ELECTRICAL RESISTIVITY CHANGES AND THERMAL ARRESTS ACCOMPANYING THE AGE HARDENING OF ALUMINUM ALLOYS

Thesis For The Degree of M. S.

FRED L. REYNOLDS

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THESIS

Chemical engineering

Electrical Resistivity Changes

and

Thermal Arrests

Accompanying the Age Hardening

of

Aluminum Alloys

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Thesis

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in Partial Fulfillment

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of

Master of Science

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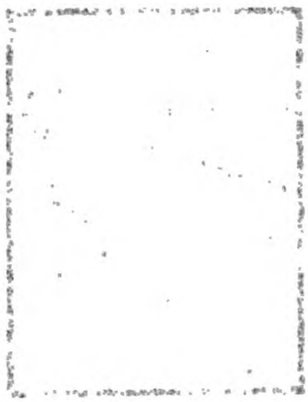
THESIS

TO MY FATHER

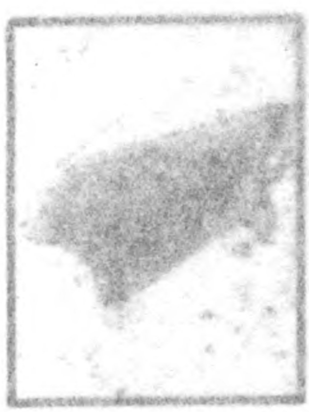


Cu [illegible]

INTERMETALLIC COM[illegible]

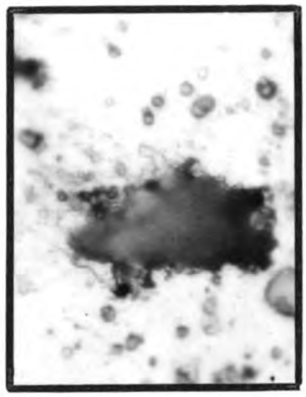
[illegible]1350

FeMnCu(?)



[illegible]

$CuAl_2$



Mg_2Si

INTERMETALLIC COMPOUNDS

x1650

FeMnCu(?)

Mg_2Al_3

INTRODUCTION

About a year and a half ago, the writer's interest was first fixed on the peculiar properties that some of the light metal alloys display when properly heat treated. The property that some of the aluminum alloys possess, of age hardening after being quenched from just below the eutectic point, is well known. The phenomenon was first observed by Wilm of Germany in his work in 1903-11.

For several years this was unexplained, and it remained so until the work of P. D. Merica and his co-workers in 1919[1]. At that time, the idea of the keying effect of the hard $CuAl_2$ particles in the groundmass of aluminum was advanced. This conclusion was based upon the thermal arrests that were observed on reheating a quenched unaged specimen of duralumin. It was believed that these arrests were evidences of a precipitation of the particles of $CuAl_2$ of a very highly dispersed nature and of colloidal size. Furthermore, the maximum hardness that could be produced was dependent on an average critical sizeof the precipitated particles. Later, (1921-23) Hanson and Gayler, working at the National Physical Laboratory, submitted the theory that Mg_2Si was a much more important influence in the age hardening than $CuAl_2$[2]. However, we have alloys such as "25s" which are free from Mg_2Si and hardened by $CuAl_2$ alone. Conversely, alloys such as "51s" contain Mg_2Si alone as the hardening constituent, age considerably at room temperature. It is noteworthy that the former does not age appreciably at room temperature, but requires elevated temperatures to bring about this effect.

The theories advanced by these workers, links well with the slip interference theory advanced by Jeffries and Archer (1921)[3]. Although the proof submitted in favor of the precipitation theory is largely of an indirect nature, it has been generally accepted by present day metallurgists. Perhaps the main objection to the theory of precipitation as applied to the age hardening of duralumin is the apparent anomaly of electrical resistance changes during age hardening+.

When a specimen is given the solution treatment i.e. quenched from just below the eutectic temperature, the resistance shows a decided increase which conforms to the idea given below+. However, on ageing the alloy its resistivity continues to increase slightly.

With these facts in mind, the following work was undertaken to discover, if possible, this apparent exception to an otherwise plausible theory.

\+ It has been considered that in general the resistivity of an alloy is increased when an aggregate is changed to a solid solution, and conversely that the resistivity is decreased when a solid solution decomposes into an aggregate.[4]

The author wishes to express his indebtedness to E. H. Dix, Jr., of the Aluminum Company of America for the suggestion of the problem, and to H. E. Publow, Instructor and friend, under whose direction this work has been carried out.

Many thanks are due to R. S. Archer of the Aluminum Company of America for his kindly advice and assistance.

June 1929. Fred L. Reynolds

INTRODUCTION TO EXPERIMENTAL WORK

When the work was first started in duralumin, there was no fabricated stock of known composition at hand. Accordingly, the several metals required were collected together and sixty (60) test bars were cast and machined for the study. The casting and study of the cats alloys constituted the first experiment of this work.

Later, by suggestion of E. H. Dix, Jr., the investigation of electrical resistivity of rolled duralumin on ageing was undertaken. The 17s metal selected was kindly supplied by the Aluminum Company of America. This investigation of the electrical resistivity changes during the process of age hardening after the solution treatment, and the accompanying hardness, constituted the second experiment.

The work of P. D. Merica and his associates on the thermal arrests in the heating of unaged specimens, indicated that there was room for further investigation along this line. Since duralumin is rather complex in its constitution, it was considered that this study might better be carried out with a pure copper-aluminum alloy. This study of the thermal critical points in a pure copper-aluminum alloy made up the third experiment.

EXPERIMENT No. 1

This experiment was devoted to the cast alloys of the composition given in Table I. Sixty of these bars were made up and machined for the tests described herein:

Table I

	Alloy No.1	Alloy No.II	Alloy No. III
Aluminum	95.4%	94.25%	98.25%
Copper	4.0	4.0	- -
Manganese	0.6	0.6	0.6
Magnesium	- -	0.8	0.8
Silicon	- -	0.35	0.35

The alloy additions were made as follows: Copper was added by first making a 50-50 Copper-Aluminum alloy and adding this to the molten aluminum to get the desired percentage of copper in the melt. In this connection, the 50-50 Copper-Aluminum alloy, as cast, was found to be very hard and brittle. Its fracture was brilliant and had the characteristic aluminum color. The alloy was made by adding molten copper to superheated molten aluminum and a very uniform mixture obtained.

Magnesium ribbon was added directly to the melt before casting. Care was taken to keep the magnesium under the surface of the melt until the alloy was formed.

Powdered manganese was added to a molted bath of aluminum having about 20% of superheat. Thus an alloy of 10% manganese and 90% aluminum was obtained. This alloy was used to make manganese additions to the melts. This alloy seemed to be much tougher and harder than pure aluminum, but not as hard as the copper alloy.

Powdered silicon was added directly to the melt before casting. The melt was superheated about 10% before these additions were made.

The test bars were sand cast on end, four in a mold from a sprue in the center. After several unsuccessful attempts, it was found that the gates must be cut very heavy. Another item to which little attention was paid at the time of casting, is the casting temperature. This should be just above the melting point. Otherwise, the metal is very porous. Many of the fractures of the bars obtained show porosity, shrink holes, brown oxide, or chalky surfaces. Hence, the physical tests as given here are inferior to the intrinsic qualities of the metals. Many of the test bars broke in the head, due to shrinkage in the top end of the cast bar.

