Spring 5-20-1955

A Study of Certain Ferromagnetic Alloys in the System Copper-Manganese-Gallium

Harold L. Coolidge

A STUDY OF CERTAIN FERROMAGNETIC ALLOYS IN THE SYSTEM COPPER-MANGANESE-GALLIUM

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Harold L. Coolidge

A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of the

Requirements for the Degree of

Bachelor of Science in Metallurgical Engineering

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Four alloys, with compositions near Cu_2MnGa, were heat treated and magnetic measurements were obtained on a ferromagnetic torsion balance. The specimens were also examined microscopically to observe the structure.

Using the experimental results as obtained an attempt was made to construct a magnetic contour map for the area adjacent to the Cu_2MnGa alloy. It is believed that such a map may help in future work on the Cu-Mn-Ga system.

INTRODUCTION

In 1898, F. Heusler discovered ferromagnetic properties in certain Cu-Mn-Al and Cu-Mn-Sn alloys. O. Heusler found that the ferromagnetic alloys in the Cu-Mn-Al system were due to a ternary beta phase having a body-centered cubic structure. In the Cu-Mn-Al system, the strongest ferromagnetism was found to occur in the alloy Cu_2MnAl. Magnetic alloys, composed of non-magnetic constituents, are thus called Heusler alloys. It was found that other ferromagnetic alloys could be produced by replacing the Cu with Ag, or by replacing the Al with Sn, As, B, Bi, Sb, or Zn.

Hames (1,2) and Eppelsheimer (1) showed the presence of ferromagnetic alloys in the Cu-Mn-In and Cu-Mn-Ga systems, in alloys with compositions near Cu_2MnIn and Cu_2MnGa. The ferromagnetism in the Cu-Mn-In system was due to a ternary beta phase. Hames found that the alloy Cu_2MnGa wa s only feebly magnetic; and was unable to determine the crystal structure. The ferromagnetism in the Cu-Mn-Zn system was also due to a ternary beta phase.

Earlier work by Hames (2) and Auberlinder (3) has shown that the Cu-Mn-Ga system contains a ferromagnetic phase. This is reasonable since gallium and aluminum are found in the same group in the periodic chart. The information Auberlinder obtained from X ray studies indicates that the crystal structure of Cu_6MnGa_2 was very close to an ideal hexagonal close packed. The crystal structure showed some slight irregularities which Auberlinder "attributed to the formation of precipitates of the same crystallographic

system".

Hames found two alloys, G_2 and G_3 (Table I), which were magnetic after proper heat treatment. The magnetic alloys had an acicular structure resembling martensite.

TABLE I

COMPOSITIONS OF HAMES' ALLOYS

Atomic Per Cent

	G_2	G_3
Cu	62.4	57.6
Mn	15.1	18.5
Ga	22.5	23.9

Auberlinder (3) found that three alloys, designated 1a, 6a, and 12 (Table II), were ferromagnetic.

TABLE II

COMPOSITION OF AUBERLINDER'S ALLOYS

Atomic Per Cent

	1a	6a	12
Cu	65.4	71.5	66.85
Mn	11.5	7.1	11.00
Ga	23.1	21.4	22.15

Auberlinder performed most of his work on alloy number 12. His work included the bracketing of the annealing temperature at which a change in the magnetic properties occurs. He found three distinct temperature ranges in which the magnetic properties and microstructures were found to differ.

The alloys annealed below 575°C were not ferromagnetic, and had a microstructure composed of a matrix with a fine dispersoid. The alloys annealed between 575° and 585°C were ferromagnetic and had a matrix of fairly coarse particle size. When annealed above 585°C, the alloys were magnetic and showed a characteristic martensitic structure. Auberlinder found that those alloys which showed the strongest ferromagnetism had a martensitic structure.

PURPOSE OF THE INVESTIGATION

The purpose of this investigation was to further study ferromagnetic Cu-Mn-Ga alloys, and to attempt the construction of a magnetic contour map for alloys with a composition near Cu_2MnGa. The information obtained by Hames and Auberlinder will be used in this determination.

EXPERIMENTAL METHODS

First, a Cu-Mn binary alloy was prepared. A set of ternary alloys was then prepared, heat treated in various ways, and the degree of ferromagnetism determined using a magnetic torsion balance. Metallographic studies were carried out on the alloys to show the relationship between ferromagnetism and structure.

Materials

Copper. The copper used in this investigation was electrolytic copper. The purity was assumed to be higher than 99.9 per cent. Before using, the Cu was cleaned by dipping in 50 per cent nitric acid, rinsing with distilled water and drying.

Manganese. The manganese used was a product of the General Chemical Company, New York, N.Y. The assay of the manganese is shown in Table III.

TABLE III

MANGANESE ASSAY

Minimum assay of Mn	99.0%
Sulfur compounds (as SO_4)	0.10%
Iron	0.0015%
Heavy metals (as Pb)	0.003%
Heavy metals (as Ni)	0.01%
SiO_2	0.02%
Alkali & Earth metals (as sulfates) ..	0.03%

Gallium. The gallium was kindly loaned by the Anaconda Copper Mining Company. Since the Ga had been used by Auberlinder in his determinations, it was necessary to recover the metal from his scrap. This recovery was accomplished using quantitative analysis procedures as outlined by Scott (4) and Treadwell (5). The electrolysis was carried on in a highly basic sodium gallate solution. The electrolized gallium served as the cathode, and a platinum plate served as the anode.

During the electrolysis, the electrolyte was checked to determine when the electrolysis was complete. This was accomplished by neutralizing the solution with HCl to precipitate the Ga as $Ga(OH)_3$. When no precipitate formed the electrolysis was considered complete.

The purity of the gallium was assumed to be above 99 per cent. Befor using, the gallium was washed in a 10 per cent solution of HNO_3. The washing not only removed some of the impurities but also helped to coagulate the gallium.

Equipment

Furnaces. Five furnaces were used in this experiment. The furnace used to melt the alloys was of the gas-blower type built by the Denver Fire Clay Company of Denver, Colorado. The other four furnaces were used to heat the samples.

Three of the four heat treating furnaces were built by the Hevi Duty Electric Co., Milwaukee, Wis. Two of these furnaces were rated at 1440 watts and controlled by Pyr-O-Vane controllers built by the Minneapolis-Honeywell Co., Minneapolis, Minn. The third was rated at 5000 watts and controlled by a Wheelco Capacitrol built by the Wheelco Instrument Co. of Chicago, Ill.

