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

By Chiuyo Hisatsune.

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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 γ -, δ -, ϵ -, η -, and θ , respectively. Some years ago G. D. Preston,⁷⁾ E. R. Jette, A. Westgren, and G. Phragmén⁸⁾, and Ichiji Obinata,⁹⁾ and more recently A. J. Bradley and Phyllis Jones¹⁰⁾ 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 nichrome-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 platinum-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

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 $\text{FeCl}_2 + 20$ c.c. conc. $\text{HCL} + 950$ c.c. Alcohol) or Iodine solution (1.2 grs $\text{I} + 1.2$ grs $\text{KI} + 1.2$ c.c. $\text{H}_2\text{O} + 97$ 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 develop the figures:

(1) Cupric chloride 10 grs + MgCl_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 I, and plotted in Fig. 2. Some examples of the cooling curves are given in Fig. 3.

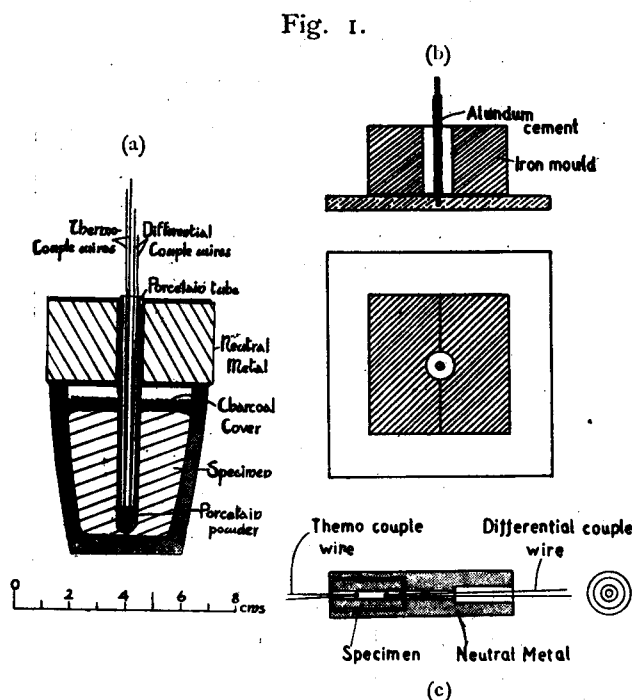


Table 1.
Results of Thermal Analysis.

Composition (by analysis) %		Points of change or arrest											
Copper	Aluminium												
94.96	5.00	1068					77.03	Remainder	950	850	670	563	
94.02	Remainder	1056					76.81	"	942	845		570	
91.98	"	1042	1037					76.35	Remainder	932	843		575
90.08	"	1041	970					76.10	23.72	925	846		583
88.87	"	1048						75.80	Remainder	920	848		590
88.01	"	1050					75.44	24.42	914	850		584	
85.93	13.87	1048	1037	826	780		75.00	Remainder	906	830	585	554	
85.40	14.50	1045						74.00	"	890	848	610	590
84.70	Remainder	1043	970					73.10	"	865	840	617	584
84.10	"	1037						72.20	"	852		620	589
83.68	"	1035	960	795					72.02	"	845	622	584
83.40	"	1034	1020	846	795		71.16	"	828		625	584	
83.10	"	1032	1018	950	838		70.60	"	823		620	582	
82.60	"	1026	1020					70.42	"	813	622	584	
82.41	"	1025	1020					70.00	29.77	813	622	584	
82.15	"	1020					69.13	Remainder	798	623	586	550	
82.00	17.92	1018					68.00	"	777	624	586	550	
81.50	Remainder	1016					66.95	"	756	624	583	550	
81.00	"	1010	958					65.80	"	738	623	588	
80.70	"	1007					63.20	"	696	628	593	530	
80.50	"	1005					61.50	"	670	623	591	540	
80.10	"	1000					60.12	"	655	624	591		
80.00	"	994	958					59.08	"	643	624	591	
79.80	"	993	960	865					57.32	"	624	593	
79.48	"	988	950	855					56.72	"	620	591	
79.16	20.73	984	958	852	678		55.77	"	609			592	
79.00	Remainder	982	960	851	675		54.84	"	602			592	
78.80	"	981	950	848	676		54.77	"	600			592	
78.00	"	968	958	846	680		54.22	"	596			592	
77.42	"	955	958	846	670		53.84	"	592			590	
							52.10	"	590			545	
							48.80	"	587			547	
							44.28	"	584			548	
							40.03	"	572			548	

Fig. 2.

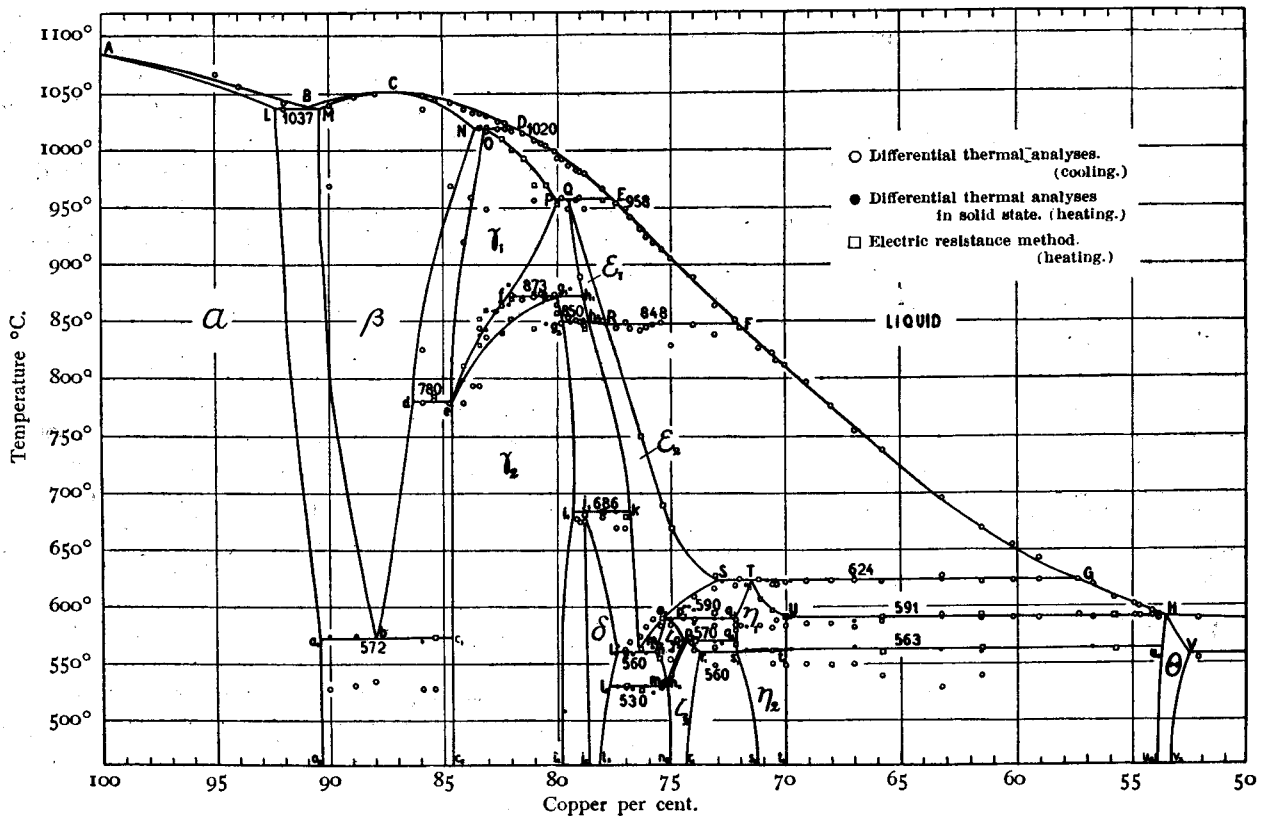
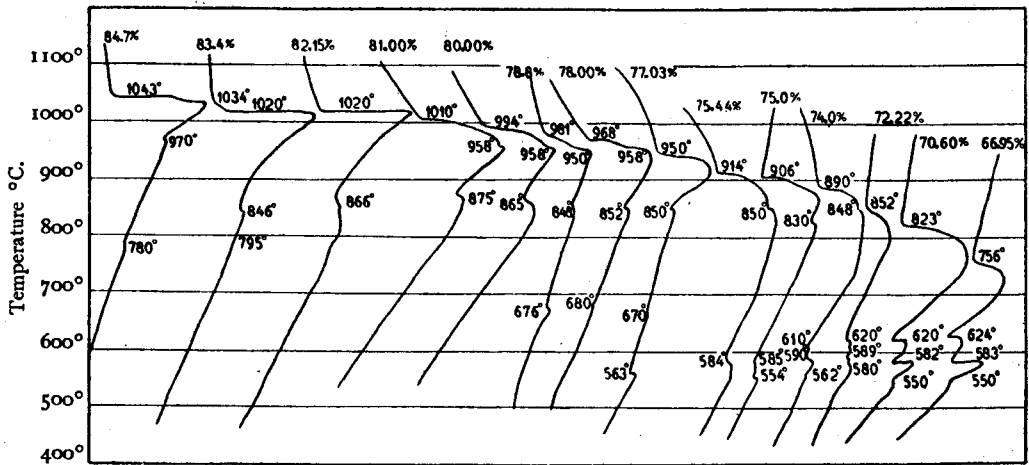