The bars were machined to the standard test size and soaked in a furnace at 945°F for three hours. After that time they were quenched in water and started to age. Half of them aged at 105°C and the other half at room temperature. As the ageing progressed, tensile tests were made. The results of these tests are given in Tables II, III and IV.

Table II

Physical Properties of Alloy No. 1

	22°C			105°C		
Time Aged	Ultimate lbs/sq.in	% Red. of Area	% Elong. in 2"	Ultimate lbs/sq.in	% Red of Area	% Elong. in 2"
4 hrs				13700	Broke in head	
1 Day	17450	5.0	3.7	19220	3.7	3.1
4 Days	13500	Porous		20000	Broke in head	
8 "	15700	3.0	4.2		Porous metal	
90 "	17200	3.7	4.7	21000	"	"
150 "	17250	-	4.5	24250	"	"
180 "	15500	Chalky		18875	Chalky	

Table III

Physical Properties of Alloy No. II

	22°C			105°C		
Time Aged	Ultimate lbs/sq.in	% Red. of Area	% Elong. in 2"	Ultimate lbs/sq.in	% Red of Area	% Elong. in 2"
4 hrs				13,500	Porous metal	
1 Day	15,500	6.4	.09	13,500	"	"
4 Days	14,000	Porous		25,000	2.7	1.6
8 "	14,000	Badly porous		24,000	Head pulled	
90 "	14,000	Porous metal		28,000	Porous metal	
150 "	15,000	"	"	29,500	"	"
180 "	16,250	"	"	24,050	"	"

Table IV

<u>Physical Properties of Alloy No. III</u>

Time Aged	22°C Ultimate lbs/sq.in	22°C % Red. of Area	22°C % Elong. in 2"	105°C Ultimate lbs/sq in	105°C % Red of Area	105°C % Elong. in 2"
4 hrs				25,300	3.15	
1 Day	28,550	2.5	1.5	28,000	Defective	
4 Days	20,000	Shrink in head		30,550	2.7	1.6
8 "	23,700	Porous		29,300	Head pulled	
90 "	24,000	"		32,200	-	1.5
150 "	24,550	Woody fracture		27,500	-	2.0
180 "	23,140	Slightly porous		30,250	-	-

From the above tables it is quite evident that alloy No. III isthe most dependable of the three. This is hardened by Mg_2Si. Although room temperature seems to bring out the properties better on this alloy than the others, better results are obtained when the ageing takes place at 105°C. Since no particular care was taken in the casting of this alloy, it seems to be much more dependable than the others.

SUMMARY

The test bars that were made up are very inferior and should not lead one to form an erroneous conception as to te quality of these metals.

The primary effect of copper is to produce hardness in aluminum.

The primary effect of manganese is to produce toughness in the cast metal.

If molding practice is watched carefully and the metal is poured at the correct temperature, sound castings will result, especially in the Mg-Si-Al alloy.

Experiment No. II

This experiment dealt with the electrical resistivity changes of rolled duralumin during aging after the solution treatment. The chemical analysis of the strip used was as follows:

Copper	4.0%
Magnesium	.5%
Manganese	.6%
Silicon	.35%
Iron	.5%
Aluminum (by difference)	94.05%

The structure of the annealed metal is shown in Fig. I and Ia. Two strips, 3/8" x 14" were cut from a sheet of rolled stock .035" thick. The apparatus for making these measurements is shown in Fig. II. A current of 6 - 10 amps., supplied by a direct current generator, was passed thru the strip. The drop in potential across the strip was measured by a potentiometer set-up as shown. The resistance of the strip was computed from these data, using Ohm's law.

After the solution treatment was given, one of the strips aged at room temperature, while the other was aged in a drying oven at 105°C. The resistivity changes are tabulated in Table V and expressed graphically in Fig. III.

In conjunction with the resistance measurements, the hardness was observed. The changes in hardness are tabulated in Table V and plotted in Fig. V.

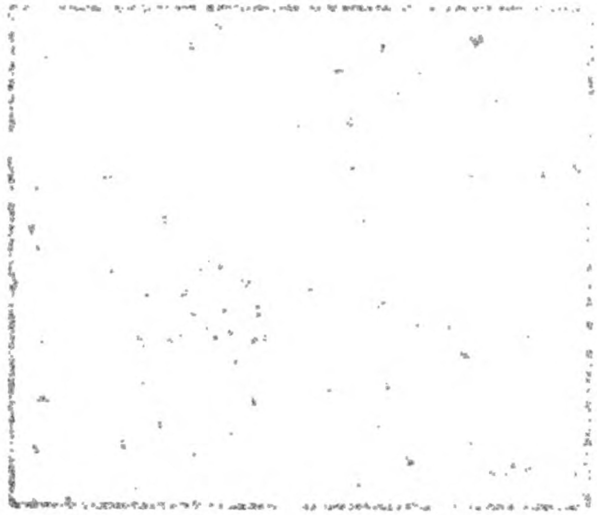


FIG I [illegible]

ANNEALED [illegible]

FIG 1a x160[illegible]

