On the Ternary Silver Alloys

II The System of Silver, Aluminium and Zinc

By

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Reports on the ternary system of silver, aluminium and zinc seem still to be lacking in the literature. The author investigated the full system but here will give a description of the silver-rich part only, because all the other alloys are brittle and liable to get tarnished, and have no practical value.

For the purpose of this investigation, the author's[1] diagram on Ag–Zn, Isihara's[2] on Al-Zn and Petrenko's[3] on Ag–Al were used without any modification.

Tab. 1

Alloy No.	Wt.-%			phase
	Ag	Al	Zn	
1	92.35	4.85	2.80	α+β
2	90.35	6.91	2.74	α+β
3	87.52	9.88	2.60	β
4	81.62	15.82	2.56	β
5	75.61	19.83	4.56	β + eutec.
6	70.43	24.65	4.92	β + eutec.
7	40.62	34.77	24.61	Al + eute .
8	50.78	44.41	4.81	Al + eutec.
9	94.65	3.11	2.24	α
10	79.42	0.98	19.60	α
11	78.45	1.74	19.81	α+β
12	75.65	4.33	19.52	β
13	70.34	10.11	19.55	β
14	68.55	11.73	19.72	β + eutec.

I Preliminary Experiments

Kahlbaum's pure aluminium and zinc and electrolytic silver were used as materials. Changes of composition by volatilization and oxidation were prevented as much as possible in the following way: The zinc was fused under molten sodium chloride in a porcelain crucible. It was kept slightly below its boiling point and well stirred while first the aluminium and then the silver were thrown into the crucible in small pieces. Some

1 These Memoirs, **12**, 347 (1929).
2 Zeits. Anorg. C. **46**, 47 (1905).
3 J. Inst. M. **33**, 73 (1925).

of the silver-rich alloys thus prepared were analysed with the results given in Tab. 1.

The compositions of the alloys, except those in Tab. 1, are due to the quantities of the constituent metals mixed and are not the values actually obtained by analysis.

In order to get a rough idea of the fields existing at ordinary temperatures, the following alloys were prepared and their microstructures tested.

Through the microscopical examination of these alloys, the author got a rough idea about the structures at ordinary temperatures in the silver-rich part of the ternary system. They correspond exactly to those of the binary systems Ag–Al and Ag–Zn; for example, the β solid solution of the Ag–Al system unites with β of the Ag–Zn system, thus forming the ternary β-solution, and in consequence the $\alpha+\beta$ of the Ag–Al system unites with $\alpha+\beta$ of the Ag–Zn, and also forms the ternary $(\alpha+\beta)$.

II The Ternary Equilibrium Diagram

In order to establish the ternary equilibrium, a number of sectional diagrams, Fig. 1—Fig. 6, were drawn, the data being as given in Tab. 3—Tab. 8.