Fig. 3.



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.

Equilibrium lines	The kind of reactions	Temp. °C.	The range of concentration Cu %
<i>LBM</i>	Eutectic reaction $\text{melt} \rightleftharpoons \alpha + \beta$	1037	92.4-90.4
<i>NOD</i>	Peritectic reaction $\text{melt} + \beta \rightleftharpoons \gamma_1$	1020	83.7-82.0
<i>PQE</i>	Peritectic reaction $\text{melt} + \gamma_1 \rightleftharpoons \epsilon_1$	958	80.0-77.6
<i>RF</i>	Polymorphic reaction $\epsilon_1 \rightleftharpoons \epsilon_2$	848	77.5-72.0
<i>STG</i>	Peritectic reaction $\text{melt} + \epsilon_2 \rightleftharpoons \eta_1$	624	73.0-57.3
<i>UH</i>	Peritectic reaction $\text{melt} + \eta_1 \rightleftharpoons \theta$	591	70.0-53.5
<i>VTW</i>	Eutectic reaction $\text{melt} \rightleftharpoons \theta + \kappa$	548	52.5-5.7
<i>a₁b c₁</i>	Eutectoid transformation $\beta \rightleftharpoons \alpha + \gamma_2$	572	90.3-84.5
<i>de</i>	Eutectoid transformation $\gamma_1 \rightleftharpoons \beta + \gamma_2$	780	85.4-84.5
<i>f g₁ h₁</i>	Peritectoid transformation $\gamma_1 + \epsilon_1 \rightleftharpoons \gamma_2$	873	82.2-78.9
<i>g₂ h₂</i>	Polymorphic transformation $\epsilon_1 \rightleftharpoons \epsilon_2$	850	79.8-78.5
<i>i₁ j₁ k</i>	Peritectoid transformation $\gamma_2 + \epsilon_2 \rightleftharpoons \delta$	686	79.2-76.8
<i>l₁ m₁ n₁</i>	Eutectoid transformation $\epsilon_2 \rightleftharpoons \delta + \zeta_1$	560	77.4-75.7
<i>l₂ m₂ n₂</i>	Eutectoid transformation $\zeta_1 \rightleftharpoons \delta + \zeta_2$	530	77.8-75.2
<i>o₁ p₁ q₁</i>	Peritectoid transformation $\epsilon_2 + \eta_1 \rightleftharpoons \zeta_1$	590	75.4-72.2
<i>o₂ p₂ q₂</i>	Peritectoid transformation $\zeta_1 + \eta_1 \rightleftharpoons \zeta_2$	570	74.4-72.1
<i>r₁ s₁</i>	Polymorphic transformation $\eta_1 \rightleftharpoons \eta_2$	560	73.8-72.1
<i>t₁ u₁</i>	Polymorphic transformation $\eta_1 \rightleftharpoons \eta_2$	563	70.0-53.7

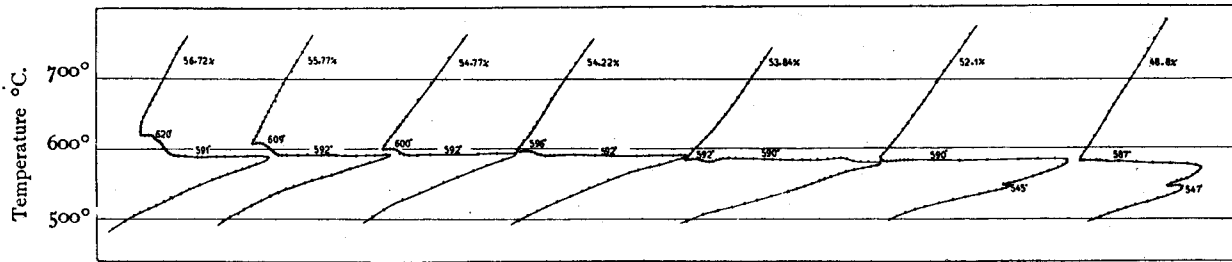
As shown in Fig. 2, the invariant equilibrium

reactions observed on solidification almost agree with the result obtained by Stockdale, although there exists a slight modification in our diagram. The reactions $\text{Melt} \rightleftharpoons \alpha + \beta$ at 1037° (LBM) and $\text{Melt} + \epsilon_1 \rightleftharpoons \epsilon_2$ at 848° (RF) have been admitted by most investigators, and the reactions $\text{Melt} + \beta \rightleftharpoons \gamma_1$ at 1020° (NOD) and $\text{Melt} + \gamma_2 \rightleftharpoons \epsilon_1$ 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° (*g₂ h₂* 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 ϵ_1 , and below it ϵ_2 .

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 CuAl_2 compound crystallizes directly from the melt or not. Fig. 4 shows the cooling curves of alloys of the composition near CuAl_2 compound. The present writer has found that an alloy of the exact composition CuAl_2 has a freezing interval of nearly 5° and contains two phases at 500°, a fact already demonstrated by Stockdale.¹¹⁾ The θ phase near CuAl_2 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 α , 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 $g_1 h_1$; 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

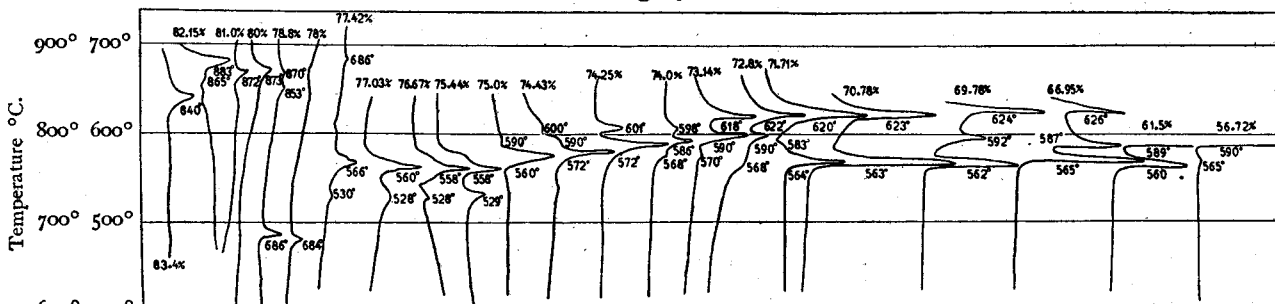
minute. The results of the experiments are given in Table 3, and plotted in Fig. 2.

