

Revision of the Equilibrium Diagram of the Copper-Zinc System.

By

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Despite the enormous literature on the Cu-Zn diagram since Roberts-Austen¹, there are still many points left for better determination. The author undertook therefore to try a full revision of the diagram, treating it in five parts as described in the following lines.

For the preparation of the alloys, he took electrolytic pure copper and the zinc *pur.* of Kahlbaum. In order to avoid the change in %-compositions by volatilization, the zinc was first fused under molten sodium chloride in a porcelain crucible, and while it was kept at temperatures a little lower than the boiling point, the copper was gradually thrown in small pieces into the melt and well stirred, the temperature being then, if necessary, raised. The alloys thus prepared generally underwent only a slight loss and were found on analysis to contain 0.2-0.5% Zn short of a given composition. He gives therefore as the compositions of the alloys, except those in Table I, the figures calculated from the mixed quantities of the constituent metals and not those actually obtained from analysis.

¹ 4th report to the Alloys Research Committee of the Institute of Mechanical Engineers, 31-100 (1897).

Table I.

%Cu used for alloying.	%Cu after ¹ alloying.	%Cu used for alloying.	%Cu after ¹ alloying.
1	1.40	40	40.23
2	2.13	41	41.21
12	12.31	42	42.37
13	13.72	43	43.42
14	14.38	44	44.19
15	15.50	45	45.31
20	20.78	50	50.45
21	21.43	51	51.52
22	22.19	56	56.26
23	23.41	57	57.18
24	24.36	60	60.32
25	25.37	65	65.16
26	26.46	67	67.43
29	29.62	68	68.76
30	30.30	70	70.52
31	31.24	80	80.47

I. The Exact Positions of the Liquidus, Solidus and Peritectical Lines.

As to the positions of the liquidus and the peritecticals, Roberts-Austen's determinations are generally believed so accurate, that no subsequent work could modify them in any way. Though this was found to be mostly true, yet there were some discrepancies inevitable differences in the author's results, as given in Table II:—

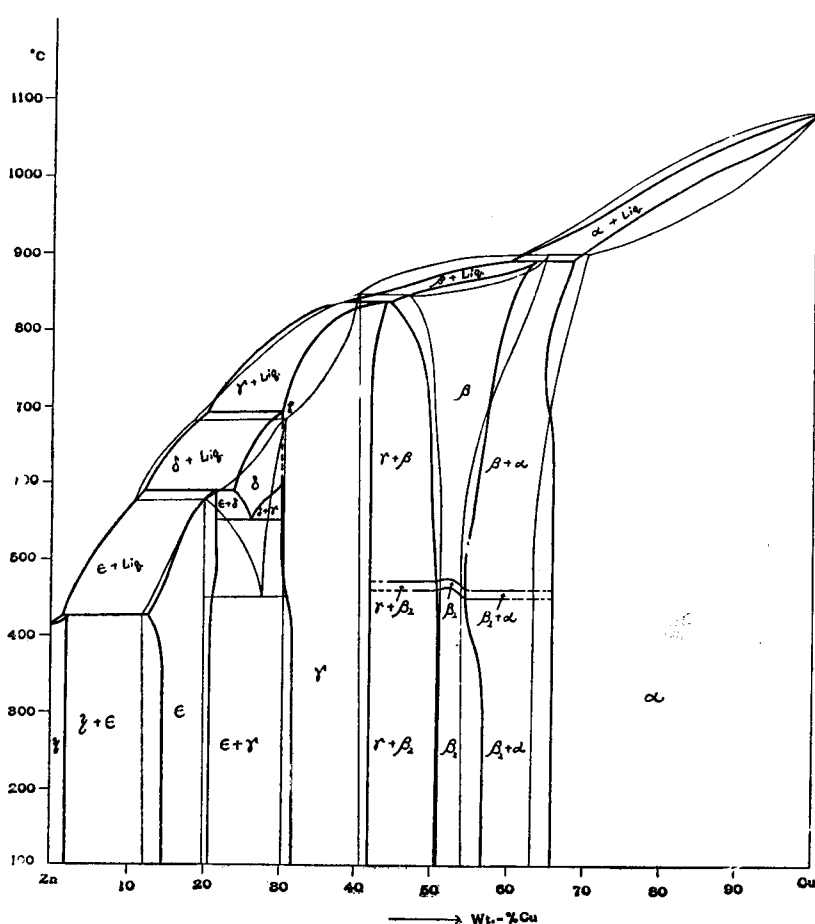
¹ The Cu only was determined electrolytically.

Table II.

Wt.-%	Liquidus.	Solidus.	Peritectic.		Wt.-%	Liquidus.	Solidus.	Peritectic.	
Cu.	°C	°C	°C	Sec.	Cu.	°C	°C	°C	Sec.
0	—	419 (m.p.)	—	—	46	858	848	—	—
0.5	421	419 ?	—	—	48	866	854	—	—
1	422	—	420 ?	?	50	868	862	—	—
2	430	—	422 ?	?	53	881	868	—	—
3	455	—	423	20	55	886	876	—	—
5	496	—	423	30	57	890	878	—	—
7	533	—	423	27	59	890	885	—	—
8	550	—	422	24	60	890	883	—	—
10	574	—	424	13	61	898	?	892	?
12	595	—	424	5	62	899	?	896	4
14	626	450	589	4	63	902	—	894	6
16	652	505	588	6	64	904	—	892	5
18	674	560	592	9	66	916	—	893	3
20	692	585	592	13	68	928	—	893	2
22	722	—	693	2	70	947	904	—	—
			592	5					
24	742	602	692	2	71	948	916	—	—
26	764	651	692	2	72	956	928	—	—
28	778	680	692	2	74	964	930	—	—
30	794	—	695	1	77	984	958	—	—
32	810	756	—	—	80	998	978	—	—
34	816	795	—	—	83	1011	990	—	—
36	824	810	—	—	85	1022	1000	—	—
38	830	824	—	—	87	1036	1009	—	—
40	838	828	834	3	90	1040	1022	—	—
42	839	—	833	4	95	1068	1048	—	—
44	850	840	—	—	100	1084 (m.p.)	—	—	—

In accordance with these determinations, the following diagram, Fig. 1, was plotted, in which the changes in the solid phases are also given for the sake of convenience, though their data have not yet been mentioned. Shepherd's diagram¹ is also plotted, with the same abscissae, in thinner lines; this is intended to show how the author's results deviate from the hitherto known data.

Fig. 1.



As is evident from the diagram, there are six sets of the liquidus and solidus, the temperatures of which were easily determined from well marked breaks in their cooling curves. The two relating to 60-100%

¹ Journal of Physical Chemistry, 8, 6, 421(1904).

Cu and 42-61% Cu run much narrower and lie enclosed in Shepherd's curves; the remaining four relating to 20-42% Cu, 12-20% Cu, 2-12% Cu and 0-2% Cu are usually in coincidence with Shepherd's, except that the two solidi for 30-43% Cu and 23-31% Cu come out much higher.

The peritecticals, except that for 20-30% Cu at 692°, could easily be determined, as each of them showed usually a definite length of time for crystallization. In the case excepted, there are no two saturation-points as usual; they coincide at a point (f). In such an irregular case, things are not to be expected to go on normally.

The presence of the peritectical for 40-45% Cu at 835°, as asserted by Roberts-Austen as well as by Shepherd but not by Tafel¹, was manifest through the arrests clearly shown in the author's cooling curves. The concentration of the peritectic must lie at 42% Cu, because there was the longest arrest, and, furthermore, the boundary line for γ at the right hand side meets exactly at this point, as will be shown in a later chapter,

The time of arrest for the horizontal line at 423° ranging from 2% to 13% Cu has its maximum at 5% Cu, becoming smaller as it goes to the right. Whether the horizontal line is a peritectic or a eutectic reaching to 0% Cu is doubtful, because the η -field is too narrow and the nature of the curves of solidification can not be ascertained by reason of their lying too near to the horizontal. That it is a peritectical, may, however, be concluded from the following considerations:—

1. The temperature of the horizontal was determined as lying a little higher than the melting point of zinc.

2. If the horizontal be eutectical, the alloys within 0-2% Cu must show a two-phased structure. An alloy with 0.1% Cu, when quenched at 430°, *i. e.* a little higher than the melting point of zinc, showed a structure like a eutectic, as shown in Photo. 1. This occurs even in the case of pure zinc; Photo. 2. Since the zinc, when suddenly cooled, has a tendency to crystallize in fine needles, expelling the impurities in their intervening space, the resulting structure may apparently seem like a eutectic, but it becomes quite homogeneous on being annealed for a few minutes.

3. The alloys within 2-13% Cu must have a bistructure consisting of $\eta + \epsilon$. The alloy with 2.13% Cu was quenched once at 440° (Photo. 3) and then at 430° (Photo. 4). Both structures are eutectical,

¹ Metallurgie, 378 (1908).

