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IN THE
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by

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THE RATE OF PRECIPITATION OF $CuAl_2$ IN THE SILVER RICH Cu-Ag-Al ALLOYS

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INTRODUCTION

Age- hardening was first observed by Wilm [1] in 1911. He discovered that Aluminum, when alloyed with 3.5% Cu, 0.5% Mg, and 0.5% Mn, and quenched from a temperature of 500° C possessed the property of hardening appreciably if it were allowed to remain at room temperature for a few days. Subsequent investigation showed that not only was the hardness increased, but the tensile strength greatly increased by this "ageing" process. Aluminum alloys of this type, known generally as duralumin, have been widely used during the past twenty years, especially in aeroplane, dirigible, and automobile construction. The light weight and high tensile strength of these alloys make them especially desirable for such construction.

Not only has the use of these alloys been extensive, but the discussion of the cause for this age-hardening phenomenon has been hardly less so. Merica, Waltenberg, and Scott[2] first advanced the opinion that the hardening was due to a finely dispersed precipitate of $CuAl_2$. It has been definitely shown by X-ray analysis that precipitation actually occurs, and this theory of critical dispersion of the dissolved substance along the slip planes of the metal increasing the hardness has been adopted generally by Jeffries & Archer,[3] Harder,[4] and other leading metallurgists of today.

Corson,[8] in 1925, successfully age-hardened alloys other than those of aluminum. He succeeded in hardening copper containing percentages of Iron-, Cobalt-, and Nickel-Silicides up to 5%.

Various other investigators have since confirmed the observations of Corson and considerable work has been done on other metals. Precipitation hardening has opened up a wide field for investigation, fraught with possibilities of commercially important alloys.

More recently, investigation of the age-hardening of silver alloys have been carried on, and some encouraging results have been obtained. With a sterling silver containing 7.5% $CuAl_2$ that was quenched from 650°C and subsequently annealed at 325°C, Wise[5] obtained a tensile strength of approximately 80,000 lbs. in ^{2}. Gregg,[6] with a silver alloy containing 3% $CuAl_2$ that was quenched from 875°C and annealed at 371°C obtained a maximum hardness of 95 on the Rockwell "E" scale.[7]

The most favorable results in the age-hardening of silver have been obtained with the use of $CuAl_2$ as the alloying material. In view of the low price of silver, an increased use of this metal in industry may be anticipated and with this, further research for age-hardening alloys of the metal.

The work submitted in this paper was done to determine the rate of precipitation of $CuAl_2$ in the silver-rich Ag-Cu-Al alloys. It is generally recognized that the electrical conductivity of age-hardening alloys changes as precipitation takes place, and by the change in electrical conductivity of the alloy, the minimum age-hardening temperature was determined. The rate of precipitation was also investigated by the change in conductivity of the alloy when annealed at different temperatures.

In order to determine the best annealing temperature at which to age-harden the alloys, hardness tests on specimen annealed for different lengths of time at different temperatures were made. The results of all these experiments are submitted herewith.

EXPERIMENTATION

The purity of the silver used in these experiments was found to be 99.9% and of the aluminum 99.+%. Electrolytic copper was used and no analysis of it was made.

To facilitate the addition of copper and aluminum to the silver in the right proportions, a compound of $CuAl_2$ was prepared by melting together 46 parts by weight of aluminum and 54 parts by weight of copper, in a graphite crucible in an electric furnace. The crucible was kept covered, and to prevent oxidation of aluminum, the metals were covered with powdered charcoal. The compound was cast and used in the preparation of the silver alloys to be investigated.

Two separate alloys were prepared for the electrical conductivity tests, one with 3% $CuAl_2$ and one with 4% $CuAl_2$. In the preparation of these alloys the $CuAl_2$ was placed in the bottom of a graphite crucible, the silver was placed on top of the $CuAl_2$ and the mass covered with powdered charcoal. The crucible was kept covered until the metals were molten, when it was removed for two half minute intervals while the molten metals were stirred with a silica tube to insure a homogenous mixture. These melts were cast into wire bars, in carbon molds. The bars, approximately 3mm square and 5cm long, were hammered and drawn through a succession of dies to give a wire about 0.6 mm in diameter. Frequent annealing was found to facilitate both drawing and hammering. Without annealing, the alloy should showed a tendency to scale and split.