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.

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_1h_1 , at 873°, caused by the peritectoid reaction $\gamma_1 + \epsilon_1 \rightleftharpoons \gamma_2$. 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 $fPQh_1g_1$ above the fg_1h_1 line and in the field $g_2g_1h_1h_2$ below the line g_1h_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_1h_1) must be attributed to a invariant reaction as $\gamma_1 + \epsilon_1 \rightleftharpoons \gamma_2$. Since the field efg_1e 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 $\gamma_1 + \epsilon_1 \rightleftharpoons \gamma_2$ and the latter might be due to a polymorphic transformation $\epsilon_1 \rightleftharpoons \epsilon_2$. Some polymorphic transformation which takes place along g_2h_2RF 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_jk at 686° is due to the peritectoid transformation $\gamma_2 + \epsilon_2 \rightleftharpoons \delta$, 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 perhaps 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 $l_1m_1n_1$ denotes the eutectoid transformation $\epsilon_2 \rightleftharpoons \delta + \zeta_1$, 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 differential thermal analyses the present writer could clearly find the line $o_1p_1q_1$ at which the peritectoid transformation $\epsilon_2 + \gamma_1 \rightleftharpoons \zeta_1$ 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 $\epsilon_2 + \gamma_1 \rightleftharpoons \zeta_1$ at 590°C, $\zeta_1 + \gamma_1 \rightleftharpoons \zeta_2$ at 570°C and the invariant line due to the polymorphic transformation $\gamma_1 \rightleftharpoons \gamma_2$ at 560°C. Because the above three reactions occurred in succession, three definite arrests in thermal curves were not observed.

The horizontal $o_2p_2q_2$, denoting the peritectoid transformation $\zeta_1 + \eta_1 \rightleftharpoons \zeta_2$, was obtained from heating curves. It was also found readily in cooling curves, though the results were rather irregular.

The eutectoid transformation $\zeta_1 \rightleftharpoons \zeta_2 + \delta$, shown by the horizontal $l_2m_2n_2$, 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 $l_2m_2n_2$. 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_1t_1 at about 560°. This line s_1t_1 , denoting a polymorphic transformation $\eta_1 \rightleftharpoons \eta_2$ 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_1s_1 and t_1n_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 $\zeta_2 + \eta_2 \rightleftharpoons \gamma_1$ and $\gamma_1 + \zeta_2 \rightleftharpoons \zeta_1$ 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

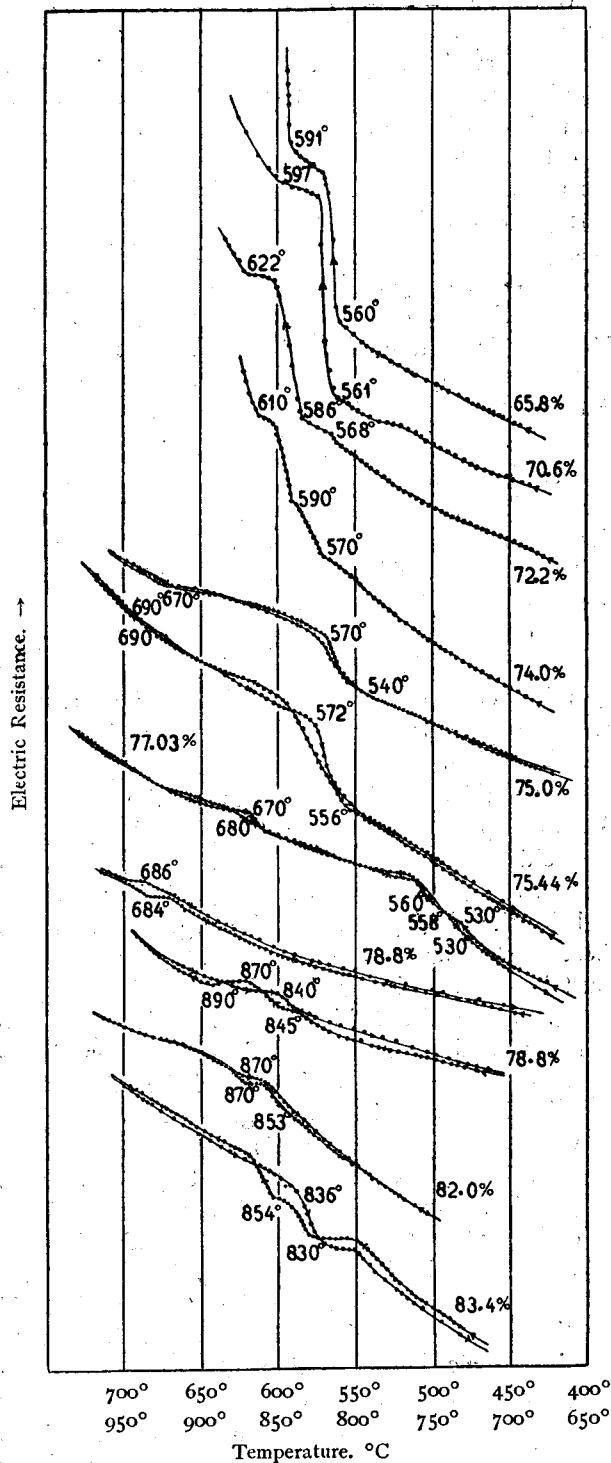
Copper %	Points of arrests or change °C			
85.40	574	(538)	784	(780)
84.10	816	(800)	920	
83.40	830	854	(836)	1020
83.10	840	860	(840)	1020
82.41	840	866	(850)	1010
82.00	853	870	(870)	1000
81.50	872	(868)	995	
81.00	844	(850)	876	(878) 970
80.50	850	(870)	970	
80.00	858	(876)	956	(958)
78.80	684	(686)	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 $\gamma_1 \rightleftharpoons \gamma_2$ phases and the peritectoid reaction $\gamma_2 \rightleftharpoons \gamma_1 + \epsilon_1$ were not clearly confirmed in this investigation: these transforma-

Fig. 6.



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 $\gamma_2 \rightleftharpoons \gamma_1$ 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 $\gamma_2 \rightleftharpoons \gamma_1 + \epsilon_1$ was distinctly ascertained at 870°C on heating. On cooling only one change was found at 870°C.

The peritectoid reaction, $\delta \rightleftharpoons \epsilon_2 + \gamma_2$, 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, $\epsilon_2 \rightleftharpoons \delta + \zeta_1$ 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, $\gamma_1 \rightleftharpoons \gamma_2$, 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 Broniewski¹²⁾ in 1912. By the measurement of specific conductivity he found four intermetallic compounds, i.e., Cu₃Al (87.5% Cu), Cu₃Al₂ (77.82%), CuAl (70.11%), and CuAl₂ (53.97%). His results are not enough 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 mm. 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°.