The fourth furnace, used for heat treatment, was built by the C. I. Hayes, Inc., Providence, R.I. This furnace is rated at 7920 watts and controlled by a Wheelco Capacitrol.

Metallography. The photomicrographs which appear in this report were taken on a Reichert Universal Camera Microscope made by C. Reichert, Wien, Austria.

Magnetic Torsion Balance. Magnetic measurements were made on a ferromagnetic torsion balance which was designed and built by Willner (6) and Moen (7). This apparatus was constructed to measure the "specific intensity of magnetization" which is the magnetic moment per gram.

When a ferromagnetic sample is suspened between the poles of the electromagnet, it is acted upon by the magnetic

field and in turn develops a magnetic moment. The following sketch illustrates how a sample, suspended in the magnetic field of the torsion balance, developes a torque.

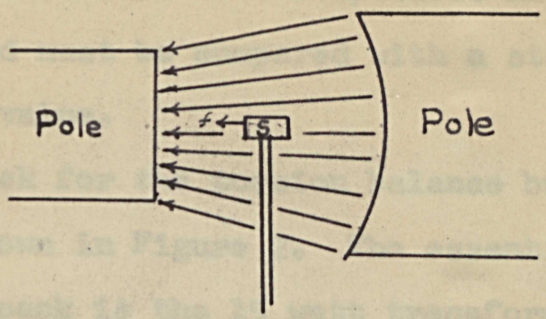

Fig. 1 - How Magnetic Force is Developed on Sample

To obtain a constant gradient, the poles of the electromagnet were made different sizes. The larger pole has a concave face.

The force (f) on a ferromagnetic specimen (s) is directly proportional to the mass (m) of the specimen; the specific intensity of magnetization (σ) of the specimen; the field strengh (H) and the rate of variation of magnetic field strength along the polar axis of the magnet (dH/dX);

$$f = m\sigma HdH/dX$$

The force, which is exerted on the suspended sample, is determined indirectly by placing a torque in the opposite direction on the suspension wire. By utilizing a suitable scaling system, in this case a graduated dial, the restoring force can be measured.

This apparatus is capable of making accurate magnetic measurements; however, the results obtained are not comparable with the results from another apparatus, because the

unit is not capable of producing a sufficient high field strength to insure complete saturation of the specimen. Therefore, it would not be correct to say that the saturation specific intensity of magnetization was measured. The restoring force is a measure of the specific intensity of magnetization, and must be compared with a standard to obtain an absolute value.

The power pack for the torsion balance burned out and was rebuilt as shown in Figure 2. The essential difference in the new power pack is the 15 watt transformer which supplies the filaments, of the 5U4 tube, with constant voltage. The transformer should prevent failure of the power pack in the future.

Preparation of Alloys

Copper-Manganese Binary Alloys. To obtain a material with a lower melting point than either Cu or Mn, an alloy of Cu and Mn was first prepared. A known weight of copper was melted in the gas-blower furnace, and a known weight of manganese was added. This scheme was used to prevent excess oxidation of the manganese. The material was melted in a fire clay crucible obtained from the Denver Fire Clay Co., Denver, Colo. There appeared to be little or no reaction between the alloys and the crucible.

The binary alloy was shotted to make weighing, in the preparation of the ternary alloys, easier. The binary alloy thus prepared was intended to be 89 per cent Cu and 10 per cent Mn. This ratio was selected so that only Ga would have to be added to produce the first ternary alloy. No analysis

