1946

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Recommended Citation

Barnett, William James, "The age hardening of copper-manganese-nickel alloys" (1946). *Masters Theses*. 4774.
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THE AGE HARDENING OF COPPER-MANGANESE-NICKEL ALLOYS

By

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A

THESIS

submitted to the Faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1946

Approved By

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Engineering and Ore Dressing

LIST OF ILLUSTRATIONS

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Introduction

The Bureau of Mines in conjunction with their Electrolytic Manganese Alloys program has developed a series of age hardening copper-manganese-nickel alloys having properties which compare favorably with those of copper-beryllium alloys. The alloy now being produced commercially is of the following composition: 60%Cu-20%Mn-20%Ni. Average physical properties for this alloy are as follows:

CONDITION	YIELD STR. psi.	TENSILE STR. psi.	ELONG. %	ROCK. HARD.
Annealed	37,000	84,000	39.0	B74
60% CR	124,000	127,000	3.2	C25
Annealed-Aged 750°F-24hrs.	150,000	165,000	5.0	C45
60% CR-Aged 750°F-24hrs.	165,000	190,000	2.0	C50

An unusual and highly desirable characteristic of these alloys is their insensitiveness to rate of cooling from the solution temperature. Air cooled and water quenched samples will have identical time hardness curves on being aged. Instead of requiring closely controlled conditions characteristic of many age hardening alloys, these alloys cannot be subjected to a thermal mechanical handling which will prevent hardening on their being subsequently heated to the aging temperature.

The reaction of these alloys to heat treatment is of such an unusual nature that the following investigation was undertaken to attempt to clarify the hardening mechanism of these alloys.

The alloys used in this investigation were those along the psuedo-binary Cu-MnNi line between 100% Cu and 45% Cu. Special emphasis was placed on the 60%Cu-20%Mn-20%Ni alloy since this composition is being produced commercially.

The effect of various aging and solution treatments and cold work on the hardness, resistivity, lattice parameter, and microstructure were determined.

SURVEY OF LITERATURE ON THE COPPER-MANGANESE-NICKEL SYSTEM

Constitution of the Binary Systems- The most recent equilibrium diagrams for the binary Cu-Mn, Cu-Ni, and Mn-Ni are as follows:

SYSTEM	WORKERS
Cu-Mn	Dean, Long, Graham, Potter, and Hayes (1)
Cu-Ni	Guertler and Tammann (2)
Mn-Ni	(3)

These equilibrium diagrams are shown in Figure 17.

The alpha-gamma solid solubility line of the copper-manganese diagram has been accurately determined but below this solid solubility line there exist several structural anomalies, principally in the region 50%-75% Manganese, which cannot be explained by the present diagram.

The Nickel-Manganese diagram as shown is only a tenative diagram. Ordered lattices have been established at compositions corresponding to MnNi and $MnNi_3$.

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(1) R. S. Dean, J. R. Long, T. R. Graham, E. V. Potter, and E. T. Hayes: Copper Manganese Equilibrium System, Transactions, American Society for Metals, Vol. 34, p. 443.

(2) N. B. Pilling and T. E. Kihlgren: Constitution of Copper Nickel Alloys, Metals Handbook, 1939 edition, p. 1353.

(3) M. Hansen: Aufbau der Zweistofflegierungen, Fig. 365.

MnNi (corresponding to the delta solid solution of the equilibrium diagram) exists above 600°C as a face centered cubic structure, while below 600°C it exists as an ordered face centered tetragonal structure.

The Copper-Nickel equilibrium diagram has been definitely confirmed as a continuous series of solid solutions crystallizing on a face centered cubic lattice.

Constitution of the Ternary System- Very little work has been done on the ternary Copper-Manganese-Nickel system. The liquidus and solidus surfaces of the Cu-Mn-Ni system were determined by N. Parravano (4) in 1913. (See Figure 17) No ternary diagram has been worked out for the equilibrium relationships in the solid state.

Electrical Properties- In 1925 N. B. Pilling (5) determined the electrical properties of Cu-Mn-Ni alloys. He found that manganese was the principal element determining resistivity. Any copper-nickel alloy increases in resistance if manganese is added to it. Both

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(4) N. Parravano; Die Ternaren Legierungen Von Eisen-Nickel-Mangan, Nickel-Mangan-Kupfer, Eisen-Mangan-Kupfer, Internationale Zeitschrift fur Metallographie, Vol. 4, 1913, Figs. 22 & 23, p. 184.

(5) N. D. Pilling: Some Electrical Properties of Copper-Manganese-Nickel Alloys, Transactions, Amer. Electrochem. Soc., Vol. 48, 1925, p. 171.

copper-manganese and nickel-manganese alloys are but little affected by adding either nickel or copper, respectively. Resistivity measurements were made on specimens vacuum cast in a 3.2mm. bore silica tube. The temperature conditions were so arranged that the metal would freeze about as soon as the column reached full height. Since the results of Pilling were based on alloys made from aluminothermic manganese(94.6%Mn, 1.75%Fe, 1.52%Si, and 1.80%Insoluble) the reported data shall be considered qualitatively rather than quantitatively.

R. S. Dean and C. T. Anderson (6) reported on the electrical properties of Cu-Mn-Ni alloys made from electrolytic manganese. Their data on resistivity of alloys water quenched from 1650°F compare favorably with that of Pilling for "as cast" bars. In addition to this it was shown that aging of certain of these alloys, principally those along the psuedo-binary Cu-MnNi line, results in a marked decrease in resistivity. A decrease in resistivity upon aging was also noted in alloys in the immediate vicinity of the ordered $MnNi_3$ composition.

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(6) R. S. Dean and C. T. Anderson: The Alloys of Manganese-Copper and Nickel: The Electrical Resistance and Temperature Coefficient of Electrical Resistance, Transactions, American Society for Metals, Vol. 29, 1941, p. 899.

Hardness- Very little work has been reported in the literature upon the hardness of manganese-copper-nickel alloys. R. S. Dean and C. T. Anderson (7) found

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(7) R. S. Dean and C. T. Anderson: The Alloys of Manganese-Copper and Nickel: Hardening in the psuedo-binary Cu-MnNi system, Transactions, American Society for Metals, Vol. 29, 1941, p. 808.

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an area extending from approximately 12.5%Mn and Ni, balance copper to 90%Ni-10%Mn and 10%Ni-90%Mn in which alloys could be hardened by water quenching from 1650°F and reheating to temperatures between 425°F to 450°F. A maximum hardness of 53 Rockwell "C" was developed in an alloy of 30%Cu-35%Mn-35%Ni. Maximum hardening is found in alloys having a manganese to nickel atomic percent ratio of 1:1.

Physical Properties- Physical properties of Cu-Mn-Ni alloys having compositions of 20%Mn-20%Ni, 22%Mn-22%Ni, and 24%Mn-24%Ni the balance being copper were reported by R. S. Dean and associates. (8)

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(8) R. S. Dean, J. R. Long, T. R. Graham, and C. W. Matthews: Age Hardening Copper-Manganese-Nickel Alloys, Transactions, American Society for Metals, Vol. 34, 1945, p.481.

Tensile strengths as high as 210,000psi. were developed. The physical properties of these alloys compare favorably with those of copper-beryllium alloys.

A more comprehensive review of the physical properties of solution treated and age (temper) hardened alloys containing up to 30% each of nickel and manganese (electrolytic manganese) was presented by Maurice Cook and W. O. Alexander.(9)

Hardness values in excess of 500 (diamond pyramid hardness) were obtained with several of the alloys, the maximum value being 586. These results checked the work of R. S. Dean and associates. The optimum heat treating cycle consisted of a solution treatment of 2 hours at 800°C and reheating to a temper-hardening temperature of 450°C for 2 to 7 days. Alloys containing more than 7% each of nickel and manganese are hardenable, the extent of hardening increasing with the nickel and manganese contents. For a given total nickel plus manganese content the maximum hardening effect is obtained in alloys containing equal proportions of these two elements.