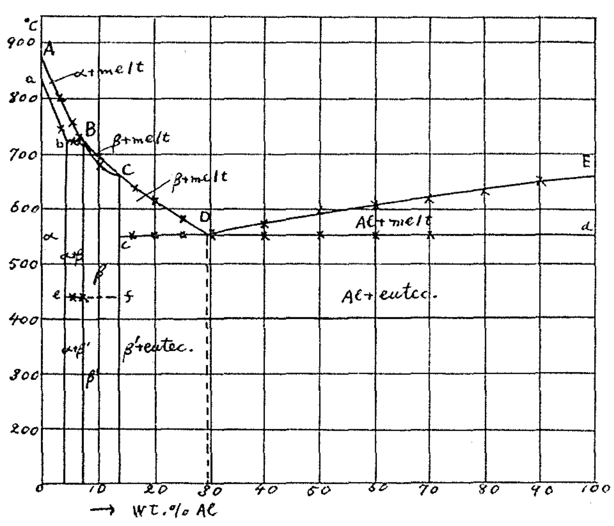
Tab. 2

Alloy No.	Wt.-%			phase
	Ag	Al	Zn	
15	92	3	5	$\alpha+\beta$
16	90	5	5	$\alpha+\beta$
17	87	7	5	$\alpha+\beta$
18	85	10	5	β
19	80	15	5	β + eutec.
20	75	20	5	β + eutec.
21	70	25	5	β + eutec.
22	60	35	5	Al + eutec.
23	45	50	5	Al + eutec.
24	65	10	25	β
25	60	15	25	β + eutec.
26	45	30	25	Al + eutec.
27	68	2	30	β
28	65	5	30	β
29	62	8	30	β
30	60	10	30	β + eutec.
31	50	20	30	β + eutec.
32	40	30	30	Al + eutec.
33	25	70	5	Al + eutec.
34	62	3	35	β
35	60	5	35	β
36	58	7	35	β
37	55	10	35	β + eutec.
38	57	3	40	β
39	55	5	40	β
40	52	8	40	β + eutec.
41	51	3	46	β
42	50	5	45	β
43	17	73	10	Al + eutec.
44	88	2	10	α
45	87	3	10	α
46	85	5	10	$\alpha+\beta$
47	83	7	10	$\alpha+\beta$
48	80	10	10	β
49	78	12	10	β
50	75	15	10	β + eutec.
51	65	25	10	β + eutec.
52	50	40	10	Al + eutec.
53	40	50	10	Al + eutec.
54	84	1	15	α
55	83	2	15	α
56	82	3	15	$\alpha+\beta$
57	80	5	15	$\alpha+\beta$
58	77	8	15	β
59	75	10	15	β
60	73	12	15	β
61	65	15	20	β + eutec.
62	60	25	15	β + eutec,
63	50	35	15	Al + eutec.
64	35	50	15	Al + eutec.
65	60	20	20	β + eutec.
66	55	35	10	Al + eutec.
67	40	40	20	Al + eutec.
68	74	1	25	$\alpha+\beta$
69	70	5	25	β
70	67	8	25	β

Tab. 3: Al–(90% Ag + 10% Zn) Section

Alloy No.	Wt.-%			°C				
	Ag	Al	Zn	Liquidus	Solidus	Peritectic	Eutectic	Trans.
71	87	3	10	801	741	—	—	—
72	85.2	5	9.8	762	—	720	—	437
73	83.7	7	9.3	731	—	721	—	438
74	81	10	9	692	677	—	—	—
75	78	13	9	665	654	—	—	—
76	75.5	16	8.5	638	—	—	550	—
77	72	20	8	610	—	—	550	—
78	67.3	25	7.7	580	—	—	553	—
79	63	30	7	555	—	—	554	—
80	58.4	35	6.6	569	—	—	553	—
81	54	40	6	570	—	—	554	—
82	45	50	5	597	—	—	554	—
83	36	60	4	603	—	—	553	—
84	27	70	3	617	—	—	553	—
85	18	80	2	630	—	—	—	—
86	9	90	1	645	—	—	—	—