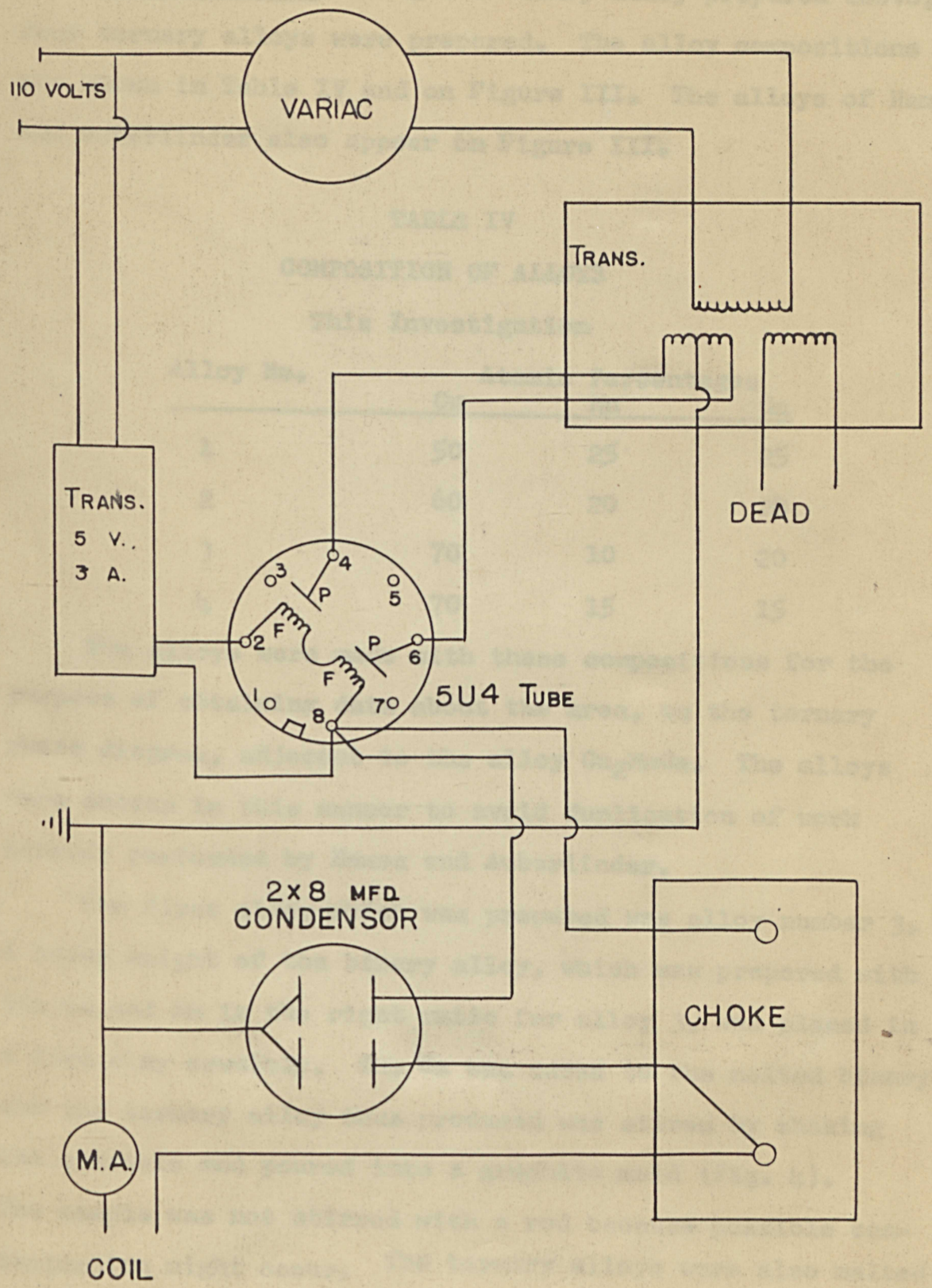

FIG. 2 - POWER PACK FOR TORSION BALANCE

was performed to determine the exact composition.

Ternary Alloys. Using the binary alloy prepared above, four ternary alloys were prepared. The alloy compositions are shown in Table IV and on Figure III. The alloys of Hames and Auberlinder also appear on Figure III.

TABLE IV

COMPOSITION OF ALLOYS

This Investigation

Alloy No.	Atomic Percentages		
	Cu	Mn	Ga
1	50	25	25
2	60	20	20
3	70	10	20
4	70	15	15

The alloys were made with these compositions for the purpose of obtaining data about the area, on the ternary phase diagram, adjacent to the alloy Cu_2MnGa. The alloys were chosen in this manner to avoid duplication of work already performed by Hames and Auberlinder.

The first alloy which was prepared was alloy number 3. A known weight of the binary alloy, which was prepared with the Cu and Mn in the right ratio for alloy 3, was placed in a fire clay crucible. The Ga was added to the melted binary and the ternary alloy thus produced was stired by shaking the crucible and poured into a graphite mold (Fig. 4). The sample was not stirred with a rod because possible contamination might occur. The ternary alloys were also melted in the gas-blower furnace.