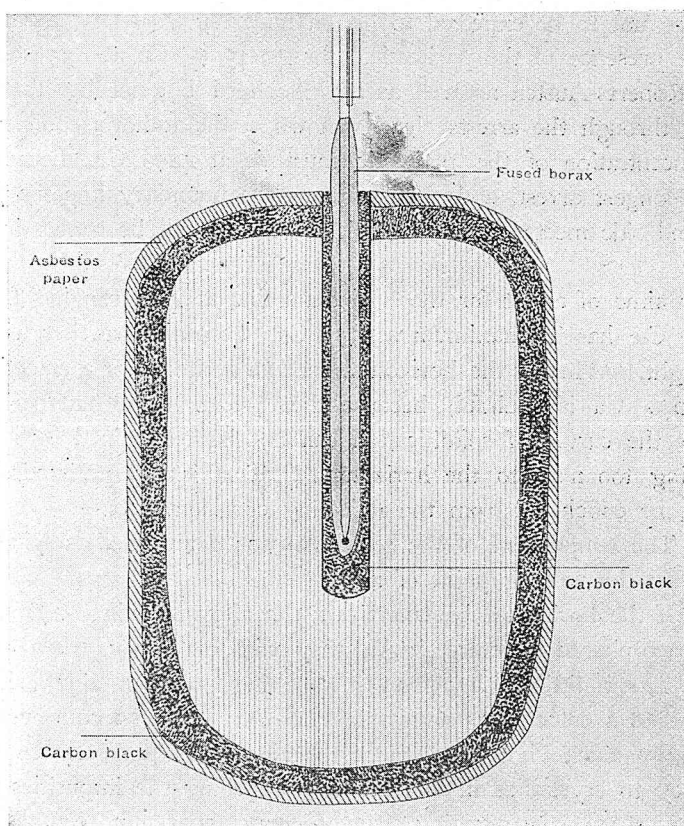
but they are changed on being annealed at 400° into a new bistructure of $\eta + \epsilon$, as shown in Photo. 5.

4. Similar experiments were repeated with the alloys of 3.18% Cu and of 8.28% Cu with the same result: *cf.* Photos. 6, 7, 8 and 9.

II. The Transformation of β into β_1 and β_2 .

As to the nature of the thermal effects at 470° , the views hitherto published have never yet been shown to be conclusive. The leading

Fig. II.



features is that the eutectoidal theory was proposed by Carpenter and Edwards¹, but was opposed by Desch², Hadson³ and many others. The author's results partly agree with those of Desch in that these thermal effects are due to the transformation of β into β_1 , and partly differ in a new

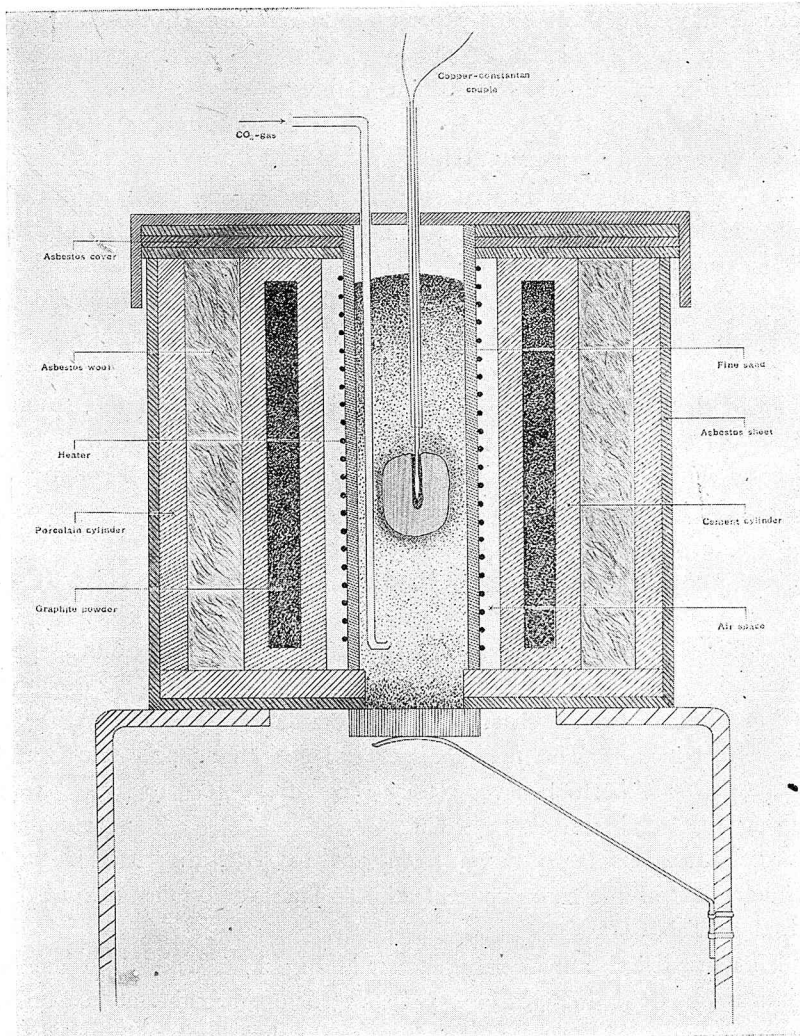
¹ The Journal of the Institute of Metals, 5, I, 127 (1911).

² Ibid, 5, I, 171 (1911); 7, I, 70; 8, II, 51 (1912).

³ Ibid., 12, II, 89 (1914).

fact that β_1 undergoes another transformation into β_2 at about 10° lower.

Fig. III.



Since the thermal effects due to the transformation of the β -constituent are very feeble, it was necessary to take the following precautions for their determinations:—

Each sample, 25 grms. in weight, was prepared upright in the middle with a bore reaching to its interior, into which was inserted a thermo-couple of copper-constantan, of which the hot junction was covered with fused borax to a length a little outside of the bore, serving both

as an insulator and a protector against oxidation. The remaining part of the bore was filled up with lamp black, and the outer surface of the specimen was also thickly smeared with it, the whole being then completely enveloped with asbestos-paper as shown in Fig. II. This was then placed deep in the middle of fine sand contained in a vertical electric resistance furnace. Beside the specimen, there was also placed a slender porcelain tube open at both ends, through which a current of dry carbon dioxide was passed: *cf.* Fig. III.

In order to have the thermal changes at 470° come out as evidently as possible in the cooling curves, it was necessary to make the sample keep the most suitable rate of cooling. The column of sand helps in this, and the carbon dioxide, which is used properly for protection against oxidation, will also do so, if its velocity be well regulated. As to the temperatures to which the samples should be heated before measurement, they should never be higher than 500° . If this protection be neglected and the specimen heated, for example, above 1000° , the cooling curves would run nearly horizontal when we come to 470° , the point of transition becoming thereby almost inexplicit. The quantity of the sample must also be large: 25 grms. is perhaps the minimum allowable.

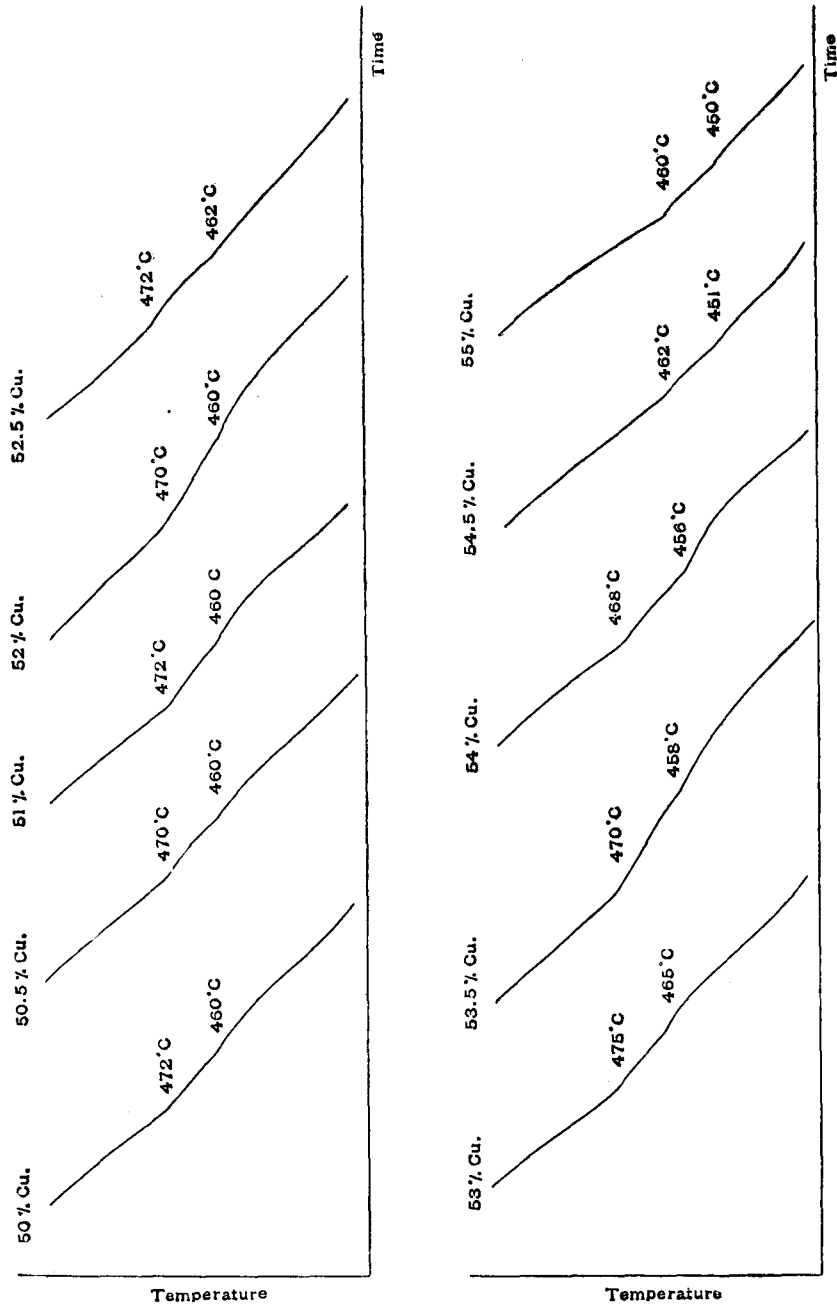
The samples tested were 40-70% Cu. The thermal effect at 470° was remarkable between 42-65% Cu, but then quite unexpectedly, another effect was observed at about 10° lower within the same range of concentration. The cooling curves from 50% Cu to 55% Cu are reproduced in Fig. IV, from each of which the existence of two breaks is easily to be ascertained. The first changes did not take place at a constant temperature as hitherto believed; they range from 460° to 475° , the latter being the maximum at 53% Cu.