The wires were wrapped around a ½ in. silica tube, 4½ in. long and fastened by a nickel wire. The ends of the silver wires were left free to enable connections to the busbars to be made direct. For quenching this wire, the wrapped tube was heated in an electric tube furnace. A reducing atmosphere was maintained by dipping the wire in lubricating oil, and by placing charcoal in each end of the furnace tube and sealing the ends with glass wool to prevent excessive circulation of air through the tube. No oxidation or etching was apparent on the surface of either wire. The quenching was done in water at about 20°C. Annealing at temperatures above 250° was done in the electric tube furnace, with similar precautions against oxidation. All temperatures in the tube furnace were read with a nickel-iron thermocouple. Annealing at temperatures below 250°C was done in an oil bath, the temperatures being measured by means of a mercury thermometer.

All electrical resistance measurements were made with a Wheatstone bridge, fitted with brass busbars and copper connecting wires, attached directly by means of two way clamps to the ends of the silver wire. The temperature at which the resistance was read was kept constant at 24°C by means of an insulating oil bath.

In the hardness tests, the alloy containing 3% $CuAl_2$ was prepared in the same way as the alloys for wire, but was cast in carbon mold into a bar 2 mm thick by 1.5 cm wide. This bar was cold rolled to give a thickness of

1 mm. It was then cut into 33 specimens and these were heated in the electric tube furnace for 1 hour at 800°C and quenched in water.

Specimen were annealed for various lengths of time at temperatures of 300°, 400°, and 500°C. The hardness tests were made on a Rockwell machine, "B" scale, using a 100 Kg load and a 1/16 in. ball.

TABLE I

The change in Electrical Resistance of the 3% $CuAl_2$ alloy, quenched from 800°C.

Length of wire - 100 cm

Diameter of wire - 0.06 cm

Time of Heating (Minutes)	Resistance (ohm's)	Change in Reisistance (%)
Cold Worked	.864	
15	.804	6.9%
45	.690	20.1%
60	.690	20.1%

TABLE II

The change in the Electrical Resistance of the 3% $CuAl_2$ alloy, annealed at 225°C.

Length of wire - 100 cm

Diameter of wire - 0.06 cm Quenched from 800°C.

Time of Heating (Minutes)	Resistance (ohm's)	Change in Resistance (%)
0	.690	
30	.675	2.1%
60	.672	2.6%
90	.664	3.7%
120	.663	3.9%
150	.660	4.4%
180	.656	5.0%
210	.656	5.0%

TABLE III

The Change in the Electrical Resistance of the 3% $CuAl_2$ alloy, annealed at 250°C.

Length of wire - 100 cm

Diameter of wire - 0.06 cm Quenched from 800°C

Time of Annealing (Minutes)	Resistance (ohm's)	Change in Resistance (%)
0	.680	
30	.647	4.9%
60	.645	5.1%
90	.634	6.7%
120	.637	6.4%
180	.639	6.0%

TABLE IV

The Change in the Electrical Resistance of the 4% $CuAl_2$ alloy annealed at 650°C.

Length of wire - 70 cm

Diameter of wire - 0.06 cm Quenched from 800°C.

Time of Heating (Minutes)	Resistance (ohm's)	Change in Resistance (%)
	.768	
30	.605	21.3%
90	.575	25.0%
120	.536	30.1%
150	.518	32.5%
210	.500	34.9%
240	.482	37.2%
270	.474	38.3%
300	.461	40.0%
360	.445	42.0%
420	.434	43.5%

TABLE V

The Change in the Electrical Resistance of the 4% $CuAl_2$ alloy, annealed at 200°C.

Length of wire - 65 cm.

Diameter of wire - 0.06 cm. Quenched from 800°C.