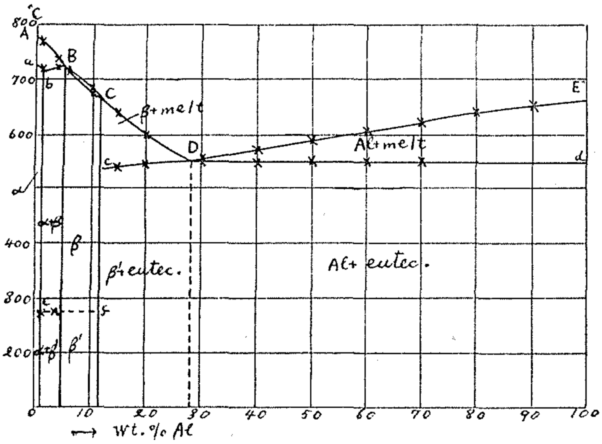
Fig. 1: Al–(90% Ag + 10% Zn) Section



Tab. 4: Al-(80%Ag+20%Zn) Section

Alloy No.	Wt.-%			°C				
	Ag	Al	Zn	Liquidus	Solidus	Peritectic	Eutectic	Trans.
87	79.2	1	19.8	770	713	—	—	—
88	78.3	2	18.7	758	—	712	—	275
89	76.8	4	19.2	732	—	713	—	276
90	75	6	19	712	710	—	—	—
91	72	10	18	681	676	—	—	—
92	68	15	17	640	—	—	538	—
93	64	20	16	598	—	—	543	—
94	56	30	14	543	—	—	544	—
95	48	40	12	565	—	—	546	—
96	40	50	10	575	—	—	544	—
97	32	60	8	602	—	—	545	—
98	24	70	6	617	—	—	545	—
99	16	80	4	621	—	—	—	—
100	8	90	2	643	—	—	—	—

Fig. 2: Al-(80%Ag+20%Zn) Section



Tab. 5: Al-(70%Ag+30%Zn) Section

Alloy No.	Wt.-%			°C		
	Ag	Al	Zn	Liquidus	Solidus	Eutec.
101	68	3	29	700	696	—
102	65	7	28	693	689	—
103	63	10	27	660	—	536
104	56	20	24	577	—	538
105	49	30	21	541	—	537
106	42	40	18	562	—	536
107	35	50	15	580	—	536
108	28	60	12	600	—	537
109	21	70	9	616	—	537
110	14	80	6	630	—	—
111	7	90	3	642	—	—

Fig. 3: Al–(70% Ag + 30% Zn) Section

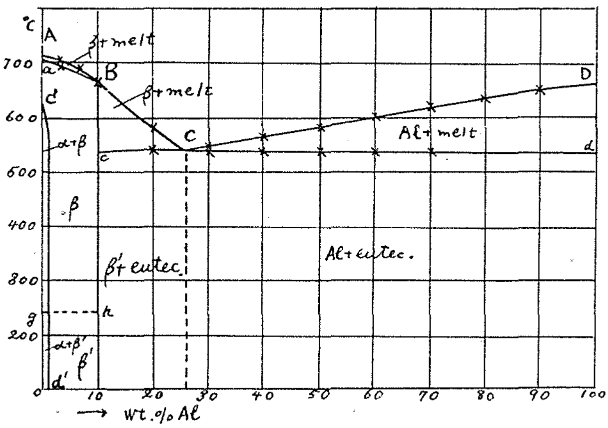


Fig. 4: Al–AgZn Section

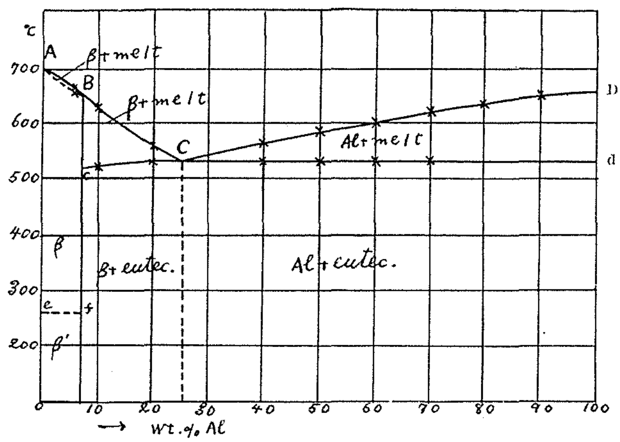
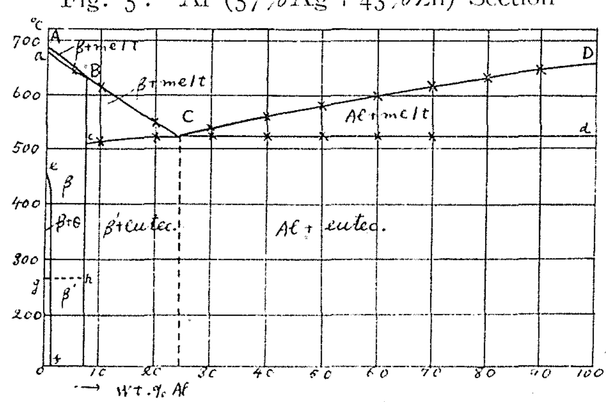