Structure and Proposed Hardening Mechanism-

R. S. Dean(10) and associates found two different types

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(9) Maurice Cook and W. O. Alexander: The physical Properties and Temper-Hardening Characteristics of Copper-Nickel-Manganese Alloys, The Journal of the Institute of Metals, Vol. 13, June 1946, p. 381.

(10) R. S. Dean, J. R. Long, T. R. Graham, and C. W. Matthews: Age Hardening Copper-Manganese-Nickel Alloys, Transactions, American Society for Metals, Vol. 34, 1945, p. 486.

of structures developed depending upon the aging temperature. When aged at temperatures up to and including 750°F, a finely divided precipitate appears in the grain boundary areas and gradually spreads throughout the grains. Aging at 840°F and above produces a grain boundary phase that has but little tendency to spread through the grains themselves.

The precipitate responsible for the hardening has not been identified as yet. Dean and Anderson have suggested that an ordered phase corresponding to MnNi may be formed, and its formation at the aging temperature brings about the hardening.

There are definite changes in electrical resistance with aging, the resistivity dropping from 87 to 67 microhms per centimeter cube when aged from the solution treated state and from 88 to 63 microhms per centimeter cube when aged from the cold worked condition.

Fragmentary data indicate that these alloys undergo a volume change at the aging temperature.

Preparation of the Alloys

The compositions of the alloys used in this investigation are listed in Table I.

Alloys 1 to 9 were available from another previous investigation. They had received the following treatment:

Cast as 5/8" rounds--hot worked--
1300°F-1hr.-WQ--Swaged to 0.250" Diam.--
1300°F-1 hr.-F'ce. Cooled 1°F/hr.

Alloys 10, 12, 13, 14, and 15 were melted in 200 gram heats in an induction furnace using an alundum crucible, and cast as 5/8" rounds in a copper chill mould. 60%Cu-20%Mn-20%Ni scrap was used as the base alloy with suitable additions of either copper shot or a master MnNi alloy to obtain the desired composition. Before casting the melt was deoxidized by the addition of 0.5% aluminum. These bars were shaken out hot and placed in a furnace at 1650°F, held for approximately 24 hrs. and water quenched. Any section showing evidence of piping was cut off. After soaking for 2 hrs. at 1650°F each bar was hot worked by means of a hammer and anvil. Each bar was reduced approximately 25% in cross-section during the hot working operation. After solution treating at 1300°F-2hrs.-WQ the bars were swaged cold in steps (with suitable intermediate anneals) to 0.250" diameter.

Alloy 11 was available as 3/4" bars which were swaged cold with intermediate anneals to 0.250" diameter. Some 0.250" diameter rods in the solution treated

(1200°F-WQ) and cold worked condition were acquired from the Drever-Harris Corp. Three (3) bars of this composition 5/8" diameter and 4" long were cast for use as dilatometer specimens.

TABLE I

ALLOY COMPOSITIONS

Number	Percent Copper	Percent MnNi
1.	93.3	6.7
2.	90.0	10.0
3.	86.7	13.3
4.	83.3	16.7
5.	80.0	20.0
6.	76.7	23.3
7.	73.4	26.6
8.	70.0	30.0
9.	66.7	33.3
10.	63.0	37.0
11.	60.0	40.0
12.	57.0	43.0
13.	54.0	46.0
14.	50.0	50.0
15.	45.0	55.0

Effect of Aging Temperature and Time on The Hardness and Resistivity of 60/20/20 Cu-Mn-Ni Alloy

Previously the changes in hardness (11) with aging temperature for 60/20/20 had been determined. These results are listed in Table II and shown graphically in Figure 1.

Since the solid reaction rates are known to be extremely low in the copper manganese system, the effect of time at temperature was determined. The change in electrical resistivity with change in aging time at 825°F was taken as a criterion for measurement of the rate of reaction. A rod of 60/20/20 was solution treated at 1650°F-2hrs.-WQ and then aged at 825°F. At various intervals the aging was interrupted by water quenching and the resistivity determined. The results are shown graphically in Figure 2.

Although the resistivity had not reached a constant value even after 175 hours at the aging temperature it was considered necessary to utilize an aging time of 24 hours in future work.

Effect of Aging Temperature- Although it is known that cold working accelerates age hardening reactions the first set of bars were aged in the solution treated.

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(11) C. Y. Clayton: Unpublished material completed by Advanced metallurgy students at the Missouri school of Mines.

state, 1650°F-2hrs.-WQ. This was done in order to avoid masking or firther complicating the fundamental reactions. The hardness values and resistivity data are listed in Table II and shown graphically in Figure 3.

Increasing the aging temperature above 600°F results in a gradual increase in hardness and decrease in resistivity until a maximum hardness of RC36 and minimum resistivity of 55.2 x 10^{-6} ohm-cm. is reached at 825°F. Increasing the aging temperature to 900°F lowers the hardness slightly to RC26 and increases the resistivity to 75 x 10^{-6} ohm-cm. Raising the aging temperature to 1000°F lowers the hardness to RB38 but has but little effect on the resistivity.

Another set of bars were aged in the "as swaged" condition, the previous treatment being water quenching from 1200°F. The hardness and resistivity values for this treatment are also listed in Table II and shown graphically in Figure 4.

The cold working results in a lowering of the aging temperature for maximum hardness, RC45, from 825°F to 600°F and also an increase of 9 points in the RC hardness. The hardness remains constant from 600°F to 840°F, while the resistivity dropped sharply to 62.8 x 10^{-6} ohm-cm. at 600°F, reaching a minimum of 53.8 x 10^{-6} ohm-cm. at 810°F. Increasing the aging temperture above 840°F resulted in a marked softening and increase in resistivity until at 1000°F the

TABLE II
The Effect of Aging Temperature on the Hardness And Resistivity of 60/20/20 Cu-Mn-Ni Alloy

Aging Temp. °F	H.W.-WQ1200*	H.W.-WQ1200* CR 50%	1650°F-2hrs.-WQ**		1200°F-2hrs.-WQ** Swaged Cold	
	Rock. Hard.	Rock. Hard.	Rock. Hard.	Resistivity ohm-cm.x10^{-6}	Rock. Hard.	Resistivity ohm-cm.x10^{-6}
None	RB60	RB88	RB22	77.8	RC23.5	79.9
400	RB60	RB90	--	----	--	----
500	RB62	RB95	--	----	RC25	78.5
600	RB68	RC21	RB52	77.3	RC45	62.9
690	--	--	--	----	RC44.5	56.4
700	RB77	RC35	RB89	72.2	--	----
750	--	--	RC21.5	68.5	--	----
800	RC26	RC44	--	----	--	----
810	--	--	--	----	RC47	53.8
825	--	--	RC35	55.3	--	----
840	--	--	--	----	RC47	54.5
900	RB67	RC40	RC26	75.2	RC42.5	56.6
1000	RB56	RC26	RB39	77.0	RB66	78.5
1100	RB55	RB71	--	----	RB61	77.7
1200	RB54	RB40	--	----	--	----