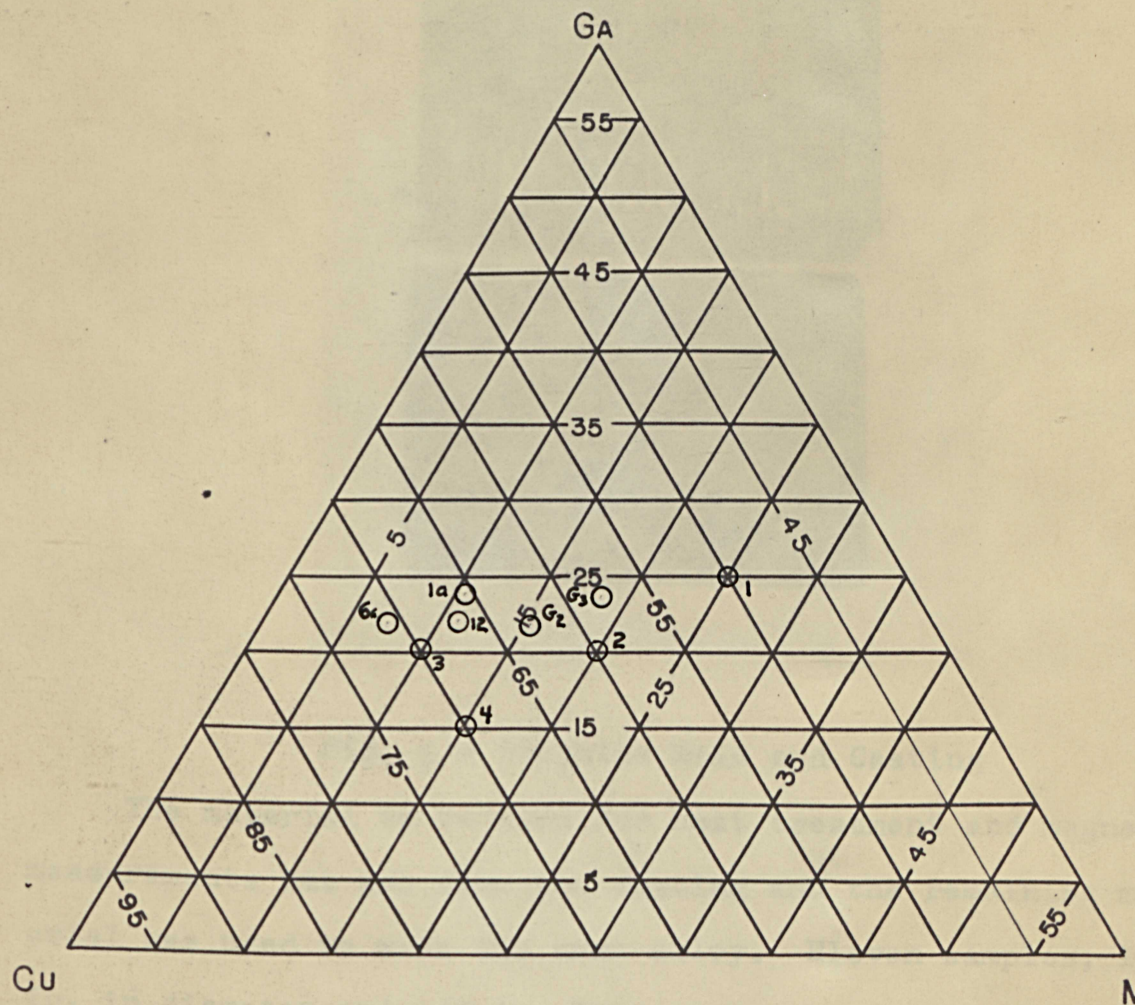

FIG. 3 — CU-MN-GA PHASE DIAGRAM

TERNARY COMPOSITION DIAGRAM

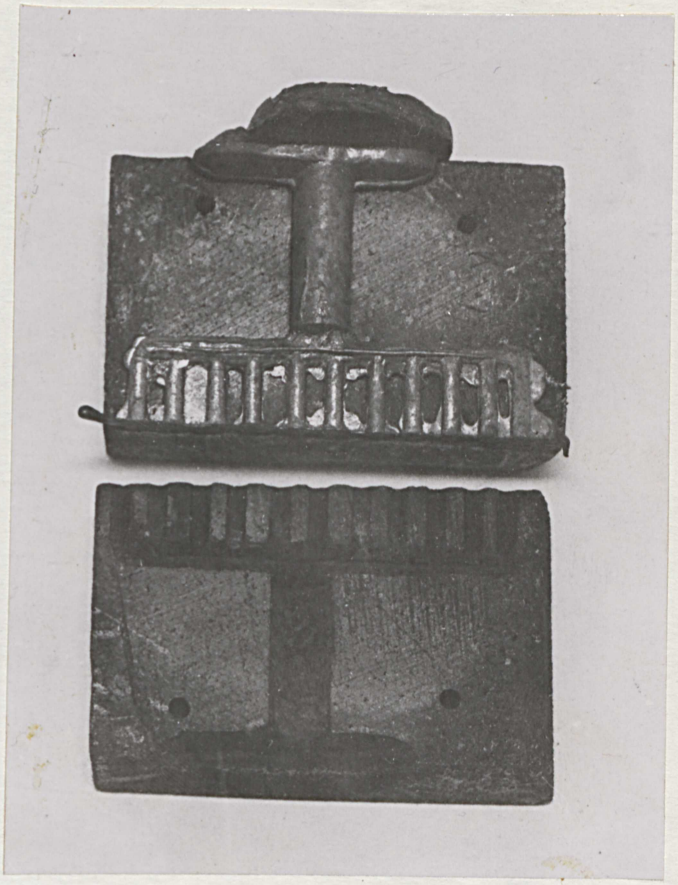

Fig. 4 - Graphite Mold and Casting

The material to be used for heat treatment and magnetic measurements was cut from the casting and the remaining material was used to make the next alloy. Eleven samples, 1/16 in. in diameter and 1/2 in. long, were obtained from each alloy.

The excess material from alloy 3 was melted and Mn and Ga were added to produce alloy 1. Again the samples were cut and the excess material was used to prepare the next alloy.

Alloy 2 was prepared by adding a known weight of Cu to alloy 1. The samples were cut and the excess material was used to prepare alloy 4. Alloy 4 was prepared by adding Cu to alloy 2. The alloys were made in this order to utilize

the waste material from the previous alloy. The alloys were not chemically analysed.

Heat Treatment

Heat treatment was carried out on all of the alloys. The results of heat treatment worked out by Auberlinder were used to determine the schedule.

The samples were sealed in quartz tube after evacuating the air with an ordinary water aspirator. An oxygen-gas burner was used to melt the quartz glass.

The samples were homogenized before the heat treatment schedule was started. This was accomplished by placing the samples in a furnace with the temperature at 600°C. After 24 hours, one of the samples was removed, quenched, polished, and examined microscopically. Since the sample was not homogeneous, the temperature was raised to 700°C for 24 hours. Again a sample was removed and quenched. When examined under the microscope the samples appeared to be homogeneous. The remaining samples were then removed from the furnace and quenched.

Quenching was accomplished by breaking the quartz tube under water. The severity of this quench is important since it will in part determine the structure of the alloy. The samples were again sealed in quartz tube before subsequent heat treatment was performed.

The samples were heat treated as shown in Table V. The series letter was assigned for the purpose of sample identification. None of the samples melted, but several showed a

slight superficial oxidation.

TABLE V

HEAT TREATING SCHEDULE

Series	Condition	Temp. °C	Time (hr.)	Cooling
A	As Cast	---	--	--
B	Homo.	600	5	Quench
C	Homo.	600	15	Quench
D	Homo.	585	15	Quench
E	Homo.	570	15	Quench
F	Homo.	555	15	Quench
G	Homo.	750	4	Quench
H	Homo.	700	4	Quench
I	Homo.	650	4	Quench
J	Homo.	600	4	Quench

RESULTS AND DISCUSSION

Magnetic Measurements. All samples were tested on the ferromagnetic torsion balance as described in the equipment section of this report. The results of these measurements, as shown in Table VI, are given in units per gram; the unit being one scale unit on the magnetic torsion balance.

It is interesting to note that those specimens which were heat treated 4 hours at 650° to 700°C and quenched showed the greatest amount of magnetism in alloys 1 and 2. Alloys 3 and 4 showed the greatest amount of magnetism in the as cast condition.

Auberlinder found that specimens annealed above 575°C and quenched were magnetic. The four alloys considered in

this report were found to be non-magnetic when heat treated for 15 hours at 585°C. This difference in magnetic properties may be due to a difference in the quenching method, a difference in the annealing time, or a difference in the alloy composition.

TABLE VI

MAGNETIC MEASUREMENTS

Units per gram

Alloy	1	2	3	4
A	0	196.7	4.7	2.25
B	0	2.4	0	0
C	0	0	0	0
D	0	0	0	0
E	0	0	0	0
F	0	0	0	0
G	3.2	55.4	0	0
H	8.6	173.7	1	1
I	0	212.9	1.3	0
J	0	0	1	0

Using the magnetic data, as shown in Table VI, a proposed magnetic contour map (Fig. 5) of the area adjacent to the alloy Cu_2MnGa was constructed. This map is only an approximation and should not be considered accurate. The alloys of Hames and Auberlinder appear on the map, but were not considered when drawing the contours because no comparsion was avaliable for the relative amounts of magnetism. The heat treating schedule did not cover all the possible combinations; therefore, the magnetism as found on the samples is not necessarily the strongest possible value.