ANNEALED

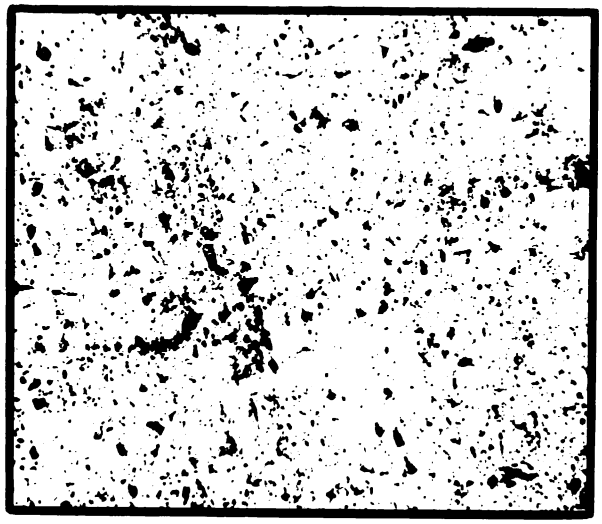


FIG I x100
ANNEALED 17S

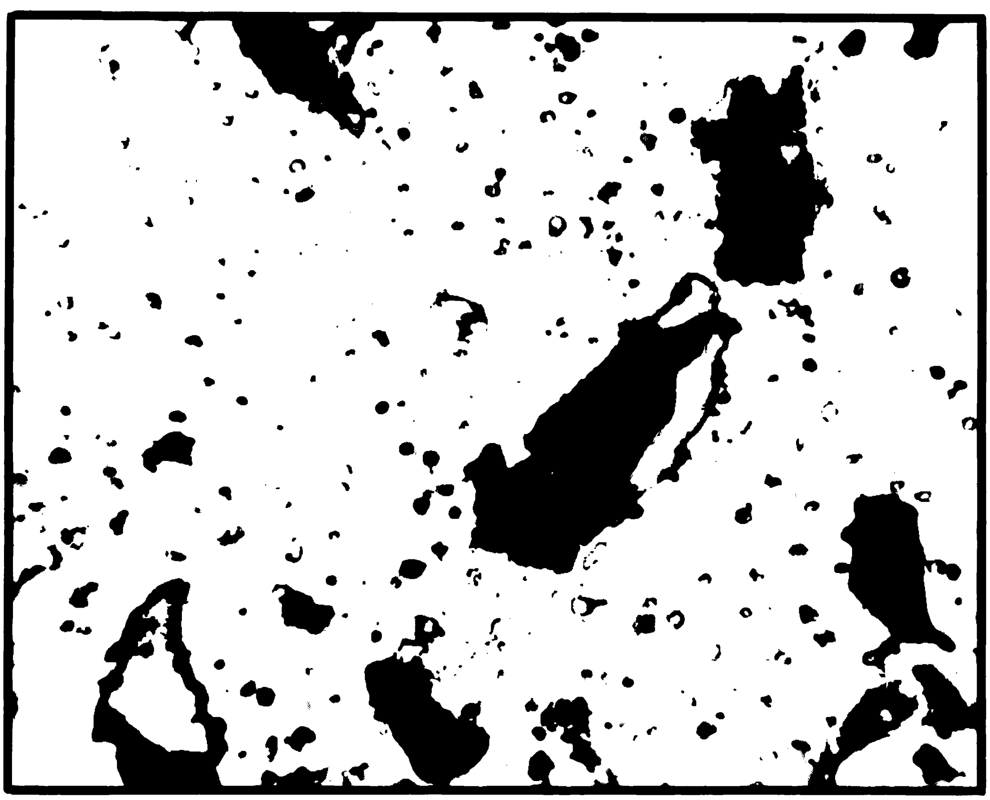
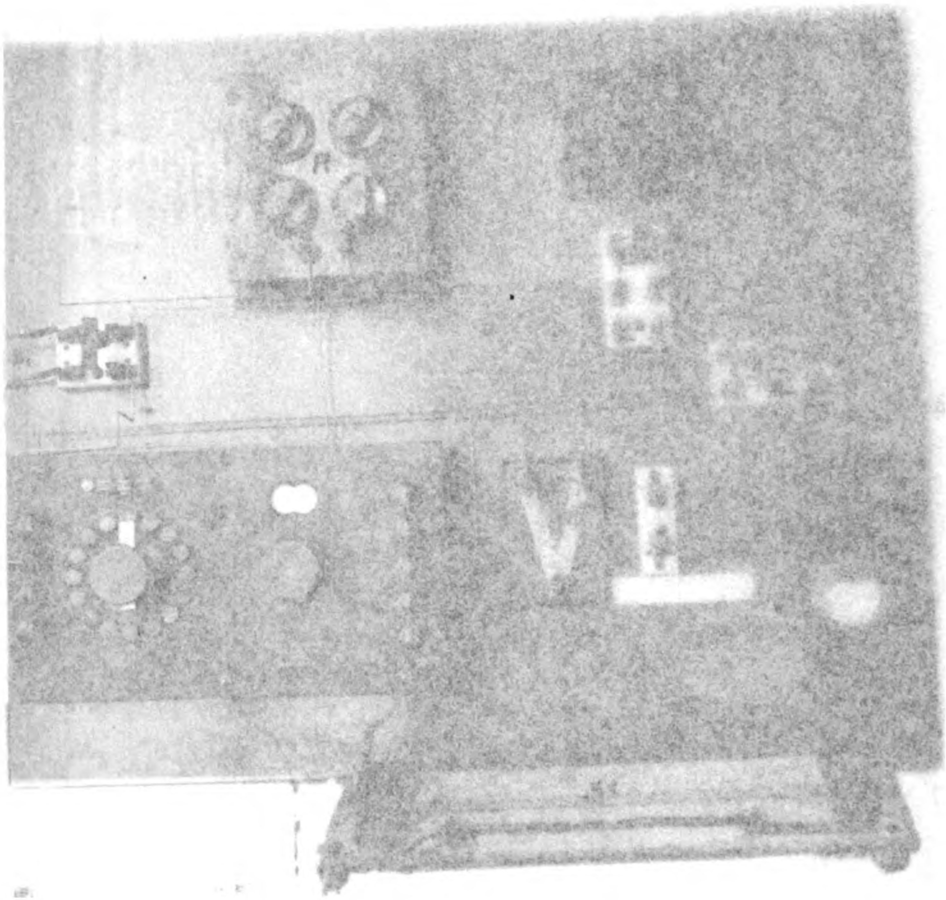


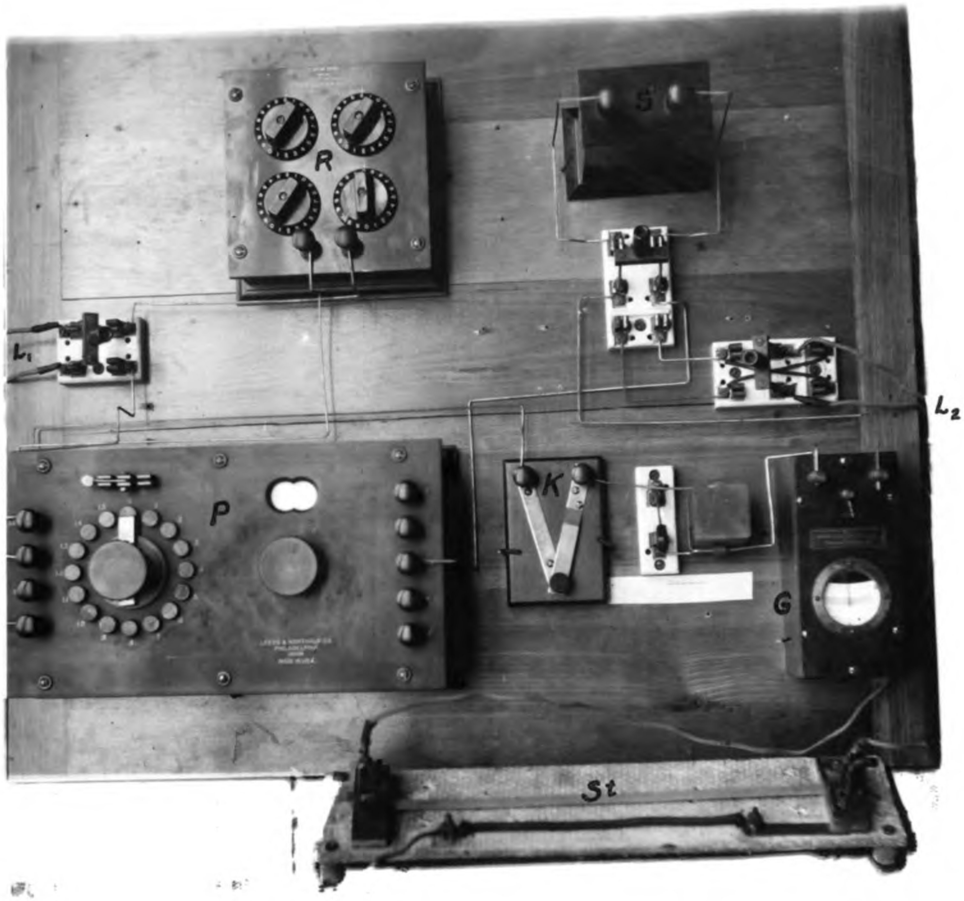
FIG Ia x1650
ANNEALED 17S



G - Galvanometer
K - Key
L - To Battery
L_2 - To Strip

P - Potentiometer
R - Resistance Box
S - Standard Cell
St - Strip Tested

FIG 1.