* Aged Six Hours
** Aged Twenty-four Hours

FIGURE 1 - EFFECT OF AGING TEMPERATURE ON THE HARDNESS OF 60/20/20 Cu-Mn-Ni ALLOY

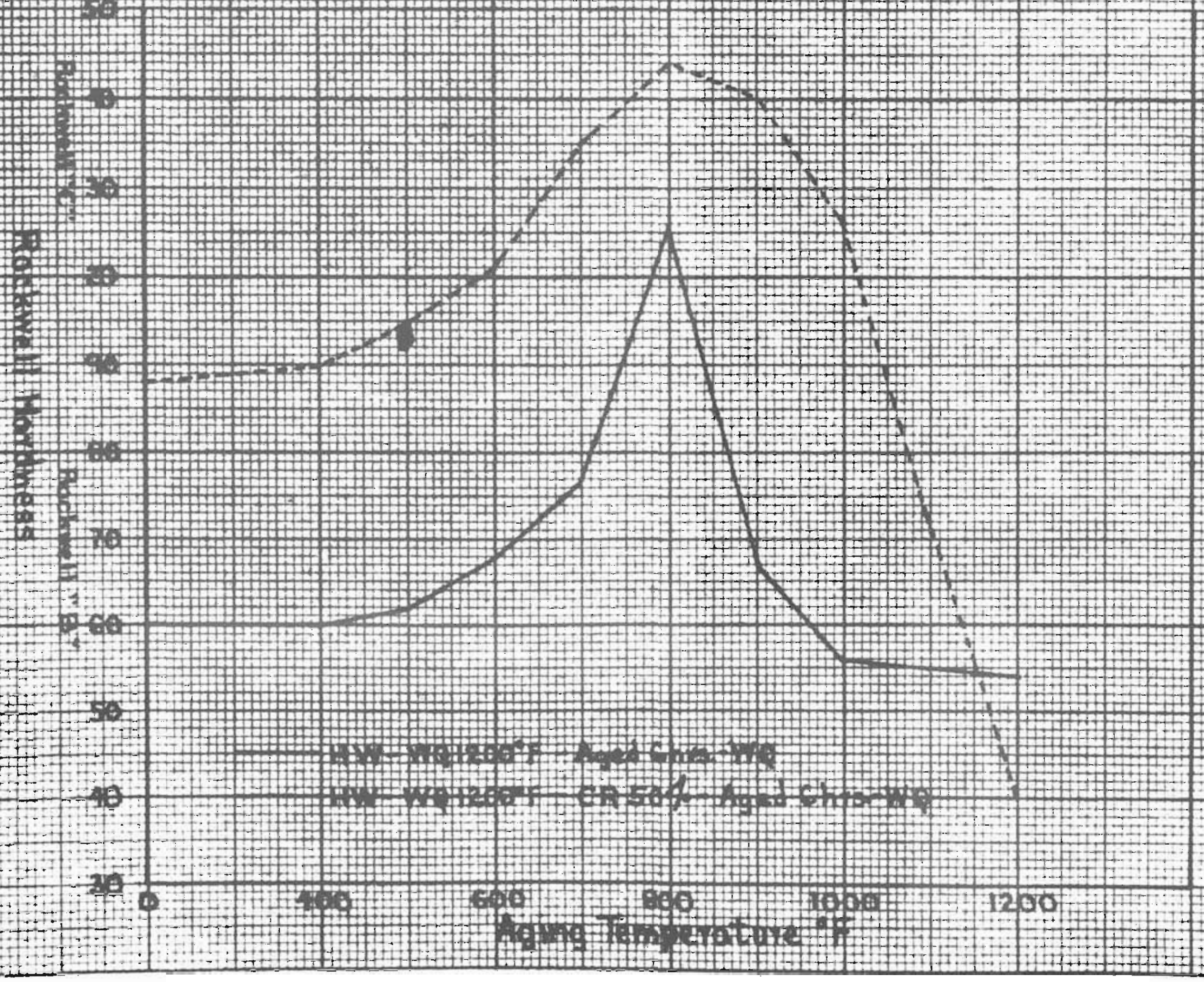
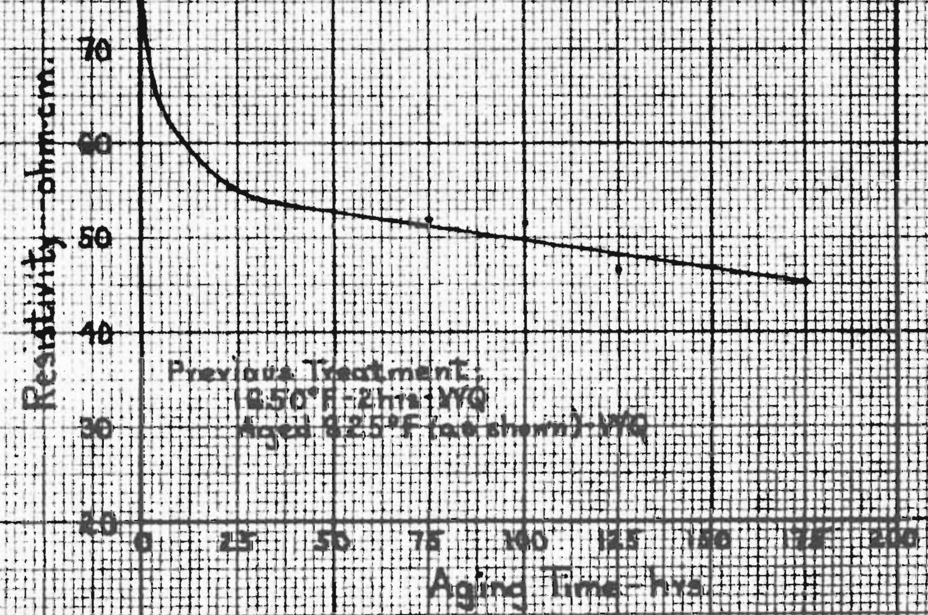
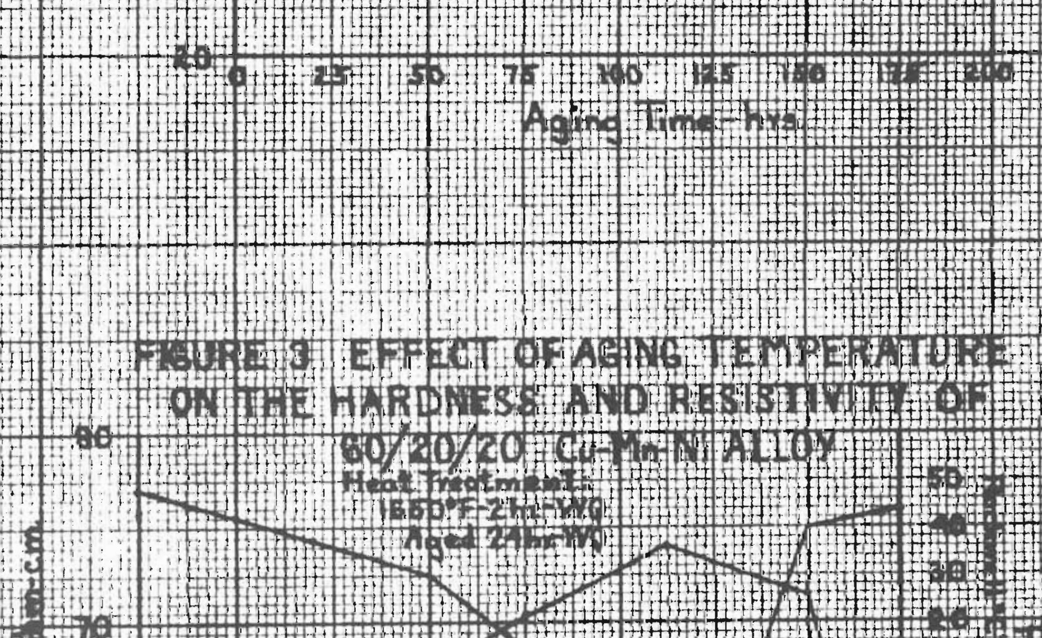


