

The Constitution of the Alloys of Copper, Aluminium, and Iron.

By

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Introduction

The effects of the addition of iron on the copper-rich aluminium-copper alloys, known generally as "aluminium-bronze", have been studied by several investigators. Dr. Asado¹⁾ has studied the mechanical properties and the microstructure of a series of copper alloys containing 6 to 15 per cent. of aluminium and a small proportion of iron, and he concludes that "the addition of iron to Al-bronze gives rise to grain refinement of the cast alloys by a peritectic reaction, $\text{Liquid} + (\text{Fe}) \rightleftharpoons (\text{Cu})$, which is observed in the binary copper-rich Cu-Fe alloys".

The grains of cast aluminium-bronze containing iron are greatly refined if the iron content exceeds about 3 per cent. This grain refinement increases markedly the tensile strength, without appreciably reducing the ductility. Taking advantage of these phenomena, Dr. Asado invented a high tension and corrosion resisting copper alloy, which is called "Arms Bronze" in our country. The composition of the Arms Bronze is as follows:

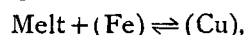
Al 8~12%, Fe 2~5%, Ni 0.5~2%,
Mn 0.5~2%, Cu Balance.

More recently, T. Tanabe and G. Koiso²⁾ have also examined a number of copper alloys containing 8 to 12 per cent. of aluminium and 0.5 to 6 per cent. of iron, and the presence of a grayish blue constituent was found to be distributed in matrix of ($\alpha + \beta$) aluminium bronzes. From these stand points they conclude that this unknown constituent refines the grain size of these cast alloys.

Thus the ternary system of Cu-Al-Fe alloys is important from the stand point of industrial uses. The equilibrium diagrams of the three binary systems, Cu-Al, Cu-Fe, and Al-Fe, may be said to have been investigated thoroughly, but the constitution copper-aluminium-iron has not been hitherto studied. The authors have therefore carried out the present investigation of this system to provide a theoretical basis for employing aluminium bronzes containing iron, and to ascertain the reason why the iron improves the strength and hardness of Al-bronzes and the possibility of precipitation hardening of the Cu-rich alloys.

The constitution of copper-aluminium alloys has been reported by one of the present writers in 1934, and more recently A.G. Dowson³⁾ has fixed accurately the position of the boundaries between β and γ phases at high temperatures, and he found a new phase to exist between 14 and 17 per cent. of aluminium. The author's previous researches, however, were sufficient for the object of the present work (i.e. up to about 15 per cent. of aluminium).

For the constitutional aspect of the copper-iron system reference has been made to the copper-iron diagram as given in Gregg and Daniloff's "Alloys of Iron and Copper". There is sufficient experimental evidence to prove that a miscibility gap exists in alloys containing from 15 to 90 per cent. of copper but the two liquid region does not intersect the liquidus. Two-liquid region is probably closed at about 20°C. above the liquidus and the solubility line expands with rise of temperature. Copper dissolves, in solid 4 per cent. of iron at 1094°C. and 0.14 per cent. or less at room temperature. At the copper side of this system a peritectic reaction,



is found to exist at 1094°C.

The iron-aluminium system has been studied by Isawa-Murakami,⁴⁾ Gwyer-Phillips,⁵⁾ Agew-Vher,⁶⁾ and Bradley-Jay.⁷⁾ It has no relation to our present investigation; hence we did not pay any consideration upon this system.

Materials Employed and Methods of Investigation.

For the purposes of this investigation, the following materials were used: Electrolytic copper of high purity, aluminium 99.8 per cent. pure, and electrolytic iron which contained the impurities; C 0.008%, Si trace, Mn 0.03%, P 0.005%, S 0.008% by analysis.

To prepare the specimens from these materials copper was melted under borax cover in a Tamman tube, heated in an electric furnace, and subsequently aluminium pieces and Cu-Fe, Al-Fe or Cu-Fe-Al alloys added according to the composition required. After stirring and skimming,

1) J. Inst. Mech. Eng. (Japan) 39 (1935) 561.

3) I. Inst. Met. advanced copy, (1937).

5) J. Inst. Met. 38 (1927) 302.

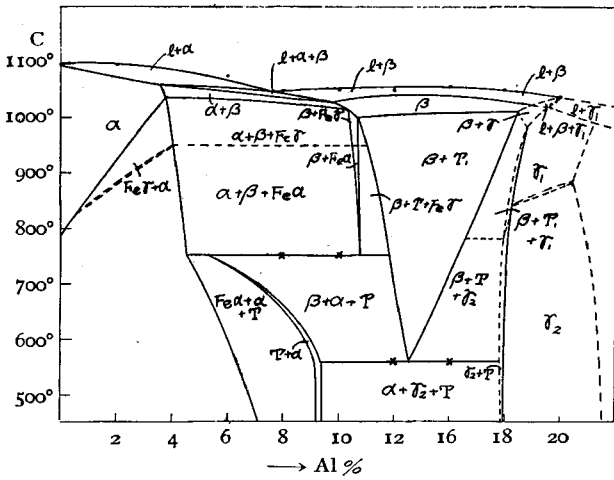
7) J. Inst. Steel Inst. 125 (1932) 339.

2) Sumitomo-Shindo-Kenkyuhōkoku Vol. 2, No. 9, p. 833.

4) Kinzoku-no-Kenkyu 4 (1927) 467.

6) J. Inst. Met. 44 (1930) 340.

Fig. 2.
2% Fe Series.



symbol • in the sectional diagrams in Fig. 2 to Fig. 6. In these Figs. the nomenclature of the constituents is used similarly as in the previous publication of the author's copper-aluminium diagrams, α , β , γ_1 , and γ_2 being the same phases as in the copper-aluminium system. In addition to them there exists a ternary intermediate phase marked as T, the nature of which will be later explained. The notation of $Fe\alpha$ and $Fe\beta$ represent the phases corresponding to the alpha and gamma-iron respectively. Fig. 2, shows a section corresponding to 2 per cent. of iron with variable content of copper and aluminium, and it is from this figure evident that the temperature of the eutectic reaction, $Liquid \rightleftharpoons \alpha + \beta$, rises by addition of iron to the copper-aluminium alloys from 1037° to the temperature $1046^\circ C$ of a peritecto-eutectic reaction, $Liquid + Fe\gamma \rightleftharpoons \alpha + \beta$.