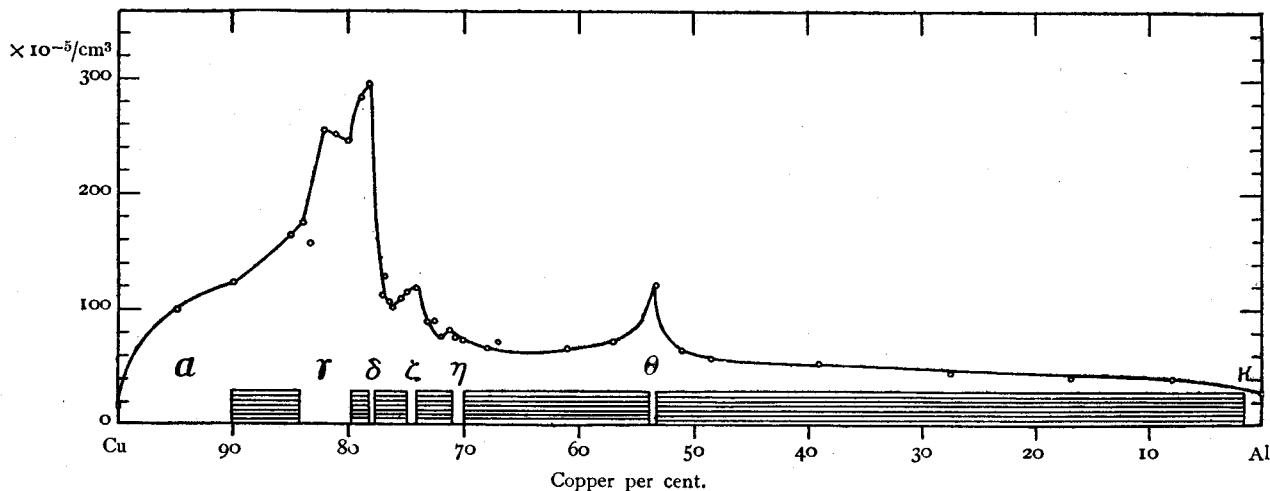
The results thus obtained are summarized in Table 5 and plotted in Fig. 7.

Table 5.
Electric resistance at 18°-20°C

Copper centent (%)	Electric Resistance $\times 10^{-6} \Omega/\text{cm}^3$	Copper centent (%)	Electric Resistance $\times 10^{-6} \Omega/\text{cm}^3$
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.



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

content. In the field of $\alpha + \gamma$ 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 minimum 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 α , 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		Phases	Remarks
	Temp. °C	Time (hours)		
85.93	900	1.0	β	nearly homogeneous phase
	850	1.0	$\beta + \gamma_1$	
	800	1.0	$\beta + \gamma_1$	
85.10	960	1.0	β	nearly homogeneous phase
	900	1.0	$\beta + \gamma_1$	
	800	1.0	$\beta + \gamma_1$	
84.10	990	0.5	$\beta + \gamma_1$	nearly homogeneous phase
	905	0.5	$\gamma_1 + \beta$	
	900	1.0	γ_1	
	850	1.0	γ_1	
	820	1.0	γ_1	
	800	4.0	γ_2	
83.68	975	1.0	$\gamma_1 + \beta$	completely homogeneous phase
	960	2.0	γ_1	
	900	2.0	γ_1	
83.40	970	1.0	γ_1	completely homogeneous phase
	960	2.0	γ_1	
	820	6.0	γ_2	
	800	4.0	γ_2	
83.10	990	1.0	γ_1	nearly homogeneous phase
	960	2.0	γ_1	
	820	6.0	γ_2	
	800	4.0	γ_2	

82.41	900	2.0	γ_1	completely homogeneous phase
	850	1.0	γ_2	
	800	4.0	γ_2	
82.00	1000	1.0	γ_1	completely homogeneous phase
	970	1.0	γ_1	
	900	2.0	γ_1	
	850	1.0	γ_2	
	800	4.0	γ_2	
81.50	926	8.0	γ_1	completely homogeneous phase (large grains)
	900	2.0	γ_1	
	850	1.0	γ_2	
81.00	920	24.0	γ_1	completely homogeneous phase (large grains are decomposed) (into small grains)
	900	18.5	$\gamma_1 + \epsilon_1$	
	850	1.0	γ_2	
80.85	945	0.5	γ_1	homogeneous phase
	900	2.0	$\gamma_1 + \epsilon_1$	
	800	4.0	γ_2	
80.50	945	0.5	γ_1	homogeneous phase
	920	24.0	$\gamma_1 + \epsilon_1$	
	900	2.0	$\gamma_1 + \epsilon_1$	
	850	8.0	γ_2	
	800	4.0	γ_2	
80.00	940	0.5	$\gamma_1 + \epsilon_1$	completely homogeneous phase
	900	18.5	$\gamma_1 + \epsilon_1$	
	850	1.0	γ_2	
	800	4.0	γ_2	
79.80	900	18.5	$\gamma_1 + \epsilon_1$	homogeneous phase
	860	10.0	$\gamma_2 + \epsilon_1$	
	840	10.0	γ_2	
	820	20.0	γ_2	
	800	4.0	γ_2	
	770	8.0	γ_2	
	740	4.0	γ_2	
720	20.0	γ_2		
79.48	860	10.0	$\gamma_2 + \epsilon_1$	completely homogeneous phase
	840	10.0	$\gamma_2 + \epsilon_2$	
	820	20.0	γ_2	
	800	4.0	γ_2	
	770	8.0	γ_2	
	740	4.0	γ_2	
	720	20.0	γ_2	
	720	20.0	γ_2	
79.16	850	8.0	$\gamma_2 + \epsilon_1$	homogeneous phase
	770	8.0	$\gamma_2 + \epsilon_2$	
78.80	900	18.5	ϵ_1	decomposed phase
	885	5.0	ϵ_1	
	800	4.0	$\gamma_2 + \epsilon_2$	
	940	0.5	$\epsilon_1 + \text{melt}$	
78.00	885	0.5	$\epsilon_1 + \text{melt}$	partially melted decomposed phase
	810	4.0	ϵ_2	
	740	4.0	$\epsilon_2 + \gamma_2$	
77.03	810	0.5	$\epsilon_2 + \text{melt}$	partially melted decomposed phase
	800	4.0	ϵ_2	
	800	4.0	ϵ_2	
	710	20.0	$\epsilon_2 + \gamma_2$	

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 $\gamma_1 + \epsilon_1$ 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 $\gamma_1 + \epsilon_1 \rightleftharpoons \gamma_2$.

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 crystals 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.

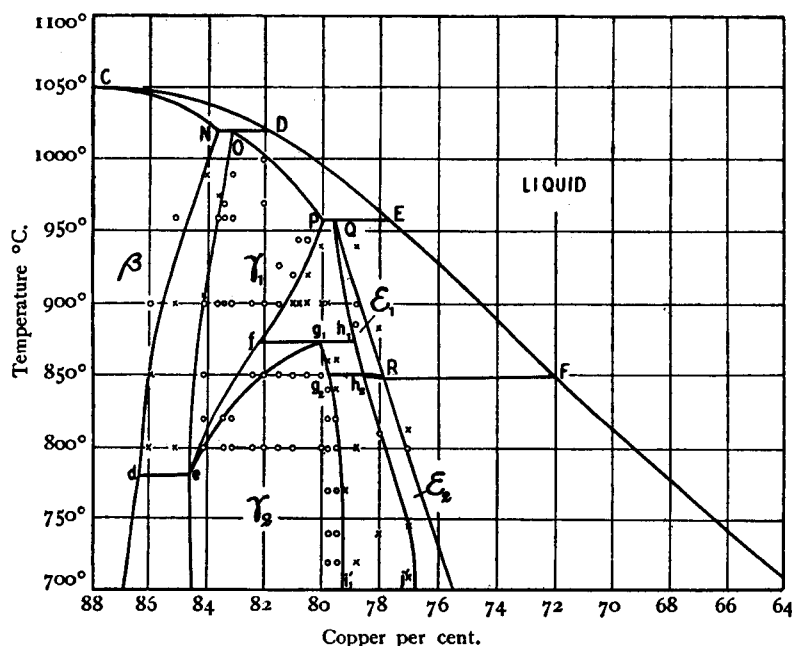
All these changes of the phases at various temperatures are graphically shown in Fig. 8.