FIGURE 2 EFFECT OF TIME AT 825°F ON RESISTIVITY OF 60/20/20 Cu-Mn-Ni ALLOY



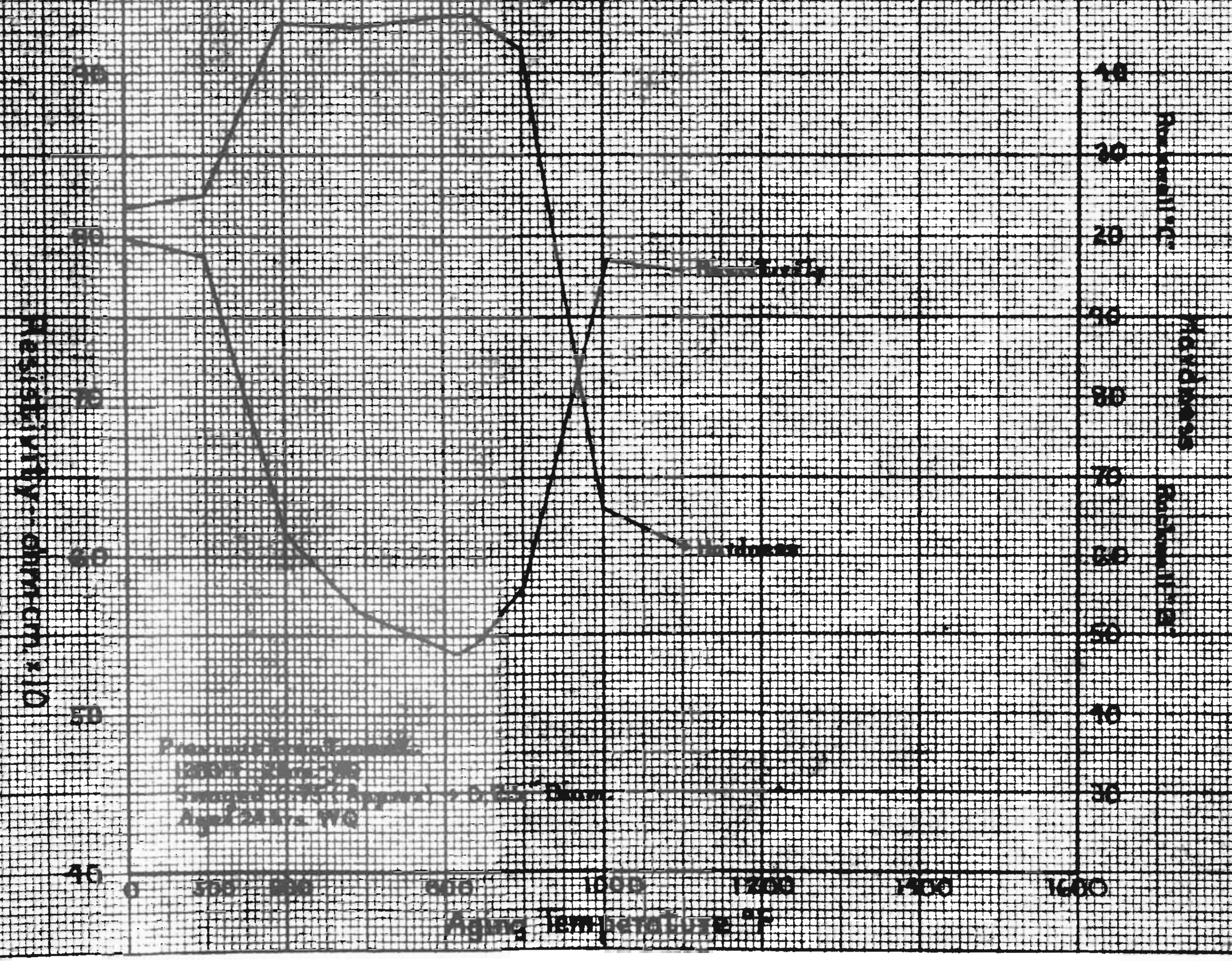
Previous Treatment:
1650°F-2hrs-WQ
Aged 825°F (as shown)-WQ

FIGURE 3 EFFECT OF AGING TEMPERATURE ON THE HARDNESS AND RESISTIVITY OF 60/20/20 Cu-Mn-Ni ALLOY



Heat Treatment:
1650°F-2hr-WQ
Aged 24hr-WQ

FIGURE 4 EFFECT OF AGING TEMPERATURE ON THE HARDNESS AND RESISTIVITY OF 60/20/20 Cu-Mn-Ni ALLOY



resistivity reached that of the original value for the unaged bars.

Effect of Cold Work on the Resistivity of Aged 60/20/20- Dean and Anderson (10) suggested that the hardening may be due to the formation and precipitation of ordered MnNi. If this assumption be true, cold work should result in a marked increase in resistivity.

The resistivity of the cold worked aged bars are listed in Table III. There is no marked increase in resistivity which would indicate the presence of an ordered lattice in either the aged or unaged bars.

Effect of Rate of Cooling from the Solution Temperature on the Hardness of Aged 60/20/20-- The "as solution treated" hardness and aged hardness of 60/20/20 after cooling from the solution temperature of 1300°F at various rates are as follows:

Rate of Cooling from 1300°F	Solution Treated	Aged 825°F
Water Quenched	RB56	RC37.5
40°F/hour	RB58	RC35
10°F/hour	RB78	RC35.5

TABLE III

Effect of Swaging after Aging on the Resistivity of 60/20/20

Ag'd. °F	1650°F-2hrs.-WQ Aged -24hrs-WQ			1200°F-2hrs.-WQ Swaged-Aged-24hrs.-WQ		
	Orig. K	%Red.	K	Orig. K	%Red.	K
500	-	-	-	78.5	19.1	78.3
600	77.3	16.5	76.4		Too Brittle	
700	72.2	13.9	71.9		" "	
750	68.5	12.0	68.5		" "	
825	55.3	19.2	55.1		" "	
900	75.2	19.8	75.9	56.6	11.3	59.2
1000	77.0	19.5	77.4	78.5	17.3	79.1
1100	-	-	-	77.7	18.4	78.5

K-Resistivity-ohm-Cm. x 10^{-6}

Dilatometric Changes on Heating- An "as cast" bar of 60/20/20 was machined to a 1/2" dilatometer specimen. Using a Rockwell Dilatometer the changes in length on heating and cooling were noted over a temperature range of 400°F-1300°F. No abnormal contractions or expansions indicative of a phase change were found.

This same specimen was then heated to 1300°F-6hrs.-WQ, heated to 825°F in the Rockwell dilatometer and the change in length on aging for 24 hours was determined.

On aging 24 hours at 825°F the specimen contracted 0.0180 inches or approximately 0.45%.

Effect of Composition on the Hardness and Resistivity of Solution treated and Aged Cu-Mn-Ni Alloys

Effect of Slow Cooling and Aging on the Resistivity of Alloys 1 to 9- Alloy compositions 1 to 9 were available in 1/4" bars which had been furnace cooled from 1300°F at 1°F/hour. The resistivity of the furnace cooled bars was determined both before and after aging at various temperatures. The results are listed in Table IV.

There was no increase in resistivity in the aged bars which would indicate the presence of an ordered lattice in the furnace cooled bars.

Effect of Composition and Aging on the Hardness and Resistivity of Alloys 4 to 15- 1/4" bars of compositions 4 to 15 were solution treated, 1300°F-3hrs.-WQ, and aged, 825°F-24hrs.-WQ. Resistivity and hardness determinations were made both before and after aging. The results are given in Table V and shown graphically in Figure 5.

In the solution treated condition both the hardness and resistivity increase directly with increasing MnNi content. This is typical for solid solution phases. In the age hardened condition no hardening is noted until a composition of 73.4%Cu-26.6%MnNi is reached. Aging of alloys having MnNi contents of 26.6% MnNi or greater results in a marked increase in hardness and decrease in resistivity.