Time of Annealing (Minutes)	Resistance (ohm's)	Change in Resistance (%)
	.420	
30	.405	3.5%
60	.400	4.7%
90	.395	5.9%
120	.392	6.6%
150	.390	7.1%
180	.388	7.6%

TABLE VI

The change in hardness of the 3% $CuAl_2$ alloy at various annealing temperatures.

Quenched from 800°C.

Annealing Temperature = 300°C.		Annealing Temperature = 400°C.		Annealing Temp. = 500°C.	
Annealing Time (Minutes)	Hardness	Annealing Time (Minutes)	Hardness	Annealing Time (Minutes)	Hardness
Quenched	12	Quenched	12	Quenched	12
5	45	5	63	5	52
25	67	15	60	15	39
35	60	30	63	30	45
45	64	60	68	60	44
60	71	90	59	90	43
90	75	135	62	120	42
150	71	180	57	180	38
210	73	210	61	240	36
		1290	40		

Figure 1.

Equilibrium diagram of Ag-Cu, Ag-Al, and Cu-Al showing pseudo-binary series Ag-$CuAl_2$

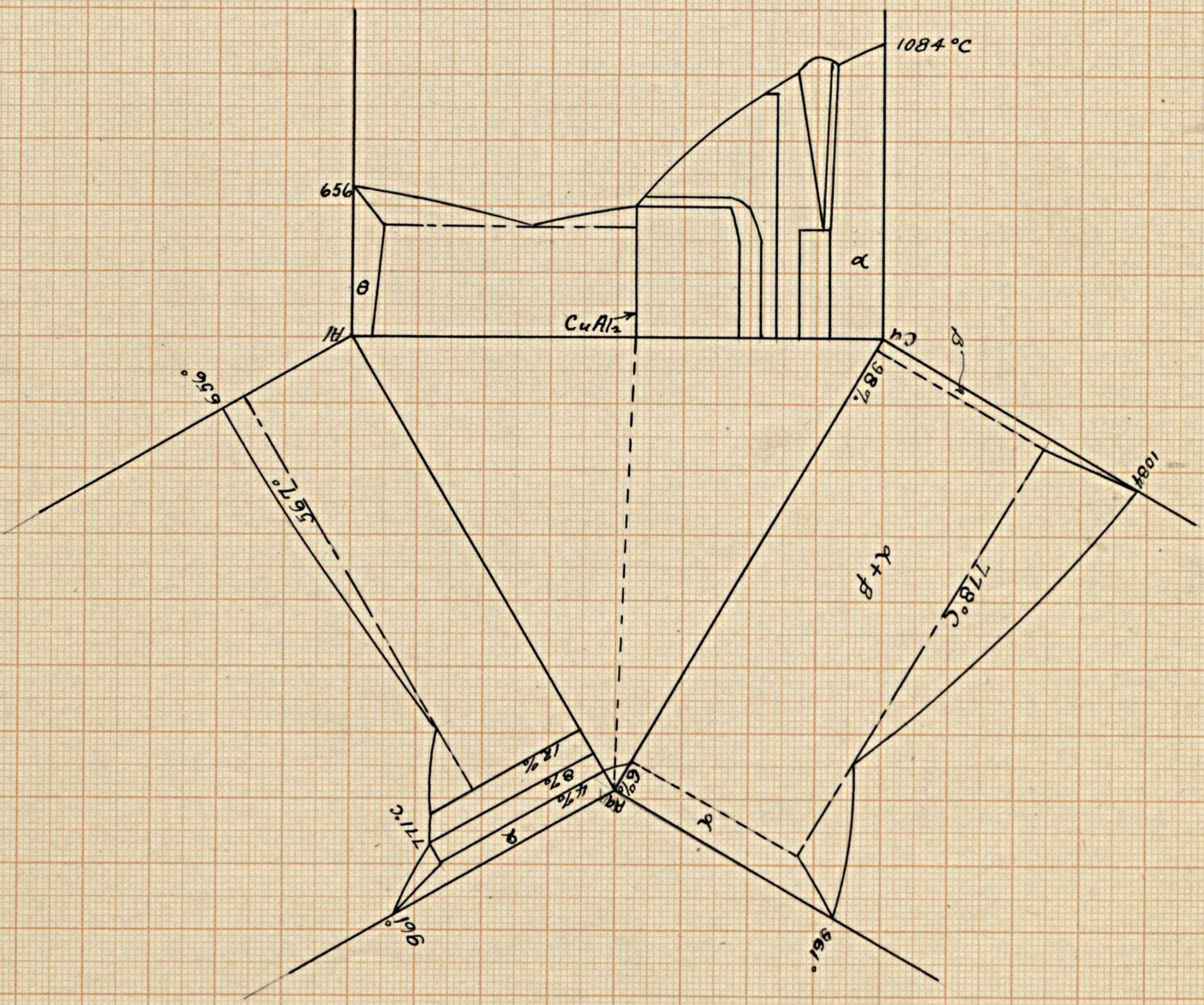


Figure 2.

Equilibrium Diagram showing solubility of $CuAl_2$ in Ag, as constructed from Figure 1.