The $Fe\alpha$ and the T constituents were observed under the microscope to be greyish blue in colour with little difference in appearance, but they are identified by the differences of crystallizing habits in primary separation as later explained.

Fig. 3.
4% Fe Series.

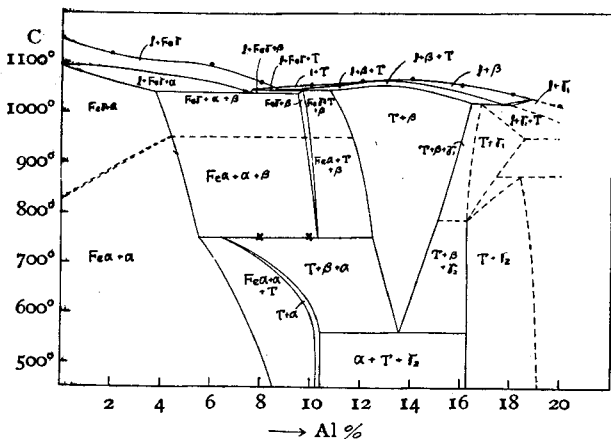
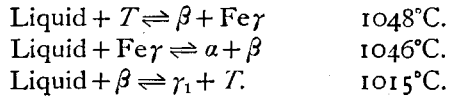


Fig. 3 represents the section of constant iron content of four per cent. The field of the primary α phase is not observed, but there exist the fields of the primary separation of $Fe\gamma$, T, β and γ_1 phases. In this section, three invariant reactions



are observed to exist.

These invariant reactions also occur in Figs. 4 and 5, which represent the constitutions of the

Fig. 4.
6% Fe Series.

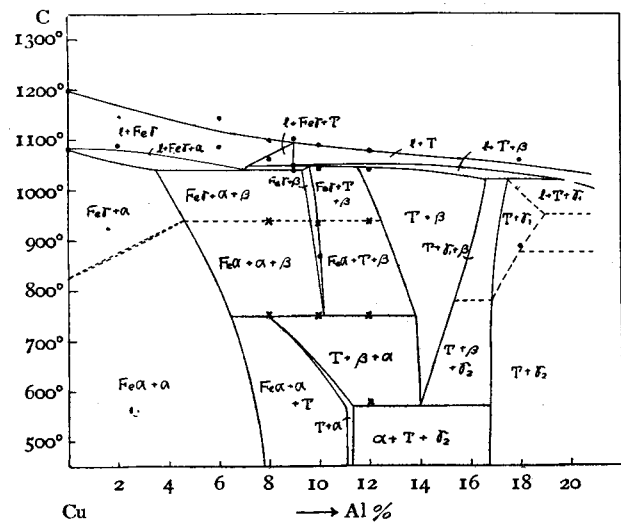
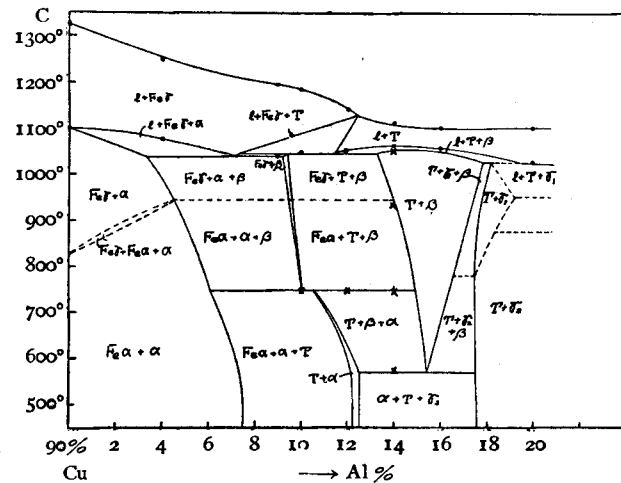


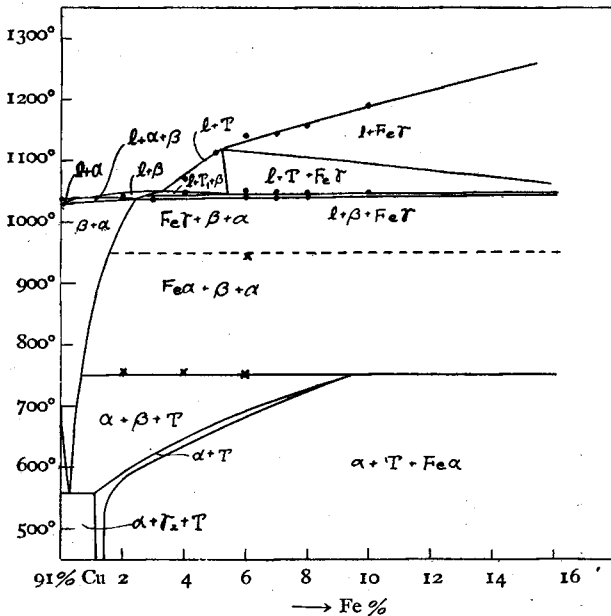
Fig. 5.
10% Fe Series.



alloys with constant iron content of six and ten per cent. respectively.

From them we see that the solid solubility of iron in the α phase decreases with fall of temperature. In figure 6, representing alloys which contain nine per cent. of aluminium with variable proportion of iron, two invariant reactions on solidification are found and the structures of alloys containing more than about two per cent. iron

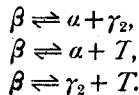
Fig. 6.
9% Al Series.



show T phase to exist and the field of $\alpha + T + \text{Fe}\alpha$ is clearly recognized by microscopical study.