G - Galvanometer
K - Key
L_1 - To Battery
L_2 - To Strip

P - Potentiometer
R - Resistance Box
S - Standard Cell
St - Strip Tested

FIG II

Table V

Time Aged	22°C Resistance	22°C Hardness	105°C Resistance	105°C Hardness
Annealed	.001370 ohms	53	.001405 ohms	53
Quenched	.001925	78	.001935	78
30 min	.001960		.002038	
1 Hr	.001993		.002058	
2 "	.002025	85	.002060	90
3 "	.002034	89	.001983	92
4 "	.002067	90	.001986	92
5 "	.002045	90	.001979	92
10 "	.002030	92	.001975	94
1 Day	.002130	93	.001972	93.5
2 Days	.002242	93	.001960	95
3 "	.002020	93	.001970	96
4 "	.002050	93	.001884	97
5 "	.002070	94	.001878	99
10 "	.002052	94	.001820	101
15 "	+.002100	94	.001773	102
20 "	.002050	94	.001798	101
30 "	.002040	94	.001752	100
45 "	.002036	94.5	.001760	100
90 "	+.002492	94	+.001820	100
120 "	.002090	95	.001735	+96
150 "	.002025	95	.001710	101

+measurement disregarded

Discussion of Results of Experiment III

Let us consider what happens to the resistivity when an annealed strip of duralumin is given the solution treatment and subsequently aged at room temperature.

The old idea that the resistivity of an alloy is increased when an aggregate is changed into a solid solution and decreased when the reverse change takes place may not be strictly true. A fundamental conception of resistance must be taken to explain these changes. The resistance of a conductor is given by theformula:

$$R = K \frac{l}{a}$$

in which R is the resistance; l is the length of the conductor; a is the cross sectional area; and K is the specific resistance. In this work, l and a were not changed since all measurements were made at the same temperature. Therefore, the resistance changes noted must be due to a change in the value of K. Since the values of K for pure aluminum, Mg_2Si, $CuAl_2$, and solid solutions of these compounds in aluminum are widely different, we must take each one into account to explain the combined or "effective specific resistance". Any explanation of the changes that occur must be made on the basis of changing values of this effective specific resistance.

In the first place, the resistivity of pure aluminum is much lower than that of either the metallic compounds[5] or of solid solutions of these compounds in aluminum[6]. Secondly, the resistivity of $CuAl_2$ is less than Mg_2Si^+. The fact that a greater increase in resistivity is observed on the strip aged at room temperature, during which only Mg_2Si is precipitated seems proof enough for this.

Referring to Fig. IVa, there exists in the annealed state large particles of intermetallic compounds surrounded by a matrix of nearly pure aluminum. A cross section of a bar os such a material could be represented as shown in the figure. Although much of the area is taken up by intermetallic compounds which have a comparatively high resistance, the matrix is of nearly pure aluminum which makes the effective specific resistance quite low.

When the alloy is given the solution treatment, these intermetallic compounds are held in a supersaturated solution of a complex nature and a cross sectional view would be homogeneous as in Fig. IVb. Work on several metals[6] show that the resistance of a solid solution is higher than its component metals. Very little, if any, work has been done in comparison of the resistivity of intermetallic compounds and solid solutions, however. The facts presented in this work show that the resistivity of these compounds are greater

+ It has been shown that in general intermatallic compounds made up of two elements which occur in the same or adjacent groups of the periodic table (as magnesium and silicon) have a high electrical resistivity. Conversely, two elements widely separated in the periodic table (as Copper and Aluminum) produce a compound of low electrical resistivity.

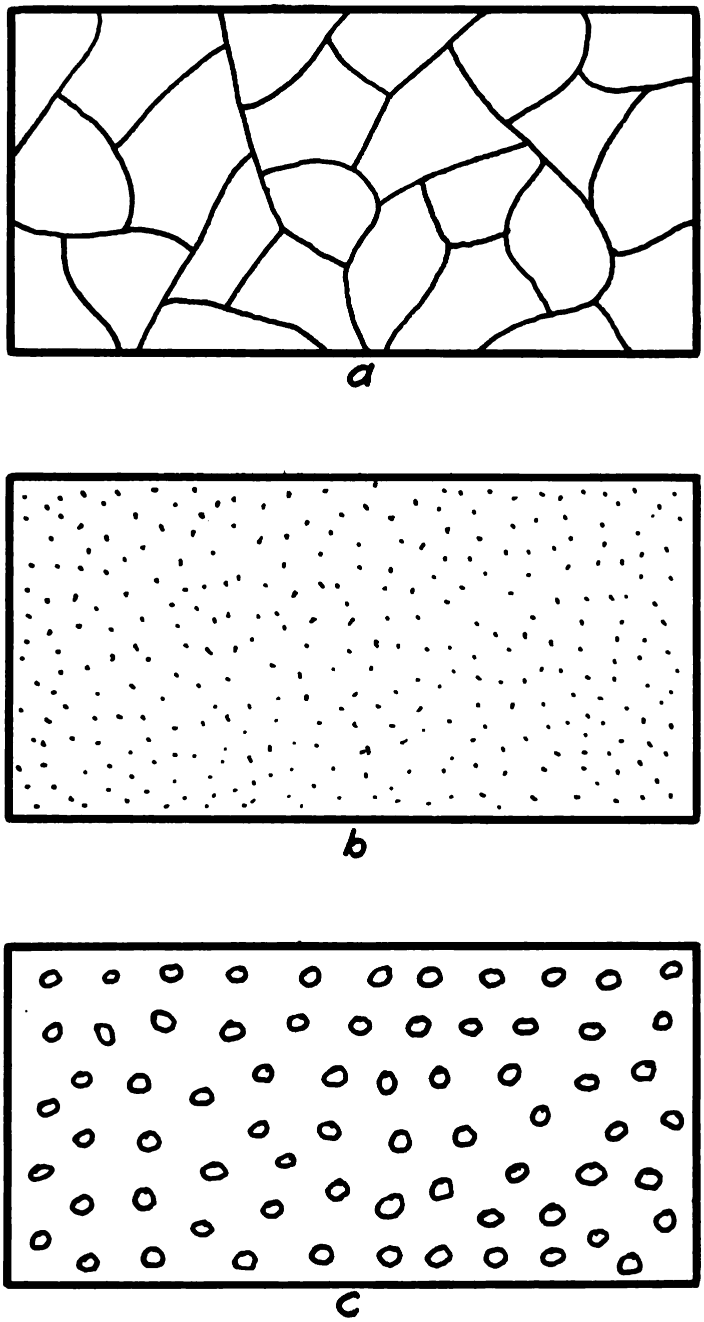


Fig IV

than their solid solutions. Since pure aluminum has a lower conductivity than its solid solutions, the solution treatment would be expected to markedly increase the resistance. This is found to be true (Fig. III).

For a short time at room temperature, the ageing precipitates Mg_2Si from solution but $CuAl_2$ is retained largely. This fact is evidenced by alloys such as "51s" which harden readily at room temperature and contain Mg_2Si alone as the hardening agent. Such alloys as "25s" with no Mg_2Si, but containing $CuAl_2$ do not harden appreciably at room temperature, but require somewhat higher ageing temperature. When the quenched piece starts to age at room temperature, we have Mg_2Si coming out of solution (Fig. IVc) which, as explained above, has a high resistivity. The $CuAl_2$ remains in solution and gives the matrix a high resistivity also. Hence, as the piece ages for a short time at room temperature, there is a further increase in resistance. As the ageing continues, more Mg_2Si and some of the $CuAl_2$ comes out of solution. This has a dual effect. First, the composition of the matrix is changed so that its resistivity is lowered and second, $CuAl_2$ is precipitated, which has a lower resistivity than the former solid solution. Therefore, ageing at room temperature for about two days, the resistivity starts to decrease. After this effect is completed (in about 4 days) a sort of an equilibrium is reached and no further change in resistance is noticed.