TABLE IV

Effect of Slow Cooling and Aging on the Resistivity of Alloys 1-9*

Alloy No.	Cooled from 1300°F@1°F/hr.	500°F 3Hr.WQ	600°F 3hr.WQ	800°F 3hr.WQ	890°F 3hr.WQ	1000°F 3hr.WQ	1200°F 3hr.WQ
1.	10.07	10.16	10.16	10.42	10.52	10.76	10.74
2.	17.81	17.27	18.23	18.41	18.77	18.81	18.84
3.	23.82	23.82	23.59	24.27	24.72	25.17	24.95
4.	29.78	29.78	29.46	30.79	31.24	31.46	32.59
5.	35.22	35.45	35.45	36.38	37.07	37.54	38.23
6.	42.87	42.40	42.63	43.56	44.72	45.64	45.65
7.	48.33	48.56	48.33	49.03	50.20	51.13	50.89
8.	54.86	54.63	55.10	55.35	56.03	58.14	57.90
9.	59.79	59.79	59.79	60.48	60.25	62.32	62.79

* All values listed ohm-cm. x 10^{-6}

TABLE V

Effect of Composition and Aging on the Hardness and Resistivity of Alloys of Cu-Mn-Ni

Alloy No.	1300°F-3hrs.-WQ		1300°F-3hrs.-WQ Aged 825°F-24hrs.-WQ	
	Rock. Hard.	K ohm-cm.x10^{-6}	Rock. Hard.	K ohm-cm.x10^{-6}
4	RB26	30.90	RB26	31.58
5	RB32	37.08	RB32.5	35.51
6	RB37	44.28	RB37	44.98
7	RB42	49.67	RB42	49.34
8	RB43	56.49	RB88.5	53.71
9	RB48	61.37	RC30	60.02
10**	RB52	70.71	RB84	52.30
11	RB56	78.74	RC37.5	53.41
12	RB62	80.06	RC42.5	52.10
13	RB63	91.71	RC43.5	60.79
14	RB67	97.83	RC45.5	64.27
15	RB72	103.06	RC47.5	67.98

** Alloy 10 results discarded due to the fact that in melting this heat was poured cold leaving considerable skull in the crucible and as a result it was an off-analysis heat.

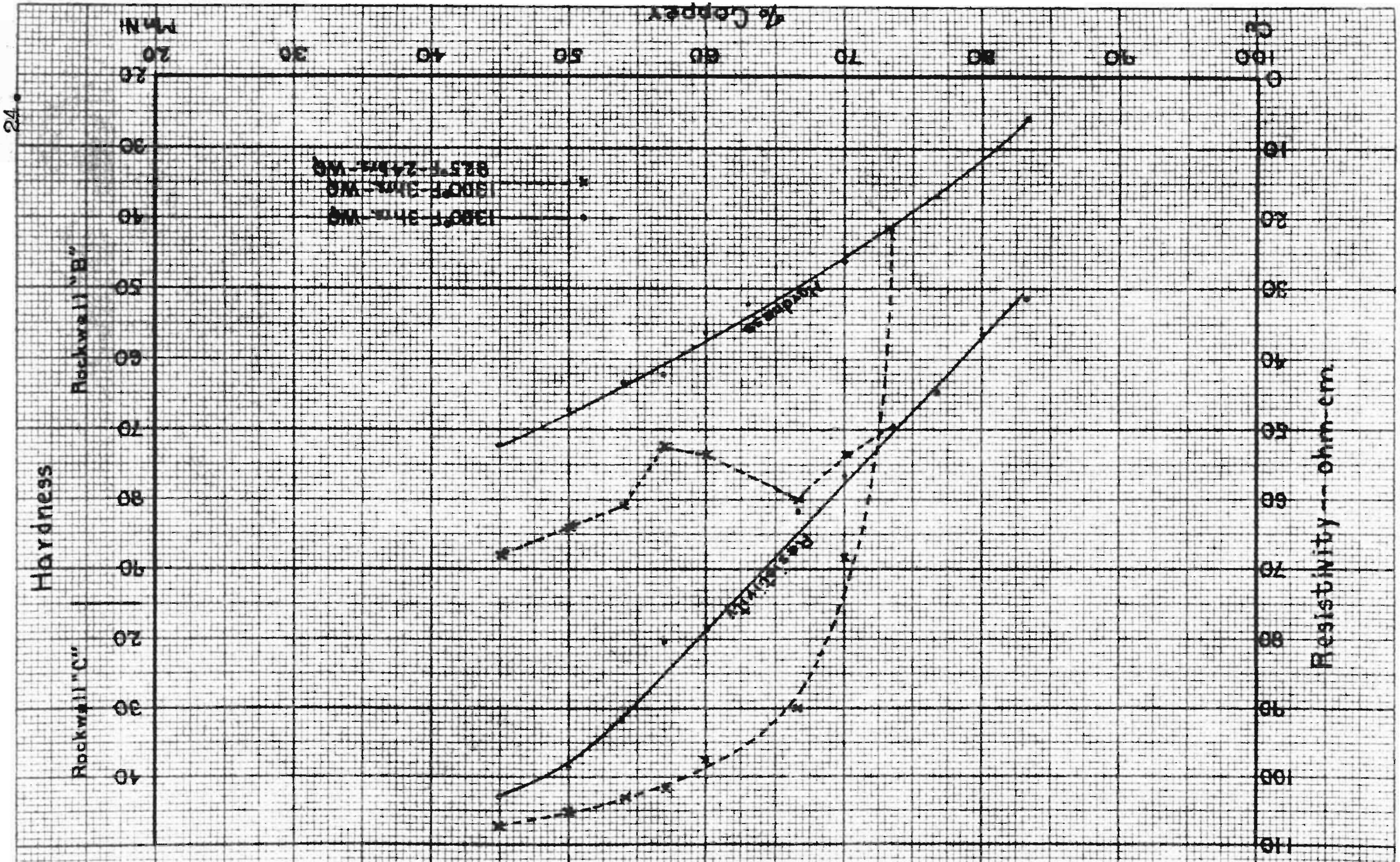


FIGURE 5 EFFECT OF AGING ON THE HARDNSS AND RESISTIVITY OF Cu-MnNi ALLOYS

Effect of Aging Temperature and Composition On the Crystal Structure of Cu-MnNi Alloys