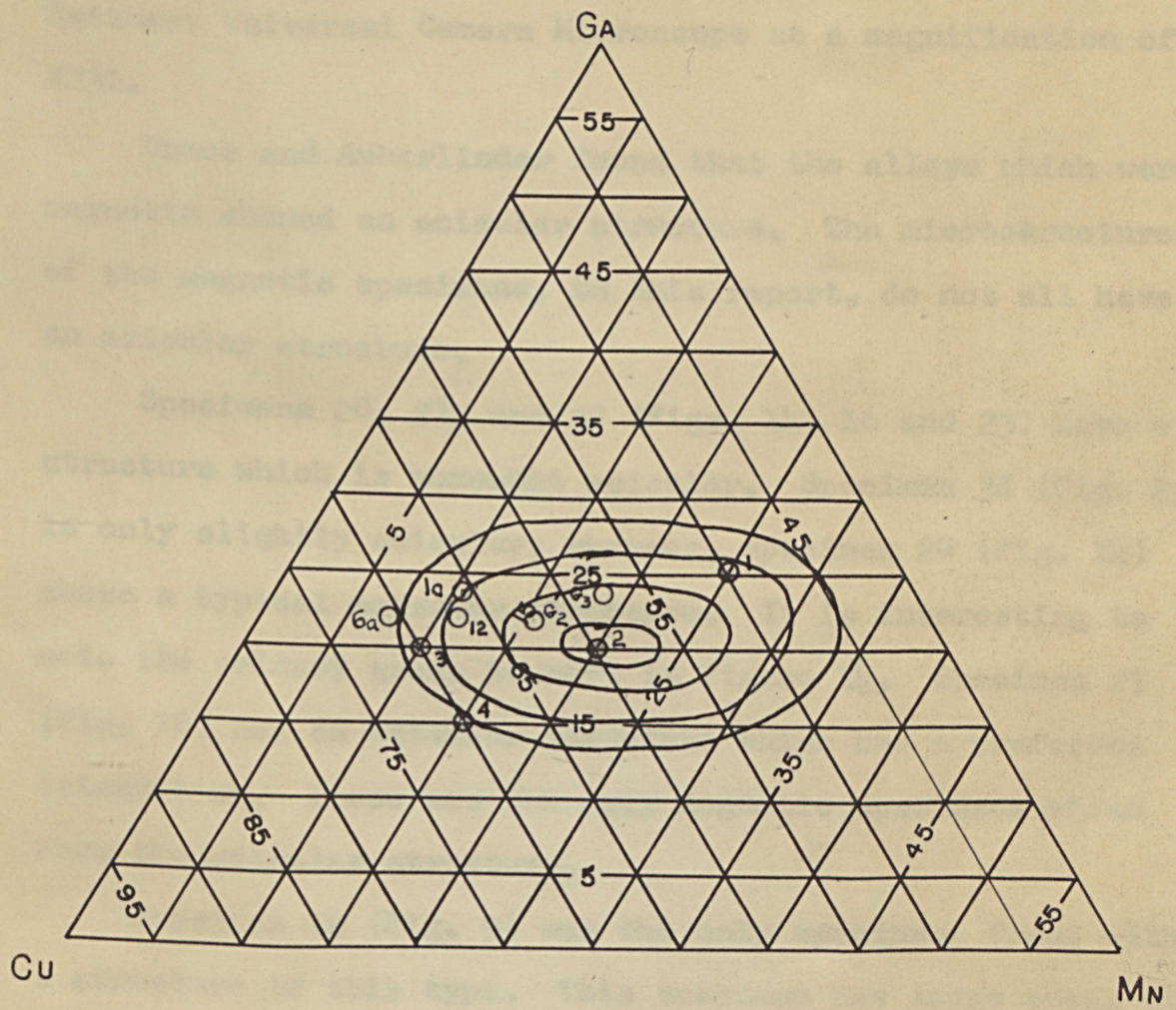

Fig. 5 — Cu-Mn-Ga Phase Diagram

Proposed Magnetic Contour Map

Metallography. Metallographic studies were carried out on the specimens which were heat treated and tested for magnetic properties. The specimens were mounted in lucite, polished, and etched with potassium bichromate. The photomicrographs (Fig. 6 through Fig. 29) were taken on the Reichert Universal Camera Microscope at a magnification of X231.

Hames and Auberlinder found that the alloys which were magnetic showed an acicular structure. The microstructures of the magnetic specimens, in this report, do not all have an acicular structure.

Specimens 2G, 2I, and 3J (Figs. 14, 16 and 23) have a structure which is somewhat acicular. Specimen 3J (Fig. 23) is only slightly acicular; whereas, specimen 2G (Fig. 14) shows a typical acicular structure. It is interesting to note the primary grain boundry in Figure 14. Specimen 2I (Fig. 16) has an acicular structure which has a preferred orientation. These are the only magnetic specimens which show the acicular structure.

Specimen 1H (Fig. 9) was the only speciment found with a structure of this type. This specimen has large areas with a structure which is nearly acicular dispersed through a matrix of a fine dispersoid. The alloy has a composition Cu_2MnGa and is slightly magnetic. It is believed that the somewhat acicular structure accounts for the slight magnetism which is found.

Specimens 1G, 2A, 2B, 2H, 3A and 3H (Figs. 8, 12, 13, 15, 18, and 21) are magnetic and have a mosaic structure showing only grain boundries. An acicular structure might

Fig. 6 - Specimen 1 A. As cast. Not magnetic. X231

Fig. 7 - Specimen 1 B. Annealed for 5 hours at 600°C and quenched at 20°C. Not magnetic. X231.

Fig. 8 - Specimen 1 G. Annealed for 4 hours at 750°C and quenched at 20°C. Slightly Magnetic. X231.

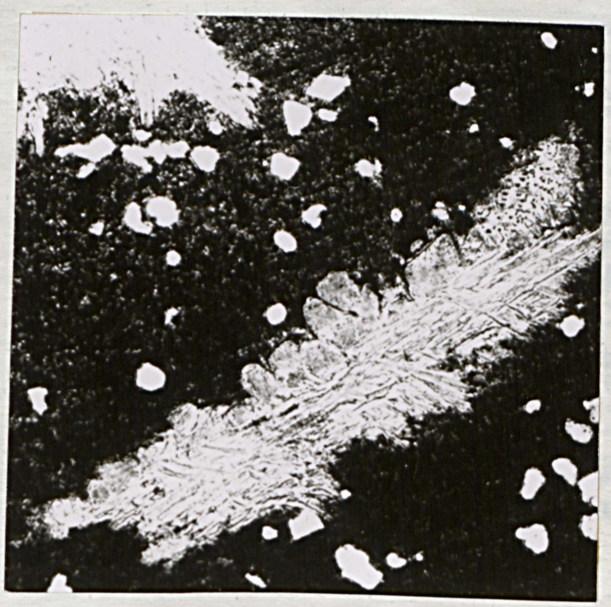

Fig. 9 - Specimen 1 H. Annealed for 4 hours at 700°C and quenched at 20°C. Slightly magnetic. X231.

