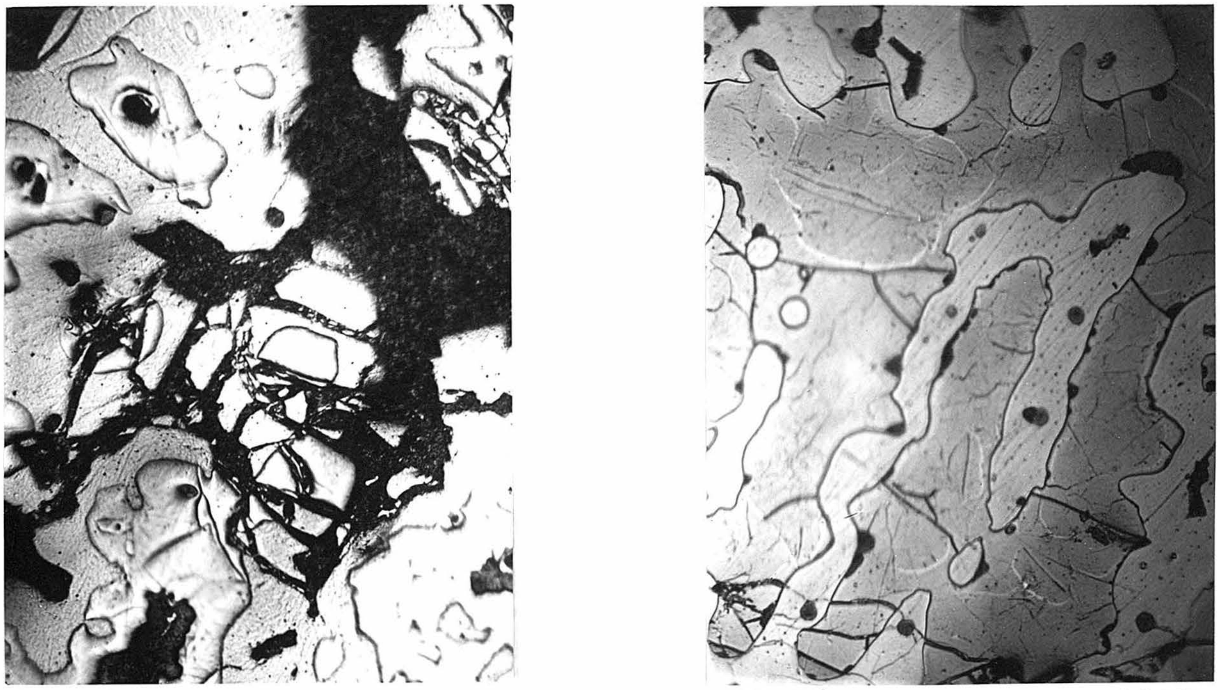
37.9% Mn 500X
A7



43.4% Mn 500X
A16

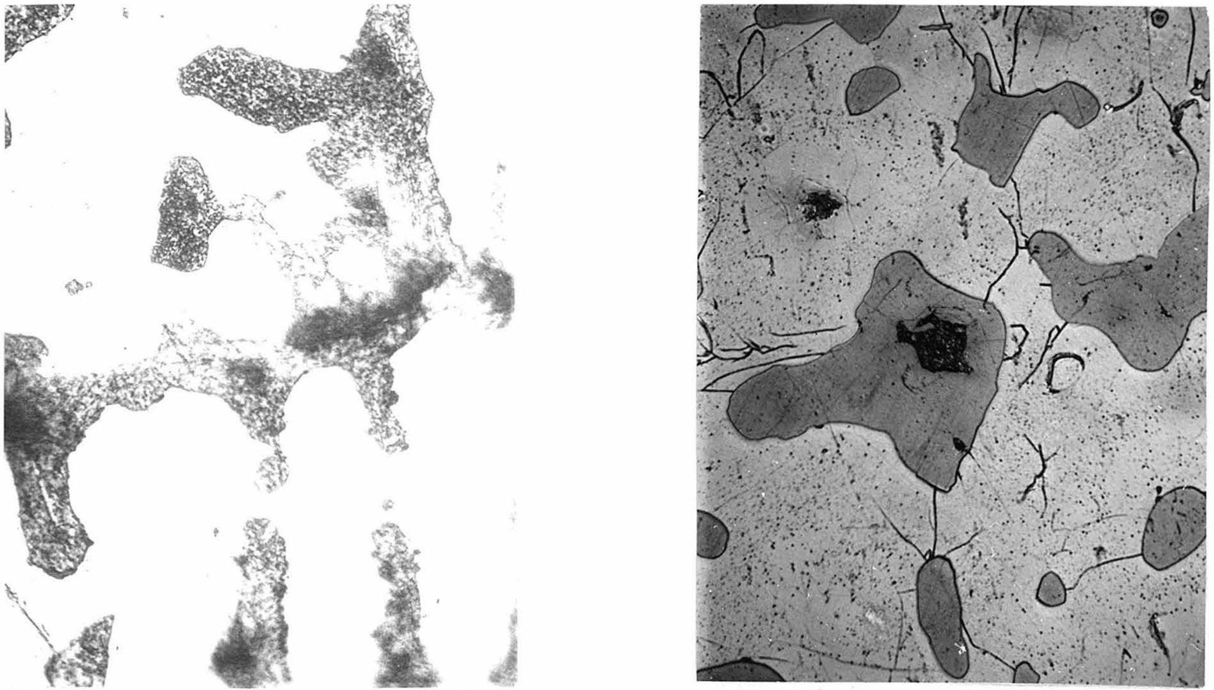
48.9% Mn 500X
A10

Fig. 10. Photomicrographs of unannealed alloys.



