On the Equilibrium Diagram of Copper-Aluminium Alloy System.*

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The equilibrium diagram of copper-aluminium alloy system has been investigated by numerous workers,[1] the most important researches in recent years being those by Carpenter and Edwards,[2] Curry,[3] Gwyer,[4] Stockdale,[5] and Tasaki.[6]

The results of these investigators especially in the concentrations and temperatures for locating the transformations from one phase to another are in glaring disagreement. The most inaccurate points of this system, on which their opinions differ, lie in the range of concentration of 16% to 50% of aluminium, i.e., the ranges between the intermetallic phases which are called the $\gamma-$, $\delta-$, $\varepsilon-$, $\eta-$, and θ, respectively. Some years ago G. D. Preston,[7] E. R. Jette, A. Westgren, and G. Phragmén[8], and Ichiji Obinata,[9] and more recently A. J. Bradley and Phyllis Jones[10] examined these alloys by means of X-rays. Again, however, the results of the X-ray analyses of this system are not in entire agreement with metallurgical investigations. Therefore, a careful study of the equilibrium diagram of this system seems to be called for.

I. Materials Employed and Preparation of Specimens.

In the present investigation the specimens were prepared from electrolytic copper and aluminium 99.8 per cent. pure. The alloys up to 30 per cent. aluminium were made under charcoal in graphite crucibles in an electric furnace, first by melting most of the copper, then adding the aluminium, and finally the remainder of copper; but in preparing the alloys containing 30 to 50 per cent. of aluminium a mother alloy of 70 per cent. of copper was used as the starting material. The melt thus prepared was agitated with a carbon electrode so as to obtain homogeneity, and then covered with new charcoal powder to protect it from oxidation. Then the melt was cooled and its cooling curve during solidification was obtained by the so-called differential method. As soon as the thermal analysis ended, the specimens were remelted, and cast into iron moulds to prepare them for the measurement of electric resistance, microscopical examination, thermal analyses, etc , in the transformation to a solid state.

All of these specimens were analyzed electrolytically in order to determine the copper content.

II. Experimental Methods.

As above described, thermal analyses were executed in two steps: the first was carried out chiefly for the observation of the phenomena of solidification, and also to find the transformation in solid state ; and the second one for the confirmation of phenomena of the transformation in solid state.

A. Thermal Analysis.

(1) *Differential method used for the investigation of phenomena during solidification.*

The usual method of differential thermal analysis was employed to take the cooling curves during solidification, and its arrangement is shown diagrammatically in Fig. 1 (a). As shown in the figure, the crucible containing the specimen was placed in a nichorme-wound electric furnace,

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1) Le Chatelier, Bul. Soc. d'Encour [4] 10 (1895) 573.
    Guillet, Rev. de Met. (1905) 568.
    Campbell and Methews, J. Amer. Soc. 24 (1902) 253, 26 (1904) 1290.
2) Proc. Inst. Mech. Eng., 1 (1907).
3) J. Phys. Chem., 11 (1907) 425.

4) Z. anorg. Chem., 57 (1908) 117.
5) J. Inst. Metals, 31 (1924) 275.
6) Kinzoku no Kenkyu, 2 (1925) 491.
7) Phil. Mag., 12 (1931) 980.
8) J. Inst. Metals, 31 (1924) 193.
9) Mem. Ryojun coll. Eng., 3 (1931) No. 4.
10) J. Inst. Metals, 51 (1933) 131.

which was heated up to a temperature about 100°C. higher than the melting point of the specimen. During cooling the difference in temperature between the specimen and a nickel piece as the neutral body was read with the deflection of a Leeds and Northrup mirror galvanometer connected to a Alumel-Chromel differential couple; and at the same time the temperature of the specimen was measured with a platin platinum-rhodium thermo-couple. The rate of cooling during solidification was regulated to about 5°C per min. by passing a small steady current through the furnace. In investigating the changes of the solid state it was made less than 5° per min., and in some cases as slow as 3° per min., in order to prevent undercooling as much as possible.

(2) *Differential method used for the investigation of the transformation in solid state.*

A specimen 25 mm. in length and 10 mm. in diameter was cast in a special iron mould, Fig. 1 (b). After proper heat treatment the specimens were inserted in a cylindrical body of nickel through which a hole was bored to hold the specimen, as shown in Fig. 1 (c). They were placed in a horizontal electric furnace, and during both heating and cooling the temperature of the specimen and the difference in temperature between the specimen and the neutral metal were measured as above described.

B. Measurement of Electric Resistance.

Specimens 6 mm. in diameter and 100 mm. in length intended for the measurement of the

Fig. 1.

change of electric resistance with the temperature were cast into an iron mould and completely annealed. The change of electric resistance of these specimens during both heating and cooling was observed in the usual way, by passing a constant current of two amperes through the specimen, the potential drop between the fixed points—namely 2–5 cm. in this experiment—being measured by a potentiometer of the Leeds and Northrup type.

In the experiments carried out in vacuum, the rate of cooling was 3°C per minute, and the rate of heating 1°C per minute.

C. Microscopic Examination.

For the microscopical study chill cast specimens 8 mm. in diameter and 100 mm. in length, whose preparation has been already described, were cut into pieces each 10 mm. in length. These specimens were annealed at the desired temperatures in an electric furnace and quenched in cold water.

Etching of the specimen was carried out with various reagents according to the composition of the alloys, i.e., an Alcoholic ferric chloride solution (30 grs $FeCl_2$ + 20 c.c. conc. HCL + 950 c.c. Alcohol) or Iodine solution (1.2 grs I + 1.2 grs KI + 1.2 c.c. H_2O + 97 c.c. Alcohol) gave fairly good results up to about 80 per cent. copper, and for the alloys of 80–70 per cent. copper the following reagents were satisfactorily employed to develope the figures:

(1) Cupric chloride 10 grs + Mg Cl_2 20 grs + HCL 20 c.c. + Alcohol to make up to 1000 c.c.

(2) Specimens attacked first with iodine solution and then with 10 per cent. nitric acid alcohol solution.

Also a good result could be obtained in etching the alloys of 80–70 per cent. copper electrolytically in alcoholic nitric acid solution.

III. Results of Thermal Analysis.

A. During Solidification.

Thermal analyses were made of a complete series of the alloys up to 50 per cent. aluminium. The crucible charges used varied in composition by step of 0.3 per cent. in the alloys containing between 84 and 70 per cent. of copper, and by the step of 1 per cent. or more in the alloys containing between 70 and 50 per cent. of copper, and they weighed 100 to 200 grs according to the composition.

The arrest or change points of cooling curves are summarized in Table 1, and plotted in Fig. 2. Some examples of the cooling curves are given in Fig. 3.
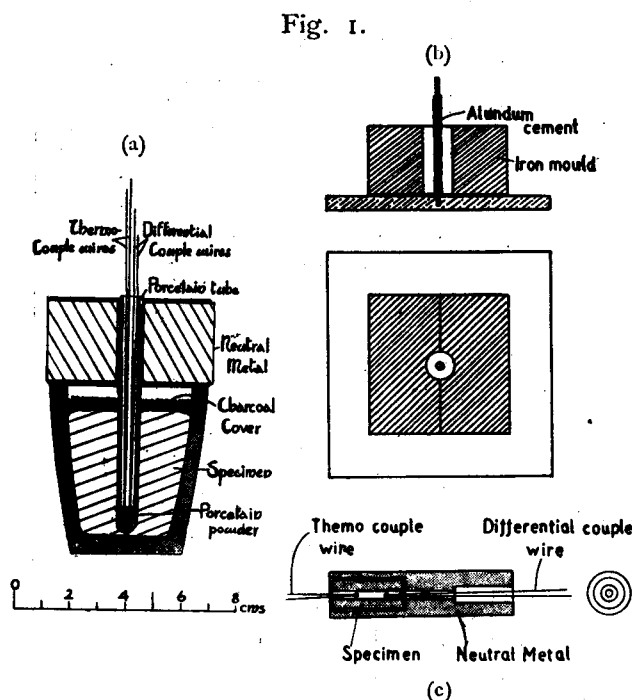
Table 1.

Results of Thermal Analysis.

Composition (by analysis) %		Points of change or arrest				
Copper	Aluminium					
94.96	5.00	1068				
94.02	Remainder	1056				
91.98	"	1042	1037			
90.08	"	1041	970			528
88.87	"	1048				531
88.01	"	1050				535
85.93	13.87	1048	1037	826	780	528
85.40	14.50	1045			782	528
84.70	Remainder	1043	970		780	
84.10	"	1037			780	
83.68	"	1035	960		795	
83.40	"	1034	1020	846	795	
83.10	"	1032	1018	950	838	
82.60	"	1026	1020		860	
82.41	"	1025	1020		865	
82.15	"	1020			866	
82.00	17.92	1018			875	
81.50	Remainder	1016			870	
81.00	"	1010	958		875	
80.70	"	1007			876	
80.50	"	1005			873	
80.10	"	1000			875	
80.00	"	994	958		865	
79.80	"	993	960		850	
79.48	"	988	950		855	
79.16	20.73	984	958	852	678	
79.00	Remainder	982	960	851	675	
78.80	"	981	950	848	676	
78.00	"	968	958	852	680	
77.42	"	955		846	670	

Copper	Aluminium					
77.03	Remainder	950		850	670	563
76.81	"	942		845		570
76.35	Remainder	932		843		575
76.10	23.72	925		846		583
75.80	Remainder	920		848		590
75.44	24.42	914		850		584
75.00	Remainder	906	830	585	554	
74.00	"	890	848	610	590	562
73.10	"	865	840	617	584	550
72.20	"	852		620	589	580
72.02	"	845		622	584	550
71.16	"	828		625	584	
70.60	"	823		620	582	550
70.42	"	813		622	584	549
70.00	29.77	813		622	584	549
69.13	Remainder	798		623	586	550
68.00	"	777		624	586	550
66.95	"	756		624	583	550
65.80	"	738		623	588	540
63.20	"	696		628	593	530
61.50	"	670		623	591	540
60.12	"	655		624	591	
59.08	"	643		624	591	
57.32	"	624			593	
56.72	"	620			591	
55.77	"	609			592	
54.84	"	602			592	
54.77	"	600			592	
54.22	"	596			592	
53.84	"	592			590	
52.10	"	590			545	
48.80	"	587			547	
44.28	"	584			548	
40.03	"	572			548	

Fig. 2.

O Differential thermal analyses. (cooling.)

● Differential thermal analyses in solid state. (heating.)

□ Electric resistance method. (heating.)