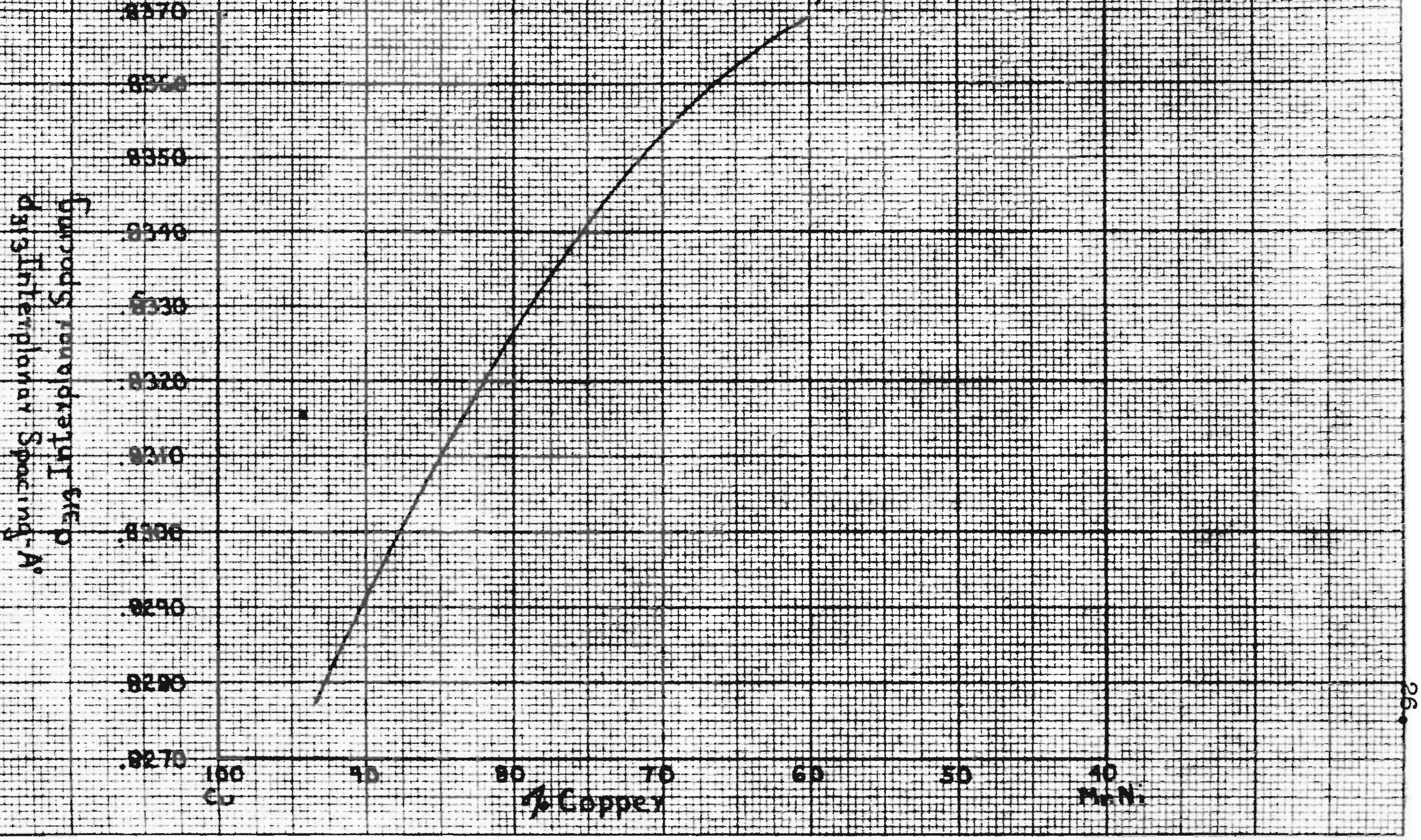
X-ray determination by both the powder and back reflection methods were made to attempt to identify the precipitated phase. Mo, Cu, and Fe target tubes were available. From an examination of their K emission wavelengths and the absorption edges of Cu, Mn, and Ni it can be seen that the most suitable radiation would be that of Fe. Due to the failure of the Fe target tube and other work being conducted at the same time the Cu target tube was used.

Cu radiation is greatly absorbed by Mn and a great deal of background fog was encountered due to the scattered radiation.

Structure of 60/20/20 Aged at Various Temperatures- Powder diffraction patterns of filings from bars in both the unaged and aged condition were identical. No evidence of a second phase was obtained. All specimens showed a Face Centered Cubic lattice. Similiar results were obtained from samples using a ground solid wedge.

Effect of Composition on the Parameter of Solution Treated Alloys- Back reflection patterns were made of alloys 1, 2, 3, 4, 5, 6, 7, 8, 9, and 11 in the solution treated condition, 1300°F-3hrs.-WQ. An electrolytic copper sample was used as a standard for determining the film to specimen distance. The variation of d_{313} plane spacing with composition is shown in Figure 6.

FIGURE 6 EFFECT OF COMPOSITION ON THE d_{313} INTERPLANAR SPACING OF THE ALPHA SOLID SOLUTION OF THE PSEUDO-BINARY Cu-MnNi System



Since precipitation of a second phase from a solvent lattice normally results in a slight contraction of the lattice of the parent solid solution, back reflection patterns were made for 60/20/20 in the solution treated condition, 1650°F-2hrs.-WQ, and after aging for 24 hrs. at 825°F. The results showed a decrease in d_{313} for the unaged sample of 0.8369A° to 0.8352A° in the aged sample. Aging not only resulted ina shrinkage of the parent lattice but also a decided broadening of the diffraction line so that the K doublet was not resolvable.

The presence of the broad, diffuse line after aging is indicative of internat strains. These strains could originate in the precipitation of very small particles of a second phase throughout the lattice of the parent solid solution, thereby distorting the parent lattice.

Microstructure

Samples were taken from each of the rods after each of the heat treatments, mounted in bakelite, polished and etched. In all cases a potassium dichromate solution of the following composition: 2 grams $K_2Cr_2O_7$, 8 cc. concentrated H_2SO_4, 4 cc. saturated NaCl solution, and 100 cc. H_2O, was used as the etchant.

The time of etching varied from specimen to specimen. In general a much longer time was necessary to etch unaged alloys. In the aged alloys the grain boundary precipitate etched very rapidly making it difficult to bring out the twinned structure within the grains.

Typical microstructures for the various treatments are shown in Figures 7 to 16.

Figures 7, 8, 9- The structures of 60/20/20 aged at 750°F, 825°F, and 900°F shows the beginning of precipitation, maximum precipitation, and partial resolution of the precipitated phase.

Figures 10 &11- Figure 10 shows the characteristic twinned polyhedral grains of a specimen of 60/20/20 water quenched from 1300°F. Figure 11 shows the structure after aging at 825°F-24hrs.-WQ.

Figure 12- Figure 12 shows the structure of 60/20/20 water quenched from 1300°F, swaged, and aged at 825°F-24hrs.-WQ. Comparing this structure with that

of Figure 11 the effect of cold work on the precipitation process can easily be seen. The cold working increases the "internal surface" of the grains by the formation of slip lines and other lattice imperfections at which precipitation may take place. Thus the precipitation in the aged cold worked specimens takes place throughout the grains rather than preferentially at the grain boundaries.

Figure 13- Figure 13 shows a duplex grain structure in an aged specimen of 60/20/20. This clearly indicates the influence of grain size on the hardening of as-solution treated specimens. Since the precipitation in strain free grains is a grain boundary process the amount of precipitation is proportional to the grain "surface area" which increases greatly with decreasing grain size.

Figures 14, 15, 16- The effect of increasing MnNi content on precipitation in alloys 4, 8, and 11 water quenched from 1300°F and aged at 825°F-24hrs.-WQ is shown. Alloy 4, which showed no increase in hardness, shows no precipitation while the amount of precipitation in alloys 8 and 11 increases with increasing MnNi content as does the hardness.