53.2% Mn 500X
A21

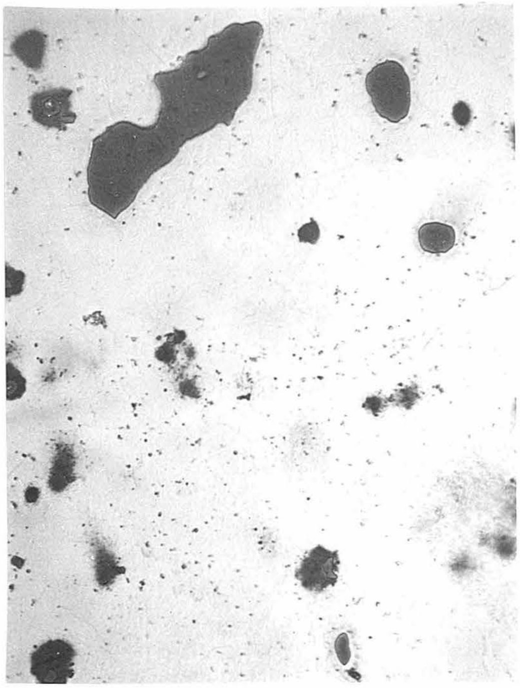
59.5% Mn 500X
A11



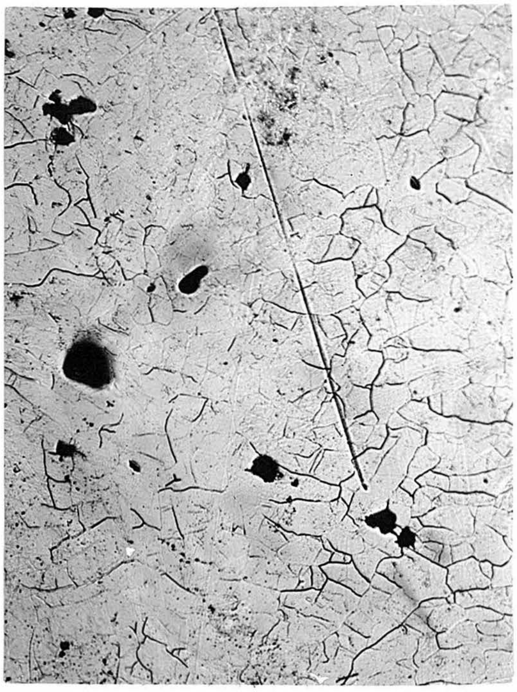
64.5% Mn 500X
A23

69.6% Mn 500X
A15

Fig. 11. Photomicrographs of unannealed alloys.