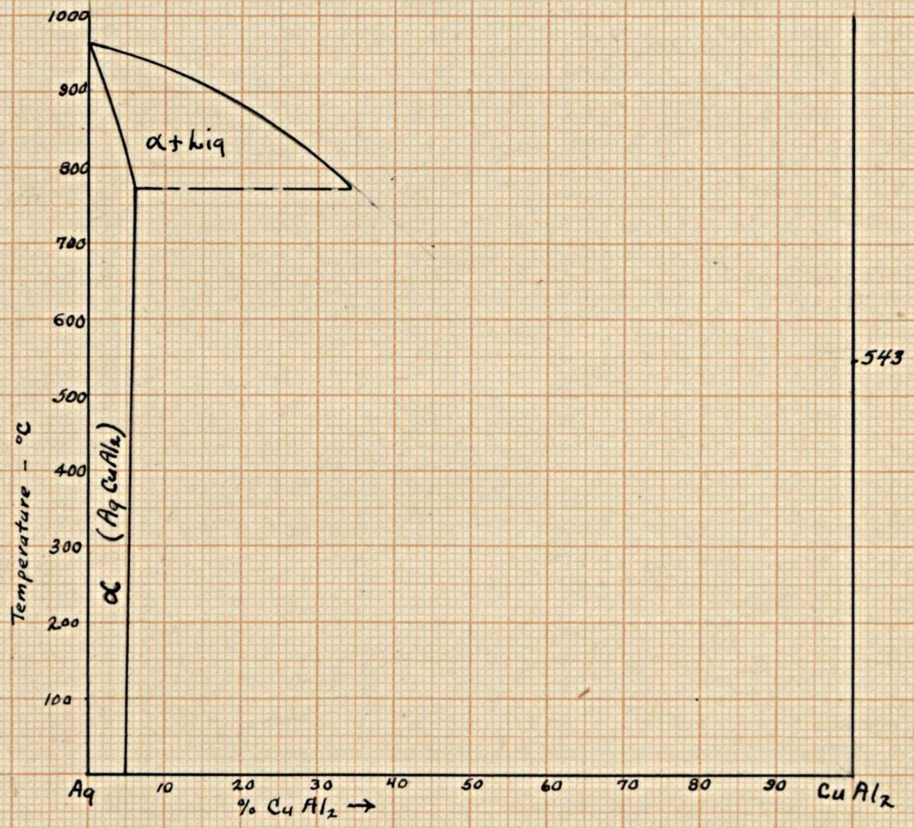
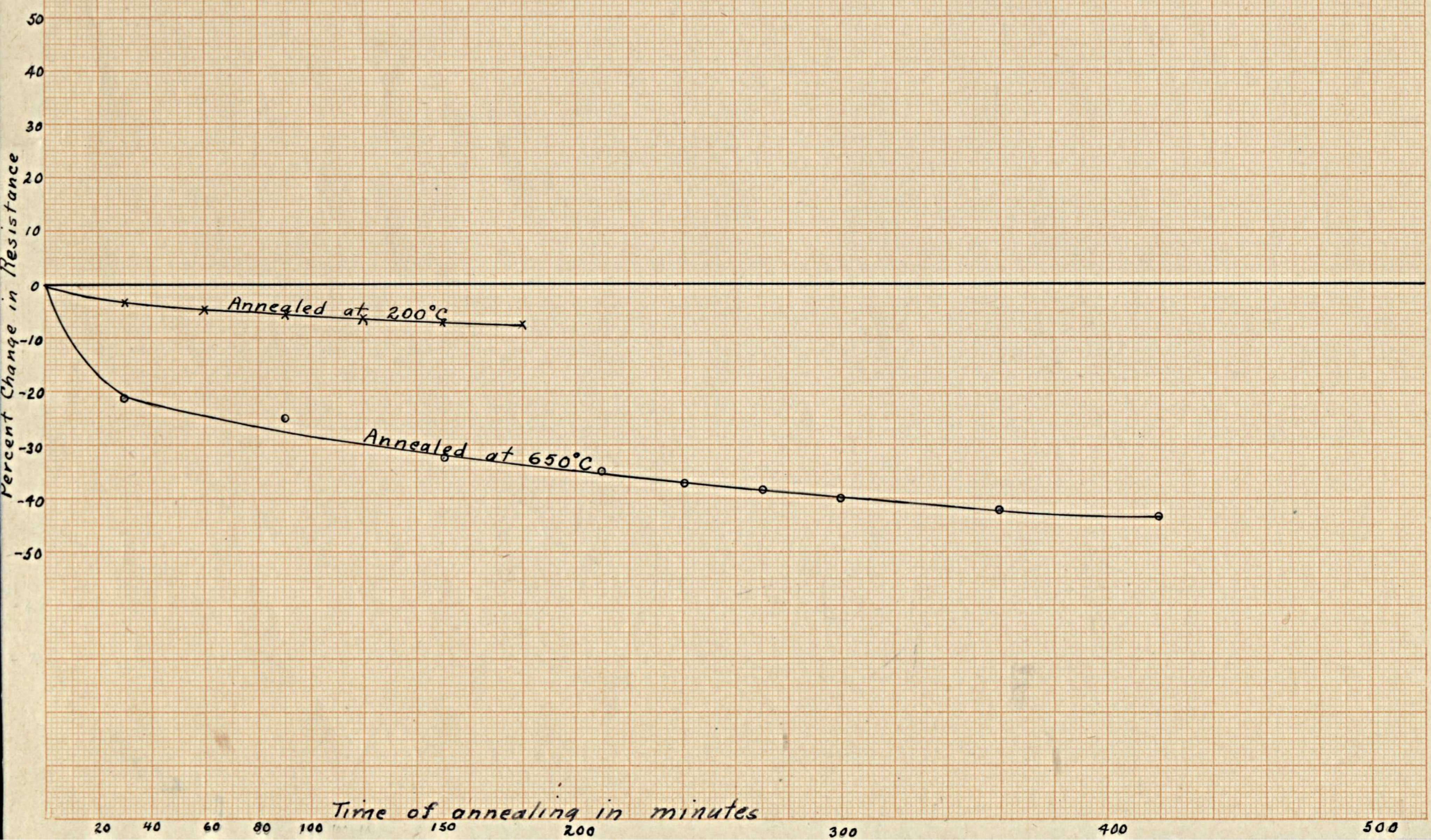


Figure 3

Effect of Annealing the 3% $CuAl_2$ Alloy on the Electrical Resistance

Figure 4

Change in Electrical Resistance in the 4% $CuAl_2$ Alloy, due to Annealing.