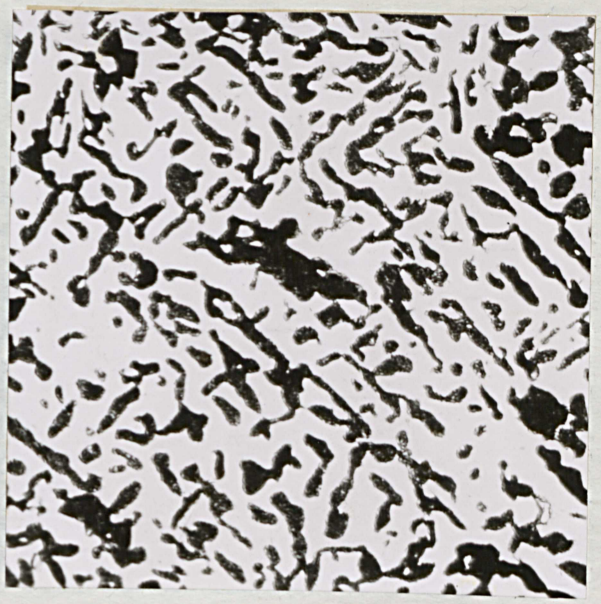

Fig. 10 - Specimen 1 I. Annealed for 4 hours at 650°C and quenched at 20°C. Not magnetic. X231

Fig. 11 - Specimen 1 J. Annealed for 4 hours at 600°C and quenched at 20°C. Not magnetic. X231.

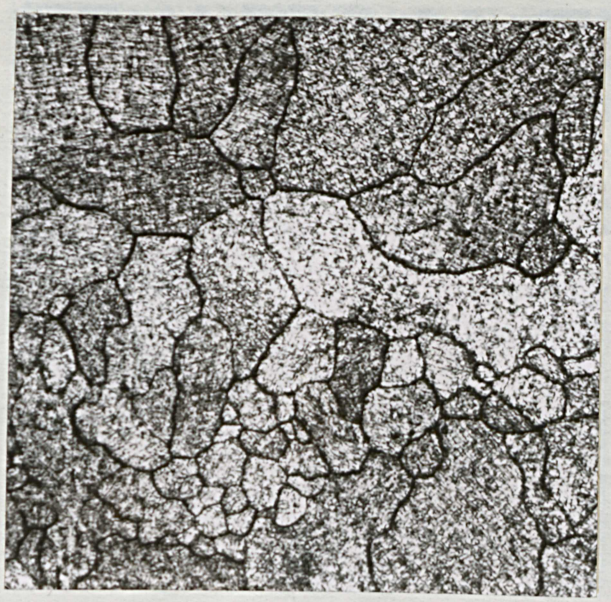

Fig. 12 - Specimen 2 A. As cast. Magnetic. X231

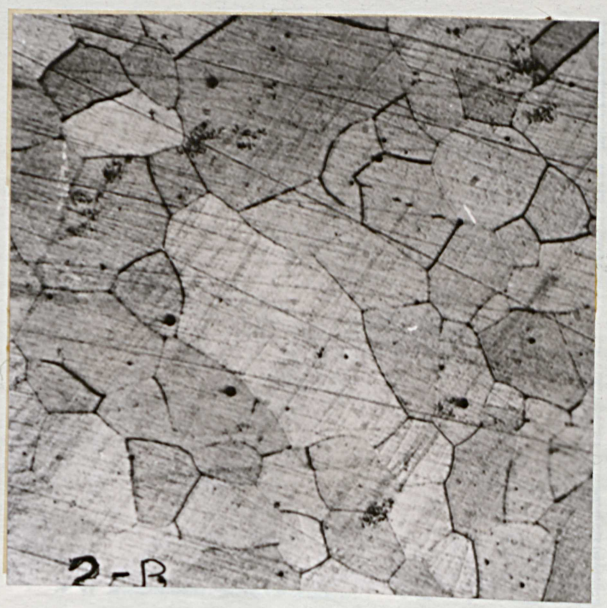

Fig. 13 - Specimen 2 B. Annealed for 5 hours at 600°C and quenched at 20°C. Magnetic. X231.

Fig. 14 - Specimen 2 G. Annealed for 4 hours at 750°C and quenched at 20°C. Magnetic. X231

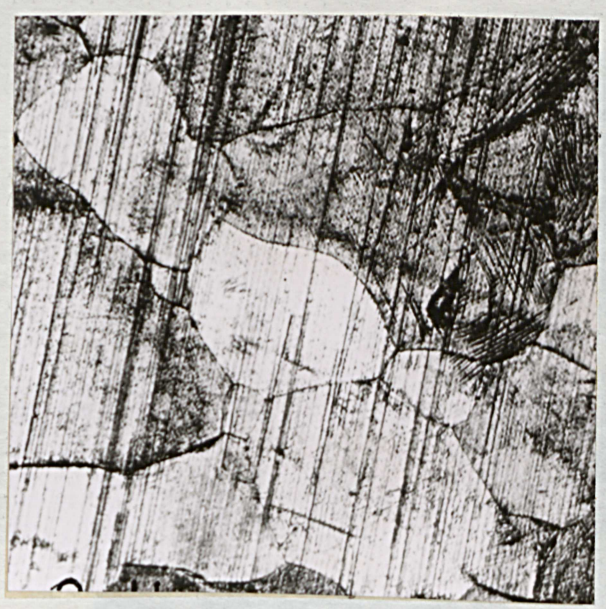

Fig. 15 - Specimen 2 H. Annealed for 4 hours at 700°C and quenched at 20°C. Magnetic. X231

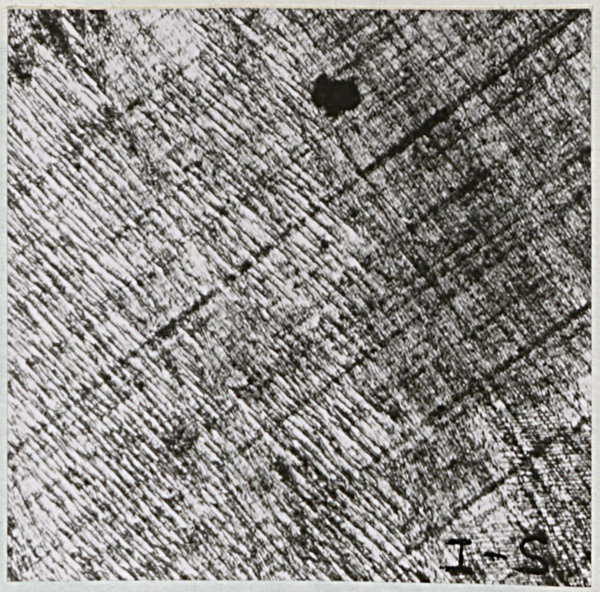

Fig. 16 - Specimen 2 I. Annealed for 4 hours at 650°C and quenched at 20°C. Magnetic. X231

Fig. 17 - Specimen 2 J. Annealed for 4 hours at 600°C and quenched at 20°C. Not magnetic. X231.