The second changes range from 450° to 465° , the latter being the maximum also at the same concentration. These determinations are summarised in Table III.

These two lines are already shown in Fig. I. Though β thus undergoes a two-fold modification, yet its structure remains at last still so homogeneous, that there can be found no points that will make these modifications distinguishable. The only proof that may point to the existence of β_1 -modification, is the peculiar property of the Muntz-metal¹, which has a black-hot breaking-point, where it is very brittle while at any other points it is too tenacious to be broken off by a single knock of a hammer.

¹ Muntz: The Journal of the Institute of Metals, 5, I. 182 (1911).

Fig. IV.



Hence, the alloys in the β -field must be forming a series of solid

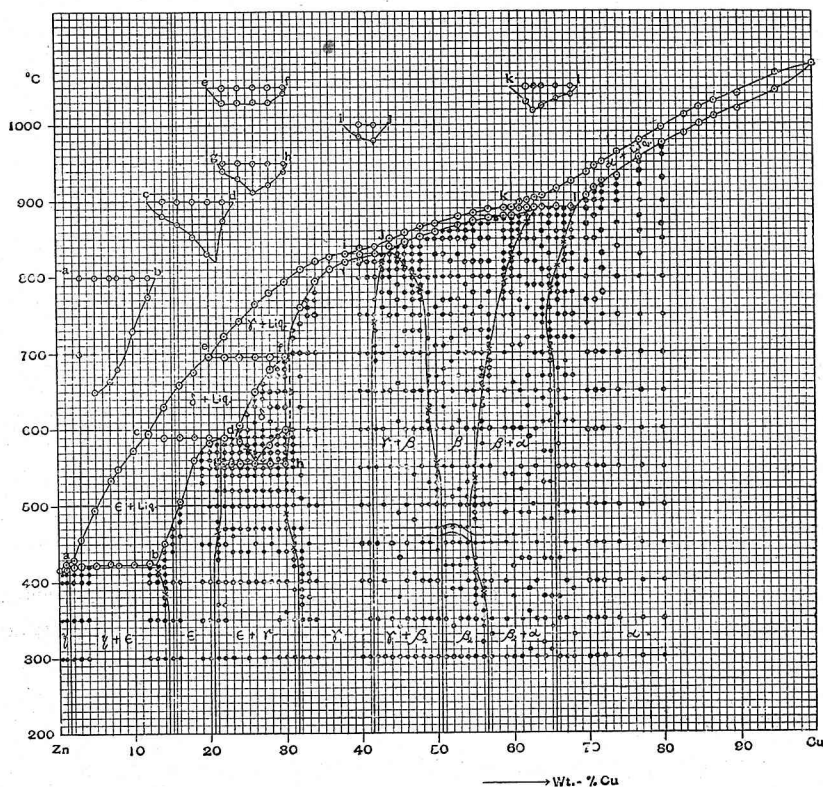
Table III.

Wt.—% Cu.	Trans. pt.		Structure as cast.
	1st °C	2nd °C	
42	?	?	$\beta_2 + \gamma$
44	472	?	$\beta_2 + \gamma$
46	471	?	$\beta_2 + \gamma$
48	470	?	$\beta_2 + \gamma$
49	470	460	$\beta_2 + \gamma$
50	472	460	$\beta_2 + \gamma$
50.5	470	460	β_2
51	472	460	β_2
51.5	470	460	β_2
52	470	460	β_2
52.5	472	462	β_2
53	475	465	β_2
53.5	470	458	β_2
54	468	456	β_2
54.5	462	451	β_2
55	460	450	β_2
56	465	452	β_2
57	460	450	$\alpha + \beta_2$
59	460	?	$\alpha + \beta_2$
61	460	?	$\alpha + \beta_2$
63	460	?	$\alpha + \beta_2$
65	?	?	$\alpha + \beta_2$

solutions, transforming themselves between the certain limits of temperatures with the maximum as Desch suggested. As to the border-lines of the β -field, they change their directions according to the solubilities of a constituent at different temperatures, so that the quenching method was found necessary for the purpose of determining them. Table VIII annexed at the end of this paper contains the quenching temperatures and their corresponding structures under the column from 33% to 70% Cu, and Fig. V shows the lines plotted in accordance with them, all the black spots

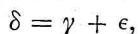
relating to the temperatures and the compositions, at which the quenching operations were carried out. Full descriptions of these boundaries will, however, be given in the fourth chapter.

Fig. V.

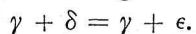


III. The Equilibrium-Curves of δ with γ and with ϵ .

As to the changes of δ in the lowering temperatures, Shepherd asserts that there goes on a eutectoid transformation at 450° :



while Tafel believes a transformation goes on at 545° ,



Such discrepancies seem, not to have attracted much attention on account of the alloys in this region having no technical importance.

The author attempted to determine the cooling curves with regard to the samples from 20% to 30% Cu under the same precautions as in

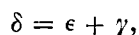
the case of β . The results are as follows:—

As is evident from the table, all the alloys lying between 20% to

Table IV.

Wt.—% of Cu.	Separation of ϵ or γ from δ .	Eutectoidal reaction.		Thermal effects of the unknown nature in ($\epsilon+\gamma$)-field	
		in °C.	in Sec.	in °C.	in Sec.
22	—	557	1	490	1
23	—	557	?	470	?
24	585	556	4	455	2
26	—	555	7	452	2
28	580 ?	555	5	456	2
30	600 ?	555	2	436	4

30% Cu show a eutectoidal transformation at 556° as their mean value; the primary thermal effects were manifest at 24% Cu, feeble at 28% Cu and 30% Cu, and none at 26% Cu. From 20% to 23% Cu, we have, as remarked before, a peritectic reaction at 590°, in which δ will come to dissolve more zinc and form ϵ partly. From these data, the reaction, which is believed to be



the pure eutectoid being at 26% Cu, must be represented in curves as shown in Fig. I. In order to have his conception confirmed, the author endeavoured to examine the changes of structures by the way of quenching, the compositions and the quenching temperatures being summarised in Table VIII in their proper columns and plotted in black spots, as shown in Fig. V. All the alloys in the δ -field are homogeneous, as shown in Photo. 11. Its boundary to γ is, however, hardly to be determined, as the latter is also homogeneous. We have, therefore, marked it provisionally in vertical dotted line.

As to the curves for the primary separation to the left of the eutectoid, an alloy with 23.41% Cu quenched at 590° shows a bistructure consisting of $\epsilon + \delta$ (Photo. 10), while an alloy with 25.37% Cu of the homogeneous δ -structure when quenched at 580° (Photo. 11), becomes bistructural when quenched at 570° (Photo. 12). To the right of the eutectoid, an alloy with 27.24% Cu, when quenched at 580°, shows the δ -structure (Photo. 13); when quenched at 570°, $\delta + \gamma$ (Photo. 14). An alloy with 29.62% Cu, when quenched at 590°, is homogeneous (Photo. 15), while it is bistructural when quenched at 580° (Photo. 16). Lastly, with regard

to the horizontal, all the alloys above stated give a eutectoidal structure when quenched at 550°; *cf.* Photos. 17, 18, 19, 20 and 21. These results are, therefore, in good accord with the conclusion obtained from studies of the cooling curves.