LIQUID

α   β   γ₁   γ₂   ε₁   ε₂   δ   η₁   η₂   ζ   θ

Temperature °C: 1100° 1050° 1000° 950° 900° 850° 800° 750° 700° 650° 600° 550° 500°

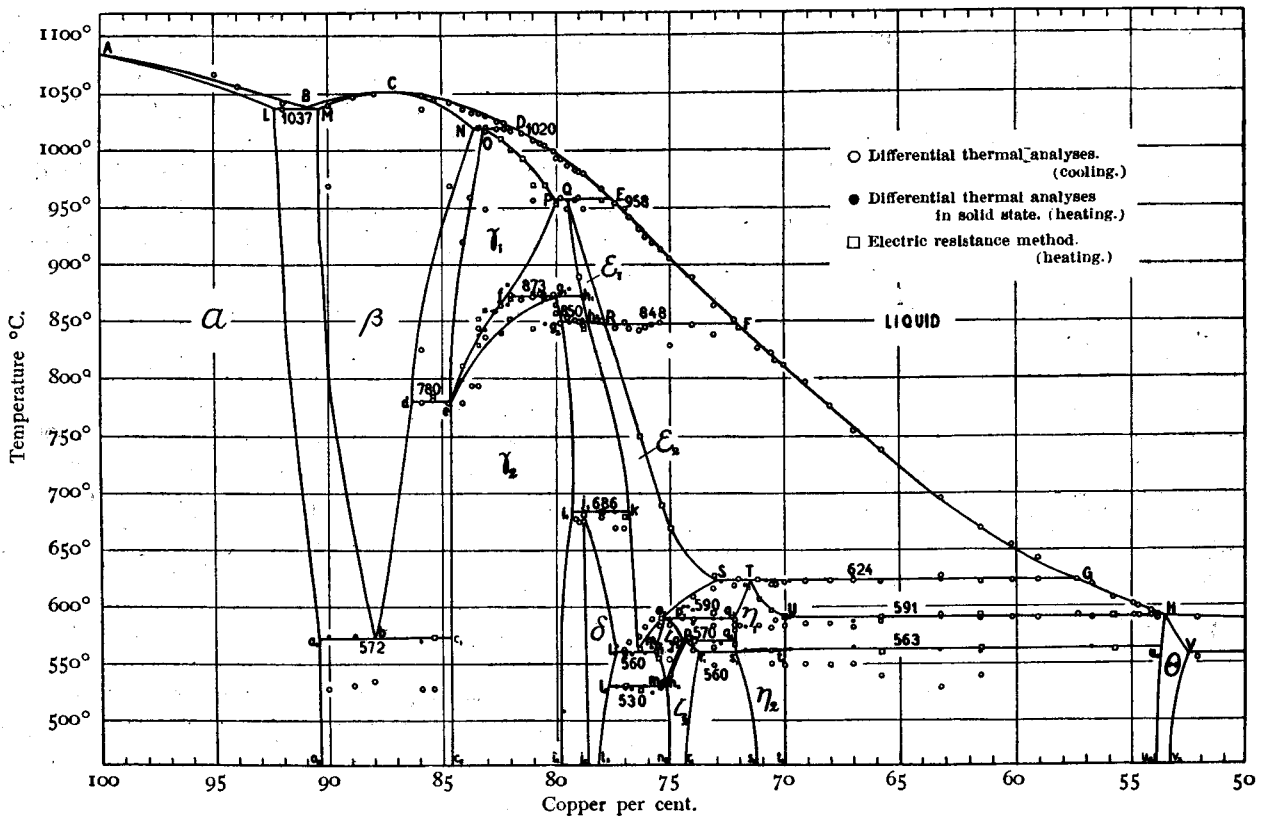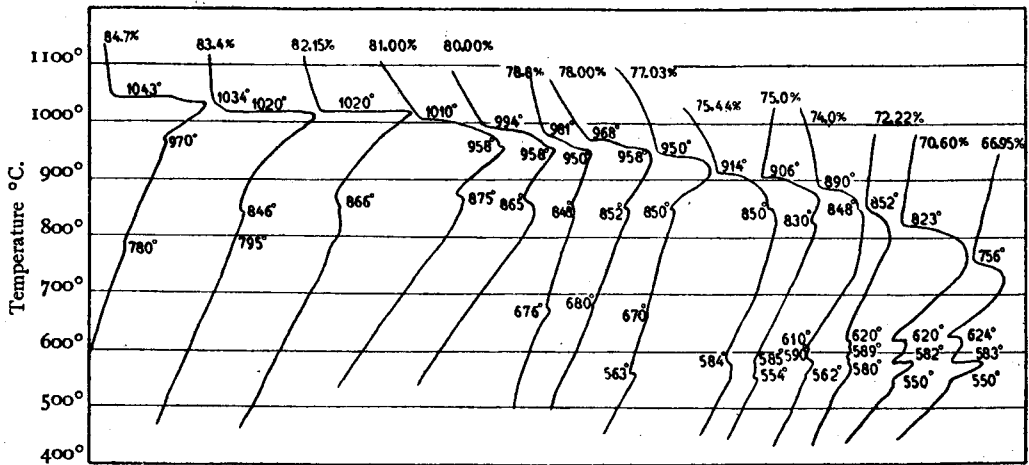Copper per cent: 100 95 90 85 80 75 70 65 60 55 50

Fig. 3.

Deflection of the Difference Galvanometer.

According to the experiments above mentioned, most of the phenomena of solidification were manifested, and many points of change or arrest were observed. The freezing point curve thus obtained agrees fairly well with the results of Stockdale. The details of the invariant equilibrium lines are summarized in Table 2.

Table 2.

| Equili-brium lines	The kind of reactions		Temp. °C.	The range of concentration Cu %
LBM	Eutectic reaction	melt ⇌ α + β	1037	92.4–90.4
NOD	Peritectic reaction	melt + β ⇌ γ₁	1020	83.7–82.0
PQE	Peritectic reaction	melt + γ₁ ⇌ ε₁	958	80.0–77.6
RF	Polymorphic reaction	ε₁ ⇌ ε₂	848	77.5–72.0
STG	Peritectic reaction	melt + ε₂ ⇌ η₁	624	73.0–57.3
UH	Peritectic reaction	melt + η₁ ⇌ θ	591	70.0–53.5
VTW	Eutectic reaction	melt ⇌ θ + K	548	52.5– 5.7
$a_1 b\, c_1$	Eutectoid transformation	β ⇌ α + γ₂	572	90.3–84.5
de	Eutectoid transformation	γ₁ ⇌ β + γ₂	780	85.4–84.5
$f g_1 h_1$	Peritectoid transformation	γ₁ + ε₁ ⇌ γ₂	873	82.2–78.9
$s_2 h_2$	Polymorphic transformation	ε₁ ⇌ ε₂	850	79.8–78.5
$i_1 j_1 k$	Peritectoid transformation	γ₂ + ε₂ ⇌ δ	686	79.2–76.8
$l_1 m_1 n_1$	Eutectoid transformation	ε₂ ⇌ δ + ζ₁	560	77.4–75.7
$l_2 m_2 n_2$	Eutectoid transformation	ζ₁ ⇌ δ + ζ₂	530	77.8–75.2
$o_1 p_1 q_1$	Peritectoid transformation	ε₂ + η₁ ⇌ ζ₁	590	75.4 72.2
$o_2 p_2 q_2$	Peritectoid transformation	ζ₁ + η₁ ⇌ ζ₂	570	74.4–72.1
$r_1 s_1$	Polymorphic transformation	η₁ ⇌ η₂	560	73.8–72.1
$t_1 u_1$	Polymorphic transformation	η₁ ⇌ η₂	563	70.0 53.7

As shown in Fig. 2, the invariant equilibrium

reactions observed on solidification almost agree with the result obtained by Stockdale, although there exists a slight modification in our diagram. The reactions Melt⇌α+β at 1037° (LBM) and Melt + ε₁⇌ε₂ at 848° (RF) have been admitted by most investigators, and the reactions Melt+β⇌γ₁ at 1020° (NOD) and Melt+γ₂⇌ε₁ at 958° (PQE) have also been found by Tasaki and Stockdale, whose explanation of them is not in agreement but the present writer supports the latter's opinions. The thermal changes which appear at 850° or 848° ($g_2\, h_2$ RF) are very definite, but under microscopic examination in solid state there is no change of structures of the alloys which were quenched from above and below this transformation. In order to account for this thermal change, the author feels sure that there is a polymorphic change in the ε phase, and so calls the phase above this transformation ε₁, and below it ε₂.

Two invariant lines STG and UH are mentioned as peritectic reactions in the above table, but alloys under these conditions show in the microscopic examination no evidence of the typical peritectic structures. The evolution of heat at these lines is very vague, and there appear two definite breaks in the liquidus at G and H. According to the facts above described the present writer concludes that there appear some special cases of the peritectic reactions along the line STG and UH.

It has been a question whether CuAl₂ compound crystallizes directly from the melt or not. Fig. 4 shows the cooling curves of alloys of the composition near CuAl₂ compound. The present writer has found that an alloy of the exact composition CuAl₂ has a freezing interval of nearly 5° and contains two phases at 500°, a fact already demonstrated by Stockdale.[1] The θ phase near CuAl₂ probably has no freezing interval, and it crystallizes directly from the melt.

Fig. 4.
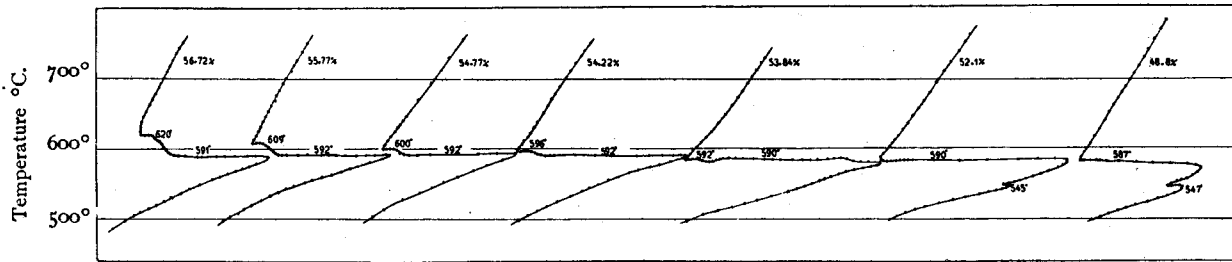
Deflection of the Difference Galvanometer.

According to the present experiments the fields of the *u, β, θ* and *κ* phases almost agree with those Stockdale. But in the alloys containing 85–50 per cent. of copper, there is a divergence of opinion about the phases and the range of their concentration. Some methods must be adopted for the accurate determination of solid transformation in the above alloys.

B. Solid Transformation.

There are two points that have not been agreed upon by Stockdale : the first is the nature of the transformation which takes place along *cf* $g_1 h_1$; and the second is the manner of the real equilibrium of the alloys containing from 20 to 30% of aluminium. For the determination of the above points, the specimens were annealed for a long time to bring them completely into the state of lower temperatures. Of the alloys, those containing 16–21% of aluminium were annealed 5 hours at 900°, cooled to 500° in the furnace, and then annealed 7 days at the latter temperature. Those alloys containing 21–54% of aluminium were annealed 10 hours at 580°, cooled to 500° slowly in the furnace, and annealed 10 days at about 500°. Then they were cooled very slowly in the furnace. Once more they were heated at about 250°C. for 1 month in an automatic regulating electric air bath. Then we obtained the heating and cooling curves of the specimens with the differential method already mentioned. The rate of heating and cooling was about 3°C per minute. The results of the experiments are given in Table 3, and plotted in Fig. 2.

Table 3. Results of Thermal Analysis

Copper %	Pointe of change or arrest °C				
90.08	575	(530)			
88.87	576	(560)			
85.93	570	(510)	780		
84.10	800	(780)			
83 40	840	(838)			
83.10	842	(830)			
82.60	860	(838)			
82.15	883	(880)	855		
81.50	872	(870)			
81.00	872	(872)			
80.70	878	(872)	860		
80.50	876	(870)	848		
80.00	873	(870)	958		
79.48	850	(848)	880	(870)	958
78.80	686	(680)	853	(850)	870
78.00	684	(678)			
77.42	530	(528)	566	(560)	686 (681)
77.03	528	(528)	560	(560)	
76.67	528	(530)	558	(565)	
76.10	530	(530)	560	(563)	
75.80	525	(530)	566	(565)	
75.44	529	(530)	558	(590)	
75.00	568	(560)	590	(590)	
74.43	572	(560)	590	600	(600)
74.25	572	(570)	601	(606)	
74.00	568	(570)	586	(590)	598 (610)
73.14	570	590	618		
72.80	568	590	622		
71.71	564	583	620		
71.16	562	624			
70.78	563	623			
70.42	563	624			
70.00	562	592			
69.78	562		592	624	
66.95	565		587	626	
63.20	563		591	624	
61.50	560		589		
56.72	565		590		

Figures in brackets show points of change or arrest on cooling

Fig. 5.