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_1i_2 , will

Fig. 8.



take the probable shape as shown in Fig. 8. From our diagram γ_2 and δ crystals are found to coexist in the field $i_2 j_1 j_2$; 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 (%)	Quenching		Phases	Remarks			
	Temp. °C	Time (hours)					
78.80	700	8.0	$\gamma_2 + \epsilon_2$	nearly homogeneous phase (twinned δ)	}	}	δ
	680	13.0					
78.00	690	24.0	$\gamma_2 + \epsilon_2$	homogeneous phase (twinned δ)	}	}	δ
	650	6.0					
77.42	610	18.0	$\delta + \epsilon_2$	almost homogeneous δ phase	}	}	δ
	600	12.0					
77.03	550	2.0	$\delta + \zeta_1$	eutectoid structure (fine grains)	}	}	$\delta + \zeta_2$
	500	1 month					
76.67	600	12.0	$\delta + \epsilon_2$	eutectoid structure	}	}	$\delta + \zeta_1$
	580	12.0					
76.10	550	2.0	$\delta + \zeta_1$	eutectoid structure (fine grains)	}	}	$\delta + \zeta_2$
	500	4 days					
84.70	640	2.0	ϵ_2	homogeneous phase	}	}	ϵ_2
	585	12.0					
84.10	565	4.0	$\epsilon_2 + \zeta_1$	eutectoid structure	}	}	$\delta + \zeta_1$
	550	2.0					
83.40	585	12.0	$\delta + \zeta_1$	eutectoid structure	}	}	$\delta + \zeta_2$
	565	4.0					
83.10	550	2.0	$\delta + \zeta_1$	eutectoid structure	}	}	$\delta + \zeta_2$
	500	4 days					
82.41	630	3.0	ϵ_2	nearly uniform structure	}	}	ϵ_2
	600	12.0					
82.00	585	12.0	ζ_1	twinned structure	}	}	$\zeta_1 + \delta$
	550	2.0					
81.50	500	1 month	$\zeta_2 + \delta$	twinned structure	}	}	$\zeta_2 + \delta$
	600	12.0					
81.00	585	12.0	ζ_1	twinned structure	}	}	ζ_1
	565	24.0					
80.50	550	2.0	ζ_1	twinned structure	}	}	ζ_1
	500	1 month					
80.00	600	12.0	ζ_2	twinned structure	}	}	ζ_2
	688	1.0					
79.80	620	10.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	600	23.0					
79.48	585	12.0	$\zeta_1 + \eta_1$	twinned structure	}	}	$\zeta_1 + \eta_1$
	550	2.0					
79.16	500	4 days	ζ_2	twinned structure	}	}	ζ_2
	600	12.0					
78.80	600	12.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
78.00	550	2.0	$\zeta_1 + \eta_1$	twinned structure	}	}	$\zeta_1 + \eta_1$
	500	1 month					
77.42	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
77.03	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	4 days					
76.67	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
76.10	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	4 days					
75.86	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
75.40	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	4 days					
75.00	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
74.57	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	4 days					
74.30	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
74.00	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	1 month					
73.14	600	23.0	$\epsilon_2 + \eta_1$	twinned structure	}	}	$\epsilon_2 + \eta_1$
	585	12.0					
72.80	550	2.0	$\zeta_2 + \eta_2$	twinned structure	}	}	$\zeta_2 + \eta_2$
	500	4 days					
72.20	600	12.0	$\eta_1 + \epsilon_2$	nearly uniform structure (widmanstätten figure)	}	}	$\eta_1 + \epsilon_2$
	585	12.0					
72.00	550	2.0	$\eta_2 + \zeta_1$	nearly uniform structure (widmanstätten figure)	}	}	$\eta_2 + \zeta_1$
	500	1 month					

* 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	γ_1 γ_1	nearly homogeneous phase (widmanstätten figure)
71.71	600	23.0	γ_1	completely homogeneous phase
	585	12.0	γ_1	
	572	6.0	γ_1	nearly homogeneous phase (widmanstätten figure)
	550	2.0	γ_2	
500	4 days	γ_2		
70.92	600	0.5	$\gamma_2 + \text{melt}$	homogeneous phase (decomposed structure)
	585	12.0	γ_1	
	550	2.0	γ_2	
	500	4 days	γ_2	
70.60	600	0.5	$\gamma_2 + \text{melt}$	homogeneous phase (decomposed structure)
	585	12.0	γ_1	
	550	2.0	γ_2	
	500	1 month	γ_2	
70.00	585	12.0	γ_1	homogeneous phase (decomposed structure)
	500	1 month	γ_2	
69.78	500	1 month	$\gamma_2 + \theta$	
69.13	500	1 month	$\gamma_2 + \theta$	
68.00	500	1 month	$\gamma_2 + \theta$	

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 $l_1 l_2 l_3$. The solubility of aluminium in the δ may decrease rapidly as the temperature falls.

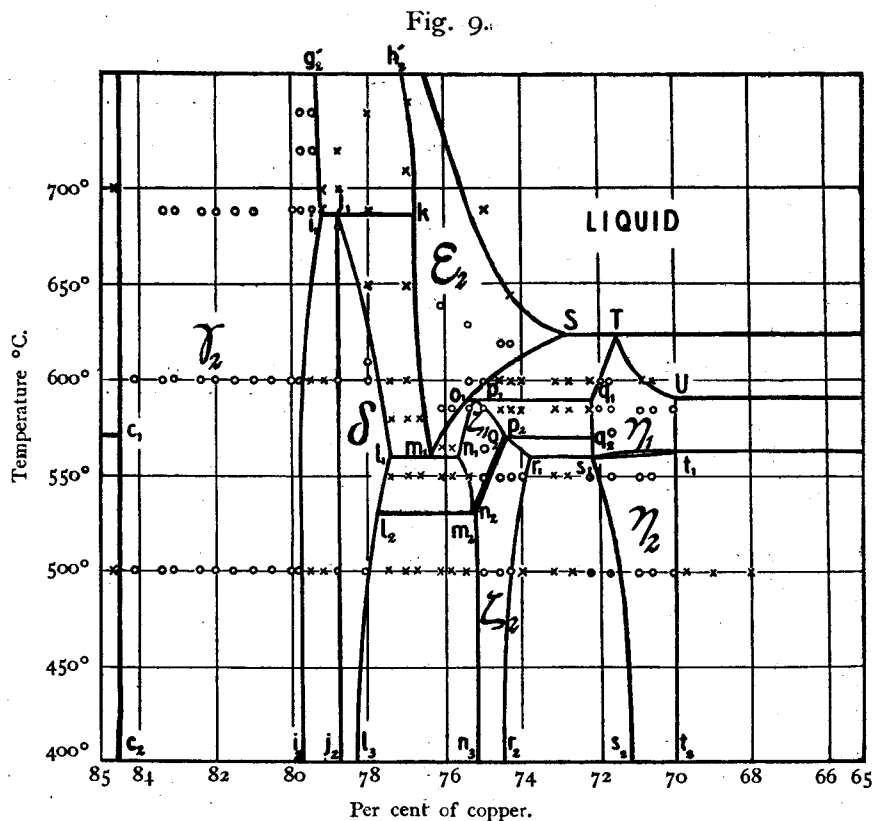
Bradely and his co-worker found the existence of a modification of the γ_2 by X-ray method, and named it the δ' phase. This δ' phase may be the same as the present writer's δ phase. The δ' phase is not a modification of the γ_2 phase, but a definite phase formed at 686°C, as already described.