Fig. 18 - Specimen 3 A. As cast. Magnetic. X231.

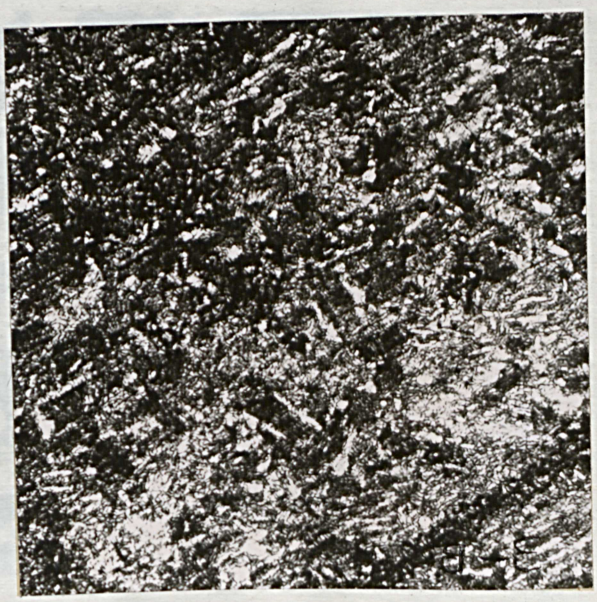

Fig. 19 - Specimen 3 B. Annealed for 5 hours at 600°C and quenched at 20°C. Not magnetic. X231.

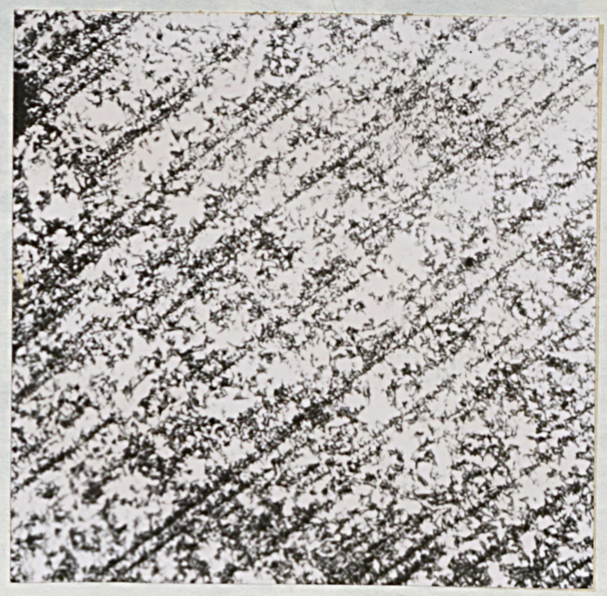

Fig. 20 - Specimen 3 G. Annealed at 750°C for 4 hours and quenched at 20°C. Not magnetic. X231.

Fig. 21 - Specimen 3 H. Annealed for 4 hours at 700°C and quenched at 20°C. Magnetic. X231.

Fig. 22 - Specimen 3 I. Annealed for 4 hours at 659°C and quenched at 20°C. Magnetic. X231

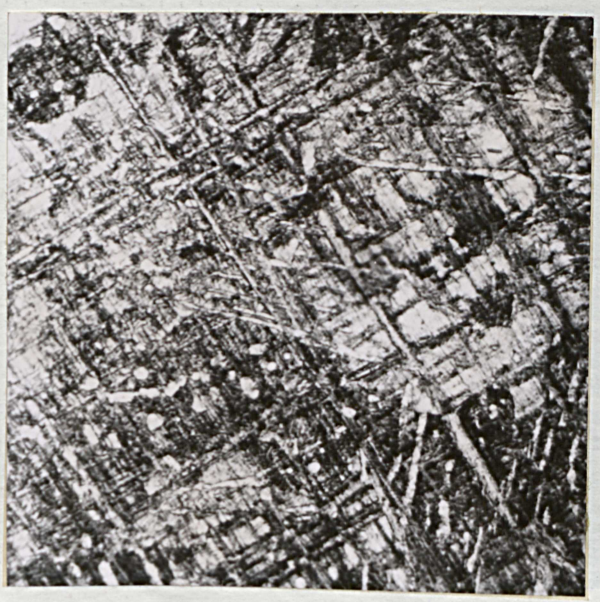

Fig. 23 - Specimen 3 J. Annealed for 4 hours at 600°C and quenched at 20°C. Magnetic. X231.

Fig. 24 - Specimen 4 A. As cast. Magnetic. X231.

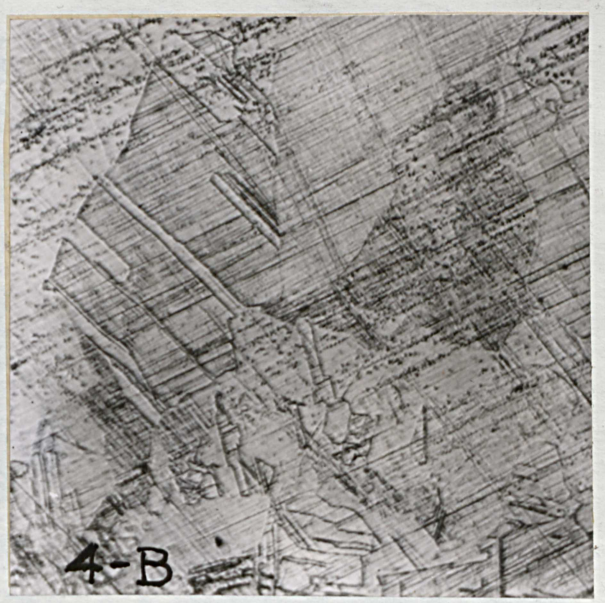

Fig. 25 - Specimen 4 B. Annealed for 5 hours at 600°C and quenched at 20°C. Not magnetic. X231.