Deflection of the Difference Galvanometer.

11) J. Inst. Metals, 52 (1933) 111.
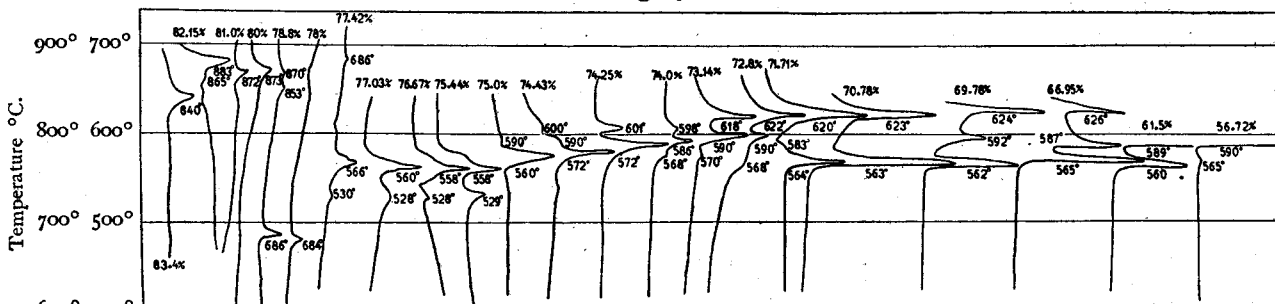
Fig. 5 shows some examples of heating curves. On heating the alloys containing 18 to 21 per cent. aluminium, an absorption of heat was observed at about 870°C, and a similar reaction was also found in lower temperature with increasing of copper content. Stockdale reported that this absorption of heat was due to a rearrangement of the atoms within the crystals. The present writer suggests that the evolution or absorption of heat of the alloys containing 84 to 82 per cent. copper along cf line may be caused by the change of a polymorphic transformation. Microscopic examination shows that the structure of the alloys quenched from above or below that line is exactly the same.

But the alloys containing 82 to 79 per cent. copper have a horizontal line $fg_1 h_1$, at 873°, caused by the peritectoid reaction $\gamma_1 + \varepsilon_1 \rightleftarrows \gamma_2$. From the results of thermal analyses, in Fig. 5 we see that this peritectoid reaction is not very sharp and is observed to occur in some temperature range even in heating and cooling at the rate of 3°C per minute. This phenomenon is further confirmed by microscopic examination, although the measurements on thermal change indicate inaccurate transformation.

The microscopic structures of the alloys in the area $fPQh_1 g_1$ above the $fg_1 h_1$ line and in the field $g_2 g_1 h_1 h_2$ below the line $g_1 h_1$ are heterogeneous, and those of the alloys below fg_1 line and in the field $fPOe$ are homogeneous. From these facts the transformation at 873° ($fg_1 h_1$) must be attributed to a invariant reaction as $\gamma_1 + \varepsilon_1 \rightleftarrows \gamma_2$. Since the field $cfg_1 e$ in which the two phases γ_1 and γ_2 must exist has not been determined by the thermal analyses and the microscopic examinations, etc., in our diagram, the line eg_1 is drawn on theoretical grounds.

The alloys containing about 79 per cent. copper have two arrests which were found by Stockdale at 865° and 846° compared with the value 873° and 850° respectively here obtained. The former arrest might be due to a peritectoid reaction $\gamma_1 + \varepsilon_1 \rightleftarrows \gamma_2$ and the latter might be due to a polymorphic transformation $\varepsilon_1 \rightleftarrows \varepsilon_2$. Some polymorphic transformation which takes place along $g_2 h_2 RF$ may exist according to the results of the thermal analyses, although the microscope discloses no change in structure.

In the range of concentration of 80 to 70 per cent. copper two new phases were found, by the existence of which the equilibrium state of this region could be logically and satisfactorily be explained. The line $i_1 j_1 k$ at 686° is due to the peritectoid transformation $\gamma_2 + \varepsilon_2 \rightleftarrows \delta$, the horizontal running from 79.3 to 76.8 per cent. copper. For instance, the thermal change at 686° in heating curves of the alloys containing 78.8 and 78.0 per

cent. copper shown in Fig. 5 is caused by this peritectoid transformation. In this reaction heating curves have been much more likely to give constant results than cooling curves. The evolution and absorption of heat due to the above reaction are the greatest in the alloys containing 78.8 per cent. copper. Therefore ; the point j_1 exists perphaps at about 78.8 per cent. copper. The existence of the constituent δ, which shows some range of solid solution, is also confirmed by the microscopic experiments as described later.

The line $l_1 m_1 n_1$ denotes the eutectoid transformation $\varepsilon_2 \rightleftarrows \delta + \zeta_1$, which has been found by many investigators. This eutectoid reaction takes place at 560°, the horizontal running from 77.4 to 75.7 per cent. copper. Above this line the ε_2 are stable and at this temperature the ε_2 phases break down to the δ and ζ phases. In the diferential thermal analyses the present writer could clearly find the line $o_1 p_1 q_1$ at which the peritectoid transformation $\varepsilon_2 + \gamma_1 \rightleftarrows \zeta_1$ takes place. As shown in Fig. 5 the thermal arrests in the heating curves of the alloys containing 75 to 72.8 per cent. copper are clearly found at 590°. According to the present equilibrium diagram, in a narrow range of temperatures which show the peritectoid transformations $\varepsilon_2 + \gamma_1 \rightleftarrows \zeta_1$ at 590°C, $\zeta_1 + \gamma_1 \rightleftarrows \zeta_2$ at 570°C and the invariant line due to the polymorphic transformation $\gamma_1 \rightleftarrows \gamma_2$ at 560°C. Because the above three reactions occurred in succession, three definite arrests in thermal curves were not observed.

The horizontal $o_2 p_2 q_2$, denoting the peritectoid transformation $\zeta_1 + \gamma_1 \rightleftarrows \zeta_2$, was obtained from heating curves. It was also found readily in cooling curves, though the results were rather irregular.

The eutectoid transformation $\zeta_1 \rightleftarrows \zeta_2 + \delta$, shown by the horizontal $l_2 m_2 n_2$, was recognized clearly in heating curves, although the arrest points at 530° were minute. This transformation, could hardly be ascribed to eutectoid reaction, because no change was found in the microscopic structures of the alloys which were quenched from above and below the line $l_2 m_2 n_2$. The heat absorption, however, was most remarkable in the alloy containing 75.44 per cent. copper. And as it gradually decreased with the decrease of aluminium content as shown in Fig. 5, it may be said to be a eutectoid reaction.

There are remarkable thermal changes in the η phase on the line $s_1 t_1$ at about 560°. This line $s_1 t_1$, denoting a polymorphic transformation $\eta_1 \rightleftarrows \eta_2$ was definitely obtained from both heating and cooling curves. The most remarkable arrest point of this reaction was observed at about 70 per cent. copper. The horizontals $r_1 s_1$ and $t_1 n_1$ are invariant lines at 560° and 563° respectively caused by a polymorphic transformation of the η

constituent. On heating, the heat absorption due to this polymorphic transformation decreases very rapidly as the content of aluminium decreases, but it gradually decreases as the content of aluminium increases. This phenomenon we recognize easily from the heating curves in Fig. 5. We see in this figure that an alloy of 66.95 per cent. copper shows a remarkable heat arrest at 565°C; but an alloy of 72.8 per cent. copper shows an inaccurate small arrest at about 568°C which corresponds to the invariant reactions $\zeta_2 + \eta_2 \rightleftarrows \gamma_1$ and $\gamma_1 + \zeta_2 \rightleftarrows \zeta_1$ occurring at the same time.

The alloy of 61.50 per cent. copper shows a perceptible small arrest at 560°; whereas the alloy containing 56.72 per cent. copper, namely, in the neighbourhood of the θ phase, shows clearly a small arrest at 565°.

IV. Results of the Measurement of Resistance.

A. In temperature range.

The nature of all invariant lines and the temperatures of some solidus lines were studied by the measurement of electric resistance of the specimens. The results of these experiments are summarized in Table 4, and plotted in the diagram of Fig. 2, where they are represented by the symbol □. Some of them are illustrated in Fig. 6.

Table 4.

Results of Electric Resistance

Copper %	Po'nts of arrests or change °C					
85.40	574	(538)	784	(780)		
84.10	816	(800)	920			
83.40	830	854	(836)	1020		
83.10	840	860	(840)	1020		
82.41	840	866	(860)	1010		
82.00	853	870	(870)	1000		
81.50	872	(868)	995			
81.00	844	(850)	876	(878)	970	
80.50	850	(870)	970			
80.00	858	(876)	956	(958)		
78 80	684	(686)	845	(840)	890	(870)
78 00	686	(686)	850	(857)		
77.03	530	(530)	560	(558)	680	(670)
76.35	527	563	(560)	750		
75.44	556	(572)	690	(690)		
75.00	540	(570)	670	(675)		
74.00	570	590	610			
73.10	565	595	628			
72.20	568	586	622			
71.16	563	608				
70.60	561	597				
70.00	563	590				
65.80	560	591				
61.50	564	593				
55.77	561	591				

Figures in brackets show points of arrest or change on cooling

From these results the following conclusions are obtained.

The polymorphic change of $\gamma_1 \rightleftarrows \gamma_2$ phases and the peritectoid reaction $\gamma_2 \rightleftarrows \gamma_1 + \varepsilon_1$ were not clearly confirmed in this investigation; these transforma-

Fig. 6.