In the field of $g'_2 i_1 j_1 k l_2 l_3$, 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 $i_1 j_1 k$, 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 $j_1 k m_1 l_1$, δ exists in equilibrium with ϵ_2 . The line $j_1 l_1$ is perhaps slightly concave at the side of the δ phase; whereas the line $k m_1$ is almost vertical, and intersects with the eutectoid horizontal $l_1 m_1 n_1$.

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 $l_3 l_2 l_1 m_1 n_1 m_2 n_2 n_3$ has been carefully determined from the structures of quench-



The δ phase is formed by the peritectoid reaction $\gamma_2 + \epsilon_2 \rightarrow \delta$ at 686°C 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 invariant reaction line $i_1 j_1 k$. 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

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 $\epsilon_2 + \eta_1 \rightleftharpoons \zeta_1$. It could not be retained as a complete uniform structure at room temperature, but showed always as a twinned structure because of the transformation $\zeta_1 \rightleftharpoons \zeta_2 + \theta$, 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 Photograph 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 \circ 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, $\eta_1 \rightleftharpoons \eta_2$, 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.

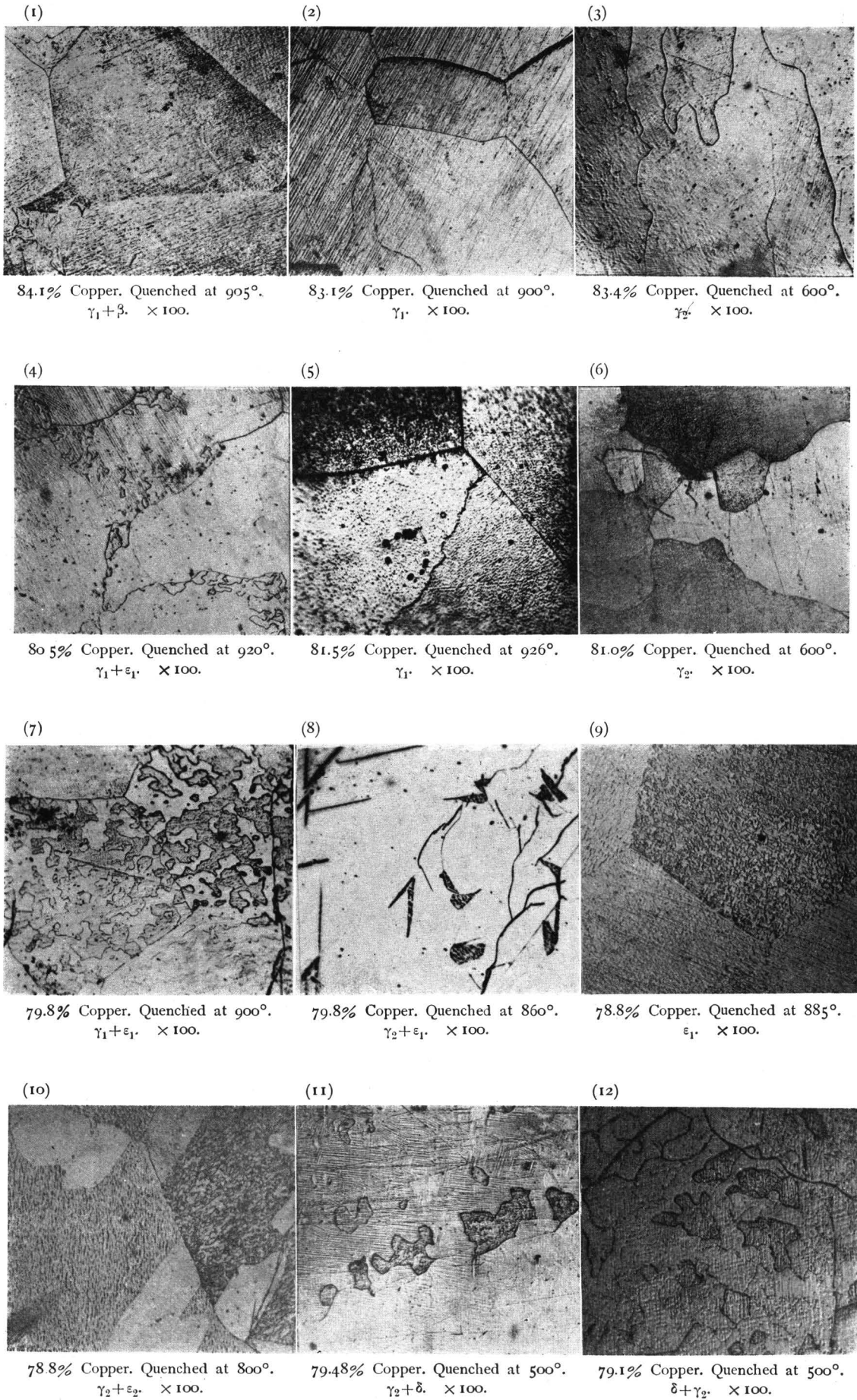
Although the field of θ phase is almost in agreement with Stockdale's recent experiments, here we will briefly comment on the results of our microscopical examinations, shown in Table 8 and plotted in the diagram, Fig 10.

Table 8.

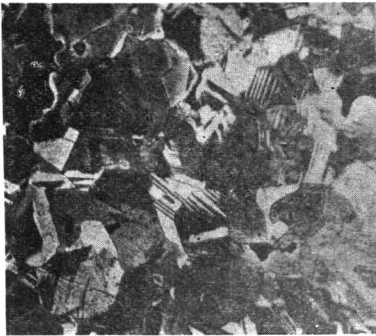
Copper Content (%)	Quenching		Phases	Remarks
	Temp. °C	Time (hours)		
65.80	618	50	Liquid + ϵ_2	There is no evidence of the peritectic reaction. dendritic ϵ_2 crystals + a little dotted η_1 crystals + θ crystals.
	585	4 days	+ η_1	
	500	10 days	$\eta_1 + \theta$	
	Furnace cooled		$\eta_2 + \theta$	
63.30	500	10 days	$\eta_2 + \theta$	dendritic ϵ_2 crystals + many dotted η_1 crystals + θ crystals.
	Furnace cooled		$\epsilon_2 + \eta_1 + \theta$	
62.30	500	10 days	$\eta_2 + \theta$	dendritic ϵ_2 crystals + many dotted η_1 crystals + θ crystals.
	Furnace cooled		$\epsilon_2 + \eta_1 + \theta$	
61.50	618	50	Liquid + ϵ_2	There is no evidence of the peritectic reaction. dendritic primary ϵ_2 crystals + many dotted η_1 crystals + θ crystals.
	585	4 days	+ η_1	
	500	10 days	$\eta_1 + \theta$	
	Furnace cooled		$\theta + \eta_2$	
56.80	585	10 days	$\eta_1 + \theta$	rod like primary η_1 crystals + many dotted η_1 crystals + θ crystals.
	500	10 days	$\theta + \eta_2$	
Furnace cooled		$\eta_1 + \theta$		
55.72	500	10 days	$\theta + \eta_2$	rod like primary η_1 crystals + dotted η_1 crystals + θ crystals.
	Furnace cooled		$\eta_1 + \theta$	
54.77	500	10 days	$\theta + \eta_2$	} completely homogeneous phase.
54.27	500	10 days	$\theta + \eta_2$	
53.73	500	10 days	$\theta + \eta_2$	
53.52	500	10 days	$\theta + \eta_2$	
53.35	500	10 days	θ	
53.00	500	10 days	θ	
52.78	500	10 days	$\theta + x$	
52.56	500	10 days	$\theta + x$	
52.10	500	10 days	$\theta + x$	