Solid Transformation:—For the determination of solid transformation annealed specimens were thermally analysed similarly as described in the previous research.* Some examples of the heating thermal curves are showed in Fig. 1. The temperatures of arrest on these curves are plotted in the vertical sections as shown in Figures 2~6, where they are represented by the symbol \times . From these figures we see that with small addition of iron to the copper-aluminium alloys the temperature of the binary eutectoid reaction, $\beta \rightleftharpoons \alpha + \gamma_2$, is lowered to 560°C ., at which a ternary eutectoid reaction, $\beta \rightleftharpoons \alpha + \gamma_2 + T$, takes place.

This invariant reaction is built up from the binary reactions corresponding to



The existence of the three phases field $\alpha + \gamma_2 + T$ is very clearly ascertained in the alloy, containing 12 per cent. of iron and 12 per cent. of aluminium, which has been slowly cooled in the furnace. The composition of the ternary eutectoid point may be about 12 per cent. of aluminium and less than 0.5 per cent. of iron. At higher temperature the solid solubility of iron in β phase may be about 2 per cent., and it decreases considerably with the lower temperature. At 1000°C an alloy containing 12 per cent. of aluminium and 2 per cent. of iron consists of an almost homogeneous β phase, but at 700°C it separates a small

quantity of T compound and its separation increases as the temperature falls to the room temperature. Another two invariant reactions, $\beta + \text{Fe}\alpha \rightleftharpoons \alpha + T$ and $\alpha + \text{Fe}\gamma \rightleftharpoons \beta + \text{Fe}\alpha$ were recognized to occur. The former reaction occurs at 750°C as seen from the results of thermal analysis as shown in Fig. 1 (9) and (10), but the temperature of the latter reaction, due to the allotropic transformation of gamma-iron to alpha-iron, could not be distinctly ascertained by direct evidence, though we described theoretically the invariant line at about 950°C in the figures.

Metallographic Investigation.

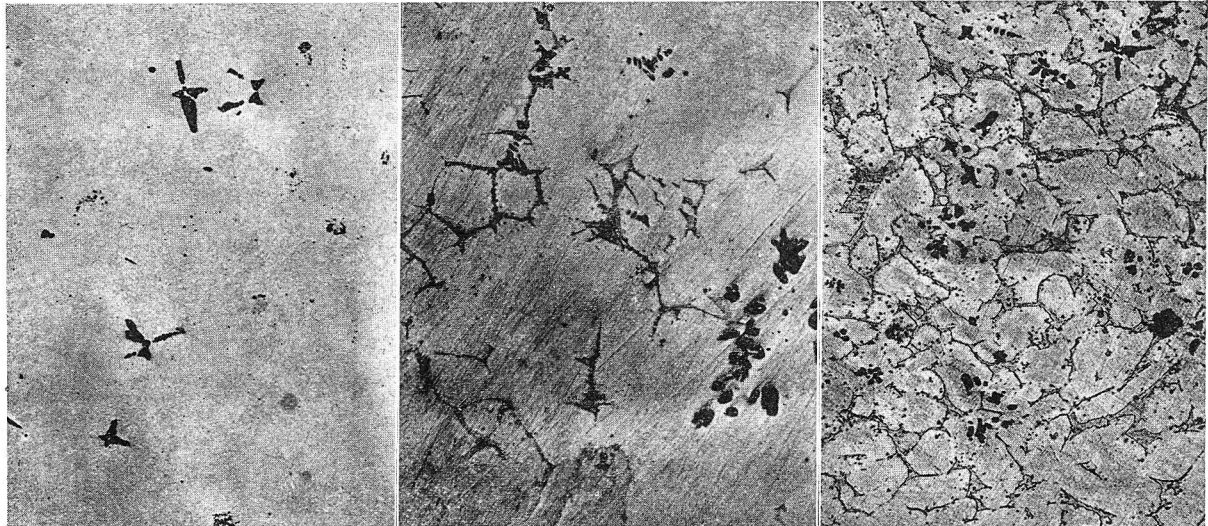
After thermal analysis, all specimens were cut or broken into pieces and one of them was examined for microscopical study to ascertain the slowly cooled phenomena. The remaining majority of pieces were remelted and cast into iron mould to prepare them for the investigation of heat treated structures by which we recognized the transformations in solid state. By the microstructures of the above mentioned alloys with reference to the results of the thermal analysis, the sectional diagrams as shown Figs. 2~6 were thus determined. The polished specimens were etched, in the majority of cases, by a solution of alcoholic acid ferric chloride solution (30 grs. $\text{FeCl}_3 + 20$ cc. Conc. $\text{HCl} + 950$ cc. Alcohol). This reagent developed the structures of α , β , γ_1 , γ_2 and alpha-iron constituents, such as they are usually observed in ordinary Cu-Al and Cu-Fe alloys, but the identification of a T constituent associated with γ_2 phase was not always distinguished by this etching. An alcoholic acetic nitric acid (An alcoholic nitric acid with acetic acid) solution was found to be suitable for distinguishing the T -Compound from γ_2 constituent in the specimens on which thermal investigations were performed.

Photograph 1 is a microstructure of an alloy containing 6 per cent. aluminium and 4 per cent. iron cooled slowly from liquid. It shows primarily crystallized dendritic gamma-iron crystals existing in the boundary of the (α) copper solid solution. The crystal habit of the primarily crystallized gamma-iron is distinguished by its rounded form from the ternary intermediate compound T , while the latter appears accicular dendrite as shown in Photograph 8. The alloy containing 6.8 per cent. of aluminium and 4 per cent. of iron, on being slowly cooled from liquid condition, consists of $\text{Fe}\alpha + \alpha + \text{a little } \beta$. This is shown in Photograph 2, under a magnification of 150 diameters, in which the large primary and fine secondary iron crystals are observed to be of

* Memoirs of the College of Engineering, Kyoto Imp. Univ. Vol. VIII, No. 2. p. 75.