Electric Resistance. →

700°	650°	600°	550°	500°	450°	400°
950°	900°	850°	800°	750°	700°	650°
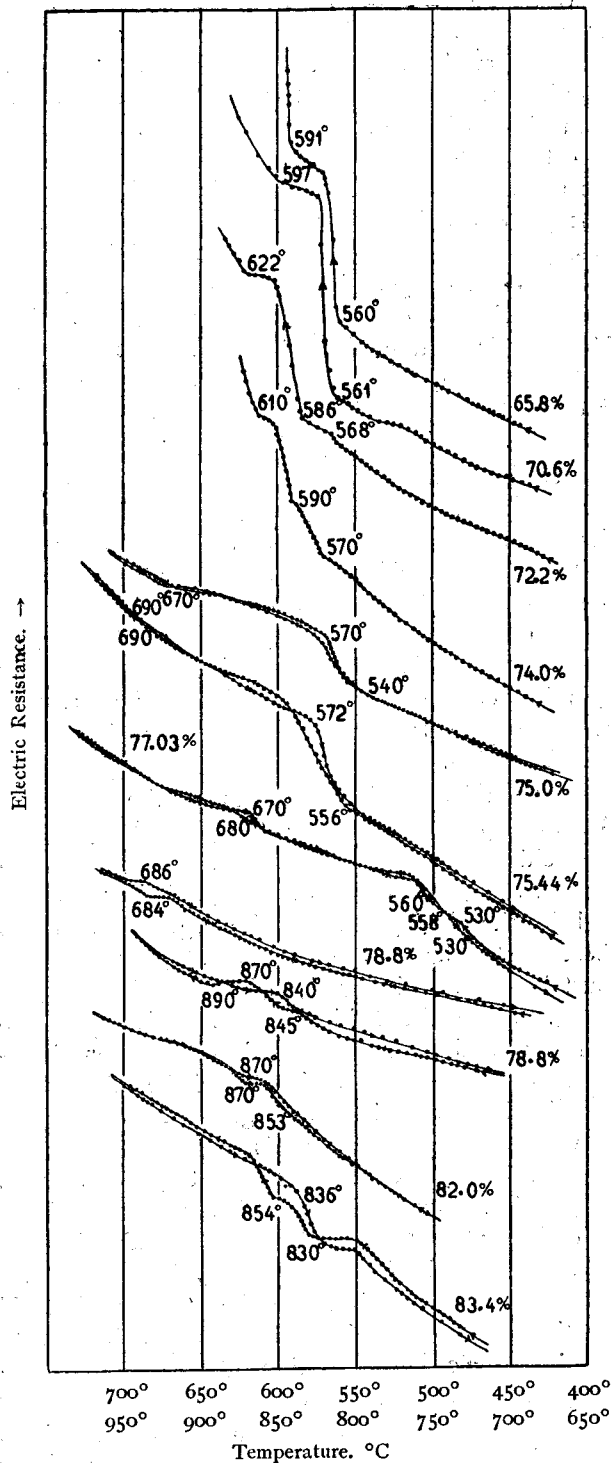
Temperature. °C

tions occurred in the same temperature range as that noted in the thermal analyses. For instance, an alloy of 83.4 per cent. copper showed on heating two rapid increases of electric resistance at 830°C and 854°, and on cooling a rapid decrease at 836°C. The first increase of resistance on heating is perhaps due to the beginning of the polymorphic transformation $\gamma_2 \rightleftarrows \gamma_1$ which ends at 854°. On cooling this polymorphic change was not manifest, but takes place in some temperature

range, with ordinary rate of cooling. In an alloy containing 82 per cent. copper the first rapid increase of resistance was very small at 853°; but the second increase owing to the peritectoid reaction $\gamma_2 \rightleftharpoons \gamma_1 + \varepsilon_1$ was distinctly ascertained at 870°C on heating. On cooling only one change was found at 870°C.

The peritectoid reaction, $\delta \rightleftharpoons \varepsilon_2 + \gamma_2$, was also confirmed by the change of electric resistance as taking place at 680°–686°. In both alloys of 78.8 and 77.03 per cent. copper the change of electric resistance owing to this peritectoid reaction was found at about 686°C as shown in Fig. 5.

Two eutectoid reactions, $\varepsilon_2 \rightleftharpoons \delta + \zeta_1$, and $\zeta_1 \rightleftharpoons \delta + \zeta_2$, took place at about 560° and 530° to 540°, respectively.

In an alloy containing 70.6 per cent. copper, a remarkable change of electric resistance, which due to the polymorphic transformation of η crystals, $\eta_1 \rightleftharpoons \eta_2$, took place at 561°, extending from about 73.5 per cent. to 53.5 per cent. copper at 560°–563°. The results as determined by this measurement agree very well with those determined by the thermal analyses. In some of the alloys the present writer determined also the solidus points by the change of electric resistance. The results are shown in Fig. 2.

B. At Room Temperature.

The electric properties of Cu-Al system were observed by Broniewski[12] in 1912. By the measurement of specific conductivity he found four intermetallic compounds, i.e., Cu_3Al (87.5% Cu), Cu_3Al_2 (77.82%), CuAl (70.11%), and $CuAl_2$ (53.97%). His results are not enongh to explain our experimental results, especially difficult is it to reveal the existence of the δ and ζ phases from his experiments. Hence the present writer measured the specific resistance of the alloys in

those concentrations. For this purpose, chill cast specimens 6 mn. in diameter and 100 mm. in length were annealed in the same way as has already been described in the paragraph III (B), in order to bring them completely into the state of the room temperature. After annealing the specific resistance of these specimens was measured at 18˚ to 20°.

The results thus obtained are summarized in Table 5 and plotted in Fig. 7.

Table 5.

Electric resistance at 18°–20°C

Copper content (%)	Electric Resistance ×10⁻⁶Ω/cm³	Copper content (%)	Electric Resistance ×10⁻⁶Ω/cm³
98.00	1.726	73.10	9.13
95.90	10.05	72.20	9.23
90.08	12.42	72.00	7.76
85.40	16.48	70.60	8.39
84.10	17.57	70.40	7.76
83.10	15.80	70.00	7.59
82.00	25.69	68.00	6.89
81.00	25.29	67.00	7.28
80.00	24.72	61.50	6.69
79.80	24.38	57.32	7.32
78.80	28.49	53.35	12.34
78.00	29.80	51.00	6.46
77.03	11.30	48.50	5.87
76.35	10.79	39.05	5.38
76.10	10.22	27.50	4.55
75.44	11.15	16.80	4.07
75.00	11.68	8.24	3.82
74.00	12.02		

As seen in Fig. 7 the resistivity of a solid solution increases from 1.724×10^{-6} to about 12×10^{-6} ohms with the increase of aluminium

Fig. 7.

Copper per cent.
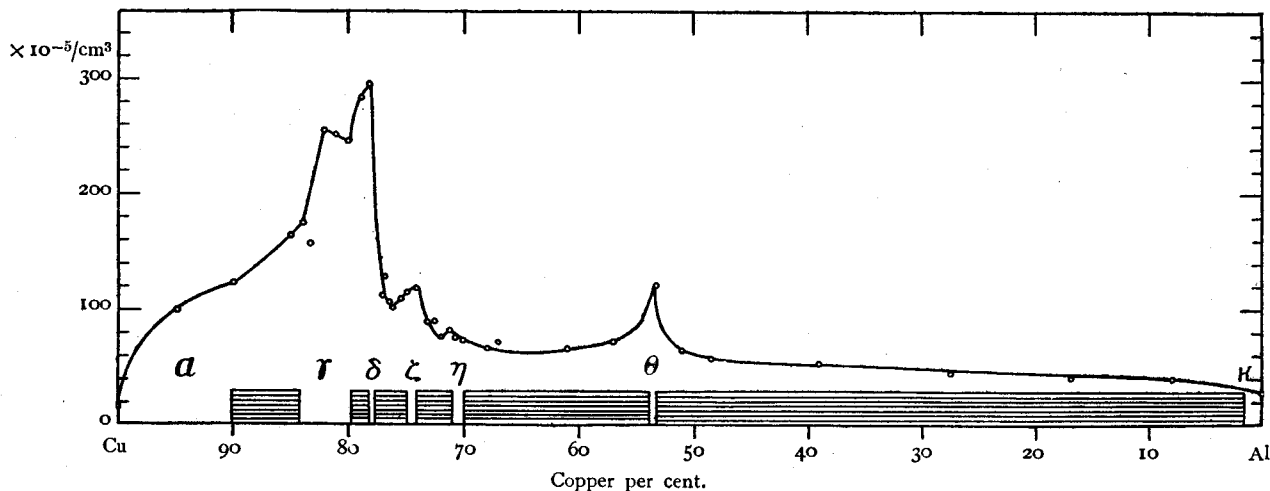
12) W. Guertler: *Metallographie*, Bd, II Teil 2 Heft 7 Lief. 2.

content. In the field of $a+\gamma$ phases the resistivity increases rapidly in the neighbourhood of the γ phase.

In the field of γ phase the resistivity-concentration curve changes to convex at the concentration axis, the maximum value of resistivity being 25.69×10^{-6} ohms in an alloy containing 82 per cent. copper.

It is significant that the maximum value of resistivity of the δ phase is 29.8×10^{-6} ohms. Beyond the δ phase the resistivity is rapidly decreased as the ζ phase appears until it shows a mininum value of 10.22×10^{-6} ohms, in a 76.1 per cent. copper alloy.

The value of θ phase—about 12.34×10^{-6} ohms at 53.35 per cent. copper—is also remarkable.

The definite high values of resistivity of both ζ and η phases—about 12.02×10^{-6} and 9.23×10^{-6} ohms, respectively—are confirmed.

V. The Microscopic Examination.

Since the phase fields of a, β and γ in alloys containing more than 85 per cent. of copper are in close agreement with those of Stockdale, they need not be further commented upon here. However, the following microstructures presented some interesting phenomena.

A. The microstructures of alloys with the concentration from 87 to 72 per cent. of copper at the temperatures above 700°C.

The phases obtained from quenching experiments are given in Table 6.

Table 6.

Copper content (%)	Quenching Temp. °C	Quenching Time (hours)	Phases	Remarks
85.93	900	1.0	β	nearly homogeneous phase
	850	1.0	β+γ₁	
	800	1.0	β+γ₁	
85.10	960	1.0	β	nearly homogeneous phase
	900	1.0	β+γ₁	
	800	1.0	β+γ₁	
84.10	990	0.5	β+γ₁	
	905	0.5	γ₁+β	
	900	1.0	.γ₁	nearly homogeneous phase
	850	1.0	γ₁	
	820	1.0	γ₁	completely homogeneous phase
	800	4.0	γ₂	
83.68	975	1.0	γ₁+β	
	960	2.0	γ₁	completely homogeneous phase
	900	2.0	γ₁	
83.40	970	1.0	γ₁	
	960	2.0	γ₁	
	820	6.0	γ₂	completely homogeneous phase
	800	4.0	γ₂	
83.10	990	1.0	γ₁	nearly homogeneous phase
	960	2 0	γ₁	
	820	6.0	γ₂	completely homogeneous phase
	800	4.0	γ₂	

Copper content (%)	Temp. °C	Time (hours)	Phases	Remarks
82.41	900	2.0	γ₁	completely homogeneous phase
	850	1.0	γ₂	
	800	4.0	γ₂	
82.00	1000	1.0	γ₁	completely homogeneous phase
	970	1.0	γ₁	
	900	2.0	γ₁	
	850	1.0	γ₂	
	800	4.0	γ₂	
81.50	926	8.0	γ₁	completely homogeneous phase (large grains)
	900	2.0	γ₁	
	850	1.0	γ₂	completely homogeneous phase (large grains are decomposed into small grains)
	800	4.0	γ₂	
81.00	920	24.0	γ₁	completely homogeneous phase
	900	18.5	γ₁+ε₁	
	850	1.0	γ₂	homogeneous phase in small g ain size
	800	4.0	γ₂	
80.85	945	0.5	γ₁	homogeneous phase
	900	2.0	γ₁+ε₁	
80 50	945	0.5	γ₁	homogeneous phase
	920	24.0	γ₁+ε₁	
	900	2.0	γ₁+ε₁	
	850	8.0	γ₂	homogeneous phase
	8)0	4.0	γ₂	
80.00	940	0.5	γ₁+ε₁	
	900	18.5	γ₁+ε₁	
	850	1.0	γ₂	completely homogeneous phase
	800	4.0	γ₂	
79.80	900	18.5	γ₁+ε₁	
	860	10.0	γ₂+ε₁	
	840	10.0	γ₂	homogeneous phase
	820	20.0	γ₂	completely homogeneous phase
	800	4.0	γ₂	
	770	8.0	γ₂	nearly homogeneous phase (twinned structure)
	740	4.0	γ₂	
	720	20.0	γ₂	
79.48	860	10.0	γ₂+ε₁	
	840	10.0	γ₂+ε₂	
	820	20.0	γ₂	completely homogeneous phase
	800	4.0	γ₂	
	770	8.0	γ₂	homogeneous phase (twinned structure)
	740	4.0	γ₂	
	720	20.0	γ₂	
79.16	850	8.0	γ₂+ε₁	
	770	8.0	γ₂+ε₂	
78.80	900	18.5	ε₁	decomposed phase
	885	5.0	ε₁	
	800	4.0	γ₂+ε₂	
	940	0.5	ε₁+melt	
78.00	885	0.5	ε₁+melt	partially melted decomposed phase
	810	4.0	ε₂	
	740	4.0	ε₂+γ₂	
77.03	810	0.5	ε₂+melt	partially melted decomposed phase
	800	4.0	ε₂	
	710	20.0	ε₂+γ₂	

Photograph 1, showing the microstructure of the alloy containing 84.1 per cent. of copper quenched from 905°C in water, gives evidence of the presence of large crystals of γ_1 and small crystals of β, the latter becoming yellowish golden-coloured when etched with a cupric chloride solution.