A similar effect is produced when the material is aged at 105°C. In this case, the quenched strip shows the same increase in resistivity over the annealed, as the previous one. However, at this temperature, both constituents precipitate. After the first few days in which we reach a maximum, we have a gradual decline in the curve. As before, we get a continued increase in the resistivity as long as the matrix has a high resistance. When the composition of the matrix approaches pure aluminum, due to precipitation, so that its resistivity begins to decline rapidly along the inverted U curve, we pass thru a maximum point on the ageing curve. Then the curve declines sharply until an equilibrium is reached between the resistivity of the precipitated compounds and the solid solution of the matrix. The slight decline in the curve after that, is due to gradual precipitation of the compound $CuAl_2$ which supposedly has a comparatively low resistivity. As a matter of fact, when the solution treatment is given an alloy of this type, we do not have complete solution of the constituents as shown in Fig. VI. However, this excess is the same in all conditions of the metal, and the changes observed are due to the constituents that do dissolve when the solution treatment is given.

The observed hardness changes shown in Fig. V seem inclined to follow the resistivity curve. The hardness of the quenched piece shows an increase over that of the annealed strip. A maximum is reached in 3 to 5 days and does not change after that time. The similarity of the resistance and hard-

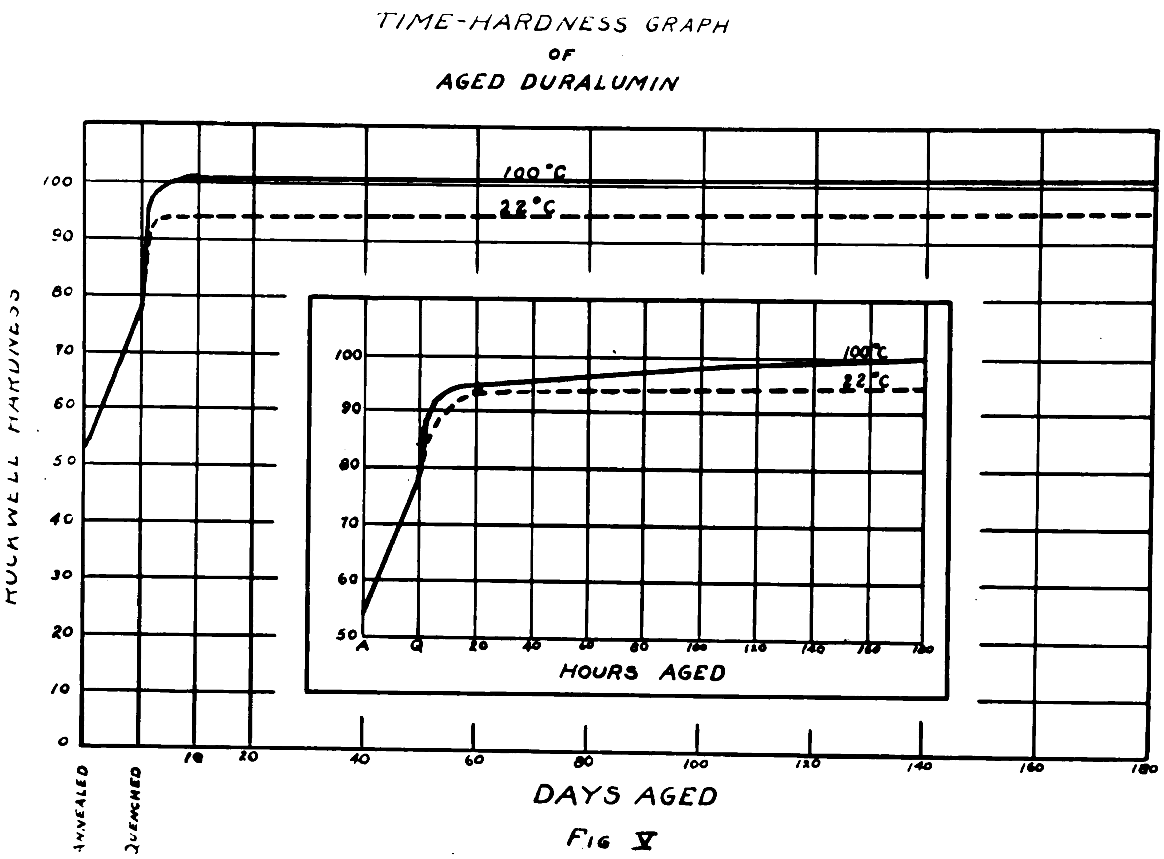

TIME-HARDNESS GRAPH
OF
AGED DURALUMIN
ROCKWELL HARDNESS
DAYS AGED
ANNEALED
QUENCHED
100°C
22°C
HOURS AGED
A
Q
0
10
20
30
40
50
60
70
80
90
100
120
140
160
180