brown colour and the β crystals of the ternary alloys are seen as a half-tone colour and they are found in the ground of the copper solid solution. Photograph 3 represents the structure of an alloy containing 9 per cent. of aluminium and 5 per cent. of iron. It is also an alloy of the similar phase field in which a medium amount of β and primary dendritic nodulus of iron crystals are shown. The microstructure of an alloy containing 10 per cent. of aluminium and 4 per cent. of iron, furnace cooled, is given in photograph 4, under a magnification of 120 diameters. It will be seen that this alloy consists of $a+\beta+T$. The latter is here observed as a small light coloured constituent in a matrix of copper solid solution. The unetched and etched structures of an alloy (10 per cent. aluminium, 6 per cent. iron) are given

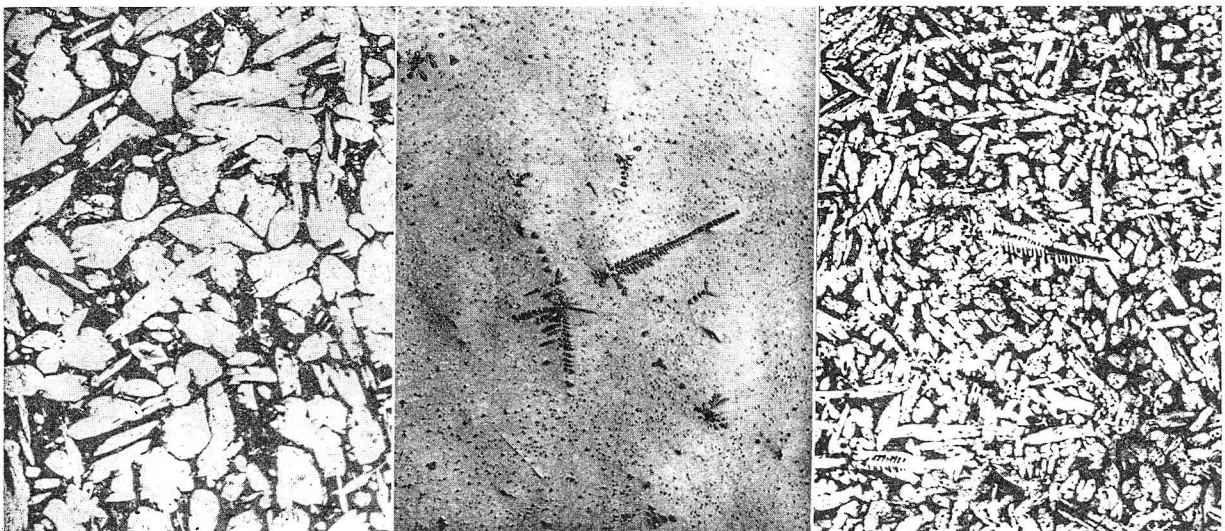
in Photograph 5 and 6 respectively. The greyish dark etching constituent is T crystal; this has come out primarily in the form of accicular needles and if it has secondarily separated, it appears in the form of fine particles, in such matrix of $a+\beta$ as usually observed in the ordinary $a+\beta$ aluminium bronze. Photograph 7 shows in a magnification of 150 diameters an alloy with fine T crystals distributed in β phase, which has been decomposed into a eutectoid mixture. In this photograph, small accicular dendrites of T crystal are uniformly distributed in the matrix of β phase. With increase in the amount of iron added to β -aluminium bronze the dendrites of T crystal are more distinctly seen as shown in photograph 8, of an alloy containing about 12 per cent. of aluminium and 8 per cent. of iron. With more addition of



(1) 6% Al, 4% Fe, Rest Cu. $\times 150$
Furnace cooled.
 $Fea+a$.

(2) 6.8% Al, 4% Fe, Rest Cu. $\times 150$
Furnace cooled.
 $Fea+a+\beta$.

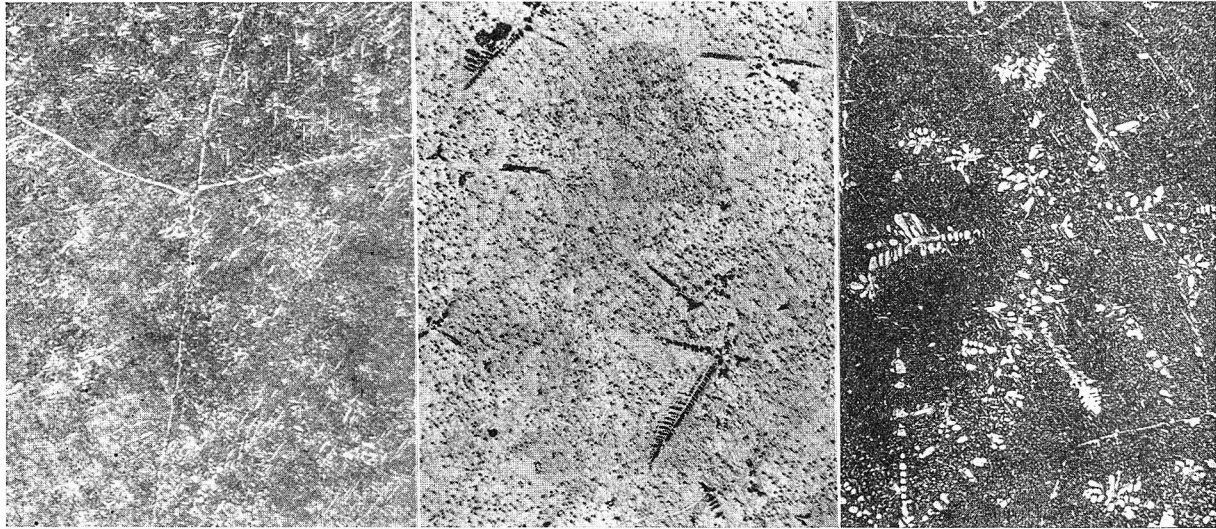
(3) 9% Al, 5% Fe, Rest Cu. $\times 120$
Furnace cooled.
 $Fea+a+\beta$.



(4) 10% Al, 4% Fe, Rest Cu. $\times 120$
Furnace cooled. $T+a+\beta$.
Etched with acetic nitric acid solution.