It was very difficult to distinguish the structures between γ_1 and γ_2. The microstructure of alloys quenched from above or below the line *ef*

were exactly the same, and were completely homogeneous as illustrated by Stockdale. This is shown in Photographs 2 and 3.

The phase boundary $\gamma_1 + \varepsilon_1$ has been carefully determined from the microstructures of the quenched specimens. By the differential thermal analyses and the measurement of electric resistance, the present writer found the invariant line fg_1h_1 corresponding to the peritectoid transformation $\gamma_1 + \varepsilon_1 \rightleftarrows \gamma_2$.

Stockdale, however, said from the results of microscopical examination that these alloys above or below the fg_1 consist of uniform solid solution. But these alloys in the field of $fPQh_1g_1f$ are heterogeneous. Evidence of this is in photograph 4, which shows the microstructure of an alloy containing 80.5 per cent. of copper quenched from 920°C in water; the large crystal is the γ_1 and some area of the decomposed ε_1 is found.

The phase boundary line Pf was also determined from the microscopical examination of quenched specimens. The alloys which were quenched from the temperatures above the line Pf were completely homogeneous. As shown in Photograph 5 the alloy of 81.5 per cent. of copper quenched from 926°C in water consists only of γ_1 crystals.

The field of $\gamma_1 + \gamma_2$ (efg_1e) could not be determined by quenching experiments. γ_2 were etched lighter or darker than γ_1, according to the orientation of crystals, and the grain size of the γ_2 crystals is smaller than that of the γ_1 crystal. Photograph 6 of a 81.0 per cent. copper alloy quenched from 600° in water shows the homogeneous γ_2 crystals.

Photograph 7 shows the structure of the

alloys containing 79.8 per cent. of copper quenched from 900°C in water in which γ_1 and ε_1 exist in about equal proportion. When the same alloy was quenched at 860°C it showed needle-like crystals of ε_1 in the ground of the γ_2 crystals, as illustrated in Photo. 8.

Since the ε_1 and ε_2 crystals were very unstable at lower temperatures, the suppression of homogeneous ε_1 crystals was impossible, and the ε_1 crystals were found to be always in decomposed structure. This is evident in Photograph 9, which is the microstructure of decomposed ε_1 cystals in the alloy containing 78.8 per cent. copper quenched from 885°C in ice-brine water. Photo. 10 shows the structure of the decomposed ε_2 and γ_2 crystals of this alloy when quenched from 800°C.

All these changes of the phases at various temperatures are graphically shown in Fig. 8.

B. The microstructures of alloys with the concentration from 86 to 65 per cent. of copper at the temperatures between 740°C and 400°C.

None of the existing diagrams for the concentrations from 80 to 70 per cent. copper are satisfactory, and the investigation of this field has been regarded as the most difficult. Stockdale concluded that there are three intermetallic compounds of δ, ε, and η, in this range; and Tasaki reported the existence of phases δ, Cu_5Al_3, ε, and CuAl. Besides these phases the present writer has determined from the microstructures the existence of the new phases δ and ζ as they have been already confirmed by the thermal analyses and the measurement of electric resistance. The changes of these phases are summarized in Table 7 and graphically shown in Fig. 9.

The existing field of the γ_2 crystals at 500° was confirmed by the microstructures of specimens after being annealed for one month in an automatic regulating electric furnace. From this experiment it was found to extend from about 84.5 per cent. to 79.8 per cent. of copper. In an alloy containing 81.0 per cent. of copper there existed no structure similar to that reported by Tasaki, and in the whole range of the 84 to 80 per cent. of copper the structures were always homogeneous. The alloys containing 80–79.8 per cent. of copper showed twinned structure of γ_2 when quenched from above 500°C. These twinned structures were perhaps caused by the change of solubility of the γ_2 crystals. The slope of the $\gamma_2 - (\gamma_2 + \delta)$ boundary, namely the line $i_1 i_2$, will

Fig. 8.
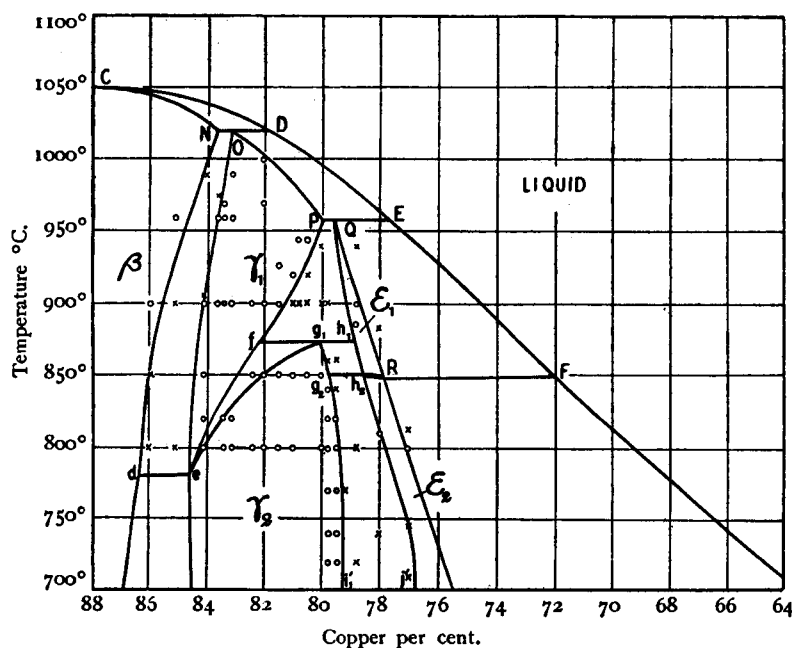
Copper per cent.

take the probable shape as shown in Fig. 8. From our diagram γ_2 and δ crystals are found to coexist in the field $i_2\,i_1\,j_1\,j_2$; however, Stockdale reported that the γ_2 phase* exists over the entire range from 84 to about 77 per cent. of copper. Photos. 11 and 12 show the microstructures of the 79.48 and 79.1 per cent. copper alloys, respectively, both of which were annealed for 1 month at 500°C and quenched in water. The evidence in these photos. that they are composed of the γ_2 and δ constituents supports our opinion. Since these figures are difficult to develop, special case was taken in the selection of the etching reagent. For this purpose an iodine solution or a nitric acid alcoholic solution was found to give the best results.

Table 7.

Copper content (%)	Temp. °C	Time (hours)	Phases	Remarks
84.70	700	12.0	$\gamma_2+\beta$	
	500	1 month	$\gamma_2+\alpha$	
84.10	600	120	γ_2	} completely homogeneous phase
	500	1 month	γ_2	
83.40	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
83.10	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
82.41	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
82.00	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
81.50	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
81.00	688	24.0	γ_2	} completely homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
80.50	600	120	γ_2	} completely homogeneous phase
	500	1 month	γ_2	
80.00	688	24.0	γ_2	completely homogeneous phase
	600	120	γ_2	} twinned homogeneous phase
	500	1 month	γ_2	
79.80	688	24.0	γ_2	} twinned homogeneous phase
	600	120	γ_2	
	500	1 month	γ_2	
79.48	688	24.0	γ_2	twinned homogeneous phase
	600	120	$\gamma_2+\delta$	
	500	1 month	$\gamma_2+\delta$	
79.16	700	8.0	$\gamma_2+\varepsilon_2$	
	688	24.0	$\gamma_2+\varepsilon_2$	
	600	120	$\gamma_2+\delta$	
	500	1 month	$\gamma_2+\delta$	

Copper content (%)	Temp. °C	Time (hours)	Phases	Remarks
78.80	700	8.0	$\gamma_2+\varepsilon_2$	
	680	13.0	δ	} nearly homogeneous phase
	600	120	δ	(twinned δ)
	500	1 month	δ	
78.00	690	24.0	$\gamma_2+\varepsilon_2$	
	650	6.0	$\delta+\varepsilon_2$	
	610	18.0	δ	
	600	120	δ	homogeneous phase (twinned δ)
	500	1 month	δ	nearly homogeneous phase
77.42	600	120	$\delta+\varepsilon_2$	
	580	12.0	$\delta+\varepsilon_2$	almost homogeneous δ phase
	550	2.0	$\delta+\zeta_1$	} eutectoid structure
	500	1 month	$\delta+\zeta_2$	(coarse grains)
77.03	650	6.0	$\delta+\varepsilon_2$	
	600	120	$\delta+\varepsilon_2$	
	580	12.0	$\delta+\varepsilon_2$	
	550	2.0	$\delta+\zeta_1$	} eutectoid structure
	500	1 month	$\delta+\zeta_2$	(fine grains)
76.67	580	12.0	$\delta+\varepsilon_2$	eutectoid structure
	550	2.0	$\delta+\zeta_1$	} eutectoid structure (fine grains)
	500	4 days	$\delta+\zeta_2$	
76.10	640	2.0	ε_2	} homogeneous phase
	585	12.0	ε_2	
	565	4.0	$\varepsilon_2+\zeta_1$	
	550	2.0	$\delta+\zeta_1$	} eutectoid structure
	500	1 month	$\delta+\zeta_2$	
75.86	585	12.0	ε_2	
	565	4.0	$\varepsilon_2+\zeta_1$	
	550	2.0	$\delta+\zeta_1$	} eutectoid structure
	500	4 days	$\delta+\zeta_2$	
75.40	630	3.0	ε_2	} nearly uniform structure
	600	120	ε_2	
	585	12.0	ζ_1	twinn d structure
	550	2.0	$\zeta_1+\delta$	
	500	1 month	$\zeta_2+\delta$	
75.00	600	120	ε_2	
	585	12.0	ζ_1	
	565	24.0	ζ_1	} twinned structure
	550	2.0	ζ_1	
	500	1 month	ζ_2	
	688	1.0	ε_2+melt	
74.57	620	10.0	ε_2	twinned structure
	600	23.0	$\varepsilon_2+\eta_1$	
	585	12.0	$\zeta_1+\eta_1$	
	550	2.0	ζ_2	} twinned structure
	500	4 days	ζ_2	
74.30	620	10.0	ε_2	twinned structure
	600	23.0	$\varepsilon_2+\eta_1$	
	585	12.0	$\zeta_1+\eta_1$	
	550	2.0	ζ_2	} twinned structure
	500	4 days	ζ_2	
74.00	600	120	$\varepsilon_2+\eta_1$	
	585	12.0	$\zeta_1+\eta_1$	
	550	2.0	$\zeta_2+\eta_2$	} twinned structure
	500	1 month	$\zeta_2+\eta_2$	
73.14	600	23.0	$\varepsilon_2+\eta_1$	
	585	12.0	$\zeta_1+\eta_1$	
	550	2.0	$\zeta_2+\eta_2$	
	500	4 days	$\zeta_2+\eta_2$	
72.80	600	23.0	$\varepsilon_2+\eta_1$	
	585	12.0	$\zeta_1+\eta_1$	
	550	2.0	$\zeta_2+\eta_2$	
	500	4 days	$\zeta_2+\eta_2$	
72.20	600	120	$\eta_1+\varepsilon_2$	
	585	12.0	$\eta_1+\zeta_1$	
	550	2.0	$\eta_2+\zeta_1$	} nearly uniform structure
	500	1 month	$\eta_2+\zeta_2$	(*widmanstätten figure*)

* It is to be noted that the nomenclature of Stockdale and of the present writer are different.