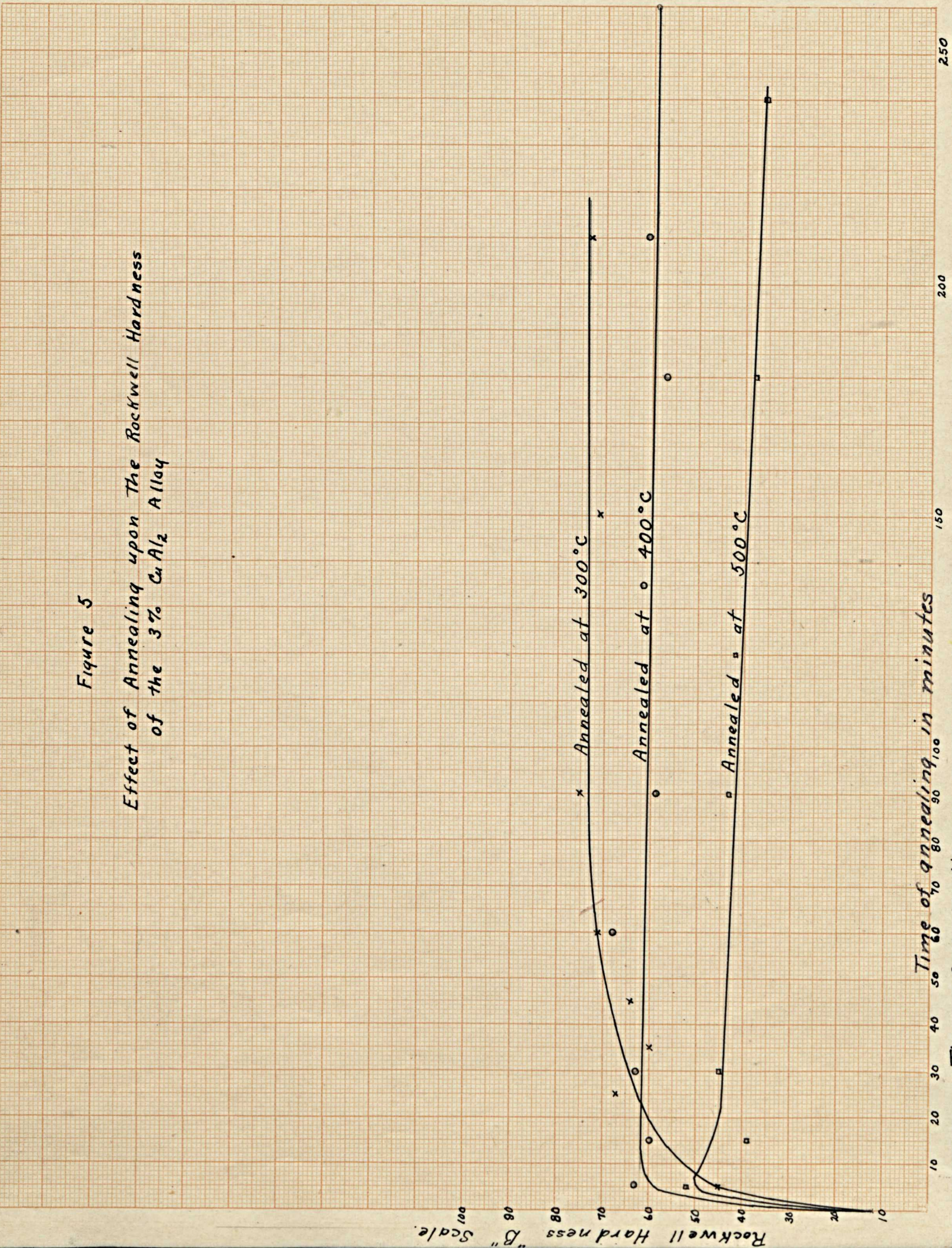


Figure 5
Effect of Annealing upon The Rockwell Hardness of the 3% CuAl2 Alloy
Annealed at 300°C
Annealed at o 400°C
Annealed ▫ at 500°C
Time of annealing in minutes
Rockwell Hardness "B" Scale.
10
20
30
40
50
60
70
80
90
100
150
200
250

DISCUSSION

The three binary alloys Cu-Ag, Cu-Al, and Ag-Al are shown in Fig. 1, with the pseudo-binary series indicated by the line connecting the Ag and $CuAl_2$ points on the equilateral triangle. No definite pseudo-binary equilibrium diagram has been worked out for the Ag-$CuAl_2$ series, but from the two branches of the binaries Ag-Cu and Ag-Al in the Ag-rich field, the diagram as shown in Fig. 2 has been constructed. This diagram indicates that the solubility of $CuAl_2$ in silver increases with temperature.