Fig. 5: Al–(57% Ag + 43% Zn) Section



Tab. 6: Al–AgZn Section

Alloy No.	Wt.-%			°C		
	Ag	Al	Zn	Liquidus	Solidus	Eutec.
112	59	5	36	667	664	—
113	56	10	34	625	—	520
114	50	20	30	651	—	528
115	43.7	30	26.3	540	—	530
116	37.4	40	22.6	560	—	531
117	31	50	19	580	—	531
118	25	60	15	599	—	530
119	19	70	11	616	—	531
120	12.5	80	7.5	631	—	—
121	6.3	90	3.7	642	—	—

Tab. 7: Al–(57% Ag + 43% Zn) Section

Alloy No.	Wt.-%			°C		
	Ag	Al	Zn	Liquidus	Solidus	Eutec.
122	54	5	41	651	647	—
123	51.2	10	38.8	612	—	513
124	45.5	20	34.5	539	—	520
125	40	30	30	533	—	523
126	34.3	40	25.7	556	—	524
127	28.5	50	21.5	580	—	525
128	25	60	15	598	—	525
129	17	70	13	614	—	524
130	11.3	80	8.7	629	—	—
131	5.5	90	4.5	641	—	—

Tab 8: Al–Ag_2Zn_3 Section

Alloy No.	Wt.-%			°C		
	Ag	Al	Zn	Liquidus	Solidus	Eutec.
132	50	5	45	647	643	—
133	47.2	10	42.8	612	—	508
134	44.6	16	39.4	556	—	512
135	42	20	38	530	—	513
136	37	30	33	530	—	517
137	34.2	40	25.8	551	—	517
138	26.3	50	23.7	578	—	516
139	21	60	19	590	—	516
140	15.8	70	14.2	613	—	516
141	10.5	80	9.5	630	—	—
142	5.3	90	4.7	640	—	—