72.00	600 585	23 0 12.0	η_1 η_1	} nearly homogeneous phase (*widmanstätten figure*)
71.71	600 585 572 550 500	23.0 12.0 6 0 2.0 4 days	η_1 η_1 η_1 η_2 η_2	} completely homogeneous phase nearly homogeneous phase (*widmanstätten figure*)
70.92	600 585 550 500	0.5 12.0 2 0 4 days	η_2+melt η_1 η_2 η_2	} homogeneous phase (*decomposed structure*)
70.60	600 585 550 500	0.5 12.0 2.0 1 month	η_2+melt η_1 η_2 η_2	} homogeneous phase (*decomposed structure*)
70 00	585 500	12.0 1 month	η_1 η_2	} homogeneous phase (*decomposed structure*)
69.78	500	1 month	$\eta_2+\theta$	
69.13	500	1 month	$\eta_2+\theta$	
68 00	500	1 month	$\eta_2+\theta$	

Fig. 9.

Per cent of copper.

The δ phase is formed by the peritectoid reaction $\gamma_2+\varepsilon_2\rightleftarrows\delta$ at 686° as already described; the composition at the triple point is 78.8 per cent. of copper, considered to be the composition at which the transformation at 686°C on the thermal curves reaches its maximum intensity. Stockdale and Tasaki failed to obtain this ivariant reaction line i_1j_1k. Photographs 13 and 14 illustrate the microstructure of the alloy containing 78.8 per cent. copper quenched from 680°C and 500°C respectively. In these photos., twinning is

observed in the δ crystals. It might be due to the change of solubility of the δ phase, i.e., the solubility of copper in δ must decrease slowly as the temperature falls.

In photograph 15, which illustrates the microstructure of the alloy containing 78 per cent. of copper, twinned δ crystals are also shown distinctly. If the same alloy is quenched from 500°C in water the structure does not become completely homogeneous as shown in Photograph 16. This would indicate that there is some change of the solubility of δ along the line $l_1l_2l_3$. The solubility of aluminium in the δ may decrease rapidly as the temperature falls.
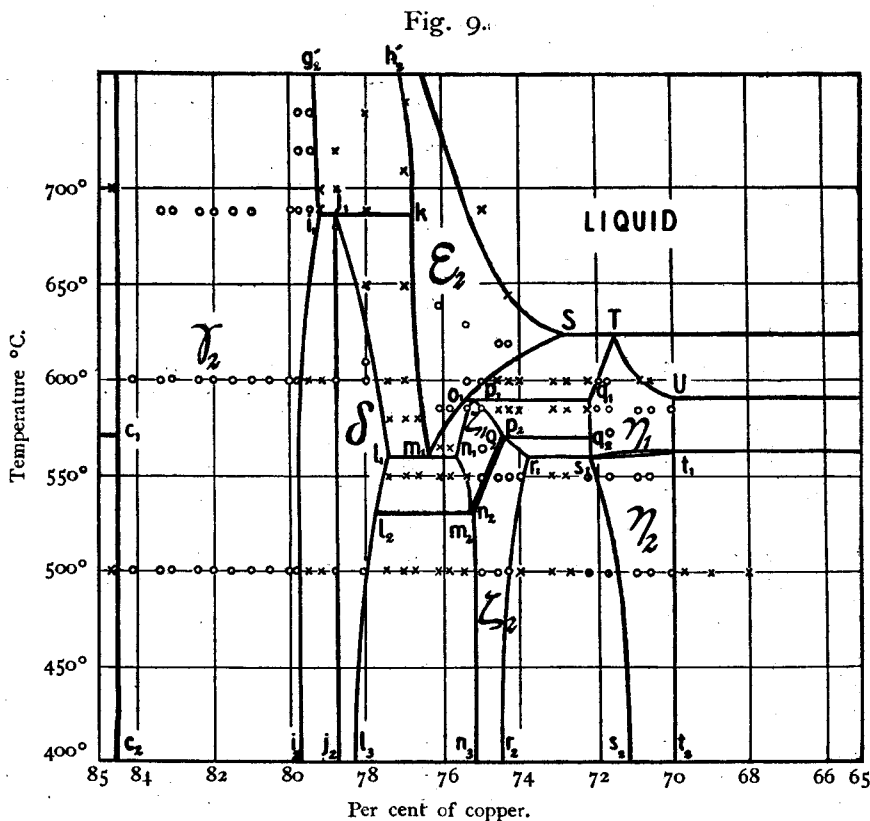
Bradely and his co-worker found the existence of a modification of the γ_2 by X-ray method, and named it the δ' phase. This δ' phase may be the same as the present writer's δ phase. The δ' phase is not a modification of the γ_2 phase, but a definite phase formed at 686°C, as already described. In the field of $g'_2i_1j_1$ kh'_2, γ_2 must coexist with ε_2, as illustrated in Photograph 17, which shows the structure of the alloy containing 78.8 per cent. copper quenched from 720°C. This indicates that the above alloy consists of γ_2 and ε_2 at the temperatures above the line i_1j_1k, and transforms into homogeneous phase at the temperatures below the line. In Photograph 18, we see also a similar heterogeneous structure of an alloy containing 78% of copper, in which γ_2 and ε_2 are present in about equal proportion.

In the field of $j_1km_1l_1$, δ exists in equilibrium with ε_2. The line j_1l_1 is perhaps slightly concave at the side of the δ phase; whereas the line km_1 is almost vertical, and intersects with the eutectoid horizontal $l_1m_1n_1$.

In Photograph 19 we see that the microstructure of an alloy containing 77.42 per cent. of copper quenched from 600°C in water shows the δ phase co-existing with a small amount of the ε_2 phase. The ε_2 phase, being unstable below 560°C, breaks down into δ and ζ_1 phases.

A typical structure of eutectoid consisting of δ and ζ_2 is shown in Photograph 20. This corresponds to the alloy containing 76.1% copper. The field indicated by $l_3l_2l_1m_1n_1m_2n_2n_3$ has been carefully determined from the structures of quench-

ed specimens. It extends from about 77.6 to 75.5 per cent. copper at 500°C. The composition at the triple point m_1 may be about 76.4 per cent. of copper, determined as the point at which the thermal change at 560° on the heating curves reaches its maximum intensity.

The microstructure of an alloy containing 75.4 per cent. copper quenched at 630°C is shown in photo. 21, in which we see only the ε_2 phase. Photograph 22 is a similar structure of the alloy with 76.1 per cent. copper quenched at 585°C. If the same alloy is quenched at 565°C, however, it transforms into two phases, as shown in Photo. 23.

The ζ_1 phase is formed at 590° by the peritectoid reaction $\varepsilon_2+\eta_1\rightleftarrows\zeta_1$. It could not be retained as a complete uniform structure at room temperature, but showed always as a twinned structure because of the transformation $\zeta_1\rightleftarrows\zeta_2+\delta$, and also because of the decrease of the solubility of both copper and aluminium in the ζ_2. As illustrated in Photograph 24, the alloy containing 75.0 per cent. copper shows a twinned ζ_2 phase. Perhaps this ζ_2 phase may be the same as that found in the hexagonal system by G. D. Preston through X-ray investigation. If the alloy containing 74.25 per cent. copper is quenched from 600°C, the ε_2 phase co-exists with the η_1 phase, as shown in Phdograph 25. Photo. 26, of an alloy containing 73.14 per cent. copper quenched from 585°, shows a heterogeneous structure of the ζ_1 and η_1 phases; whereas the same alloy quenched from 500° shows a structure of the ζ_2 and η_2 phases as in Photo. 27. Photograph 28 is a photomicrograph of an alloy with 72.2 per cent. copper quenched from 600°C, in which a small amount of the ε_2 phase exists in the boundary of the η_1 phase.

The same alloy quenched from 500°C after annealing for one month as shown in Photo. 29, a nearly homogeneous structure with *widmannstätten* figure. This figure may be produced by the separation of the other phase due to the decrease of solubility of copper in the η_2 phase. In the diagram, the symbol ⊙ represent the *widmannstätten* figures, which the present writer could not distinguish either to be homogeneous or heterogeneous.

Photo. 30 shows that the micro-structure of the alloy containing 70.92 per cent. copper has a completely homogeneous η_1 phase. If it is quenched at 600°, it begins to melt: that melt is seen in the boundary of the η_1 phase, as shown in Photo. 31. An alloy containing 70 per cent. copper quenched from 500° after annealing for one month consists of finely decomposed η_2 due to the polymorphic transformation, $\eta_1\rightleftarrows\eta_2$, as shown in Photograph 32.

Photograph 33, a microstructure of an alloy

with 68 per cent. copper, shows some amount of θ phase existing in the boundary of the decomposed η_2 phase. This θ phase is found definitely in an alloy of 69.78 per cent. copper. The existing range of η_2 solid solution extends from about 71.5 to 70 per cent. copper at 500°C, and the slope of the line s_1s_2 probably inclines as shown in the diagram.

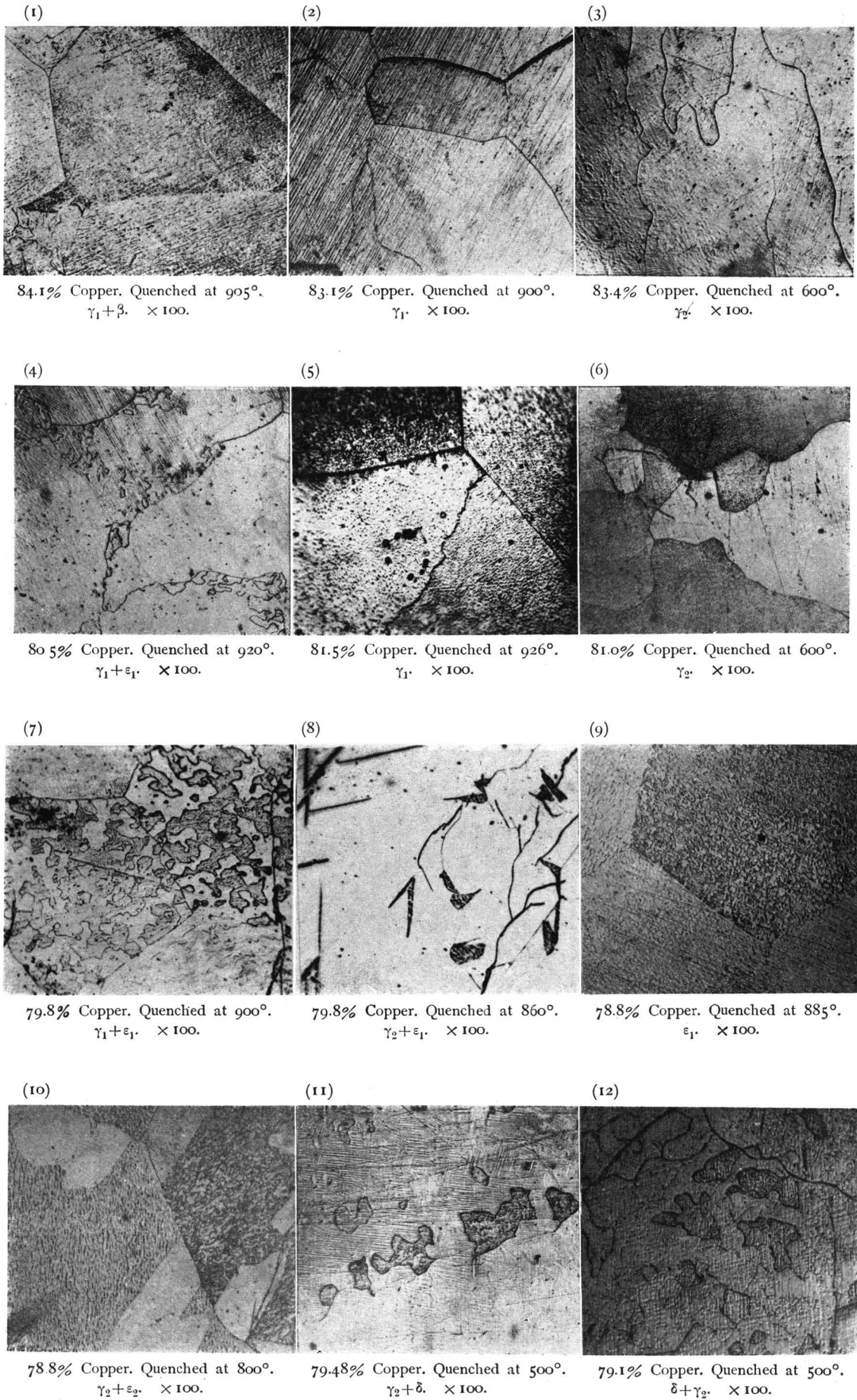## C. The microstructures of alloys with the concentration from 66 to 52 per cent. copper at the temperatures above 400°C.