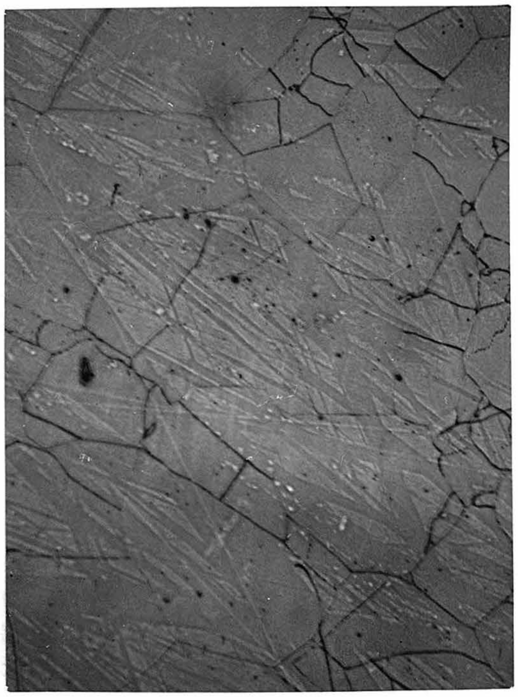


77.2% Mn 500X
A13



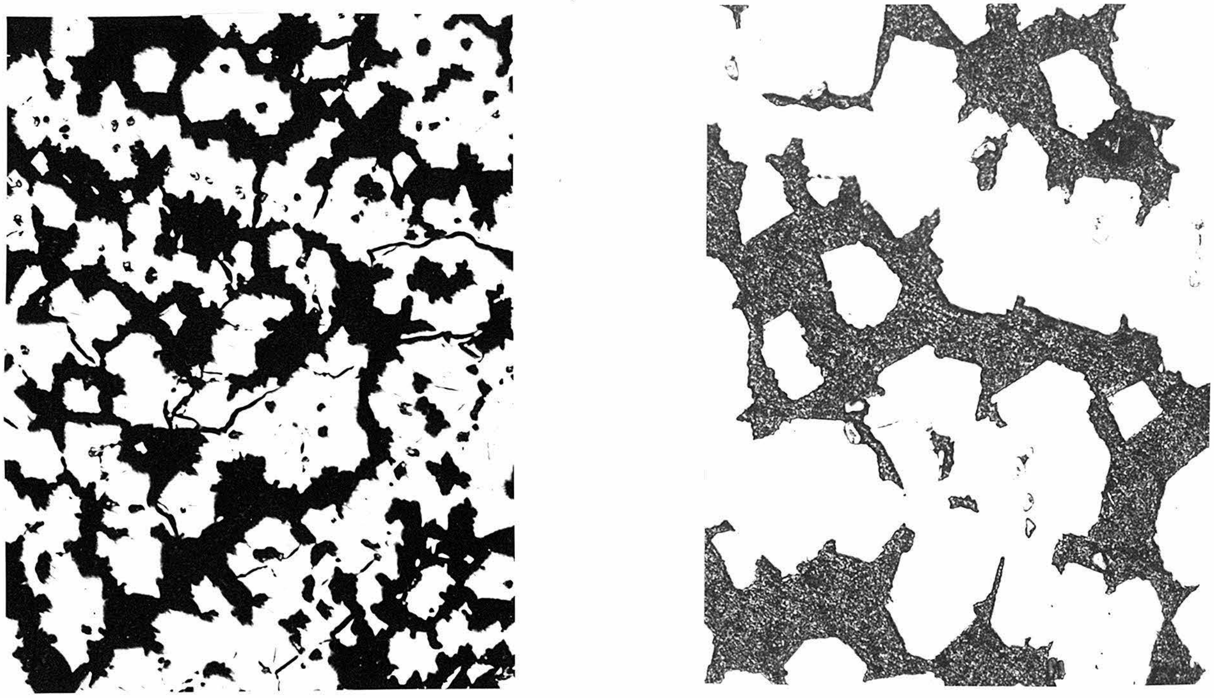
84.4% Mn 150X
A17

84.4% Mn 500X
A17



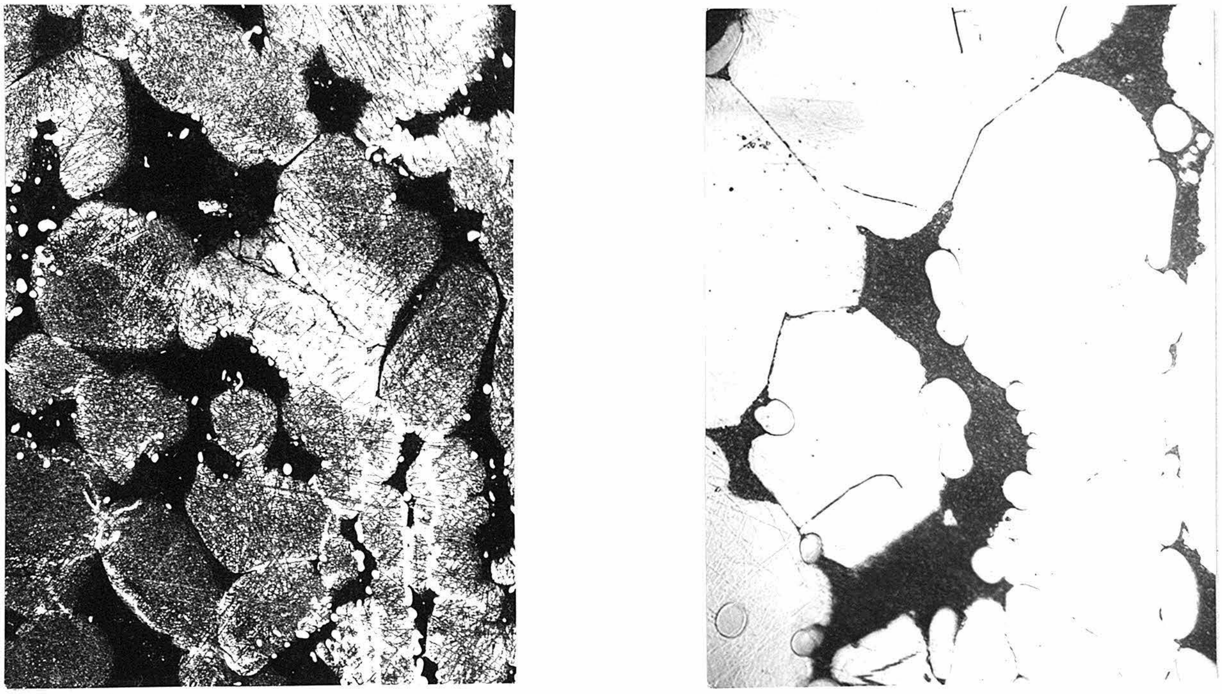
90.7% Mn 500X
A14

Fig. 12. Photomicrographs of unannealed alloys.