(5) 10% Al, 6% Fe, Rest Cu. $\times 100$
Furnace cooled.
Unetched.

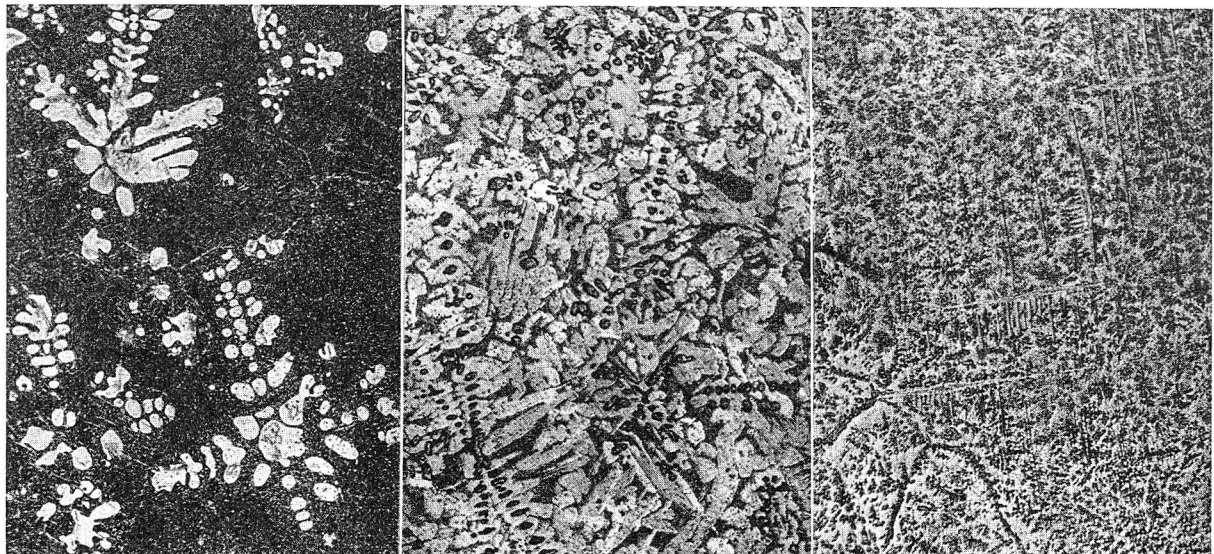
(6) The same specimen as Fig. 5,
but etched with ferric chloride solution.
 $\times 100$



(7) 12% Al, 6% Fe, Rest Cu. $\times 150$
Annealed at 500°
for 120 hrs.

(8) 12% Al, 8% Fe, Rest Cu. $\times 120$
 $T+\beta$
Unetched.

(9) 12% Al, 10% Fe, Rest Cu. $\times 120$
Furnace Cooled.
 $Fe\alpha+\beta$



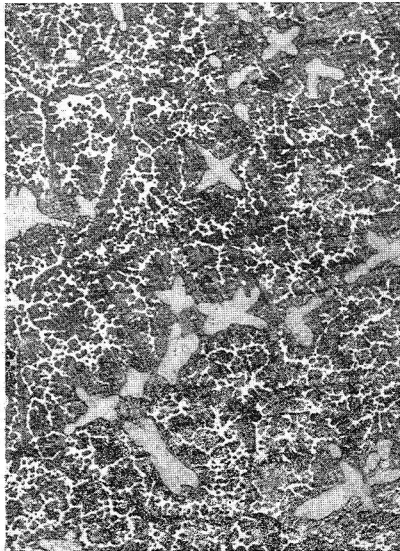
(10) 12% Al, 12% Fe, Rest Cu. $\times 120$
Furnace cooled.
 $Fe\alpha+\beta$

(11) 10% Al, 10% Fe, Rest Cu. $\times 120$
Furnace cooled. $Fe\alpha+a+\beta$.
Etched with acetic nitric acid soln.

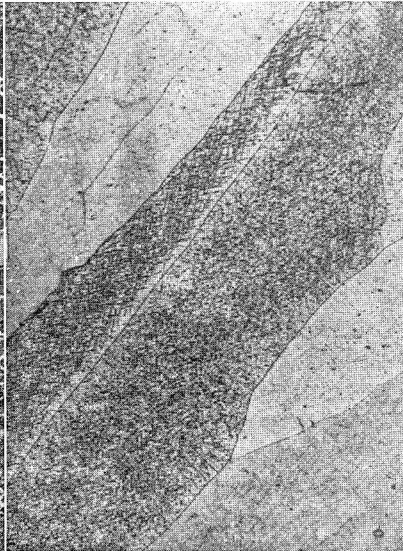
(12) 14% Al, 10% Fe, Rest Cu. $\times 120$
Furnace cooled.
 $T+\beta$

iron, gamma-iron crystals are separated out primarily, photographs 9 and 10 illustrate them. Primary crystallized gamma-iron exhibits a rounded dendrite which is decomposed by solid transformation. The fields of the primary separation of T and gamma-iron are represented respectively by HP_3P_1G and GP_1P_2C in Figure 7. The different shapes of the primary crystal in these fields are also illustrated in Photographs 11 and 12. Photograph 11 is a microstructure of an alloy containing 10 per cent. of aluminium and 10 per cent. of iron cooled in a furnace. In this figure we see that the rounded dendrite is the primary separated gamma-iron, the greyish dark constituent is the decomposed β phase, and α phase present as a constituent of yellowish colour. The microstructure of the furnace cooled alloy containing 14 per cent.