It may here be remarked that the alloys of 20—30% Cu show after the eutectoidal transition peculiar thermal effects as given in Table IV, though their nature is not yet well known; in fact, no difference in structure can be observed before and after these thermal effects. Nevertheless, they are plotted in the diagram.

IV. The Solubility Lines.

Having described reactions in the solid phases in the above two chapters, we shall now proceed to give a brief account of the solubility-lines of the different constituents with regard to each other.

1. The solubility-line of ϵ in η was found to run vertically at about 1.5% Cu. An alloy with 2% Cu shows a bistructure at ordinary temperatures as well as at 400°: for the experimental data refer to Table VIII.

2. The solubility-line of η in ϵ was found to be convex towards the right. An alloy with 14% Cu shows ϵ -structure above 390°, while it is bistructural below 380°: refer to Table VIII.

3. The solubility-line of γ in ϵ was previously believed to be vertical, except by Tafel. According to the author's determination, the line passes vertically through 21.5% Cu above 500° but thence it turns gradually to the left till 20.5% Cu and continues so to room-temperatures. An alloy with 21% Cu was, for instance, homogeneous (ϵ) above 470°, but bistructural ($\epsilon + \gamma$) below 460°: refer to Table VIII.

4. The solubility-line of ϵ in γ is also curved. It passes vertically through 30% Cu from the peritectic point of 695° to 470°, and then turns gradually to the right, passing through 31.5% Cu to room-temperatures. An alloy with 31% Cu showed, for instance, γ -structure above 450° but was bistructural below 440°: refer to Table VIII.

5. The solubility-line of β in γ starts from 830° and 43% Cu turning slightly towards the left, and from 700° passes vertically down through 41.5% Cu to the room-temperatures. An alloy with 42% Cu has, for instance, γ -structure at 750°, while it turns $\gamma + \beta$ below 730°.

6. The solubility-lines of γ and α in β have already been dealt with in the foregoing chapter in so far as they concern the stability of β at ordinary temperatures. So we understand, that, as to the boundary between γ and β , our results are nearly in accord with those hitherto

known. That between β and α , however, comes out very peculiar; an alloy with 54% Cu remains β at whatever temperatures it may be quenched, while that with 55% Cu shows ($\alpha + \beta$) between the temperatures of 530° and 420°, α being most rich when quenched at 480°. Outside of these limits, it is always homogeneous through β . The curve must, therefore, be considered as to be swelled up towards the left in those limits.

7. The solubility-line of β in α is also very peculiar. An alloy with 64% Cu is always bistructural through $\alpha + \beta$, but when quenched at 750°, it becomes poorer of β than when quenched at any other temperatures. Furthermore, we know that an alloy with 65% Cu, which is bistructural above 790° or below 700°, becomes homogeneous through α , when quenched between 780° and 710°. Hence, the line must be concave against α at temperatures between 800° and 700°.

V. The Change in the Microstructures Owing to the Oxidation and Volatilization of Zinc.

The volatilization of zinc in the copper-zinc alloys has been dealt with by Thorneycraft and Turner¹ who examined six specimens of different compositions, heated respectively in the form of turnings to 300°—900° in vacuo for 30 minutes. The author's experiment was on the same lines, differing, however, in that he cut every specimen in halves, heated one in the air and the other in vacuo to 470°—500° for 5, 25 and 50 hours. The zinc volatilised gets oxidised, though only partly in vacuo, thus forming films on the surface of the alloy or on the inner wall of the closed tube. The losses in weight were then determined on the one hand and the changes in structure on the other. Such experiments were made with eight samples, the results of which are summarised in the following Tables V and VI:—

¹ The Journal of the Institute of Metals, 12, II. 214(1914).

Table V.

Volatilization of zinc in brass annealed in sealed tubes containing air.

% -comp. of alloy.	Wt. of alloy used.	Zn- content.	Hour of anneal. at 470-500°.	Wt. after annealing.	Wt. of volatilized zinc.		Loss from total zinc in original alloy.
	in grams.	in grams.		in grams.	in grams.	in %.	in %.
Cu : 42.71 Zn : 57.29	3.1833	1.8237	5	3.1821	0.0012	0.04	0.07
			25	3.1762	0.0071	0.22	0.39
			50	3.1755	0.0078	0.25	0.43
Cu : 46.47 Zn : 53.53	3.8237	2.0467	5	3.8232	0.0005	0.02	0.03
			25	3.8210	0.0027	0.07	0.13
			50	3.8204	0.0033	0.09	0.16
Cu : 49.75 Zn : 50.25	3.5850	1.8015	5	3.5845	0.0005	0.01	0.03
			25	3.5770	0.0080	0.22	0.44
			50	3.5768	0.0097	0.27	0.54
Cu : 52.27 Zn : 47.73	3.7285	1.7797	5	3.7282	0.0003	0.008	0.02
			25	3.7260	0.0025	0.07	0.14
			50	3.7225	0.0060	0.16	0.34
Cu : 53.40 Zn : 46.60	3.4189	1.5932	5	3.4184	0.0005	0.01	0.03
			25	3.4171	0.0018	0.05	0.11
			50	3.4148	0.0041	0.12	0.26
Cu : 61.59 Zn : 38.41	4.2968	1.6494	5	4.2962	0.0006	0.01	0.04
			25	4.2951	0.0017	0.04	0.10
			50	4.2947	0.0021	0.05	0.13
Cu : 65.03 Zn : 34.97	3.2800	1.1471	5	3.2800	0.0000	0.00	0.00
			25	3.2800	0.0000	0.00	0.00
			50	3.2779	0.0001	0.003	0.008
Cu : 70.98 Zn : 29.02	4.7282	1.3721	5	4.7276	0.0006	0.01	0.04
			25	4.7250	0.0032	0.06	0.23
			50	4.7220	0.0060	0.13	0.44

Table VI.
Volatilization of zinc in brass annealed in vacuum-tubes.

% comp. of alloy.	Wt. of alloy used.	Zn-content.	Hour of anneal. at 470-500°.	Wt. after annealing.	Wt. of volatilized zinc.		Loss from total zinc in original alloy.
	in grams.	in grams.		in grams.	in grams.	in %.	in %.
Cu : 42.71 Zn : 57.29	3.7434	2.1446	5	3.7393	0.0041	0.11	0.19
			25	3.7382	0.0052	0.14	0.24
			50	3.7350	0.0084	0.22	0.39
Cu : 46.47 Zn : 53.53	2.6372	1.4117	5	2.6346	0.0026	0.09	0.18
			25	2.6339	0.0033	0.12	0.23
			50	2.6314	0.0058	0.22	0.41
Cu : 49.75 Zn : 50.25	2.5595	1.2861	5	2.5580	0.0015	0.06	0.12
			25	2.5577	0.0018	0.07	0.14
			50	2.5557	0.0038	0.10	0.29
Cu : 52.27 Zn : 47.73	3.5684	1.7032	5	3.5641	0.0043	0.12	0.25
			25	3.5635	0.0049	0.14	0.29
			50	3.5598	0.0086	0.24	0.50
Cu : 53.40 Zn : 46.60	2.9187	1.3601	5	2.9164	0.0023	0.08	0.17
			25	2.9162	0.0025	0.09	0.18
			50	2.9139	0.0048	0.16	0.35
Cu : 61.59 Zn : 38.41	4.0725	1.5642	5	4.0723	0.0002	0.004	0.01
			25	4.0715	0.0010	0.03	0.06
			50	4.0682	0.0043	0.10	0.27
Cu : 65.03 Zn : 34.97	3.6191	1.2656	5	3.6191	0.0000	0.00	0.00
			25	3.6190	0.0001	0.003	0.008
			50	3.6189	0.0002	0.005	0.02
Cu : 70.98 Zn : 29.02	3.6261	0.9623	5	3.6253	0.0008	0.02	0.08
			25	3.6226	0.0035	0.09	0.36
			50	3.6191	0.0070	0.19	0.72

As may be seen from the tables, the copper-zinc alloys, in vacuo as well as in the air lose their zinc in proportion to the length of time of annealing. This result agrees with Thorneycraft and Turner's as well as Guillet and Ballay's¹. One should, however, not be confused by the phenomenon, that when the temperatures are not sufficiently high to cause the volatilization of the zinc, the alloys may lose weight much more in the air than in vacuo, the zinc in brass then being directly oxidized by the air; but on the other hand, when the volatilization is more rapid, oxidation will go on mainly in the zinc volatilised, and the loss in weight due to the oxidation will not be conceivable on the alloy itself, so that there is observed no difference either in vacuo or in the air. There is, however, as may be seen from the tables, a remarkable exception to this rule, *i. e.* the alloy with 65% Cu does not let the zinc volatilize, however long it be heated at about 500°. This composition lies just at the boundary between α and β . It was therefore doubted if the alloys having the composition at or near the other boundary lines might also behave in a similar way, but it is not the case, as the following table shows:—

Table VII.
Volatilization of zinc in brass heated
at 470°—500° in vacuo for 50 hours.