43.4% Mn 100X
A16AQ

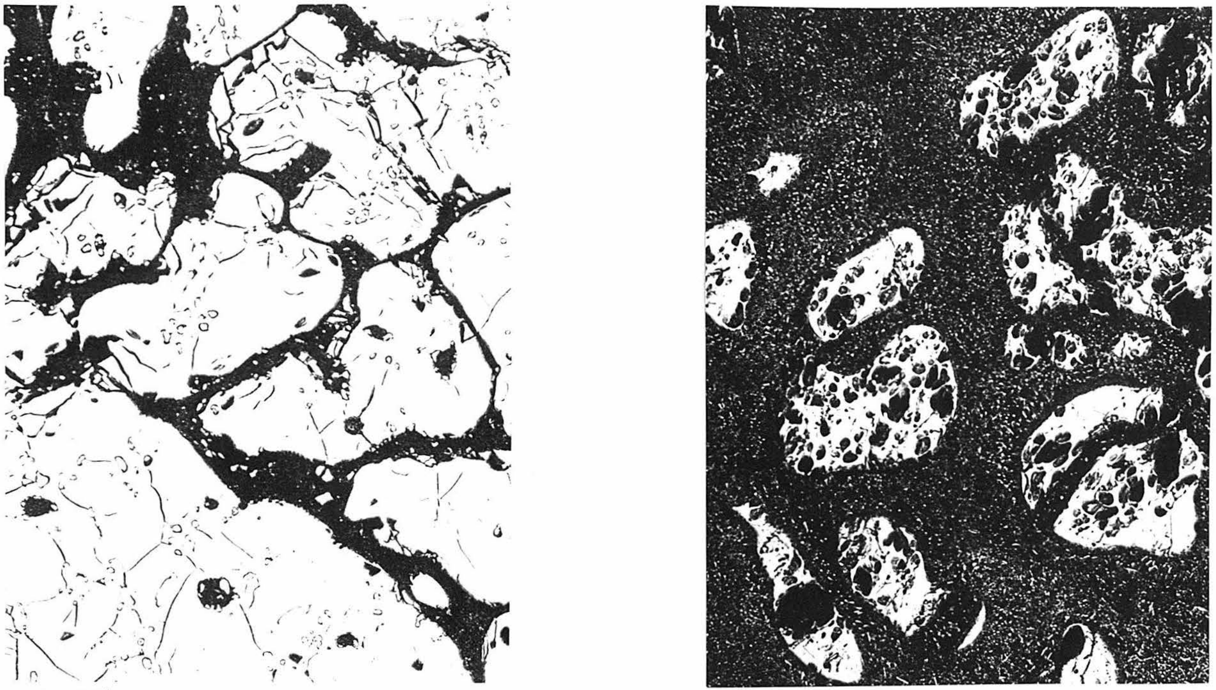
43.4% Mn 250X
A16AQ



48.9% Mn 100X
A10AQ

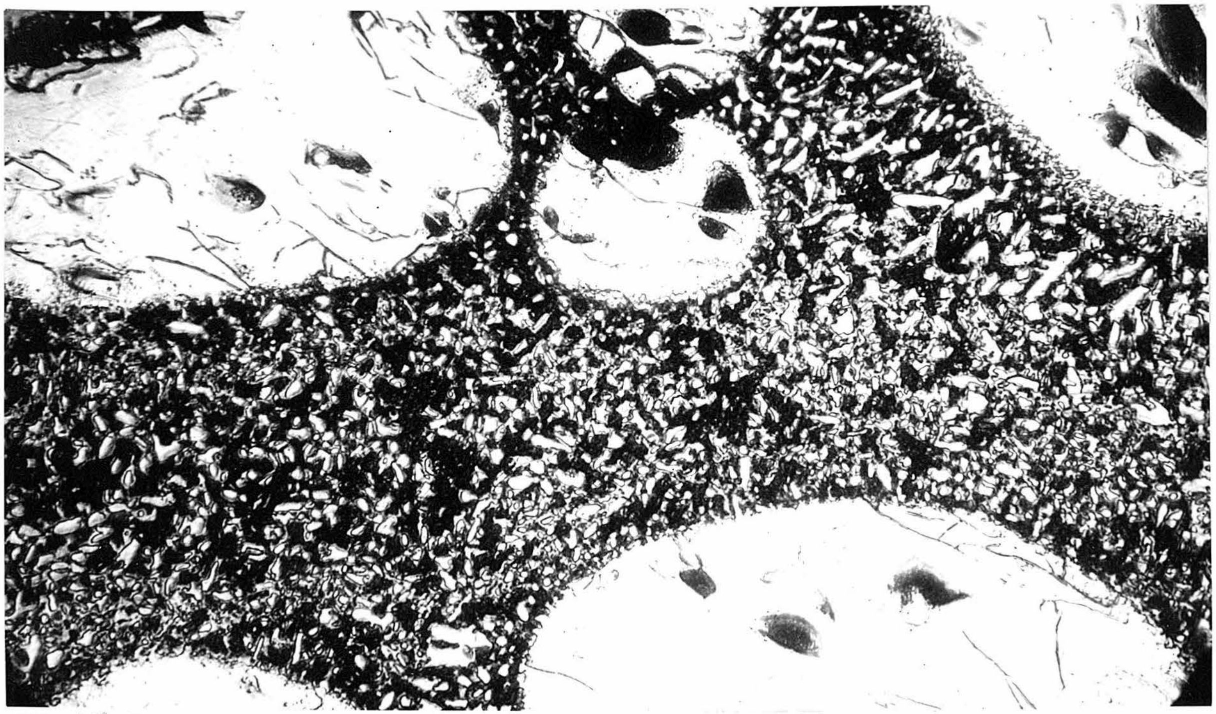
48.9% Mn 500X
A10AQ

Fig. 13. Photomicrographs of annealed and quenched alloys.