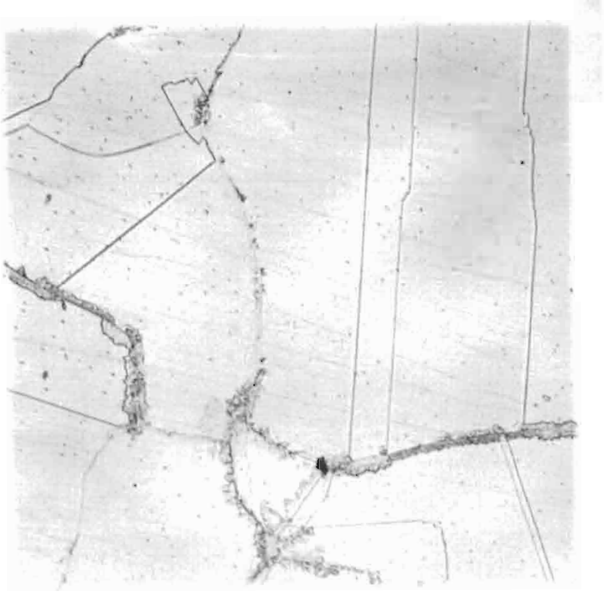


Figure 7 100X
60/20/20 1650°F-2hrs.-WQ
Aged 750°F-24hrs.-WQ
Dichromate Etch

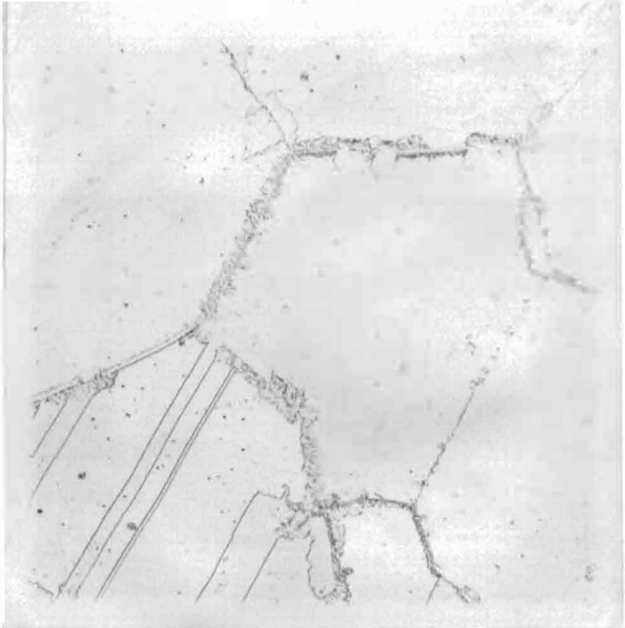


Figure 8 100X
60/20/20 1650°F-2hrs.-WQ
Aged 825°F-2hhrs.-WQ
Dichromate Etch

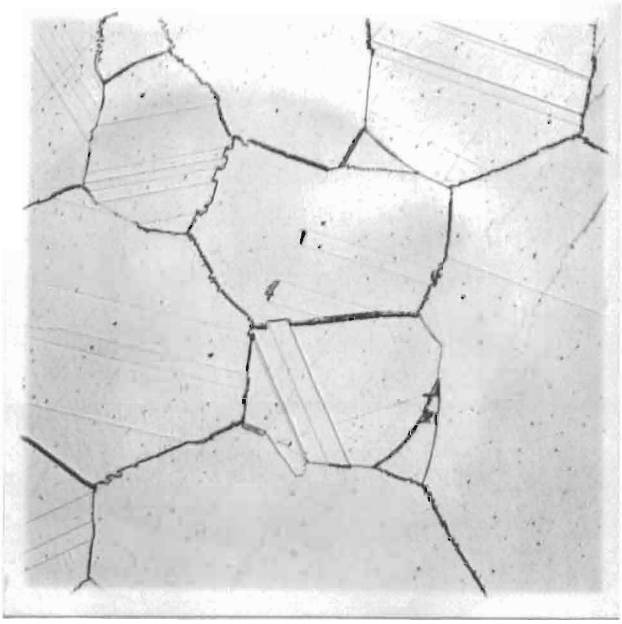


Figure 9 100X
60/20/20 1650°F-2hrs.-WQ
Aged 825°F-24hrs.-WQ
Dichromate Etch

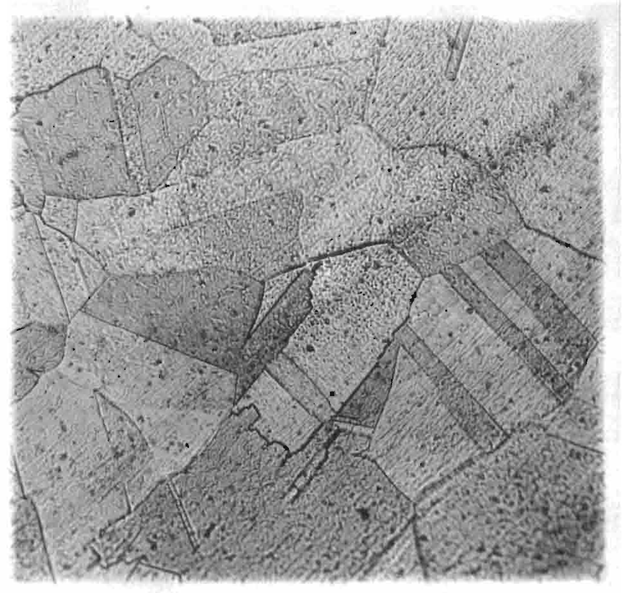


Figure 10 500X
60/20/20 1300°F-3hrs.-WQ
Aged -- None
Dichromate Etch

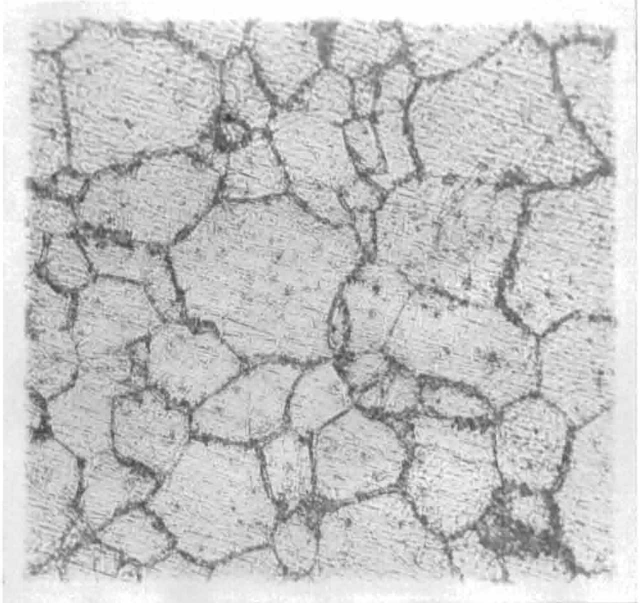


Figure 11 500X
60/20/20 1300°F-3hrs.-WQ
Aged 825°F-24hrs.-WQ
Dichromate Etch

Figure 12 500X
60/20/20 1300°F-3hrs.-WQ
Swaged-Aged 825°F-24hrs.-WQ
Dichromate Etch

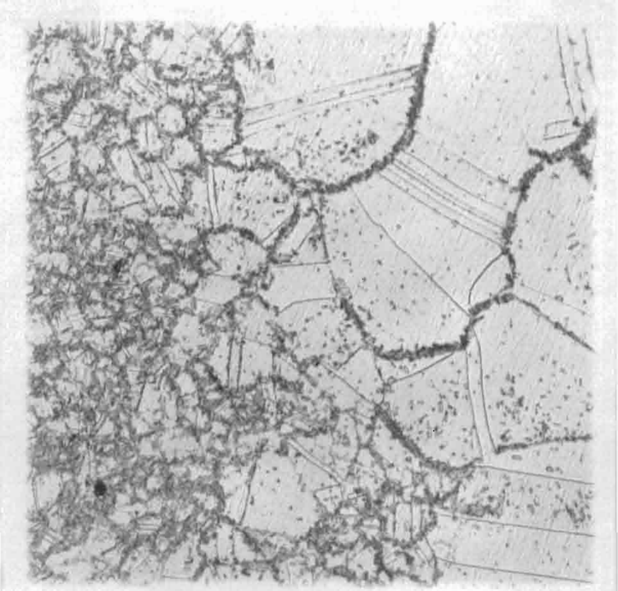


Figure 13 100X
60/20/20 Aged 825°F
Dichromate Etch

Figure 14 500X
Alloy 4-83.3% Cu
16.7% MnNi

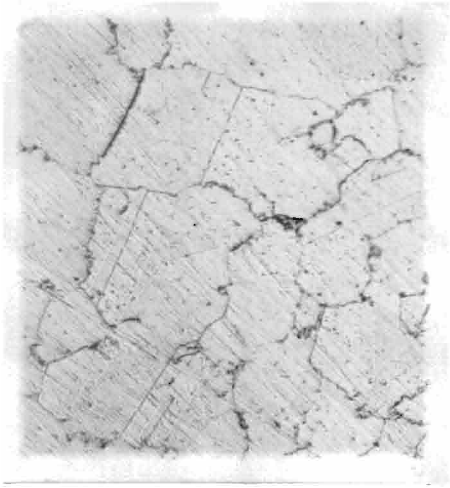


Figure 15 500X
Alloy 8-70% Cu
30% MnNi

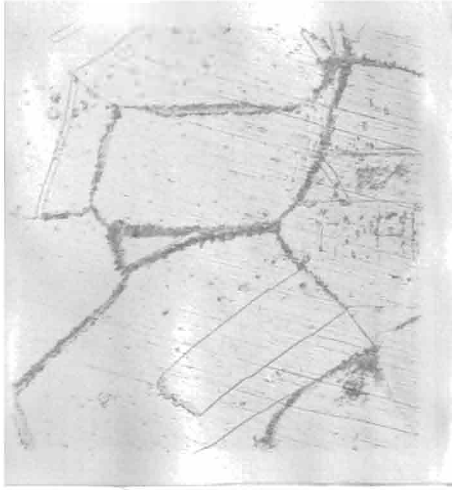


Figure 16 500X
Alloy 11-60% Cu
40% MnNi

1300°F-3hrs.-WQ
Aged-825°F-24hrs.-WQ
Dichromate Etch

Conclusions

The rate of cooling from the solution temperature has little or no effect on the final hardness of aged 60/20/20.