Although the field of θ phase is almost in agreement with Stockdale's recent experiments, here we will briefly comment on the results of our microscopical examinations, shown in Table 8 and plotted in the diagram, Fig 10.
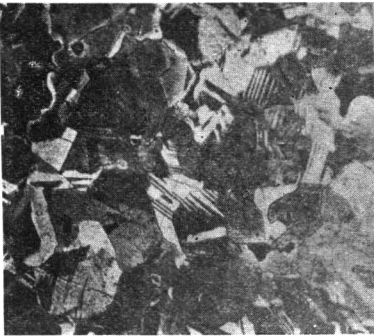
Table 8.

Copper Content (%)	Quenching		Phases	Remarks
	Temp. °C	Time (hours)		
65.80	618	50	Liquid+ε₂ +η₁	There is no evidence of the peritectic reaction.
	585	4 days	η₁+θ	
	500	10 days	η₂+θ	
	Furnace cooled		ε₂+η₁+θ	dendritic ε₂ crystals+a little dotted η₁ crystals+θ crystals.
63.30	500	10 days	η₂+θ	
	Furnace cooled		ε₂+η₁+θ	dendritic ε₂ crystals+many dotted η₁ crystals+θ crystals.
62.30	500	10 days	η₂+θ	
	Furnace cooled		ε₂+η+θ	dendritic ε₂ crystals+many dotted η₁ crystals+θ crystals.
61.50	618	50	Liquid+ε₂ +η₁	There is no evidence of the peritectic reaction.
	585	4 days	η₁+θ	
	500	10 days	θ+η₂	
	Furnace cooled		ε₂+η₁+θ	dendritic primary ε₂ crystals+ many dotted η₁ crystals+θ crystals.
56.80	585		η₁+θ	
	500	10 days	θ+η₂	
	Furnace cooled		η+θ	rod like primary η₁ crystals+ many dotted η₁ crystals+θ crystals.
55.72	500	10 days	θ+η₂	
	Furnace cooled		η+θ	rod like primary η₁ crystals+ dotted η₁ crystals+θ crystals.
54.77	500	10 days	θ+η₂	rod like η₁ crystals+dotted η₁ crystals+θ crystals.
54.27	500	10 days	θ+η₂	
53.73	500	10 days	θ+η₂	
53.52	500	10 days	θ+η₂	
53.35	500	10 days	θ.	completely homogeneous phase.
53.00	500	10 days	θ.	
52.78	500	10 days	θ+x	
52.56	500	10 days	θ+x	
52.10	500	10 days	θ+x	

From these results it is concluded that the θ phase has a narrow range of solid solution and crystallizes directly from the melt.

The ε_2 phase which crystallizes along the line $F'G$ shows a dendritic structure in cast specimens,

(1)

84.1% Copper. Quenched at 905°.
$\gamma_1 + \beta$.　× 100.

(2)

83.1% Copper. Quenched at 900°.
γ_1.　× 100.

(3)

83.4% Copper. Quenched at 600°.
γ_2.　× 100.

(4)

80 5% Copper. Quenched at 920°.
$\gamma_1 + \varepsilon_1$.　× 100.

(5)

81.5% Copper. Quenched at 926°.
γ_1.　× 100.

(6)

81.0% Copper. Quenched at 600°.
γ_2.　× 100.

(7)

79.8% Copper. Quenched at 900°.
$\gamma_1 + \varepsilon_1$.　× 100.

(8)

79.8% Copper. Quenched at 860°.
$\gamma_2 + \varepsilon_1$.　× 100.

(9)

78.8% Copper. Quenched at 885°.
ε_1.　× 100.

(10)

78.8% Copper. Quenched at 800°.
$\gamma_2 + \varepsilon_2$.　× 100.

(11)

79.48% Copper. Quenched at 500°.
$\gamma_2 + \delta$.　× 100.

(12)

79.1% Copper. Quenched at 500°.
$\delta + \gamma_2$.　× 100.

(13)

78.8% Copper. Quenched at 680°.
Twinned δ.   × 100.
(CuCl₂ solution)

(14)

78.8% Copper. Quenched at 500°.
Twinned δ.   × 100.
(Iodine solution)

(15)

78.0% Copper. Quenched at 610°.
δ.   × 100.
(CuCl₂ solution)

(16)

78.0% Copper. Quenched at 500°.
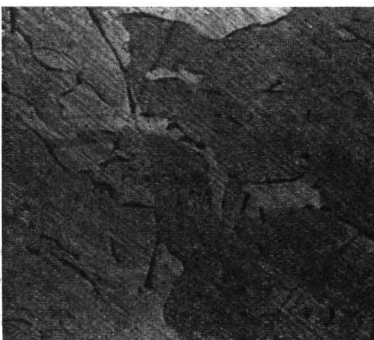Decomposed δ.   × 100.
(Iodine solution)

(17)
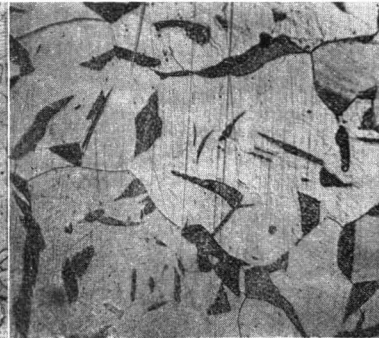
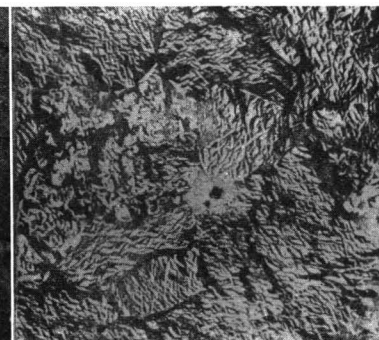78.8% copper. Quenched at 720°.
$\gamma_2 + \epsilon_2$.   × 100.

(18)
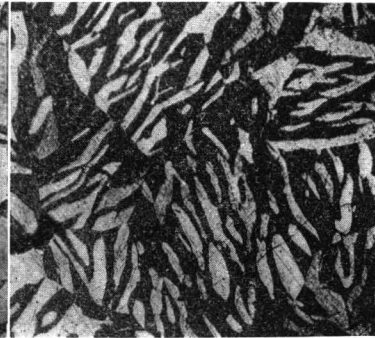
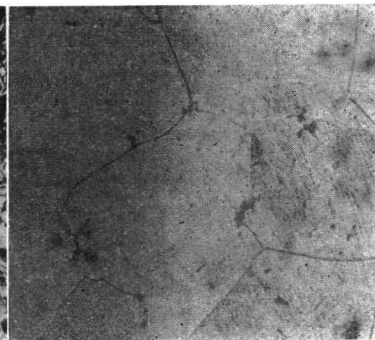78.0% Copper. Quenched at 720°.
$\gamma_2 + \epsilon_2$.

(19)

77.42% Copper. Quenched at 600°.
$\delta + \epsilon_2$.   × 100.
(CuCl₂ solution)

(20)

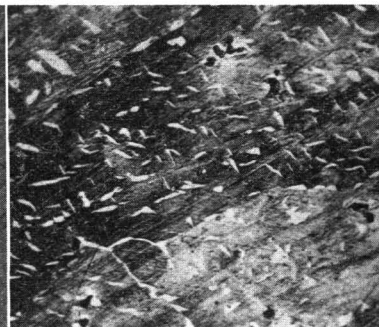76.1% Copper. Quenched at 500°.
$\delta + \zeta_2$.   × 100.

(21)

75.4% Copper. Quenched at 630°.
ϵ_2.   × 100.

(22)

76.1× Copper. Quenched at 585°.
ϵ_2.   × 100.

(23)

76.1% Copper. Quenched at 565°.
$\epsilon_2 + \zeta_1$.   × 100.

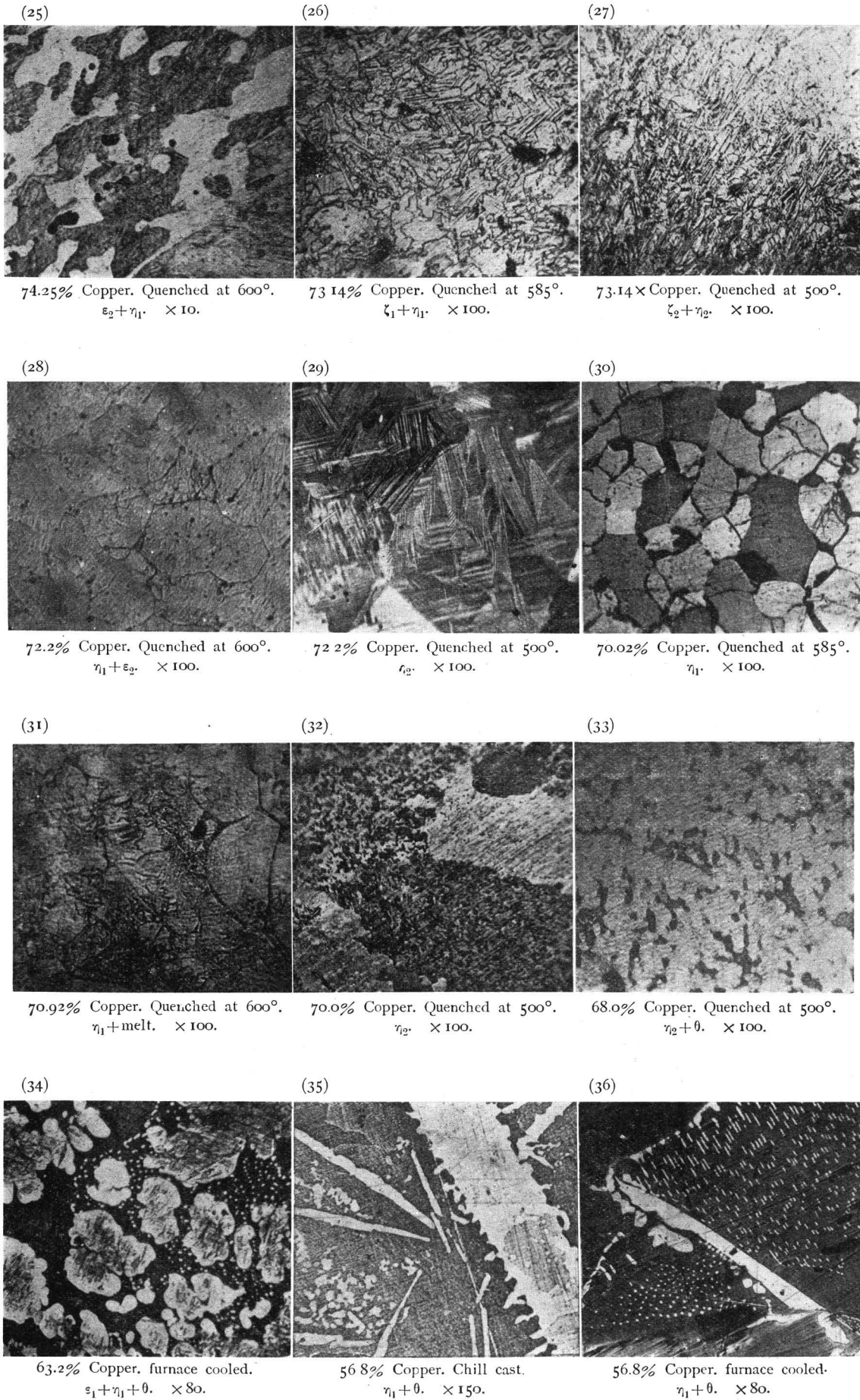(24)