Wt.—%.	Wt. of alloy before annealing.	Wt. of alloy after annealing.	Loss of zinc.	Loss of zinc.
	in grams.	in grams.	in grams.	in %.
Cu : 40.35 Zn : 59.65	3.9686	3.9591	0.0095	0.24
Cu : 50.62 Zn : 49.38	2.5273	2.5250	0.0023	0.09
Cu : 51.40 Zn : 48.60	3.1545	3.1476	0.0069	0.22
Cu : 55.54 Zn : 44.46	2.3560	2.3522	0.0038	0.16
Cu : 56.23 Zn : 43.77	4.1720	4.1649	0.0071	0.17

¹ Compt. rend., 175, 1057 (1922).

Nevertheless, we observe a remarkable change in structure in alloys heated for a long time; they get decidedly finer and more compact as shown in Photos. 22 and 23. At any rate, it seems to be difficult to give any adequate explanation for this peculiarity.

For the other alloys, which obey the above rule, the loss in weight after prolonged heating is always accompanied by changes in structure. We shall give only three representative cases, which will be sufficient to explain the changes due to the volatilization.

(I) A sample with 46% Cu, consisting of $\beta + \gamma$, as shown in Photo. 24, was cut in two parts and subjected to two series of experiments:—

a. One piece was heated at 700° in carbon dioxide for 3 hours, and quenched in water; since the zinc will go off from the surface, the structure near it must be changed into β , thereby increasing superficially the β -region: this fact is well confirmed by Photo. 25.

b. The other piece was heated in oxygen at the same temperature for 4 hours and quenched in water; the same result, as shown in Photo. 26.

(II) A sample with 53% Cu, consisting of β only, was cut in three parts and tested as follows:—

a. One piece, after being heated at 400° in vacuo for 10 days, remained unchanged, because the temperature was not high enough to cause volatilization of the zinc, while there was no oxygen to attack the alloy itself; compare Photo. 27.

b. Another piece, on being treated in the same way but in the air, lost the zinc more considerably, so that there appeared some α ; compare Photo. 28.

c. The remaining piece was heated at 700° for two days in the air. Since the temperature was very high, there was produced much more α in spite of the shortness of the time of heating; see Photo. 29.

(III) A sample with 63% Cu, consisting of $\beta + \alpha$, Photo. 30, was tested as follows:—

a. Heated two days at 800° in the air, quenched in water; β disappeared from the surface, so that there could be seen α only, as in Photo. 31.

b. The above sample was then cut transversely into two parts; one of which on being polished, showed β still present a little beneath the surface as shown in Photo. 32; this shows that the volatilization and consequently the change in structure are only superficial phenomena

not proceeding far inwards.

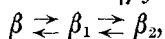
From all these results, we are convinced that Carpenter and Edward's hypothesis, that β is transformed at 470° into $\alpha + \gamma$, is not to be accepted as a fact. If the alloy containing 54.2% Cu, which consists of β with a very small amount of α , be heated for as long as 3-8 weeks, it will, according to our experience, lose zinc by volatilization and the structure of the remaining alloy must evidently be composed of $\alpha + \beta$ and not of $\alpha + \gamma$.

Summary.

1. The author's determinations agree generally with those of Roberts-Austen and the other workers as regards the liquidus and the peritecticals, but differ in that he finds that the latter at 695° between 20 and 30% Cu has only one saturation-point, and that the peritectic reaction between 0 and 12% Cu takes place at 425° , *i. e.* much higher than hitherto believed.

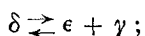
2. Many discrepancies are observed with regard to the solubility-lines.

3. The solid solution β undergoes two-fold transformations between the range of temperatures from 475° to 450° :-



the maximum of temperature being observed at 53% Cu.

4. The solid solution δ is unstable below 550° , and passes into a eutectoid:-



the $(\delta + \gamma)$ -field must therefore exist at 26-30% Cu between 590° and 560° .

5. Zinc is somewhat easily volatilized at as low temperatures as 470° , the change in the structures being then produced chiefly on the surface.

In conclusion, the author desires to express his indebtedness to Prof. M. Chikashige for his kind guidance and valuable remarks.

Table VIII.—Continued.

19%Cu.		20%Cu.		21%Cu.		22%Cu.		23%Cu.		24%Cu.		25%Cu.		26%Cu.		27%Cu.		28%Cu.	
°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.
570	ε	580	ε	590	ε	590	ε+δ	590	ε+δ	600	δ	620	δ	640	δ	660	δ	670	δ
560	ε	570	ε	580	ε	580	ε+δ	580	ε+δ	590	δ	600	δ	630	δ	650	δ	650	δ
550	ε	560	ε	570	ε	570	ε+δ	570	ε+δ	580	ε+δ	590	δ	610	δ	640	δ	630	δ
540	ε	550	ε	550	ε	560	ε+δ	560	ε+δ	570	ε+δ	580	δ	590	δ	600	δ	610	δ
530	ε	500	ε	540	ε	550	ε+γ	550	ε+γ	560	ε+δ	570	ε+δ	580	δ	590	δ	590	δ
450	ε	450	ε	520	ε	540	ε+γ	540	ε+γ	550	ε+γ	560	ε+δ	570	δ	580	δ	580	δ+γ
400	ε	400	ε	500	ε	520	ε+γ	520	ε+γ	540	ε+γ	550	ε+γ	560	δ	570	δ+γ	570	δ+γ
350	ε	350	ε	480	ε	500	ε+γ	500	ε+γ	520	ε+γ	540	ε+γ	550	ε+γ	560	δ+γ	560	δ+γ
300	ε	300	ε	470	ε	470	ε+γ	470	ε+γ	500	ε+γ	520	ε+γ	540	ε+γ	550	ε+γ	550	ε+γ
Room temp. Cast state	ε	Room temp. Cast state	ε	460	ε+γ	450	ε+γ	460	ε+γ	470	ε+γ	500	ε+γ	520	ε+γ	540	ε+γ	540	ε+γ
	ε		ε	450	ε+γ	400	ε+γ	440	ε+γ	440	ε+γ	470	ε+γ	500	ε+γ	520	ε+γ	520	ε+γ
				440	ε+γ	370	ε+γ	400	ε+γ	400	ε+γ	440	ε+γ	470	ε+γ	500	ε+γ	500	ε+γ
				430	ε+γ	350	ε+γ	300	ε+γ	Room temp. Cast state	ε+γ	400	ε+γ	450	ε+γ	470	ε+γ	470	ε+γ
				400	ε+γ	300	ε+γ	Room temp. Cast state	ε+γ	Room temp. Cast state	ε+γ	300	ε+	400	ε+γ	440	ε+γ	450	ε+γ
				370	ε+γ	Room temp.	ε+γ	Room temp. Cast state	ε+γ	Room temp.	ε+γ	Room temp.	ε+γ	Room temp.	ε+γ	400	ε+γ	400	ε+γ

			350 300 Room temp. Cast state	$\epsilon+\gamma$ $\epsilon+\gamma$ $\epsilon+\gamma$ $\epsilon+\gamma$	Cast state	$\epsilon+\gamma$				Cast state	$\epsilon+\gamma$	Cast state	$\epsilon+\gamma$	300 Room temp. Cast state	$\epsilon+\gamma$ $\epsilon+\gamma$ $\epsilon+\gamma$	Room temp. Cast state	$\epsilon+\gamma$ $\epsilon+\gamma$
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Table VIII.—Continued.