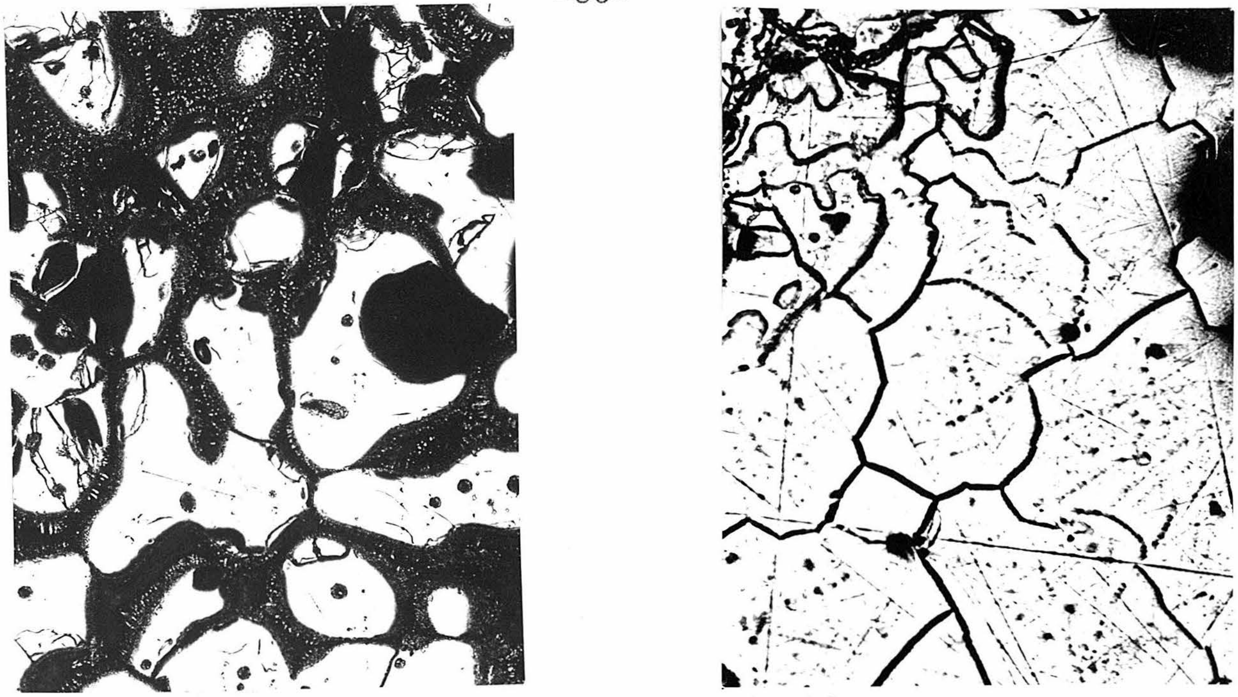
53.2% Mn 100X
A21AQ

59.4% Mn 100X
A11AQ



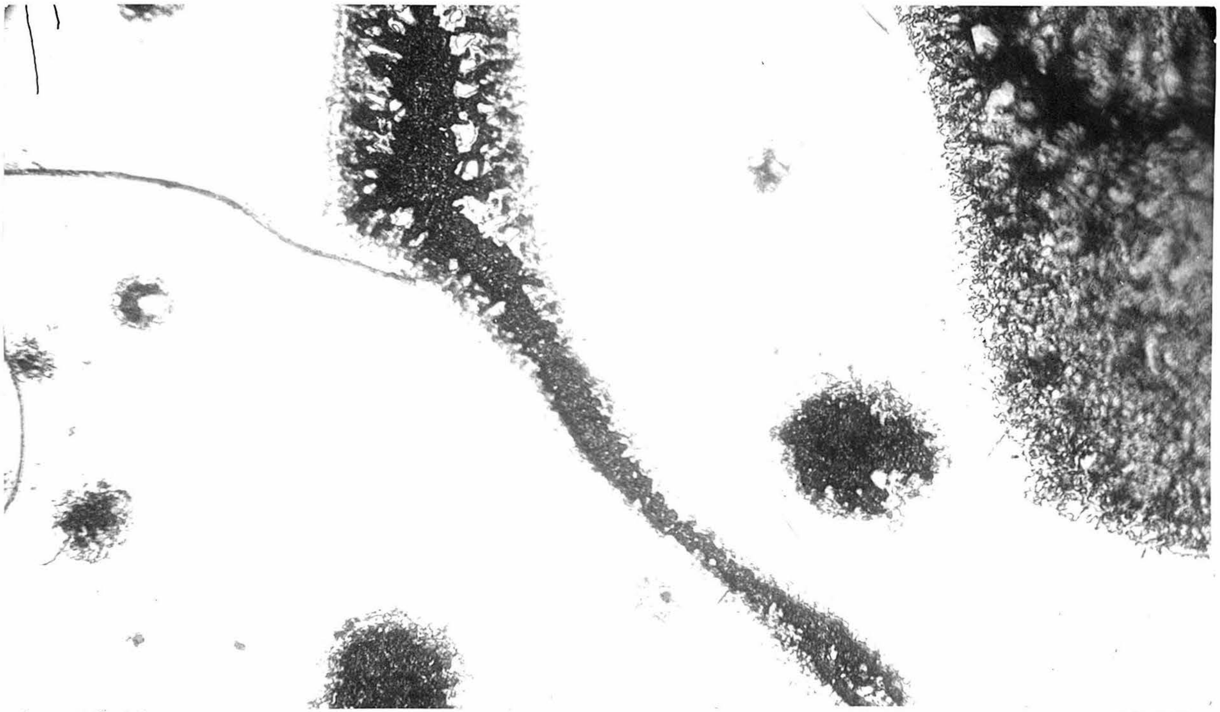
59.4% Mn 500X
A11AQ

Fig. 14. Photomicrographs of annealed and quenched alloys.