Fig V

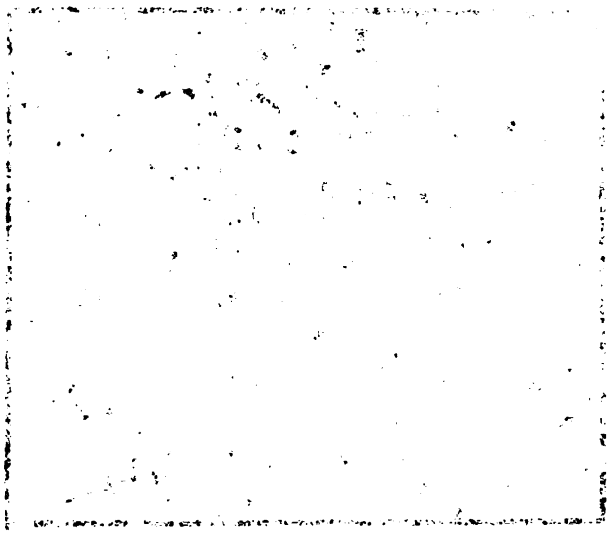


Fig [illegible] [illegible]
Quenched 17s

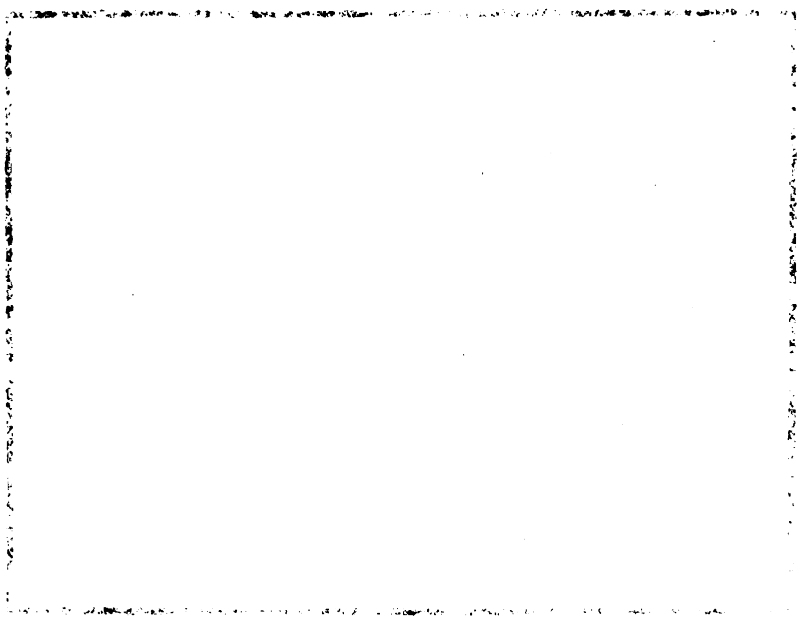


Fig [illegible]
Quenched [illegible] A

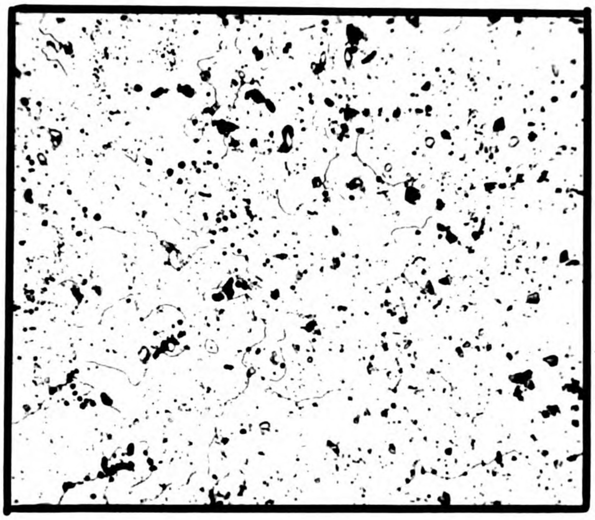


FIG VI x100
QUENCHED 17S

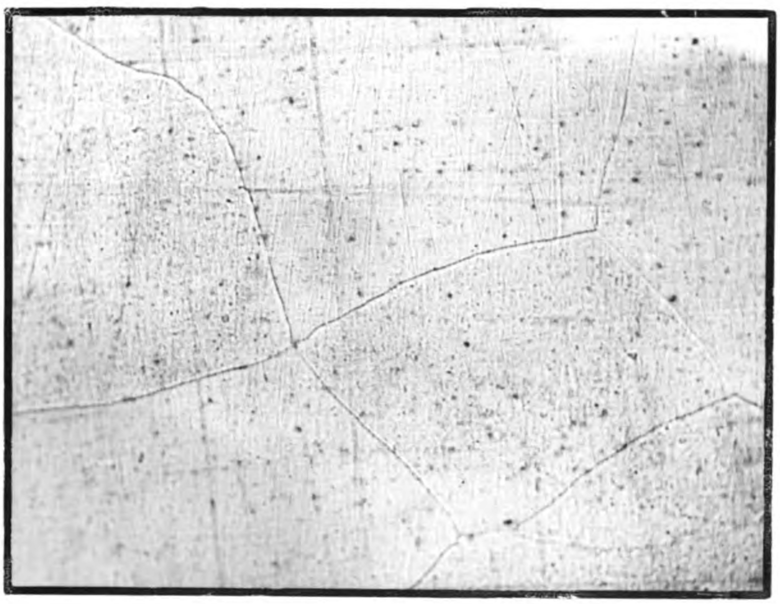


FIG VIII x100
QUENCHED Cu-Al ALLOY

ness curves stop at this point because the hardness curve does not drop back again as does the resistance curve.

Ageing at 100°C brings out the hardness of the alloy that is caused by the $CuAl_2$ constituent that is not brought out at room temperature. At the lower temperature the hardness is due mainly to the Mg_2Si compound.

SUMMARY

1. The resistivity of $CuAl_2$ is less than Mg_2Si.

2. The resistivity of a solid solution of $CuAl_2$ in aluminum is greater than that of $CuAl_2$ or aluminum.

3. The resistivity of a solid solution of Mg_2Si in aluminum is less than that of Mg_2Si, but greater than aluminum.

4. Quenching causes an increase in resistivity over the annealed condition.

5. On ageing, a continued increase in resistivity obtains, as long as the matrix has a high resistance. When the intermetallic compounds precipitate from solution and cause a sharp decrease in its resistivity, the curve drops back quickly until an equilibrium is reached. After that time, no change in resistivity is observed unless more $CuAl_2$ precipitates (at high temperature). In that case, a gradual decline in the curve is noted.

EXPERIMENT No. III

In 1919, P. D. Merica[8] and his co-workers observed thermal arrests on reheating freshly quenched aluminum alloys. This was very logically explained by assuming that the absorption of heat was caused by $CuAl_2$ precipitating from the supersaturated solution. However, they were not able to find any difference in the microstructure of a piece before and after reheating subsequent to the solution treatment. Since the material used for their work contained other elements in appreciable percentages as well as copper, it may be that their results were influenced by the presence of these other elements.

With this in mind the third experiment of the series was made to check the previous work and to supplement it with a micrographic analysis.

A copper-aluminum alloy was used which was very pure. The percentage of copper was about 5.3% with less than .05% of other impurities. The alloy was held at 1005°F for 72 hours and quenched in water to get complete solution (Fig. VIII). The thermal samples were carefully reheated on a double sand bath. The temperature was taken at equal intervals of time by a mercury thermometer inserted in a hole drilled into the piece for the purpose (Fig. VII).

This alloy was studied with a Leeds Northrup critical point recorder in an endeavor to determine the thermal arrests. This was unsuccessful however, as the points are masked in such a way that this instrument will not detect them.