75.0% Copper. Quenched at 500°.
ζ_2.   × 100.

(25)

(26)

(27)

74.25% Copper. Quenched at 600°.
$\varepsilon_2 + \eta_1$.   × 10.

73 14% Copper. Quenched at 585°.
$\zeta_1 + \eta_1$.   × 100.

73.14 × Copper. Quenched at 500°.
$\zeta_2 + \eta_2$.   × 100.

(28)

(29)

(30)

72.2% Copper. Quenched at 600°.
$\eta_1 + \varepsilon_2$.   × 100.

72 2% Copper. Quenched at 500°.
ζ_2.   × 100.

70.02% Copper. Quenched at 585°.
η_1.   × 100.

(31)

(32)

(33)

70.92% Copper. Quenched at 600°.
$\eta_1 +$ melt.   × 100.

70.0% Copper. Quenched at 500°.
η_2.   × 100.

68.0% Copper. Quenched at 500°.
$\eta_2 + \theta$.   × 100.

(34)

(35)

(36)

63.2% Copper. furnace cooled.
$\varepsilon_1 + \eta_1 + \theta$.   × 80.

56 8% Copper. Chill cast.
$\eta_1 + \theta$.   × 150.

56.8% Copper. furnace cooled.
$\eta_1 + \theta$.   × 80.

Fig. 10.

Per cent. of copper.

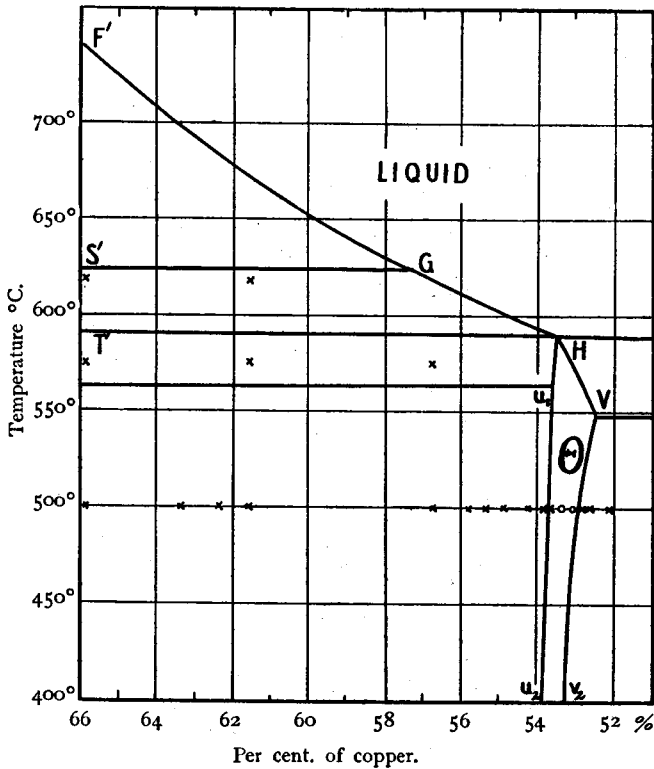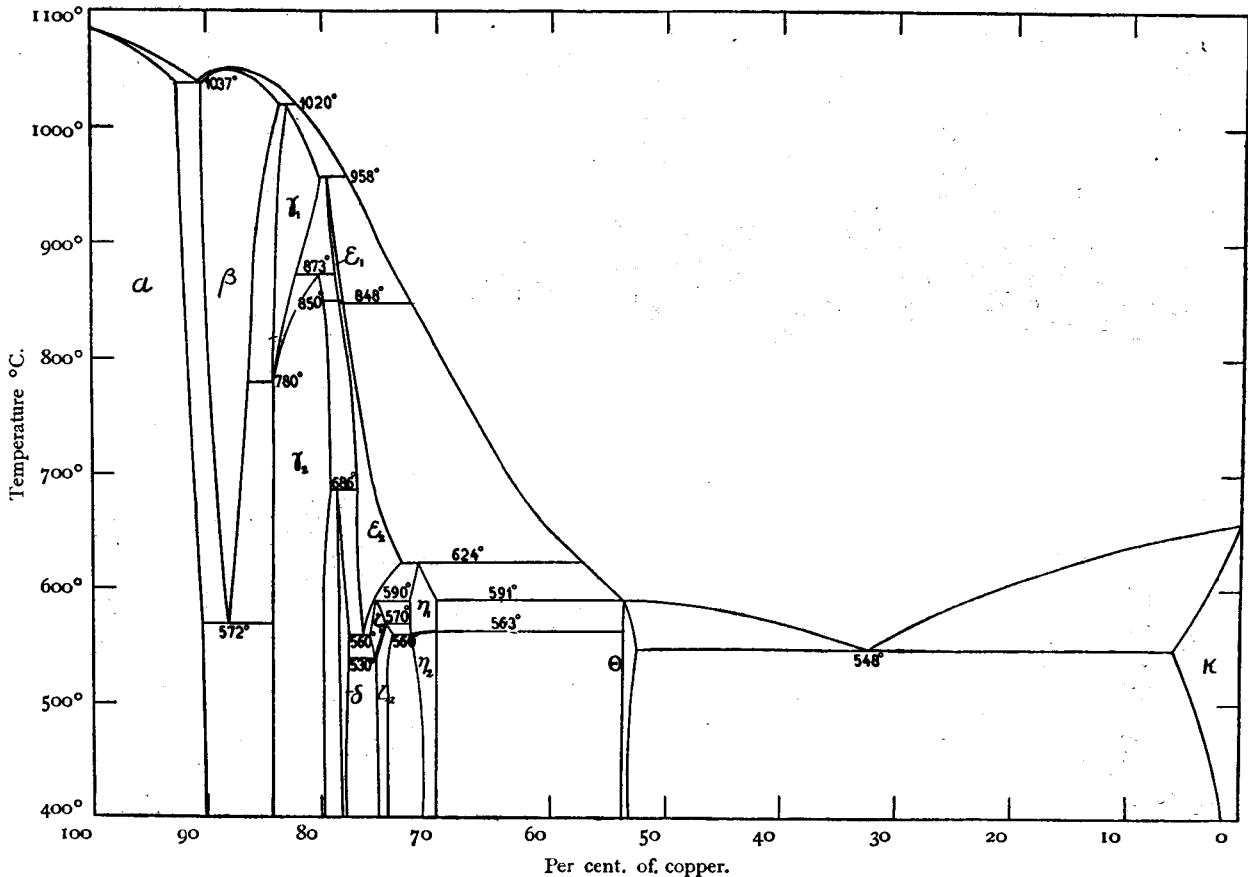where as the γ_1 phase which crystallizes along the line GH appears with rod-like structure. In

Photograph 34, of an alloy containing 63.2 per cent. copper, primary dendritic ε_2 crystals are seen to be decomposed into the γ_2 by solid transformations, and the secondarily crystallized γ_1 crystals into dotted form on the ground of the θ phase. These dotted γ_1 crystals were found in alloys from about 66 to 53.8 per cent. copper. In Photograph 35 of chill cast alloy of 56.8 per cent. copper the dotted γ_1 phase appears in somewhat irregular form. Photograph 36 of the same alloy furnace cooled illustrates similar microstructure. Even when the furnace-cooled alloys with 65.8 and 61.5 per cent. copper were again annealed at 618° for 50 hours and quenched in ice water, the form of the dotted γ_1 crystals did not change. The present writer has no satisfactory explanation for the existence of such dotted crystals, but suggests that the dotted γ_1 are formed as the result of supercooling at the invariant reaction shown by the line $T'H$ at 563°. A remarkable supercooling is found in the cooling curves as shown in Fig. 4.

VI. The Equilibrium Diagram.

The equilibrium diagram of the whole system above 400°C is given in Fig. 11, in which the notations are somewhat different from those of other authors in that the various phases are noted with Greek letters in the order of their copper

Fig. 11.

Per cent. of. copper.

content. This figure is itself a complete summary of all the present work, but the new observations made by the present writer may be summarized as follows.

VII. Summary.

(1) The equilibrium diagram of Cu-Al system had never been thoroughly ascertained. The present writer, however, has dissolved many doubtful points by means of differential thermal analyses, electric resistance method, microscopic examination; and a new equilibrium diagram as shown in Fig. 11 has been given.

(2) The liquidus of this system consists of 8 branches corresponding to the separation of α, β, γ_1, ϵ_1, ϵ_2, η_1, θ, and κ.

(3) The γ_2 phase is formed by the following reactions according to the concentration of alloys:

$$\gamma_1 \underset{\leftarrow}{\rightarrow} \gamma_2$$

$$\gamma_1 + \epsilon_1 \underset{\leftarrow}{\rightarrow} \gamma_2$$
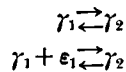
The former reaction takes place at 780°–873°C in the range of 84.5–82 per cent. copper as it has been observed by Stockdale. The latter is found by the present writer to occur at 873°C in the range of 82–80 per cent. copper.

(4) The existence of newly found δ and ζ phases is ascertained: the δ being formed by the peritectoid reaction $\gamma_2 + \epsilon_2 \underset{\leftarrow}{\rightarrow} \delta$ at 686°C; and the ζ by the peritectoid reaction $\epsilon_2 + \eta_1 \underset{\leftarrow}{\rightarrow} \zeta_1$ at 590°C. These phases form some range of solid solution, whose solubility decreases as temperature falls.

(5) The eutectoid reactions $\epsilon_2 \underset{\leftarrow}{\rightarrow} \delta + \zeta_1$ and $\zeta_1 \underset{\leftarrow}{\rightarrow} \delta + \zeta_2$ take place at 560°C and 530°C respectively.

(6) Each of the ϵ and η phases shows a polymorphic transformation. Among them the polymorphic change of η phase is evident, but that of the ϵ phase is somewhat indistinct.

(7) The θ phase crystallizes directly from the melts, and forms a narrow range of solid solution.

Acknowledgement.