Fig. 6 : Al-Ag_2Zn_3 Section

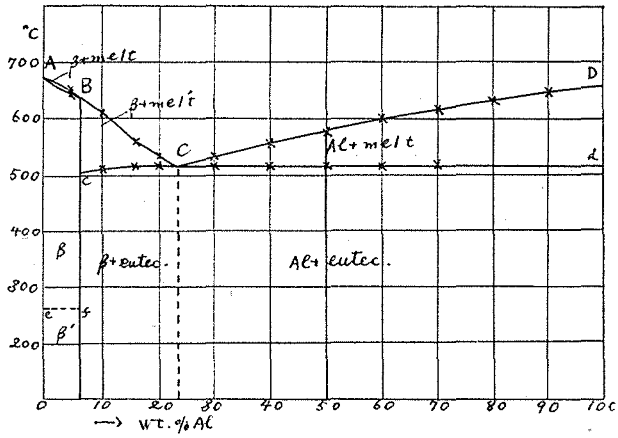
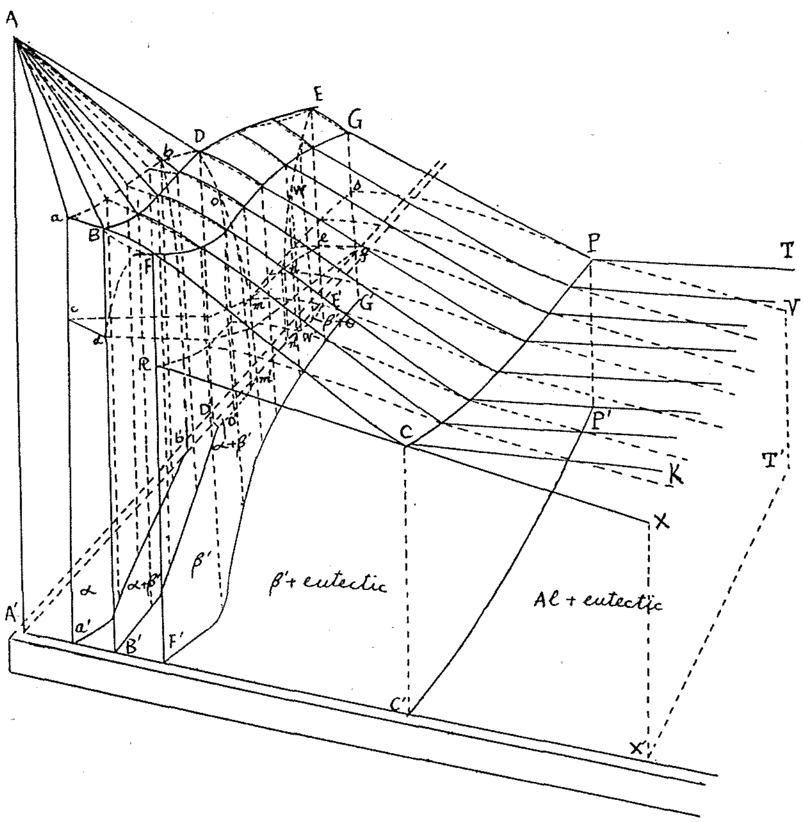
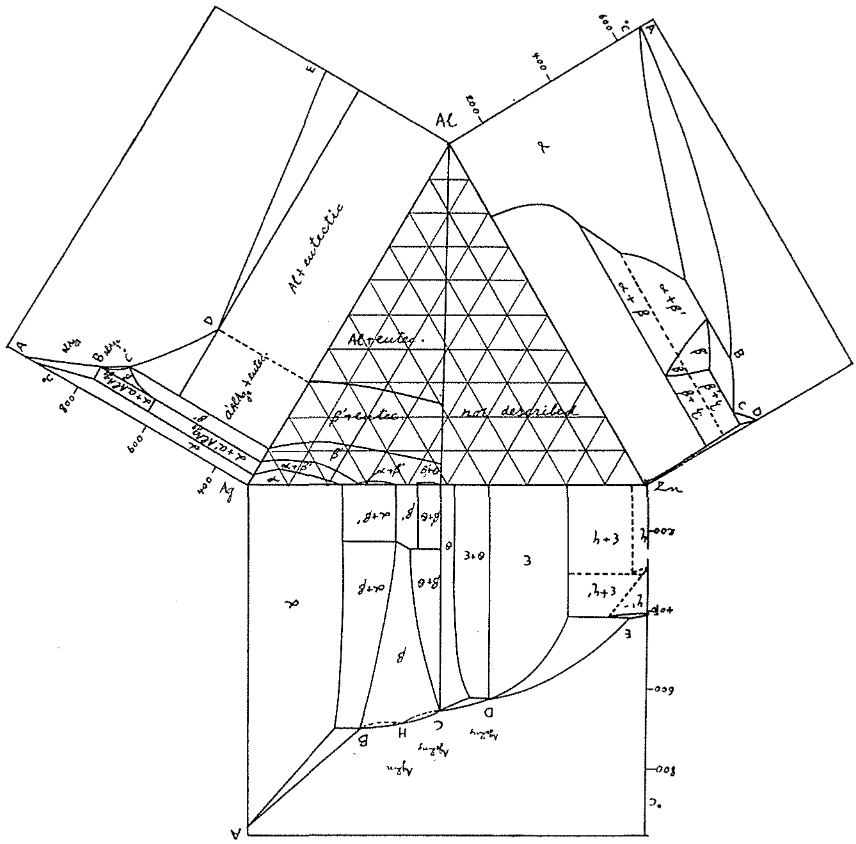


Fig. 7



On the basis of these data, the ternary equilibrium diagram, Fig. 7, as well as its projection-diagram, Fig. 8, were drawn.