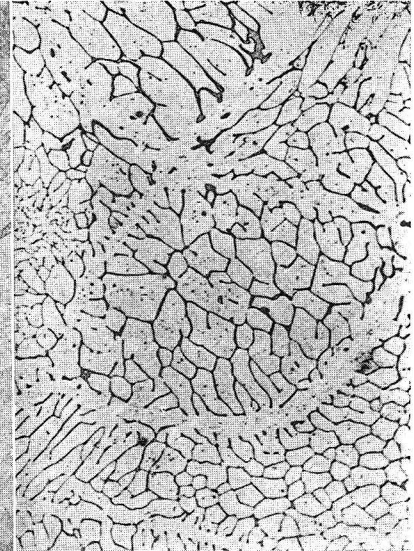
of aluminium and 10 per cent. of iron is shown in photograph 12, in which the accicular dendrite T crystals are surrounded by the matrix of the β phase. As shown in photograph 13 the alloys in the field of $P_3f_1d_1h_2$ in Figure 7 consist of the three phases, $T+\beta+\gamma$. The T phase separates primarily in dendritic form and the greyish etching constituent is the γ_2 phase and the β phase is yellowish grey. To distinguish between T and γ_2 phases an alcoholic acetic nitric acid was used for an etching as previously mentioned. The solubility of iron in the γ_2 phase was determined by microscopical examination. We see that about 2 per cent. of iron dissolves in the γ_2 phase as shown in photograph 14. This is microstructure of the alloy containing 20 per cent. of aluminium and 2 per cent. of iron, which is annealed for 8 hours



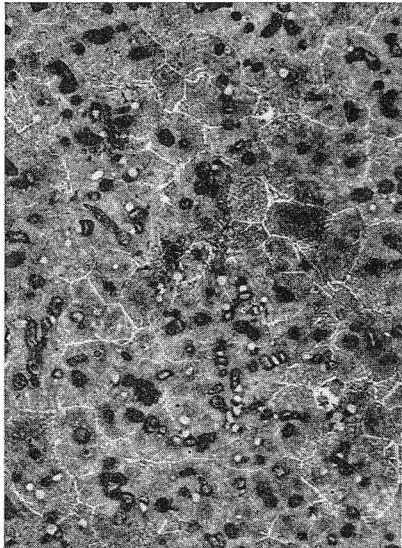
(13) 16% Al, 10% Fe, Rest Cu. $\times 120$
 $T + \gamma_2 + \beta$
 A furnace cooled specimen was etched with acetic nitric acid solution.



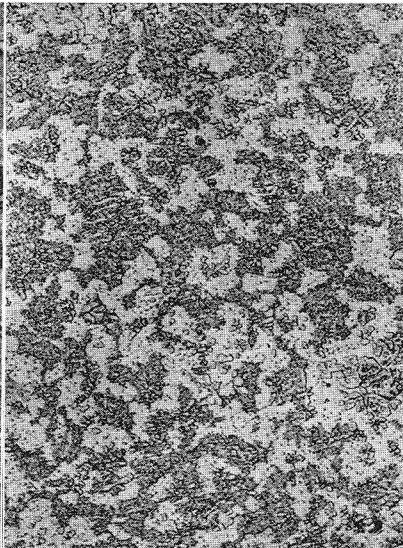
(14) 20% Al, 2% Fe, Rest Cu. $\times 150$
 Annealed for 8 hours at 800° , slowly cooled to 500° and then reannealed for a week at that temperature.
 Almost uniform γ_2 phase.



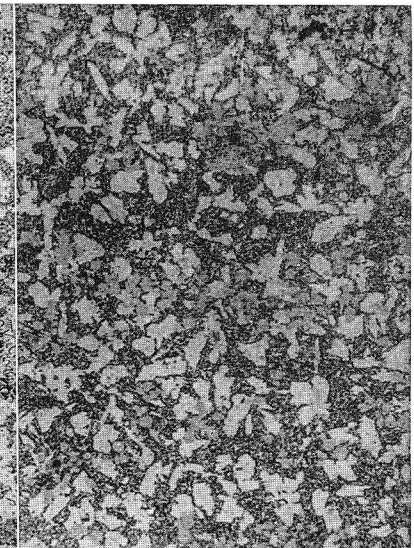
(15) 20% Al, 4% Fe, Rest Cu. $\times 150$
 The heat treatment is the same as described in Fig. 14.
 $\gamma_2 + T$.



(16) 10% Al, 10% Fe, Rest Cu. $\times 120$
 Heated at 950° for 8 hours.
 $Fe\gamma + T + \beta$.
 Etched with ferric chloride solution.



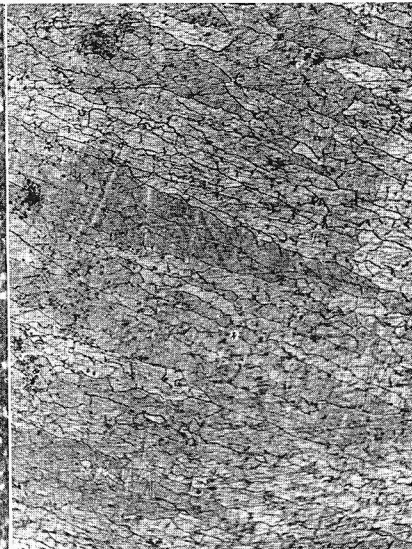
(17) 10% Al, 10% Fe, Rest Cu. $\times 200$
 Heated at 950° for 8 hrs., and reannealed at 500° for three weeks.
 $Fe\alpha + T + \alpha$.
 Etched with acetic nitric acid solution.



(18) 12% Al, 12% Fe, Rest Cu. $\times 150$.
 Heated at 900° for 24 hours, at 500° for 1 week and furnace cooled.
 $Fe\alpha + T + \alpha$.