29%Cu.		30%Cu.		31%Cu.		32%Cu.		33%Cu.		34%Cu.		40%Cu.		41%Cu.		42%Cu.		43%Cu.	
°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.
680	δ	690	δ	730	γ	760	γ	770	γ	780	γ	820	γ	820	γ	830	γ	830	γ
670	δ	680	δ	720	γ	740	γ	760	γ	770	γ	800	γ	800	γ	820	γ	820	γ
650	δ	670	δ	700	γ	700	γ	750	γ	750	γ	750	γ	750	γ	800	γ	810	$\beta+\gamma$
630	δ	650	δ	650	γ	670	γ	700	γ	700	γ	700	γ	700	γ	770	γ	800	$\beta+\gamma$
600	δ	630	δ	600	γ	630	γ	600	γ	600	γ	650	γ	650	γ	750	γ	780	$\beta+\gamma$
590	δ	600	δ	590	γ	590	γ	500	γ	500	γ	600	γ	600	γ	730	$\beta+\gamma$	760	$\beta+\gamma$
580	$\delta+\gamma$	590	$\delta+(\gamma)$	580	γ	540	γ	450	γ	400	γ	550	γ	550	γ	710	$\beta+\gamma$	740	$\beta+\gamma$
570	$\delta+\gamma$	580	$\delta+(\gamma)$	570	γ	510	γ	410	γ	350	γ	500	γ	500	γ	700	$\beta+\gamma$	700	$\beta+\gamma$
560	$\delta+\gamma$	570	γ	560	γ	470	γ	400	γ	300	γ	450	γ	450	γ	690	$\beta+\gamma$	650	$\beta+\gamma$
550	$\epsilon+\gamma$	560	γ	550	γ	440	γ	380	γ	Room temp.	γ	400	γ	400	γ	650	$\beta+\gamma$	600	$\beta+\gamma$

540	$\epsilon+\gamma$	550	γ	520	γ	430	γ	350	γ	Cast state	γ	300	γ	350	γ	600	$\beta+\gamma$	500	$\beta+\gamma$
520	$\epsilon+\gamma$	540	γ	500	γ	420	γ	300	γ			Room temp. Cast state	γ	300	γ	550	$\beta+\gamma$	400	$\beta_2+\gamma$
500	$\epsilon+\gamma$	530	γ	470	γ	410	γ	Room temp. Cast state	γ				Room temp. Cast state	γ	Room temp. Cast state	450	$\beta_2+\gamma$	300	$\beta_2+\gamma$
470	$\epsilon+\gamma$	520	γ	460	γ	400	γ									350	$\beta_2+\gamma$	Room temp. Cast state	$\beta_2+\gamma$
440	$\epsilon+\gamma$	500	γ	450	γ	390	γ									300	$\beta_2+\gamma$		$\beta_2+\gamma$
400	$\epsilon+\gamma$	480	$\epsilon+\gamma$	440	$\epsilon+\gamma$	380	γ									Room temp. Cast state	$\beta_2+\gamma$		
350	$\epsilon+\gamma$	470	$\epsilon+\gamma$	430	$\epsilon+\gamma$	370	γ										$\beta_2+\gamma$		
300	$\epsilon+\gamma$	440	$\epsilon+\gamma$	420	$\epsilon+\gamma$	350	γ												
Room temp. Cast state	$\epsilon+\gamma$	400	$\epsilon+\gamma$	390	$\epsilon+\gamma$	300	γ												
	$\epsilon+\gamma$	360	$\epsilon+\gamma$	350	$\epsilon+\gamma$	Room temp. Cast state	γ												
		300	$\epsilon+\gamma$	300	$\epsilon+\gamma$		γ												
		Room temp. Cast state	$\epsilon+\gamma$	Room temp. Cast state	$\epsilon+\gamma$														
		$\epsilon+\gamma$	$\epsilon+\gamma$	$\epsilon+\gamma$	$\epsilon+\gamma$														

Table VIII.—Continued.

44%Cu.		45%Cu.		46%Cu.		47%Cu.		48%Cu.		49%Cu.		50%Cu.		51%Cu.		52%Cu.		53%Cu.	
°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.
830	$\beta+\gamma$	850	β	850	β	840	β	840	β	850	β	850	β	860	β	860	β	860	β

820	$\beta + \gamma$	840	β	840	β	830	β	820	β	800	β	830	β	850	β	850	β	850	β
810	$\beta + \gamma$	830	β	830	β	820	β	810	β	780	β	800	β	830	β	820	β	830	β
800	$\beta + \gamma$	820	$\beta + \gamma$	820	β	810	β	800	β	750	β	760	β	800	β	800	β	800	β
780	$\beta + \gamma$	810	$\beta + \gamma$	810	$\beta + \gamma$	800	$\beta + \gamma$	790	β	720	β	710	β	770	β	770	β	770	β
750	$\beta + \gamma$	790	$\beta + \gamma$	800	$\beta + \gamma$	790	$\beta + \gamma$	780	$\beta + \gamma$	700	β	670	β	750	β	750	β	740	β
650	$\beta + \gamma$	770	$\beta + \gamma$	780	$\beta + \gamma$	780	$\beta + \gamma$	770	$\beta + \gamma$	670	β	650	β	710	β	720	β	700	β
550	$\beta + \gamma$	750	$\beta + \gamma$	760	$\beta + \gamma$	770	$\beta + \gamma$	750	$\beta + \gamma$	650	β	600	β	680	β	690	β	670	β
450	$\beta_2 + \gamma$	710	$\beta + \gamma$	730	$\beta + \gamma$	750	$\beta + \gamma$	730	$\beta + \gamma$	630	β	570	β	660	β	650	β	610	β
350	$\beta_2 + \gamma$	660	$\beta + \gamma$	700	$\beta + \gamma$	730	$\beta + \gamma$	700	$\beta + \gamma$	620	$\beta + \gamma$	560	β	630	β	600	β	560	β
300	$\beta_2 + \gamma$	610	$\beta + \gamma$	650	$\beta + \gamma$	700	$\beta + \gamma$	650	$\beta + \gamma$	610	$\beta + \gamma$	550	$\beta + \gamma$	600	β	550	β	520	β
Room temp. Cast state	$\beta_2 + \gamma$	550	$\beta + \gamma$	600	$\beta + \gamma$	650	$\beta + \gamma$	600	$\beta + \gamma$	600	$\beta + \gamma$	540	$\beta + \gamma$	570	β	510	β	500	β
	$\beta_2 + \gamma$	490	$\beta + \gamma$	550	$\beta + \gamma$	600	$\beta + \gamma$	550	$\beta + \gamma$	590	$\beta + \gamma$	530	$\beta + \gamma$	550	β	470	β_1	470	β_1
		430	$\beta_2 + \gamma$	500	$\beta + \gamma$	540	$\beta + \gamma$	500	$\beta + \gamma$	580	$\beta + \gamma$	520	$\beta + \gamma$	470	β_1	450	β_2	450	β_2
		380	$\beta_2 + \gamma$	450	$\beta_2 + \gamma$	480	$\beta + \gamma$	450	$\beta_2 + \gamma$	570	$\beta + \gamma$	510	$\beta + \gamma$	450	β_2	420	β_2	420	β_2
		340	$\beta_2 + \gamma$	400	$\beta_2 + \gamma$	410	$\beta_2 + \gamma$	400	$\beta_2 + \gamma$	560	$\beta + \gamma$	500	$\beta + \gamma$	420	β_2	390	β_2	390	β_2
		300	$\beta_2 + \gamma$	350	$\beta_2 + \gamma$	350	$\beta_2 + \gamma$	350	$\beta_2 + \gamma$	530	$\beta + \gamma$	470	$\beta_1 + \gamma$	380	β_2	340	β_2	350	β_2
	Room temp. Cast state	$\beta_2 + \gamma$	$\beta_2 + \gamma$	300	$\beta_2 + \gamma$	300	$\beta_2 + \gamma$	300	$\beta_2 + \gamma$	500	$\beta + \gamma$	440	$\beta_2 + \gamma$	350	β_2	300	β_2	300	β_2
		$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$	$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$	450	$\beta_2 + \gamma$	400	$\beta_2 + \gamma$	300	β_2	Room temp. Cast state	β_2	Room temp. Cast state	β_2
			$\beta_2 + \gamma$	$\beta_2 + \gamma$	$\beta_2 + \gamma$	$\beta_2 + \gamma$	$\beta_2 + \gamma$	$\beta_2 + \gamma$	$\beta_2 + \gamma$	400	$\beta_2 + \gamma$	350	$\beta_2 + \gamma$	Room temp. Cast state	β_2	β_2	β_2	Room temp. Cast state	β_2
										350	$\beta_2 + \gamma$	300	$\beta_2 + \gamma$	Room temp. Cast state	β_2				

									300 Room temp. Cast state	$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$	Cast state	β_2			
									Room temp. Cast state	$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$					
									Room temp. Cast state	$\beta_2 + \gamma$	Room temp. Cast state	$\beta_2 + \gamma$					

Table VIII.—Continued.