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,



(13)



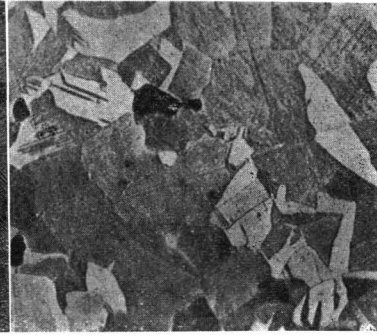
78.8% Copper. Quenched at 680°. Twinned δ . $\times 100$. (CuCl₂ solution)

(14)



78.8% Copper. Quenched at 500°. Twinned δ . $\times 100$. (Iodine solution)

(15)



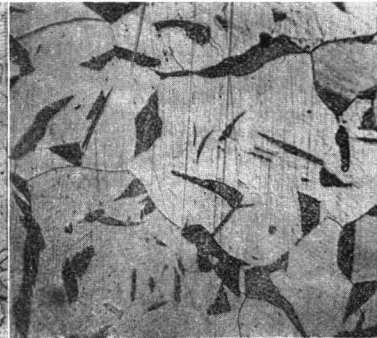
78.0% Copper. Quenched at 610°. δ . $\times 100$. (CuCl₂ solution)

(16)



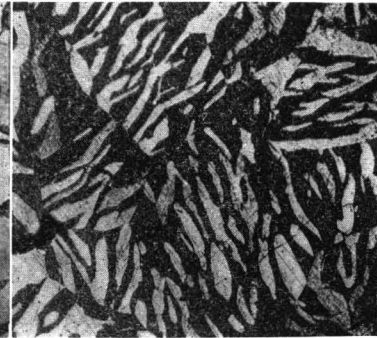
78.0% Copper. Quenched at 500°. Decomposed δ . $\times 100$. (Iodine solution)

(17)



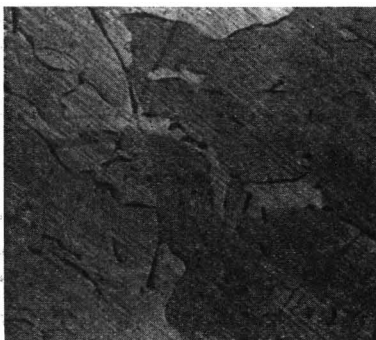
78.8% copper. Quenched at 720°. $\gamma_2 + \epsilon_2$. $\times 100$.

(18)



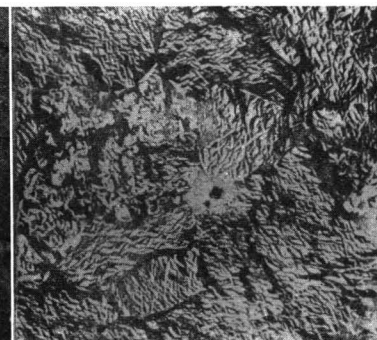
78.0% Copper. Quenched at 720°. $\gamma_2 + \epsilon_2$.

(19)



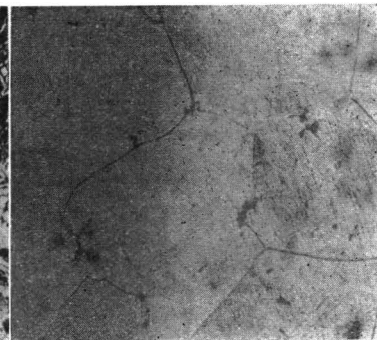
77.42% Copper. Quenched at 600°. $\epsilon + \epsilon_2$. $\times 100$. (CuCl₂ solution)

(20)



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

(21)



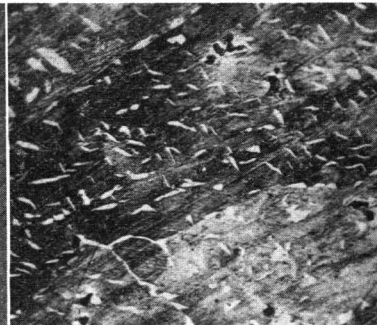
75.4% Copper. Quenched at 630°. ϵ_2 . $\times 100$.

(22)



76.1% Copper. Quenched at 585°. ϵ_2 . $\times 100$.

(23)



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

(24)



75.0% Copper. Quenched at 500°. ζ_2 . $\times 100$.