Regardless of aging temperature precipitation in strain free solution treated specimens is a grain boundary phenomenon. Therefore the amount of precipitation is greatly influenced by grain size.

Cold working before aging accelerates the precipitation process. Slip lines and other lattice imperfections produced by cold work increase the "internal surface" of the grains, thereby producing points for the nucleation of the precipitating phase throughout the grain.

The sustained maximum hardness of aged cold worked specimens over a temperature range can be explained as follows. Cold Working increases the "tendency" for precipitation causing precipitation to occur at a lower temperature. Since cold work usually results in an uneven distribution of plastic strain the minimum temperature for maximum precipitation varies from grain to grain.

Softening of aged alloys appears to be due to resolution rather than agglomeration of the precipitated phase. Resolution and recrystallization take place in an overlapping range, approximately 925°F to 1000°F.

The precipitated phase has not been identified.

The drop in resistivity on aging may be attributed to the depletion of the manganese content of the parent supersaturated alpha solid solution by the precipitation of a manganese rich phase. Pilling has shown that the resistivity of Cu-Mn-Ni alloys is principally a function of the manganese content.

Assuming the precipitated phase to be MnNi, the composition of the matrix may be approximated by comparing the d_{313} spacing (0.8352A°) of the aged specimen of 60/20/20 with the graph of Figure 6. A d_{313} value of 0.8352A° corresponds with a solid solution composition of 70% Copper-30% MnNi. The resistivity of a solid solution of this composition, from Figure 5, is 58×10^{-6} ohm-cm. compared to an actual resistivity of 53.3×10^{-6} ohm-cm.

Summary

A study of the hardening characteristics was made on alloys of the psuedo-binary Cu-MnNi system between 100% to 45% copper. Attention was focused mainly on the alloy 60%Cu, 20%Mn, 20%Ni.

The effects of cooling rate from solution temperature, cold working, aging time and temperature, and composition on hardness, resistivity, and lattice parameter were determined. The microstructures were examined and photomicrographs were taken of the typical microstructures.

In view of these facts a description of the hardening mechanism for these alloys was presented.

Further work is necessary to positively identify the precipitated phase. An X-ray study of single crystals of these alloys by the Laue method should greatly elucidate the subject.

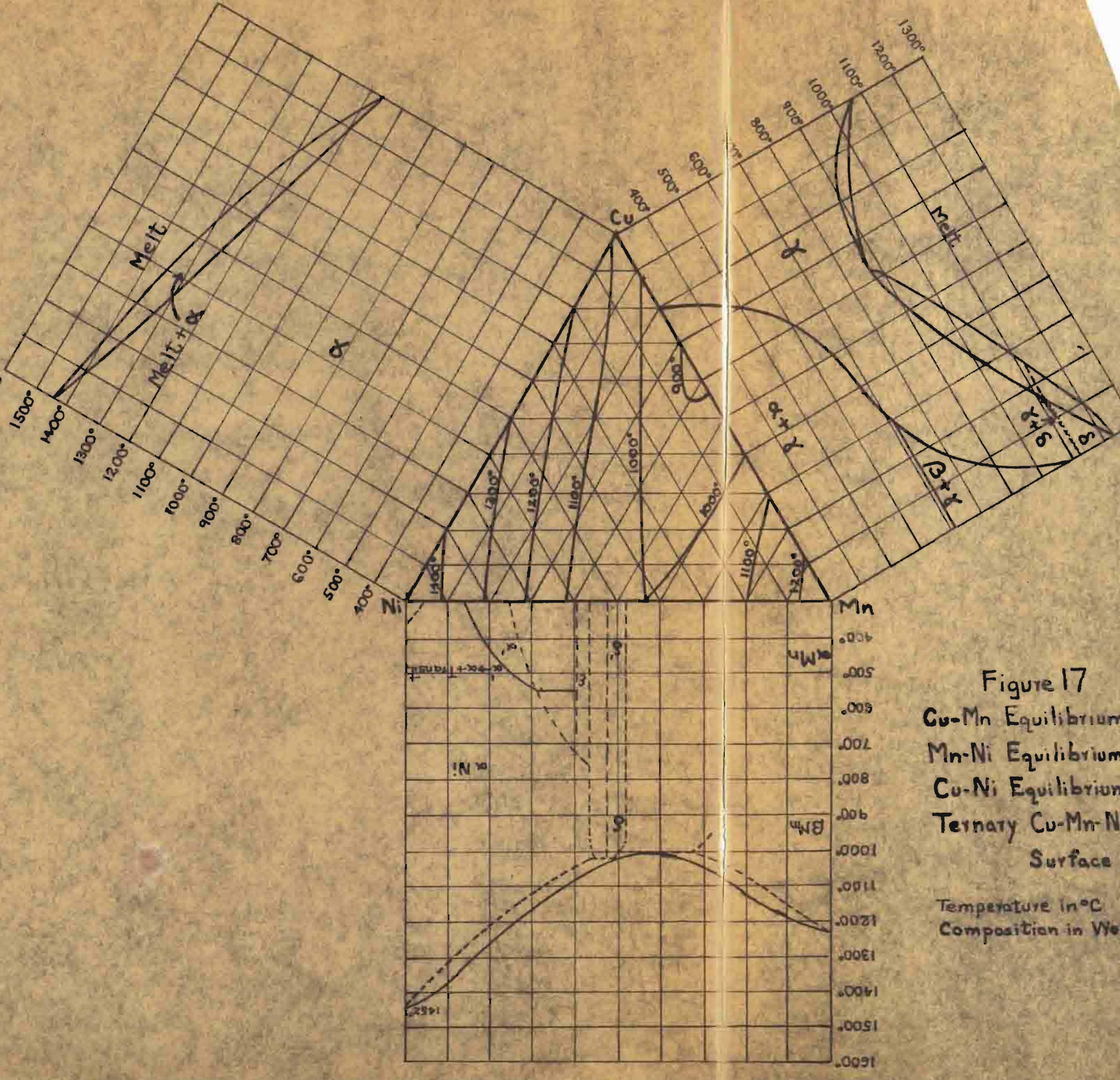


Figure 17

Cu-Mn Equilibrium Diagram

Mn-Ni Equilibrium Diagram

Cu-Ni Equilibrium Diagram

Ternary Cu-Mn-Ni Liquidus Surface

Temperature in °C

Composition in Weight %

Acknowledgment

The author wishes to thank the Missouri School of Mines & Metallurgy for providing the opportunity and facilities for carrying on this investigation, Doctor O. R. Grawe of the Geology Department for aid in the X-ray work, and Prof. C. Y. Clayton of the Metallurgical Engineering Department for invaluable advice rendered during the course of this work.

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