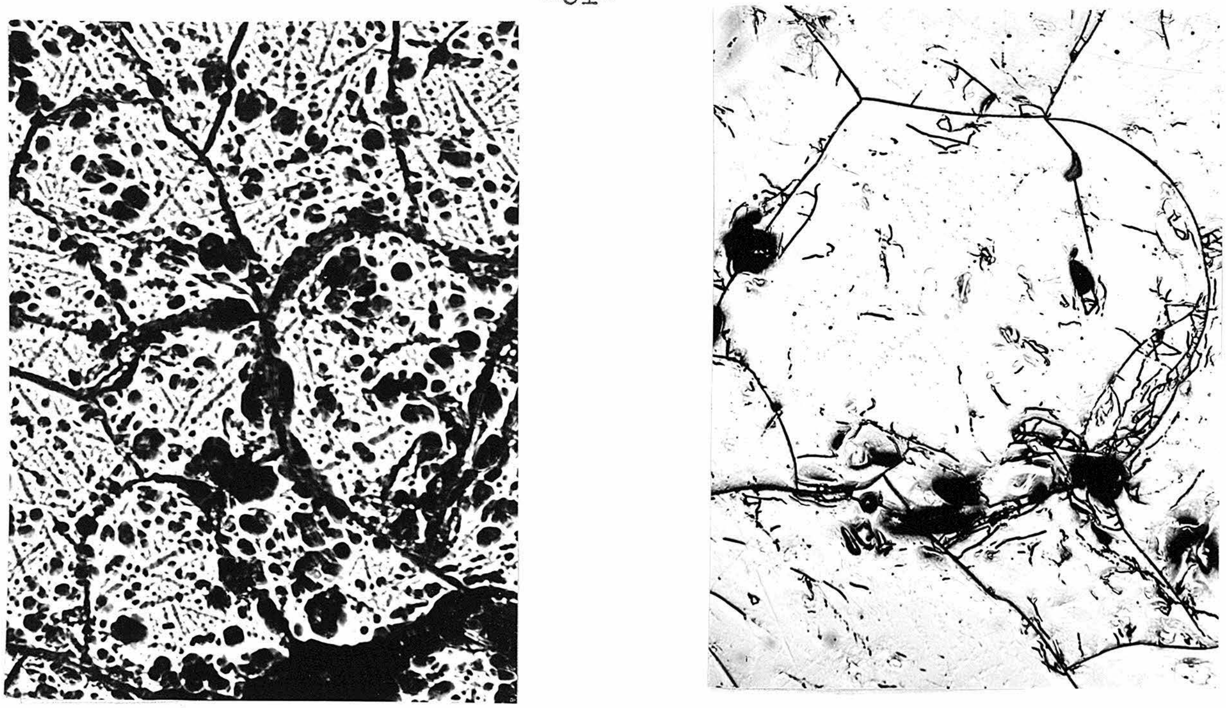
64.5% Mn 100X
A23AQ

69.6% Mn 100X
A15AQ



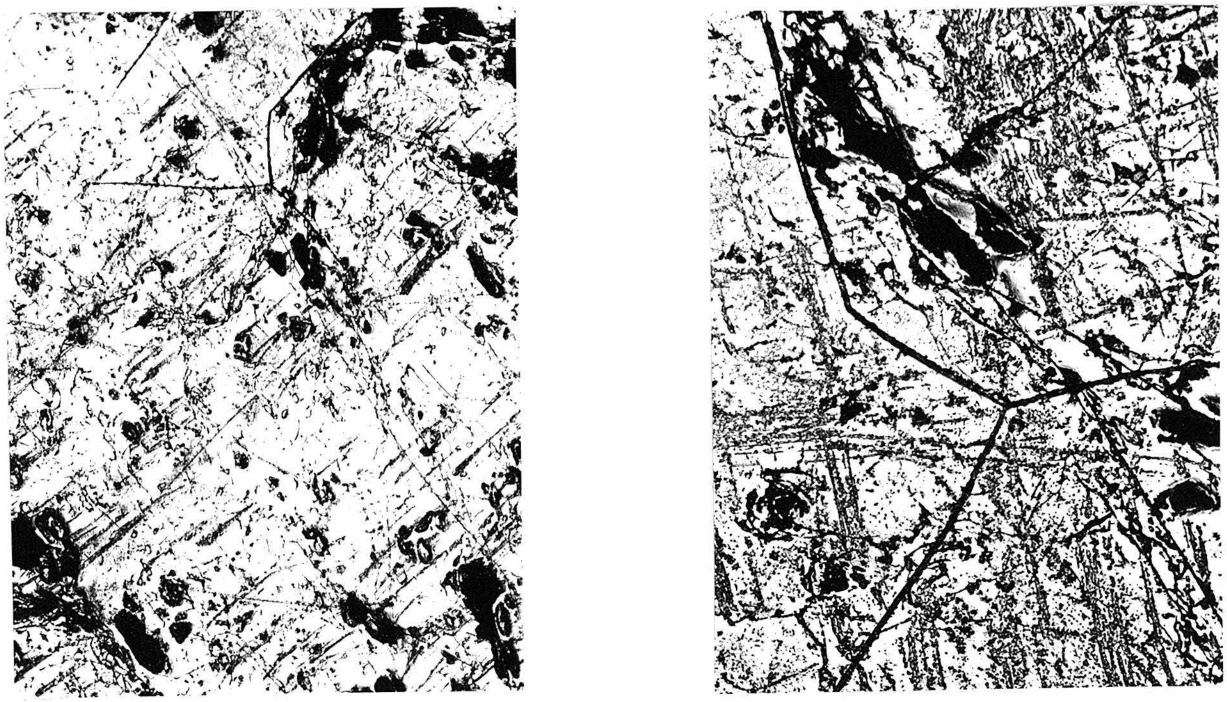
64.5% Mn 500X
A23AQ

Fig. 15. Photomicrographs of annealed and quenched alloys.