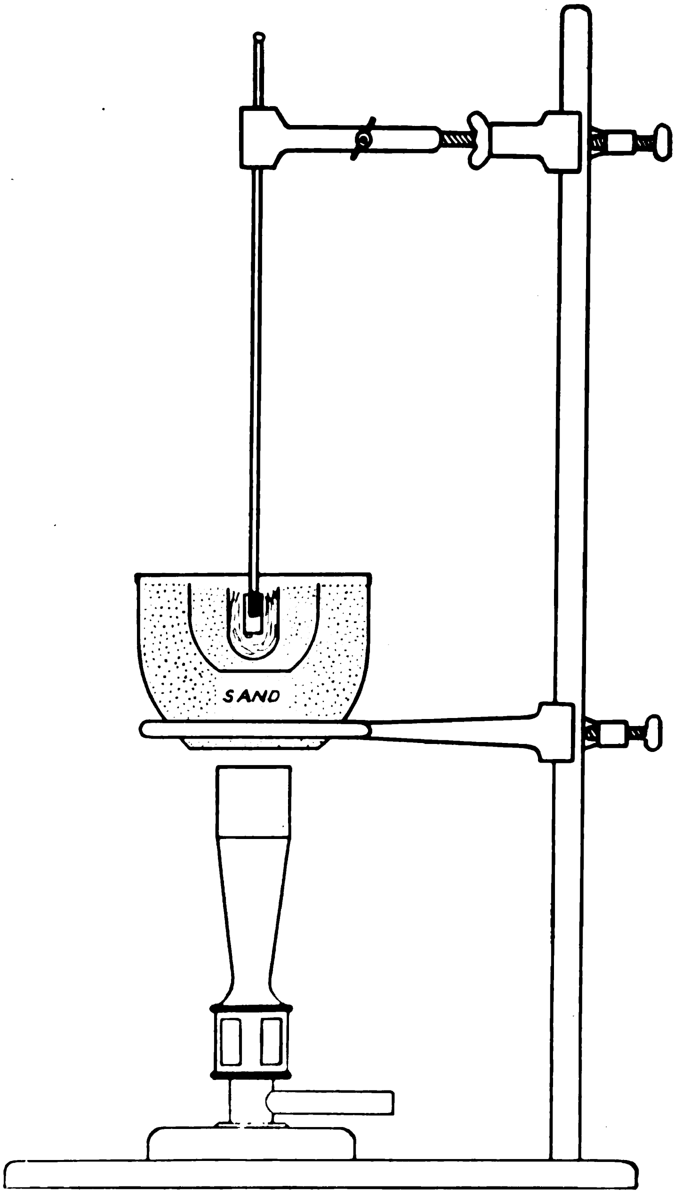


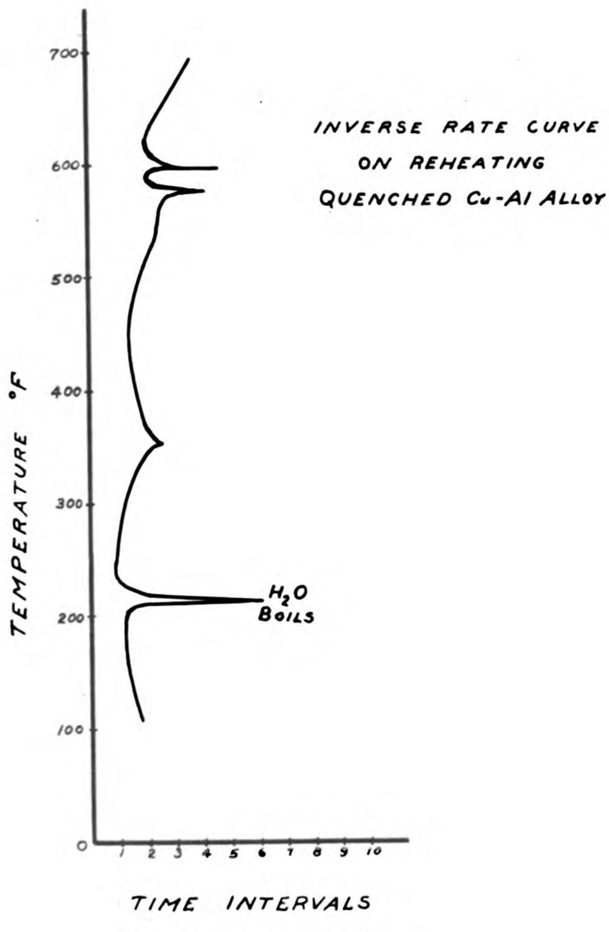
FIG VIII

CRITICAL POINT APPARATUS

Discussion of Results of Experiment III

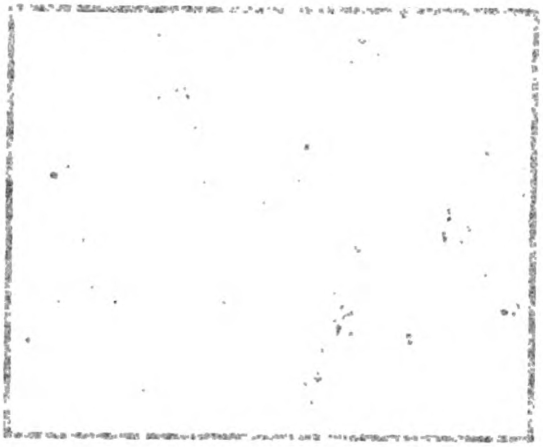
The amount of copper in the alloy used in this experiment seems to be near the limit which is soluble in aluminum at 1005°C. In fact, several authors have given the limit somewhat lower than this. However, the picture shows the complete solution has been made (Fig. VIII). The inverse rate curve is plotted for the reheating and is given in Fig. IX. The specimen was covered with water glass before reheating so that a sharp arrest is made at the boiling point of water. A slight break is noticed at 350°F which is not accounted for except by inequalities in the heating rate. At 550°F a sharp break is encountered and another appears at 600°F. This double arrest has been checked by running another sample and is confirmed by it.

Figs. X, XI, XII, show the changes that take place when this alloy is reheated at 540°F, 570°F and 600°F respectively. The first temperature (540°F) is just below the first critical point and shows almost no precipitation of $CuAl_2$. The intermediate temperature (570°F) is between the two thermal arrests and shows precipitation within the crystals. The tendency of $CuAl_2$ to precipitate at the grain boundries is not apparent in this piece. The picture in Fig. XII shows this and closely resembles the structure of the annealed specimen (Fig. XIII and XIV).



INVERSE RATE CURVE
ON REHEATING
QUENCHED Cu-Al ALLOY
TEMPERATURE °F
700
600
500
400
300
200
100
0
1 2 3 4 5 6 7 8 9 10
H_2O
BOILS
TIME INTERVALS

FIG IX



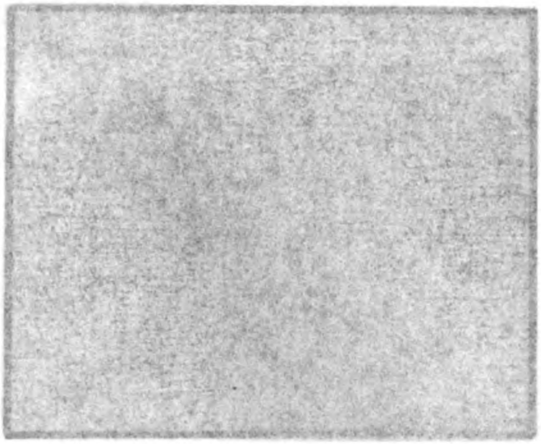
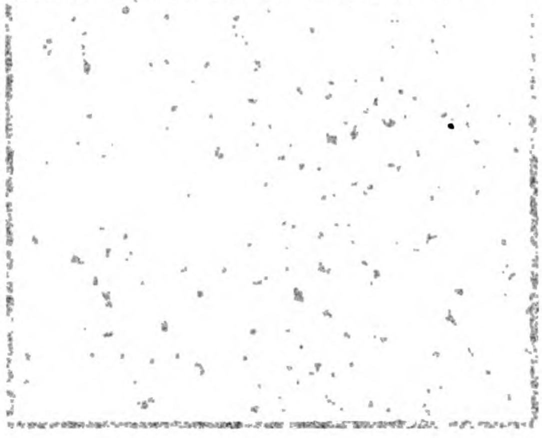


Fig XI x300
Cu-Al Alloy
Quenched [illegible]



[illegible] X300
[illegible]