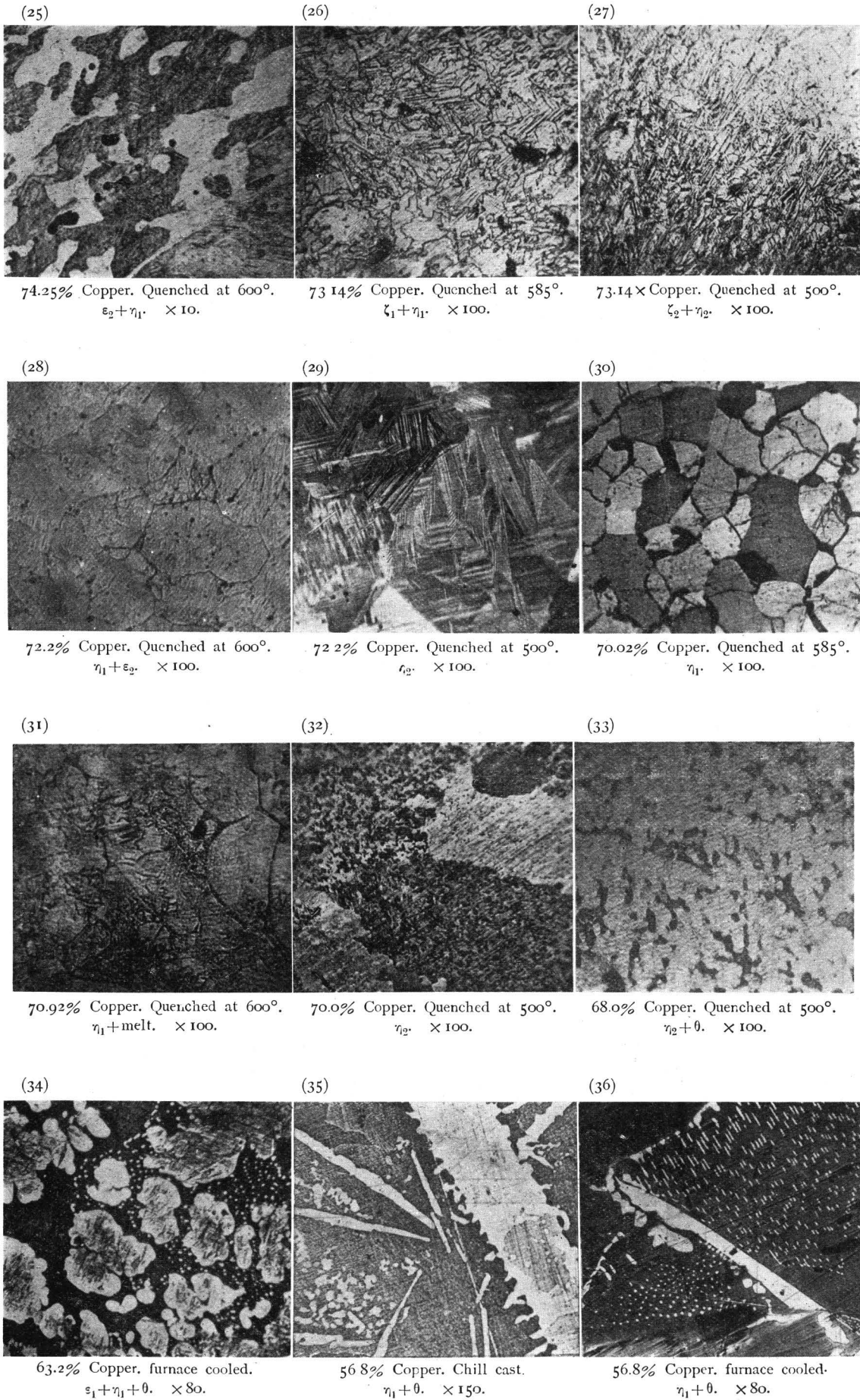
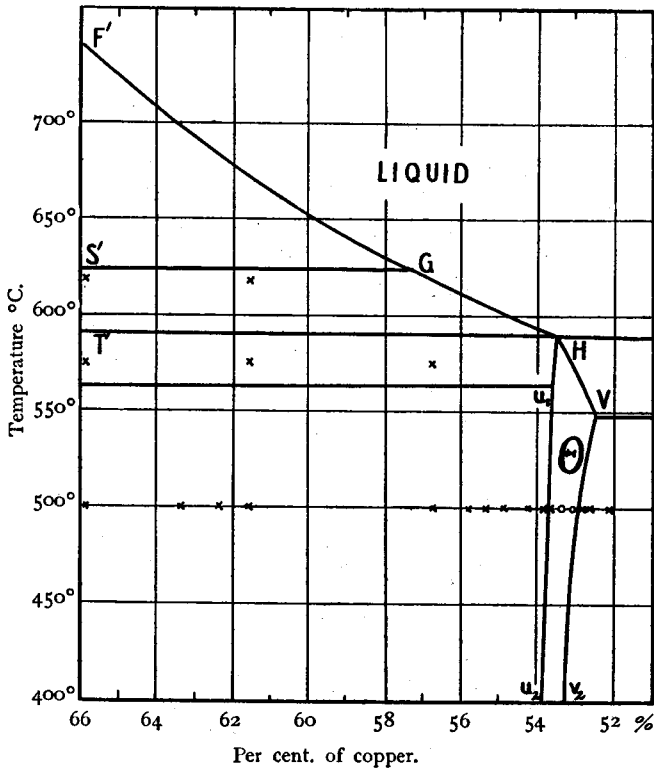


Fig. 10.



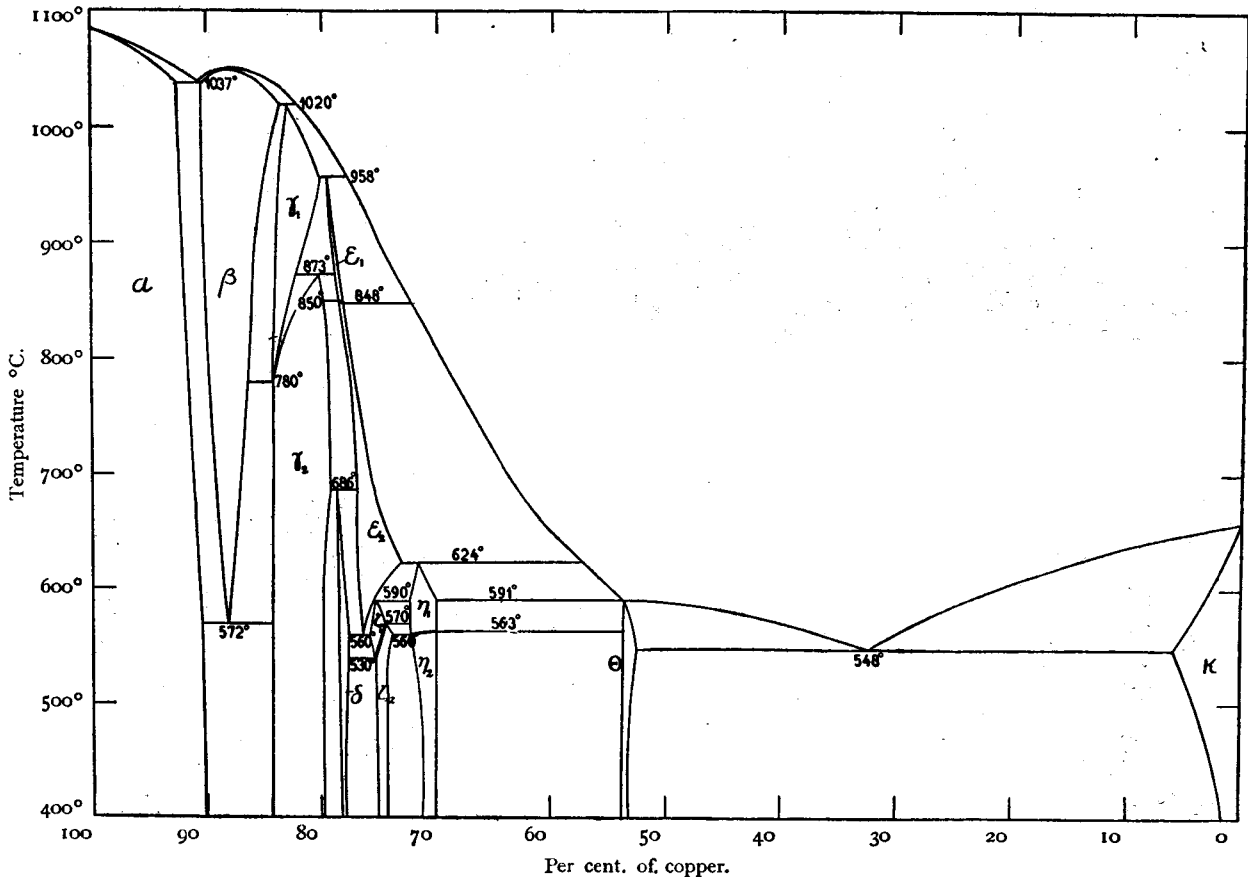
Photograph 34, of an alloy containing 63.2 per cent. copper, primary dendritic ϵ_2 crystals are seen to be decomposed into the γ_2 by solid transformations, and the secondarily crystallized γ_1 crystals into dotted form on the ground of the θ phase. These dotted γ_1 crystals were found in alloys from 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

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

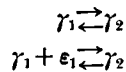
Fig. 11.



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 , γ_2 , θ , and κ .
- (3) The γ_2 phase is formed by the following reactions according to the concentration of alloys:



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 $\gamma_2 + \epsilon_2 \rightleftharpoons \delta$ at 686°C; and the ζ by the peritectoid reaction $\epsilon_2 + \gamma_1 \rightleftharpoons \zeta_1$ at 590°C. These phases form some range of solid solution, whose solubility decreases as temperature falls.
- (5) The eutectoid reactions $\epsilon_2 \rightleftharpoons \delta + \zeta_1$ and $\zeta_1 \rightleftharpoons \delta + \zeta_2$ 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.

In conclusion, the writer would like to express his cordial thanks to Prof. D. Saito and Prof. N. Nishimura, under whose guidance the present investigation was carried out, and to S. Miyoshi who gave valuable assistance.

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