54%Cu.		55%Cu.		56%Cu.		57%Cu.		59%Cu.		60%Cu.		61%Cu.		62%Cu.		63%Cu.		64%Cu.	
°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.
870	β	870	β	870	β	870	β	880	β	880	β	890	β	890	β	890	$\alpha + \beta$	890	$\alpha + \beta$
860	β	860	β	850	β	850	β	860	β	870	β	880	β	880	β	880	$\alpha + \beta$	880	$\alpha + \beta$
850	β	840	β	820	β	820	β	850	β	860	β	870	β	870	$\alpha + \beta$	850	$\alpha + \beta$	860	$\alpha + \beta$
820	β	820	β	800	β	800	β	830	β	850	β	860	β	850	$\alpha + \beta$	820	$\alpha + \beta$	840	$\alpha + \beta$
790	β	800	β	760	β	780	β	820	β	840	β	850	$\alpha + \beta$	820	$\alpha + \beta$	790	$\alpha + \beta$	810	$\alpha + \beta$
760	β	780	β	730	β	750	β	810	β	830	β	830	$\alpha + \beta$	790	$\alpha + \beta$	750	$\alpha + \beta$	790	$\alpha + \beta$
730	β	750	β	700	β	730	β	800	β	820	$\alpha + \beta$	800	$\alpha + \beta$	760	$\alpha + \beta$	700	$\alpha + \beta$	770	$\alpha + \beta$
700	β	700	β	680	β	720	β	790	$\alpha + \beta$	810	$\alpha + \beta$	770	$\alpha + \beta$	720	$\alpha + \beta$	650	$\alpha + \beta$	760	$\alpha + \beta$
650	β	650	β	670	β	710	β	780	$\alpha + \beta$	800	$\alpha + \beta$	740	$\alpha + \beta$	670	$\alpha + \beta$	600	$\alpha + \beta$	750	$\alpha + \beta$
600	β	630	β	660	β	700	$\alpha + \beta$	770	$\alpha + \beta$	780	$\alpha + \beta$	710	$\alpha + \beta$	630	$\alpha + \beta$	550	$\alpha + \beta$	740	$\alpha + \beta$
580	β	600	β	650	$\alpha + \beta$	690	$\alpha + \beta$	750	$\alpha + \beta$	750	$\alpha + \beta$	650	$\alpha + \beta$	590	$\alpha + \beta$	500	$\alpha + \beta$	720	$\alpha + \beta$

		Room temp. Cast state	β_2																
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Table VIII.—Continued.

65% Cu.		66% Cu.		67% Cu.		68% Cu.		70% Cu.		71% Cu.		72% Cu.		74% Cu.		77% Cu.		80% Cu.	
°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.	°C	phase.
890	$\alpha+\beta$	890	$\alpha+\beta$	890	$\alpha+\beta$	890	α	910	α	910	α	920	α	930	α	950	α	970	α
880	$\alpha+\beta$	880	$\alpha+\beta$	880	$\alpha+\beta$	880	α	900	α	900	α	910	α	920	α	940	α	960	α
870	$\alpha+\beta$	860	$\alpha+\beta$	870	$\alpha+\beta$	870	α	890	α	880	α	900	α	910	α	920	α	930	α
850	$\alpha+\beta$	850	$\alpha+\beta$	860	$\alpha+\beta$	860	α	870	α	850	α	890	α	900	α	900	α	900	α
830	$\alpha+\beta$	840	$\alpha+\beta$	850	$\alpha+\beta$	850	α	850	α	820	α	860	α	870	α	880	α	870	α
810	$\alpha+\beta$	830	$\alpha+\beta$	840	$\alpha+\beta$	830	α	820	α	770	α	830	α	840	α	860	α	850	α
800	$\alpha+\beta$	820	$\alpha+\beta$	830	α	810	α	800	α	700	α	810	α	800	α	830	α	800	α
790	$\alpha+\beta$	810	α	820	α	780	α	770	α	650	α	780	α	750	α	800	α	750	α
780	α	800	α	800	α	750	α	740	α	600	α	750	α	700	α	750	α	700	α
760	α	790	α	780	α	720	α	700	α	550	α	700	α	650	α	700	α	650	α
740	α	780	α	750	α	670	α	650	α	500	α	650	α	600	α	650	α	600	α
730	α	770	α	720	α	610	α	600	α	450	α	600	α	550	α	600	α	550	α

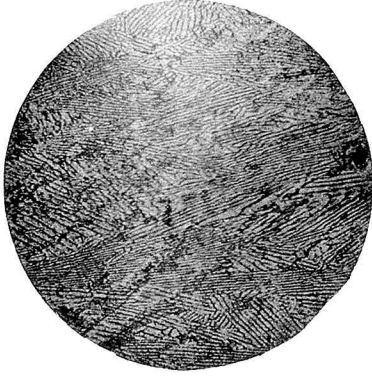


Photo. 1. Zn containing 0.1% Cu.
Quench. from 430. $\times 178$.

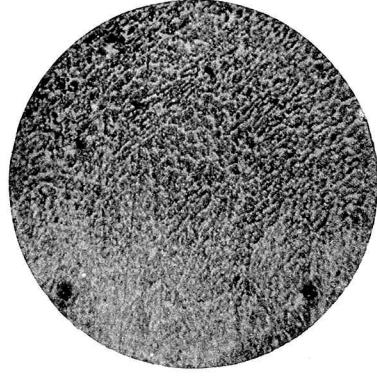


Photo. 2. Zn.
Quench. from 430. $\times 178$.



Photo. 3. 2.13% Cu.
Quench. from 440. $\times 178$.

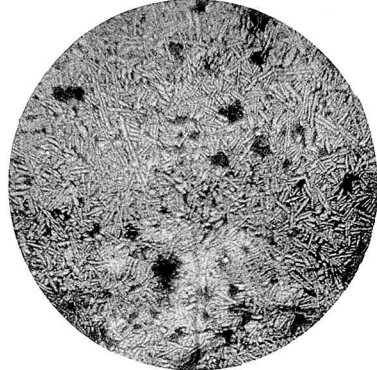


Photo. 4. 2.13% Cu.
Quench. from 430. $\times 178$.



Photo. 5. 2.13% Cu.
Anneal. at 400. $\times 178$.



Photo. 6. 3.18% Cu.
Quench. from 430. $\times 178$.



Photo. 7. 3.18% Cu.
Quench. from 400°. $\times 178$.

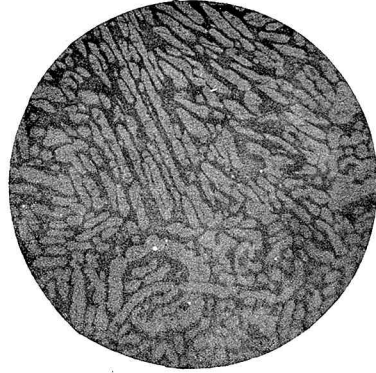


Photo. 8. 8.28% Cu.
Quench. from 440°. $\times 178$.



Photo. 9. 8.28% Cu.
Anneal. at 400°. $\times 178$.

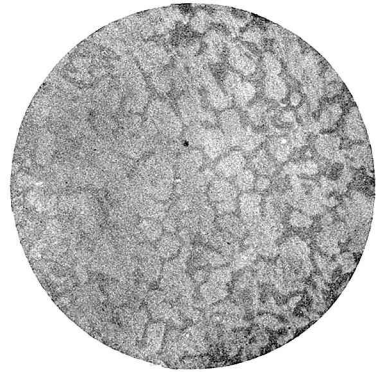


Photo. 10. 23.41% Cu.
Quench. from 590°. $\delta + \epsilon$. $\times 178$.

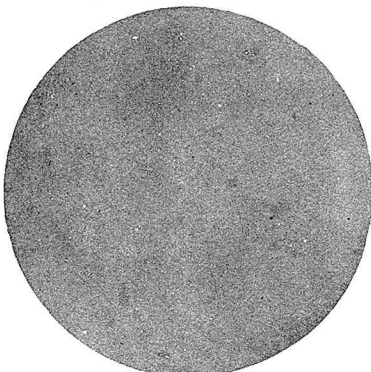


Photo. 11. 25.37% Cu.
Quench. from 580°. δ . $\times 178$.

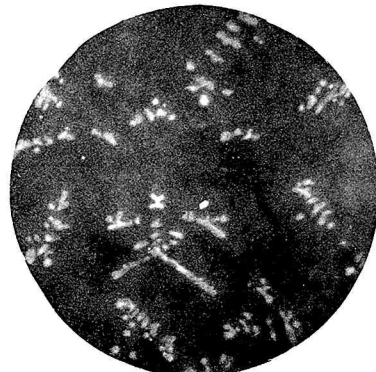


Photo. 12. 25.37% Cu.
Quench. from 570°. $\epsilon + \delta$. $\times 178$.

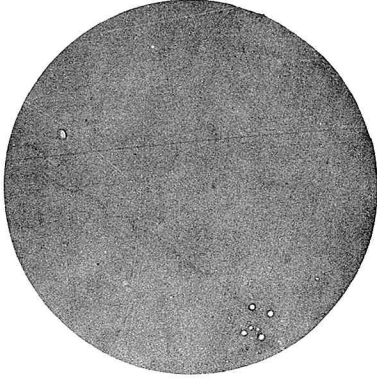


Photo. 13. 27.24% Cu.
Quench. from 580°. δ . $\times 178$.

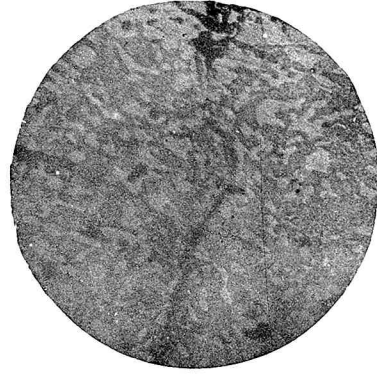


Photo. 14. 27.24% Cu.
Quench. from 570°. $\delta + \gamma$. $\times 178$.



Photo. 15. 29.62% Cu.
Quench. from 590°. δ . $\times 178$.