FIG X x300
Cu-Al Alloy
Quenched. Reheated to 540°F

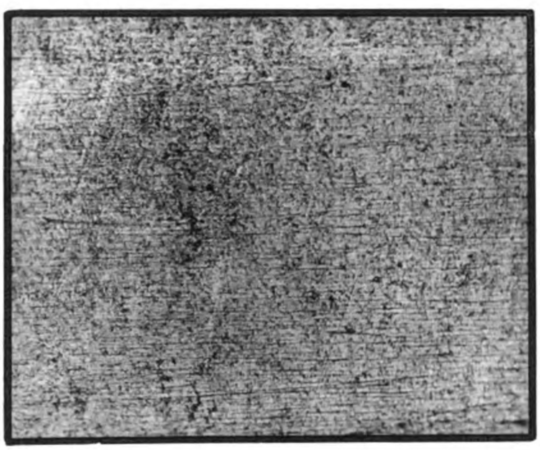


FIG XI x300
Cu-Al Alloy
Quenched. Reheated to 570°F

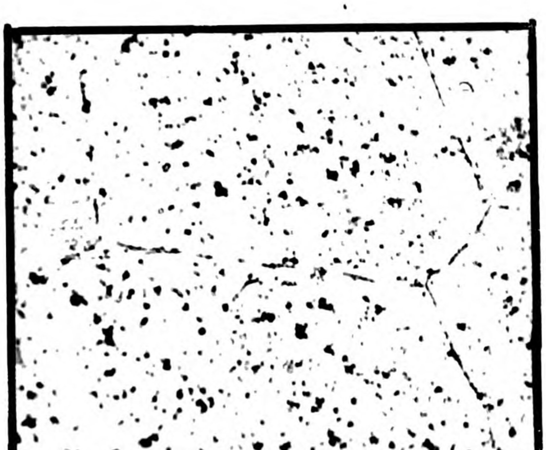
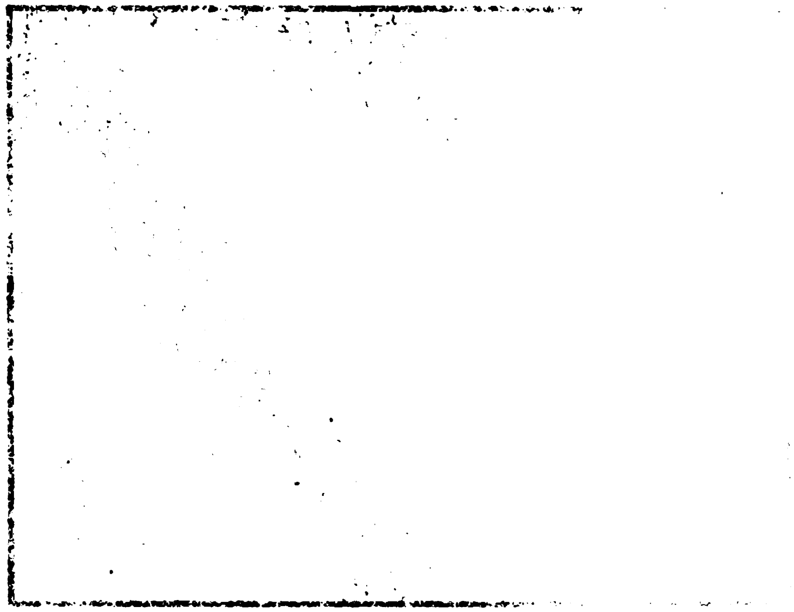
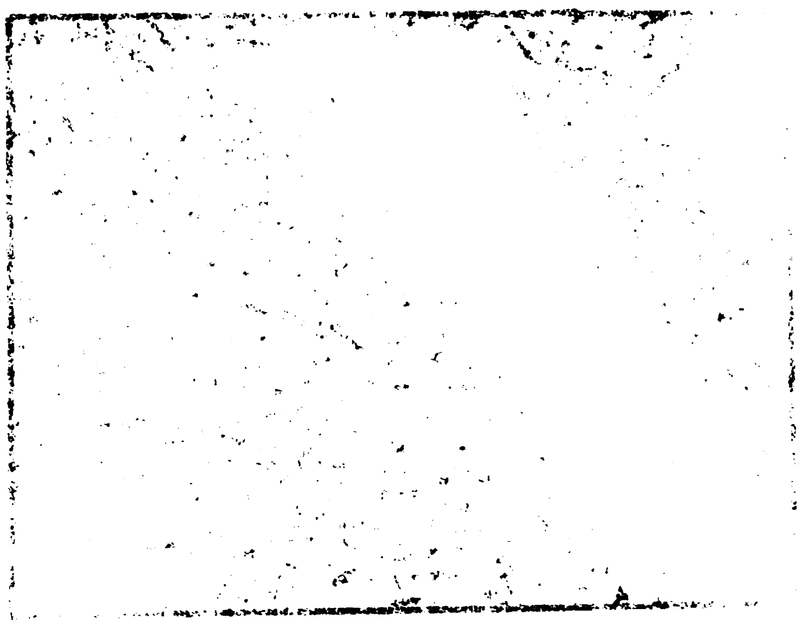


FIG XII x300
Cu-Al Alloy
Quenched. Reheated to 600°F



[illegible]
[illegible] ANNEALED Cu-Al [illegible]



[illegible]
[illegible] NEALED C [illegible]

FIG XIII x100
ANNEALED Cu-Al ALLOY

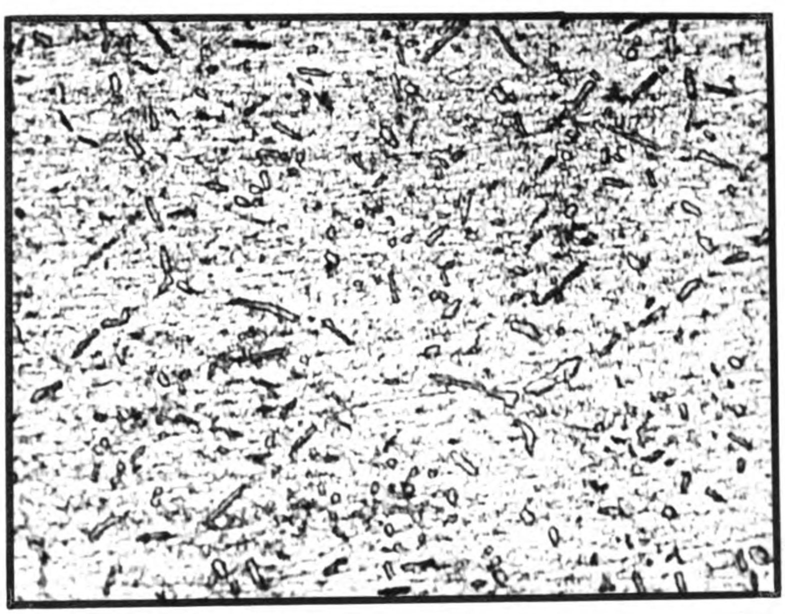


FIG XIV x500
ANNEALED Cu-Al ALLOY

The very marked difference in structure that is shown in these pictures is very evident of a reprecipitation within the metal. The tendency of precipitation at the grain boundries that Archer[4] notes is shown up in these pictures.

Summary

1. A double thermal arrest is encountered when a quenched copper-aluminum alloy is reheated. The first arrest is at 545°F and the second is at 590°F.

2. At these temperatures, $CuAl_2$ precipitates from the supersaturated solution with a tendency toform at the grain boundries.

General Summary and Conclusion

From the first experiment which was on the cast alloys of this type, it is concluded that the alloy which contained magnesium and silicon as the hardening agents was much more dependable than the others used. The other alloys might have developed the same strength if the casting had been carefully done. This series gave good results without careful precautions taken in casting.

The prime effect of copper is to produce hardness in the alloy.

The prime effect of manganese is to produce toughness in the alloy.

From the second experiment which dealt with the resistivity changes of aged duralumin, the following conclusions are drawn:

1. The resistivity of Mg_2Si is greater than the solid solution of it in aluminum.

2. The resistivity of $CuAl_2$ is less than Mg_2Si.

3. Ageing a quenched piece of duralumin for a short time increases its resistance because the Mg_2Si precipitates out. After the precipitation has gone so far as to dilute the solid solution matrix and cause its resistivity to decrease, there is a sharp drop in the curve. After that, at room temperature, an equilibrium is reached and no further change is noticed. At the higher temperature $CuAl_2$ precipitates and having a low resistivity causes a gradual decline in the curve.

From the last experiment, it is noted that a double critical is encountered on reheating a quenched piece of copper-aluminum alloy. The first is at 545°F and the second at 590°F. At these temperatures, $CuAl_2$ precipitates out and has a tendency to form at the grain boundaries.

F I N I S

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