In order to drive all of the $CuAl_2$ into solid solution in both the 3% and 4% alloys, a quenching temperature of 800°C was chosen. The resistance of the cold-worked and annealed wires are tabulated in Table I, where it is shown that the increases in resistance due to cold work has been removed. The decrease in resistance due to precipitation annealing is tabulated in Tables II, III, IV, and V, and shown graphically in Figs. 3 and 4.

These results show that annealing decreases the resistance of both the 3% and 4% $CuAl_2$ silver alloys. Figure 4 shows that the resistance decreases very rapidly at first at 650°C, and that it is still gradually decreasing at the end of 7 hours annealing, although the rate of decrease becomes less.

Figure 4 also shows that there is a gradual decrease in electrical resistance in the 4% $CuAl_2$ alloy when it is annealed at 200°C, indicating a slow precipitation of $CuAl_2$ at this temperature. The 3% $CuAl_2$ alloy, when annealed at this temperature showed no change in resistance, but a slight change at 225°C (Figure 3). From These results, it appears that the minimum annealing temperature for a 3% $CuAl_2$ silver alloy would lie somewhere between 200°C and 225°C, and minimum annealing temperature for a 4% $CuAl_2$ silver alloy slightly below 200°C. This would seem to indicate that the higher the percentage of $CuAl_2$, the lower will be the minimum annealing temperature. This is what one would naturally expect, since the greater the degree of saturation of silver with $CuAl_2$, the greater would be the tendency of the $CuAl_2$ to precipitate.

Considerable difficulty was encountered in getting the $CuAl_2$ back into solution after it had been once precipitated. Long heating at 800°C with as many as 8 quenchings were necessary to obtain a constant resistance. In no case was the resistance increased to its original value, although in all cases the resistance was appreciably increased compared to that in the annealed state. The failure to obtain a resistance equal to that before the wire was annealed may be attributed to oxidation or to grain growth. No investigation of the effect of either of these factors was attempted.

The maximum hardness obtained with the 3% $CuAl_2$ alloy was 75 on the Rockwell "B" scale. This hardness was obtained in a specimen that was annealed for 1½ hours at 300°C. The results of annealing at this temperature, as shown in Figure 5 indicate that the hardness of this alloy increases gradually up to 1½ hours and remains about constant up to 3½ hours annealing. The specimen annealed at 400°C shows a more or less constant hardness, with a very gradual decrease in hardness with protracted annealing at this temperature. With the alloy annealed at 500°C, the maximum hardness would seem to be reached within a time of less than 5 minutes. No period of annealing shorter than 5 minutes was tried. The hardness of this alloy decreases appreciably with a longer annealing time at this temperature.

CONCLUSIONS

In view of the above results, it may be said that critical dispersion and precipitation of $CuAl_2$ in the 3% $CuAl_2$ - silver alloy will take place at temperatures below 300°C but that no evidence of agglomeration of these dispersed particles at temperatures below 300°C is shown. The minimum age-hardening temperature of this alloy is between 200°C and 225°C. From these results, the most suitable temperature for age-hardening would seem to be about 300°C.

No attempt was made to determine the effect of annealing upon the grain size of the alloy, although this may have had some effect upon the final hardness, particularly with those specimens annealed at higher temperatures. Annealing at temperatures above 400°C, gives a rapid precipitation of $CuAl_2$, as is shown by the decrease in Electrical Resistance (Figure 4), but is not suitable as an annealing temperature, since specimens annealed at those temperatures are much softer than those annealed at lower temperatures (Figure 5). This is presumably due to agglomeration of precipitated particles, which does not seem to take place at lower temperatures.

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