77.2% Mn 100X
A13AQ

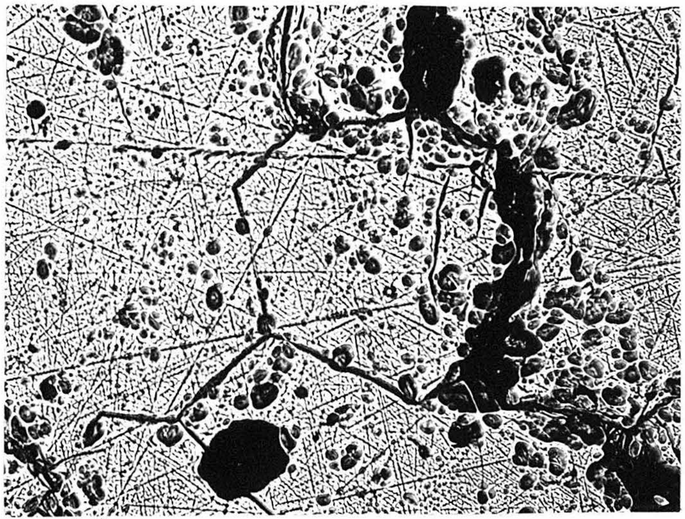
77.2% Mn 250X
A13AQ



84.4% Mn 100X
A17AQ

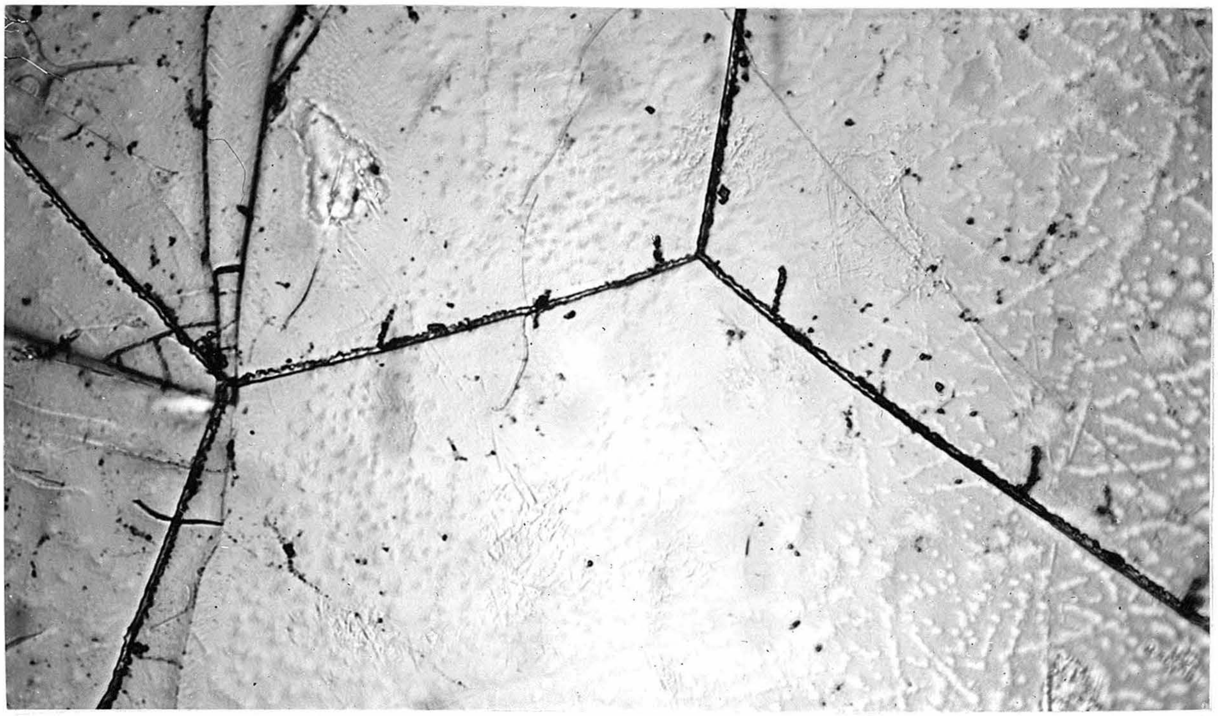
84.4% Mn 250X
A17AQ

Fig. 16. Photomicrographs of annealed and quenched alloys.



90.7% Mn 100X

A14AQ



90.7% Mn 750X

A14AQ

Fig. 17. Photomicrographs of annealed and quenched alloys.

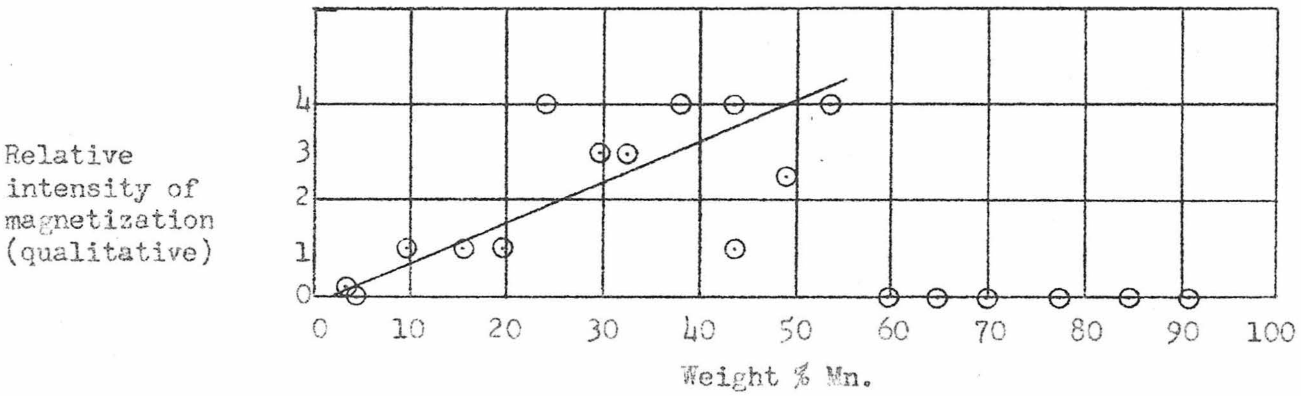


Fig. 18. Ferromagnetic Strength.