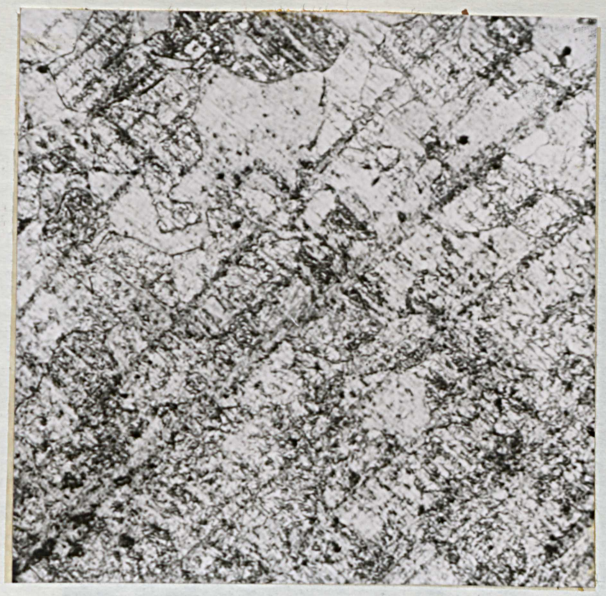

Fig. 26- Specimen 4 G. Annealed for 4 hours at 750°C and quenched at 20°C. Not magnetic. X231

Fig. 27 - Specimen 4 H. Annealed for 4 hours at 700°C and quenched at 20°C. Slightly magnetic. X231.

Fig. 28 - Specimen 4 I. Annealed for 4 hours at 650°C and quenched at 20°C. Not magnetic. X231.

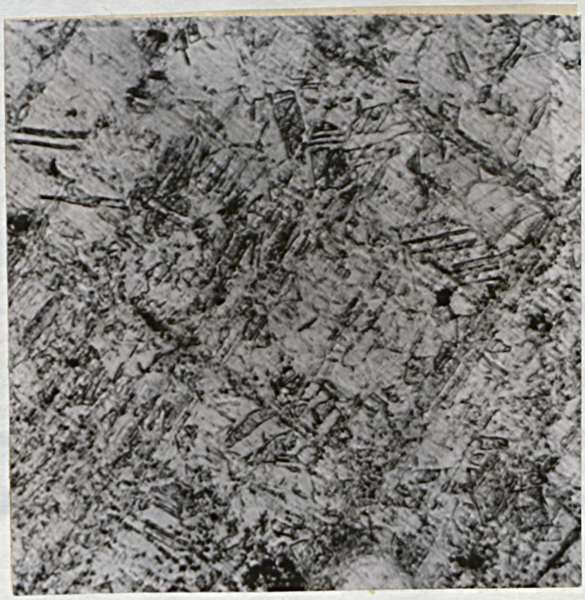

Fig. 29 - Specimen 4 J. Annealed for 4 hours ar 600°C and quenched at 20°C. Not magnetic. X231.

have been found if the annealing temperature were changed, if the annealing time were changed, or if the quenching method were changed.

Specimen 4A (Fig. 24) is magnetic and has a structure which is cored. The cored structure is typical of many cast alloys, but the structure does not seem to be typical of the other magnetic specimens.

Specimen 1B, 1I, and 1J (Figs. 7, 10, 11) are not magnetic and show a structure observed on many of the non-magnetic specimens which were not photographed. Auberlinder found a number of non-magnetic alloys which had a similar structure. These specimens show a fine two-phase dispersoid in a continious matrix.

All other specimens which are non-magnetic seem to have one thing in commom: a dispersoid of many fine crystals. It is interesting to note that many of the crystals in this type structure are twinned.

It is found, from examination of the photomicrographs, that all of the magnetic specimens do not have the same type of structure. It is also noted that those specimens which are non-magnetic have one of two types of structure 1) a dispersoid of fine crystals which have no orientation, or 2) a continious matrix with a fine dispersoid which is composed of two phases.

CONCLUSIONS

A proposed magnetic contour map (Fig. 5) has been constructed from the magnetic data gathered in this report. This map may be altered when future data is collected; however, it is believed that such a map will be helpful in future study of the Cu-Mn-Ga system.

An acicular structure is found on only three of the magnetic specimens: 2G, 2I, and 3J. Specimens 1G, 2A, 2B, 2H, 3A, and 3H are also magnetic but show no tendency toward a martensitic structure. The structure of these specimens is either one phase showing only grain boundries, or two phase showing primary grains with very small precipitates present.

It was found that the specimens which were non-magnetic have a structure composed of a fine dispersoid in a continous matrix. Therefore, it is believed that the structure of non-magnetic specimens will show a continous phase with a fine dispersoid; whereas, a magnetic specimen will have 1) an acicular structure 2) one phase showing only grain boundries, or 3) a structure showing the primary grains with very fine precipitates present. The one phase structure is shown clearly in figure 13. Figure 12 shows clearly the fine precipitates within the grain structure.

It was found that the most magnetism was obtained when the specimens were annealed between 650° and 700°C followed by quenching. However, as pointed out on page 13, not all of the alloys responded to heat treating.

ACKNOWLEDGEMENTS

This investigation was carried out under the guidance of Dr. F. A. Hames, Head of the Metallurgy Department, whom the writer thanks for much helpful advice and encourgement.

The writer also wishes to express his gratitude to Prof. R. I. Smith and Mr J. K. Dawson for the helpful advice and supporting hand which made this investigation possible.

BIBLIOGRAPHY

The numbers of the references are those referred to in the text of this report.

(1) F. A. Hames and D. S. Eppelsheimer: "Ferromagnetic Alloys in the Systems Cu-Mn-In and Cu-Mn-Ga". AIME Jl. of Metals, 185 (1949) 495.

(2) F. A. Hames: "Ferromagnetic Alloys in the Systems Cu-Mn-In and Cu-Mn-Ga". Thesis submitted to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1948.

(3) Gerard Auberlinder: "A Study of Certain Ferromagnetic Alloys in the System Cu-Mn-Ga". Thesis submitted to the Department of Metallurgical Engineering of the Montana School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering. June, 1954.

(4) W. W. Scott: "Standard Methods of Chemical Analysis", D. Van Nostrand Co., Inc., New York, 5th Ed., 2 Vol.,1939.

(5) F.P. Treadwell, and W. T. Hall: "Analytical Chemistry", John Wiley & Sons, Inc., New York, Vol. II 8theEd., 1935.

(6) Elliot Willner: "The Construction of a Ferromagnetic Torsion Balance". Thesis submitted to the Department of Metallurgical Engineering of the Montana School of Mines in partial fulfillment of the requirements for the degree of Bachelor of Science in Metallurgical Engineering. May, 1951.

(7) Oliver W. Moen: "Design and Calibration of a Ferromagnetic Torsion Balance". Thesis submitted to the Department of Metallurgical Engineering of the Montana School of Mines in partial fulfillment of the requirements for the degree of Bachelor of Science in Metallurgical Engineering. June, 1954.