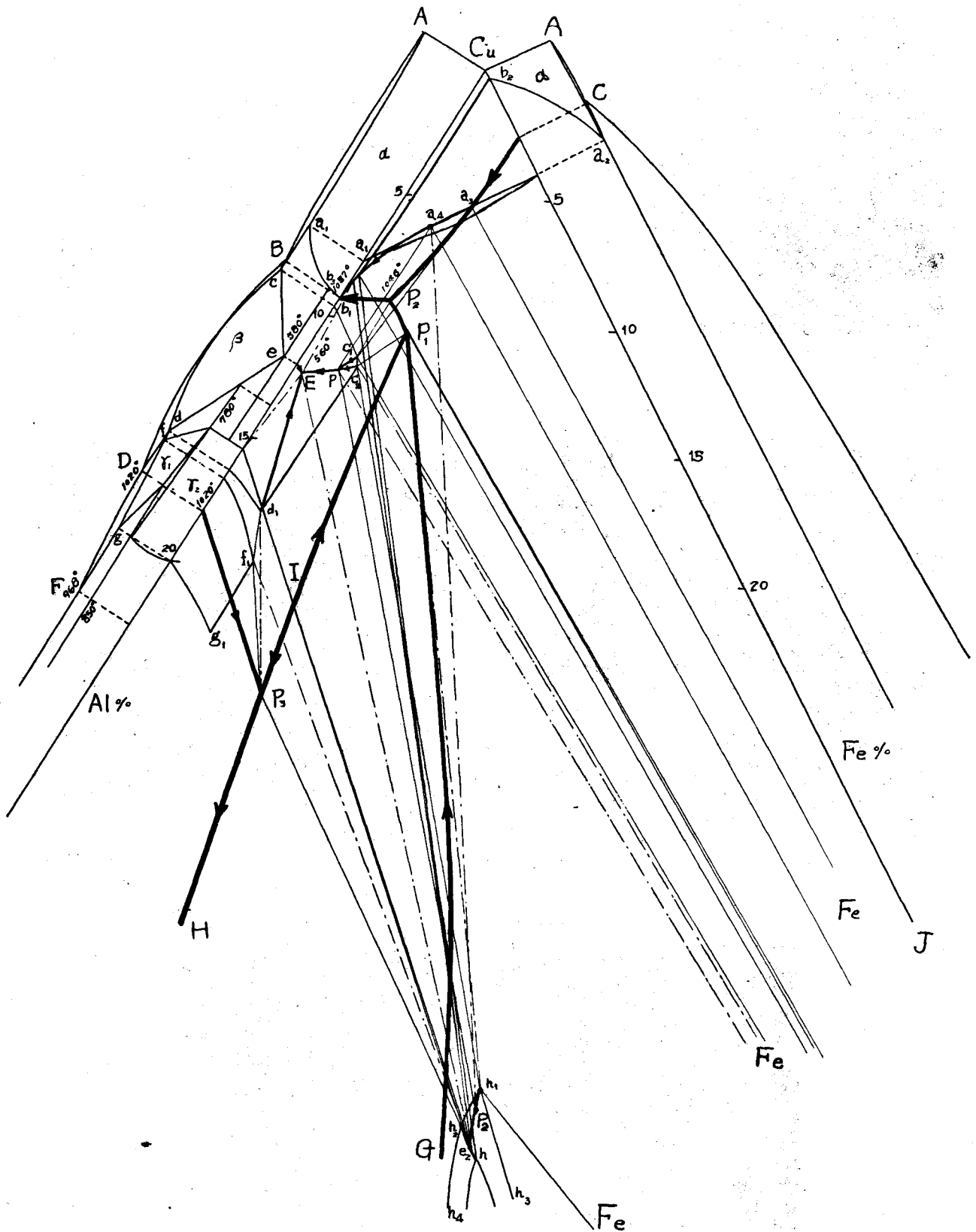


(19) 20% Al, 30% Fe, 50% Cu. $\times 150$
 Furnace cooled.



(20) The same alloy as $\times 100$
 Fig. 19, but annealed for a day at 800° .
 A uniform T phase.

Fig. 7.



at 800°C, and for a week or more at 500°C. With more than 2-4 per cent. of iron some amount of the *T* phase exists in the boundary of the γ_2 phase. This is illustrated in photograph

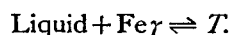
15, in which the greyish γ_2 crystals are surrounded by the network of *T*. The existence of the univariant reaction, $\beta + Fea \rightleftharpoons a + T$, at 750°C is ascertained also by microscopic examination.

Photograph 16 shows the microstructure of the alloy containing 10 per cent. of aluminium and 10 per cent. of iron which was annealed 8 hours at 950°C and quenched in water. The three phase field of $Fe\gamma+T+\beta$ due to the above described invariant reaction is distinctly observed. When the same alloy is annealed for a long time under the univariant temperature, we see that it consists of $Fea+T+a$ as shown under a magnification of 200 diameters in photograph 17.

The similar structure of the $Fea+T+a$ phases is also seen in an alloy containing 12 per cent. of aluminium and 12 per cent. of iron in photograph 18, in which the grey etching constituents are the Fea phase and the light yellowish a constituent are seen in matrix of the T phase.

The Compound T : The ternary intermediate phase T was identified under microscope and the X-ray analysis proved its existence for the alloy containing 20 per cent. of aluminium and 30 per

cent. of iron. By etching of the unannealed specimen the dendritic enveloped structure as shown in photograph 19 was found. This illustrated well that the compound T is formed by the peritectic reaction:



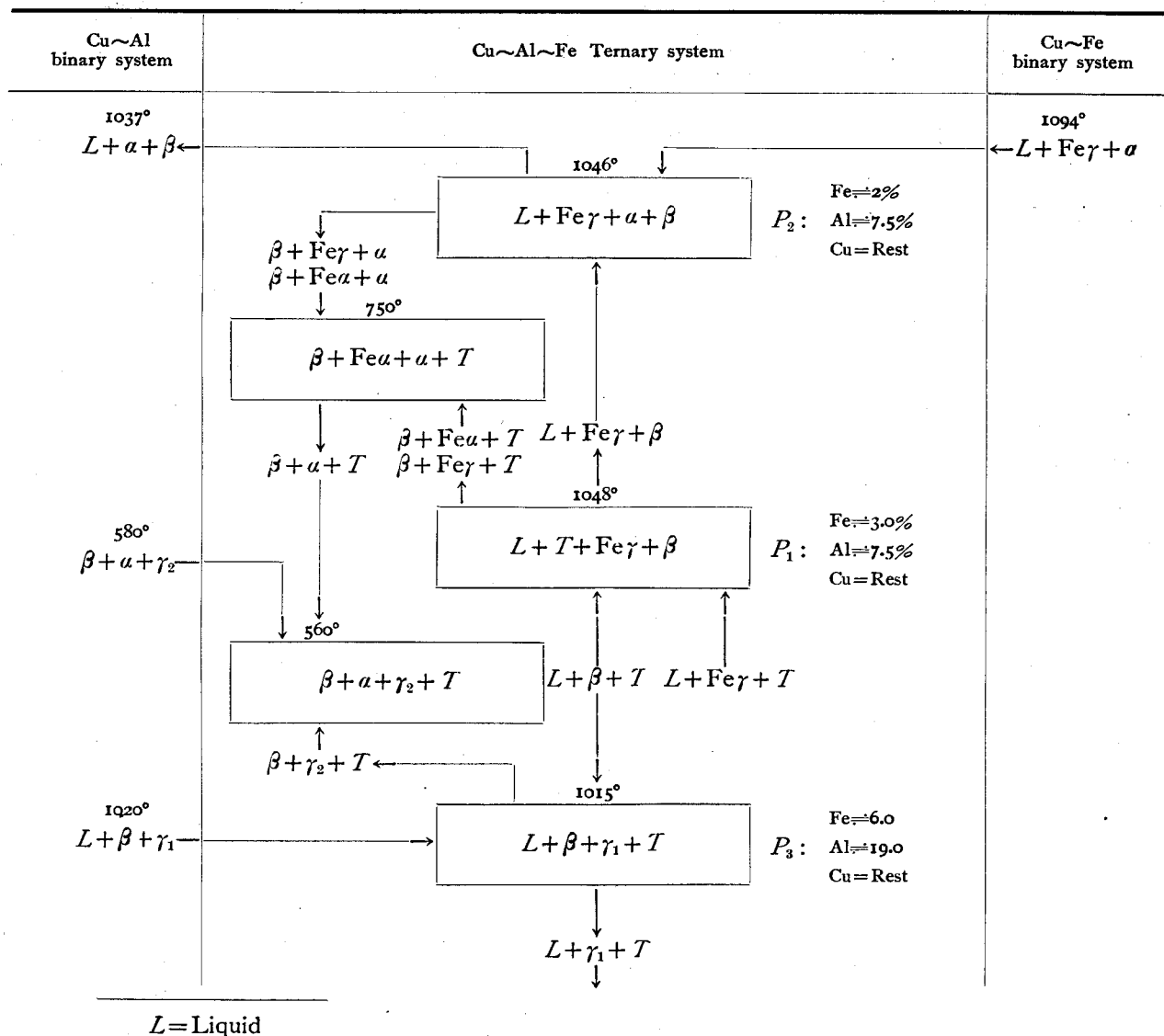
By annealing the same alloy at 800°C a day the enveloped structure was made to disappear and it was transformed into the uniform structure. This is evident in photograph 20, under a magnification of 100 diameters.

After further examination we found that this compound is of no fixed composition but formed a wide range of solid solution: 20~27% Al, 25~45% Fe, and Cu the rest.

Equilibrium Diagram.

From the results of our present experiments, an equilibrium diagram of the copper rich Cu-Al-

Table 2.



Fe system has been obtained as given in Figure 7, in which the field of ACP_2B represents the primary separation of copper rich solid solution (a) and those of $Fe\gamma$, β , γ_1 and T phases are respectively shown by JCP_2P_1G , $DP_3IP_1P_2B$, DP_3H and GP_1IP_3H . The binary complex lines showing the univariant reactions during solidification are summarized as follows.

CP_2	Liquid + $Fe\gamma \rightleftharpoons a$,
P_2B	Liquid $\rightleftharpoons a + \beta$,
P_1P_2	Liquid $\rightleftharpoons Fe\gamma + \beta$,
GP_1	Liquid + $Fe\gamma \rightleftharpoons T$,
P_3IP_1	Liquid $\rightleftharpoons T + \beta$,
DP_3	Liquid + $\beta \rightleftharpoons \gamma_1$,
HP_3	Liquid $\rightleftharpoons \gamma_1 + T$.

The quasi-binary eutectic curve P_3IP_1 has a maximum point I at about $1060^\circ C$ and it proceeds from this point to both P_1 and P_3 points. Three invariant points P_1 , P_2 and P_3 are found to exist on the liquidus surface and two points E and ϕ in solid state. The reactions of the latter two points are already explained in the paragraph of thermal analysis and microscopical study. The composition, temperature, and reacting phases of these nonvariant reactions are given in Table 2.

Conclusion.

(1) The equilibrium diagram of Copper rich Cu-Al-Fe alloys containing up to 20 per cent. of

aluminium and up to about 10 per cent. of iron was determined.

(2) A ternary phase, which the authors denote " T " was found to exist and it is formed by a peritectic reaction, $Liquid + Fe\gamma \rightleftharpoons T$.

The true nature of this ternary phase is not thoroughly examined but its existence is ascertained by microscopical examination. T phase has a large solubility of iron and aluminium. The existing range of homogeneous field extends from 20 to 27 per cent. of aluminium and from 25 to 45 per cent. of iron at room temperature.

(3) The following invariant reactions were found to exist on solidification and in the solid state.

Liquid + $T \rightleftharpoons \beta + Fe\gamma$	$1048^\circ C$.
Liquid + $Fe\gamma \rightleftharpoons a + \beta$	$1046^\circ C$.
Liquid + $\beta \rightleftharpoons \gamma_1 + T$	$1015^\circ C$.
$\beta + Fea \rightleftharpoons a + T$	$750^\circ C$.
$a + Fe\gamma \rightleftharpoons \beta + Fea$	about $950^\circ C$.
$\beta \rightleftharpoons a + \gamma_2 + T$	$560^\circ C$.

The latter ternary eutectoid reaction occurs at a temperature approximately 20° below that of the eutectoid temperature in copper-aluminium alloys.

(4) The γ_2 phase of Cu-Al system forms a range of solid solution, the maximum solubility of which with iron may be about 2 per cent. at room temperature.