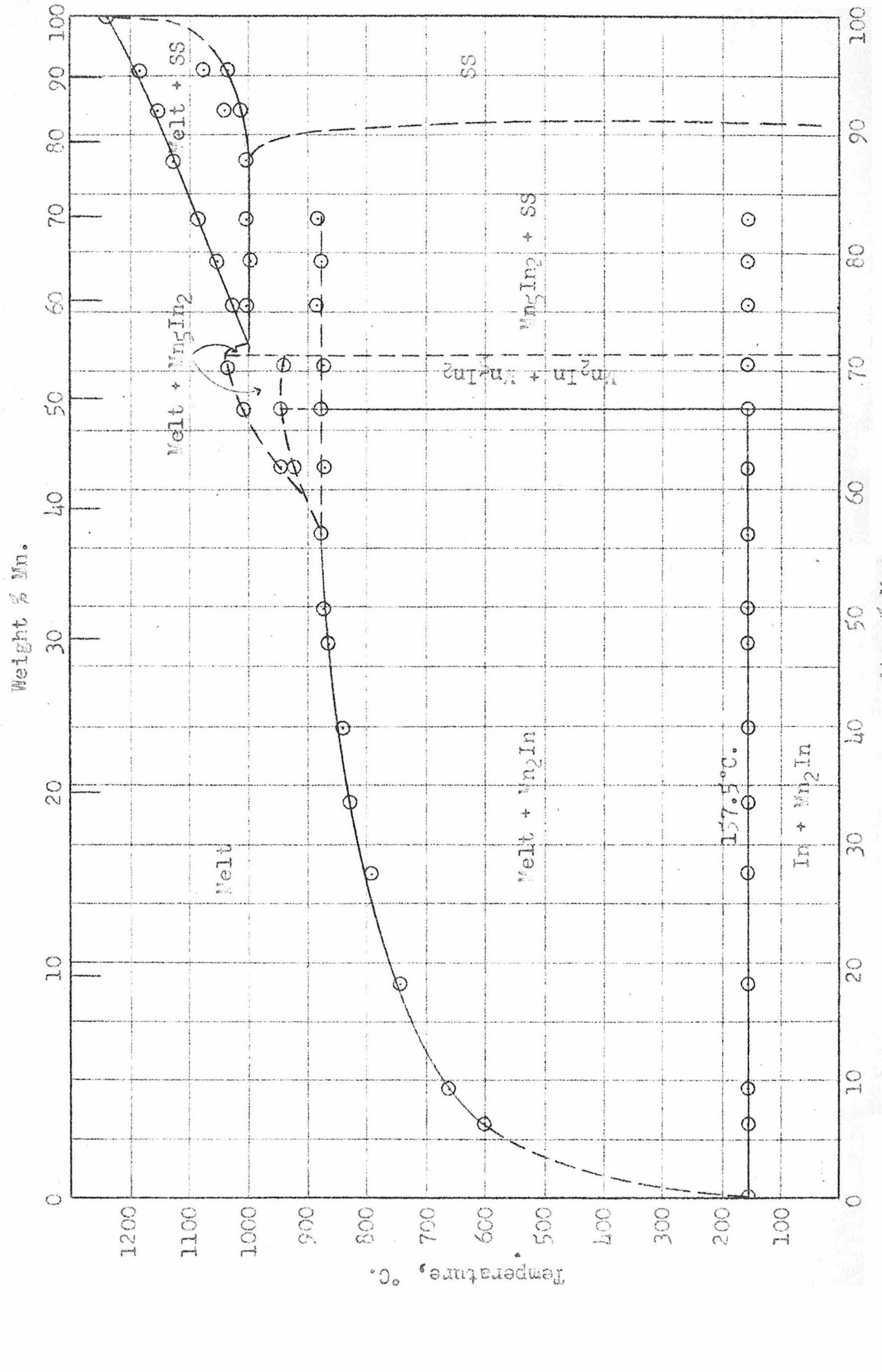


Fig. 19. Phase Diagram.

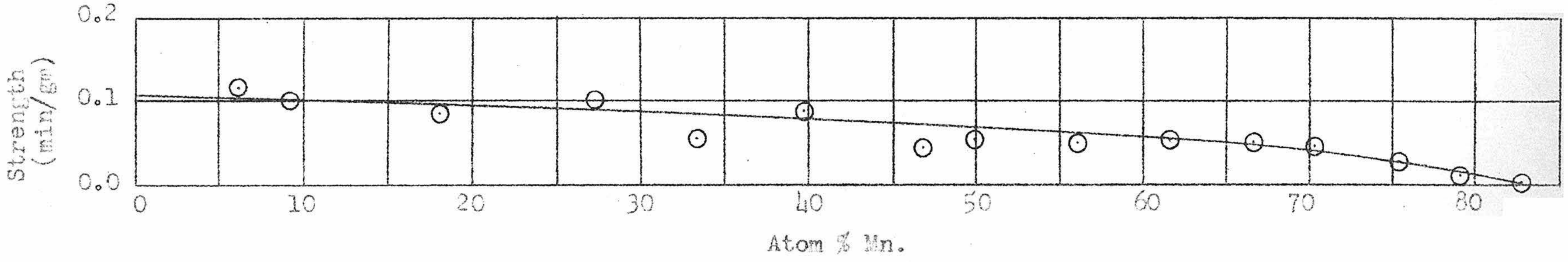


Fig. 20. Strength of Thermal Arrest at 157.5°C.