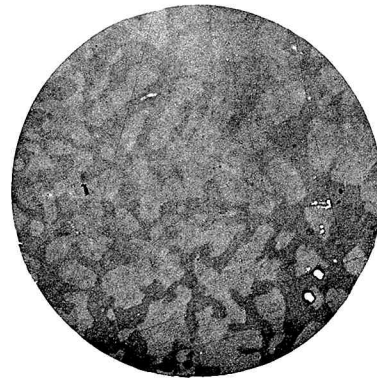


Photo. 16. 29.62% Cu.
Quench. from 580°. $\delta + \gamma$. $\times 178$.



Photo. 17. 23.41% Cu.
Quench. from 550°. $\epsilon + \gamma$ (Eutect.)
 $\times 178$.

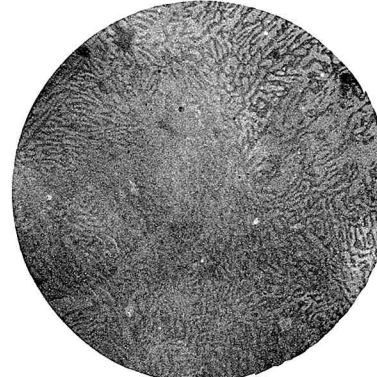


Photo. 18. 25.37% Cu.
Quench. from 550°. $\epsilon + \gamma$ (Eutect.)
 $\times 178$.

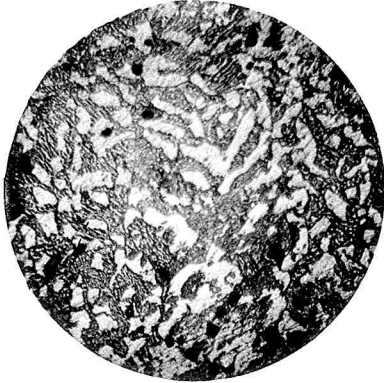


Photo. 19. 27.24% Cu.
Quench. from 550°. $\epsilon + \gamma$ (Eutect.).
 $\times 178$.



Photo. 20. 29.62% Cu.
Quench. from 550°. $\epsilon + \gamma$ (Eutect.).
 $\times 178$.

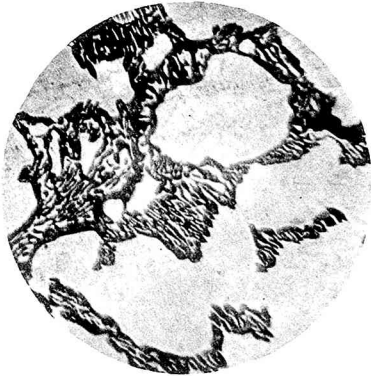


Photo. 21. The same as Photo. 20.
Magnified 300 diameters.

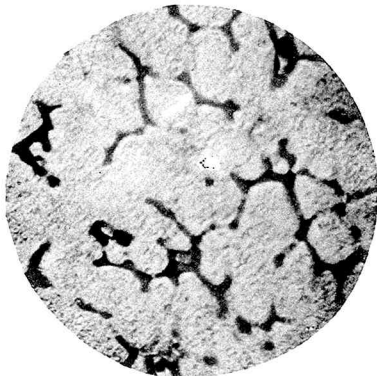


Photo. 22. 65.16% Cu.
As cast, $\alpha + \beta$. $\times 178$.

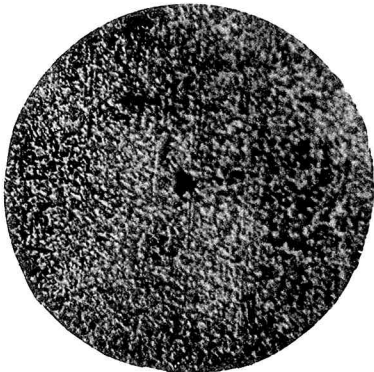


Photo. 23. 65.16% Cu.
After anneal. at 470-500° for 50
hours in vacuo. $\times 178$.

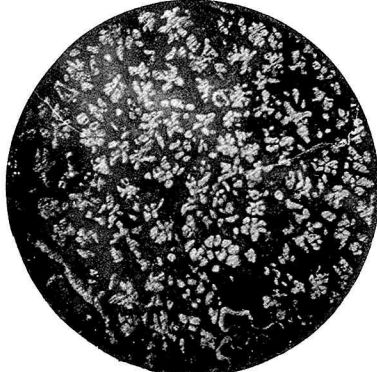


Photo. 24. 46.47% Cu.
As cast, $\beta + \gamma$. $\times 178$.

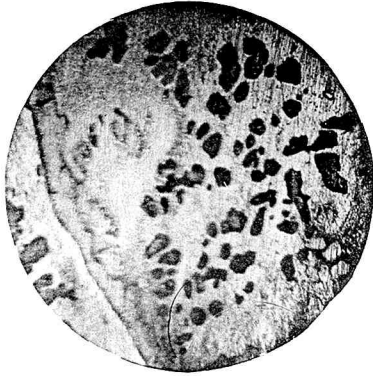


Photo. 25. 46.47% Cu.
Anneal. at 700° for 3 hours in
CO₂. $\beta + \gamma$. $\times 178$.

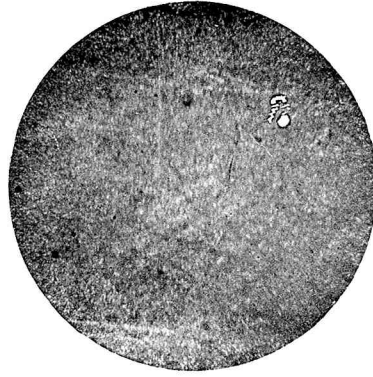


Photo. 26. 46.47% Cu.
Anneal. at 700° for 4 hours in
O₂. β . $\times 178$.

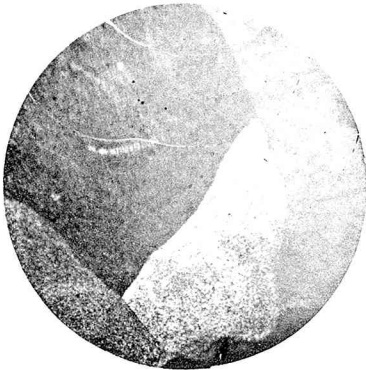


Photo. 27. 53.40% Cu.
Anneal. at 400° for 10 days in
vacuo. β . $\times 178$.

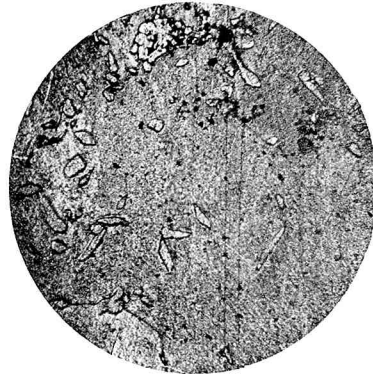


Photo. 28. 53.40% Cu.
Anneal. at 400° for 10 days in
air. $\alpha + \beta$. $\times 178$.

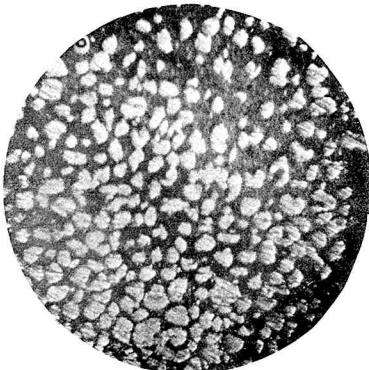


Photo. 29. 53.40% Cu.
Anneal. at 700° for 2 days in
air. $\alpha + \beta$. $\times 178$.

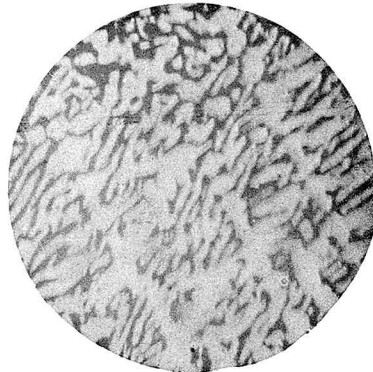


Photo. 30. 63.57% Cu.
Not annealed. $\alpha + \beta$. $\times 178$.

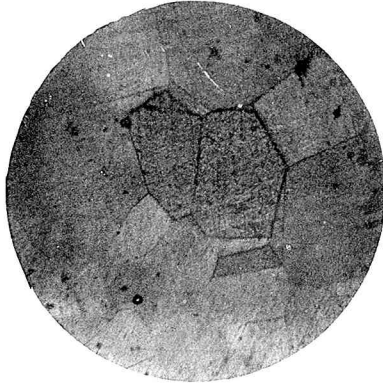


Photo. 31. 63.57% Cu.
Anneal. at 800° for 2 days in air.
a. $\times 178$.



Photo. 32. The section of the same
as Photo. 31. $\alpha + \beta$. $\times 178$.