Fig. 8



For the sake of illustration the equilibrium diagram, Fig. 7, will be divided into seven fields :—

1 The field-$A'a'b'A'$: the structure α

The α solid solution in the Ag–Zn system dissolves aluminium and forms a ternary α solid solution. The alloys in this field are all of the homogeneous α structure at ordinary temperatures. The melt begins to separate out α crystals at the temperatures below those of the liquidus surface $ABDA$ and ceases at the temperatures of the solidus surface $AabA$, where a space curve ab shows the concentration of the separated mixed crystals. The curve AB in the sectional diagrams 1 and 2 corresponds to the primary separation of α and the curve ab to its solidus. Comp. Photo 1.

2 The field-$a'B'D'b'a'$: the structure $\alpha+\beta'$

The melts of the alloys in this field, begin to separate out the α crystals at the temperatures below those of the liquidus surface $ABDA$ till they attain the temperatures of the peritectic surface $aBDba$, where a binary peritectic reaction takes place between α along the space curve ab and the melt along the space line BD, as a consequence of which the field $\alpha+\beta$ is attained at the room temperature.

The horizontal line aB shows the binary peritectic reaction, Liq.$+\alpha\rightleftarrows\beta$ in the Ag–Zn system at 710°, while the horizontal line bD shows the reaction, Liq.$+\alpha\rightleftarrows AlAg_3$ in the Ag–Al system at 770°. The temperature of the former reaction is raised by the addition of aluminium, while that of the latter is lowered by the addition of the zinc, in consequence of which both ternary reactions will meet at the temperatures between 770° and 710°. The equilibrium between the three phases, α, β and the melt, is shown by the curve BD.

The binary $\alpha+\beta$ is transformed into $\alpha+\beta'$ at 610° in the Ag–Al system while it is also transformed into $\alpha+\beta'$ at 240° in the Ag–Zn system. The temperature of the transformation with the Ag–Al system is lowered by the addition of zinc and that of the Ag–Zn system is raised by the addition of aluminium. These two transformation surfaces are connected by a line and produce a transformation surface $cdfec$. See, Photo 2 and 3.

3 The field-$B'F'G'E'D'B'$: the structure β'

The β solid solution of the Ag–Al system is produced by the mutual solution of $AlAg_2$ and $AlAg_3$. This β solid solution dissolves zinc, AgZn and Ag_2Zn_3 thus forming a ternary β solid solution. The β solid solution of the Ag-Zn system dissolves aluminium and $AlAg_2$ thus forming also a ternary β solid solution. These two ternary β solid solutions are connected by a line, in consequence of which a wide field of the homogeneous ternary β solid solution makes its appearance. The β solid solution will begin to separate itself at the liquidus surface $BFGEDB$. The curve BC in the sectional diagrams, 1 and 2, and the curve AB in the sectional diagrams, 3—6, show the separation of β.

4 The field–$D'O'm'D'$: the structure $\alpha+\beta'$

The melt in this field begins to separate β at the liquidus surface *BFGEDB* and solidifies at its solidus surface, which on the temperature being lowered, segregates α along the surface $DD'o'm'moD$ due to the decrease in solubility of α in β. This fact is confirmed by the following experiment: An alloy of 69.5% Ag, 0.5% Al and 30% Zn, quenched at 400° was seen to have a bistructure consisting of $\alpha+\beta'$ (Photo 4), while when quenched at 660°, it became homogeneously β (Photo 5). The transformation of $\beta\rightarrow\beta'$ takes place in this field at the surface *cdfec*. The curve $c'd'$ in the sectional diagram 3 corresponds to the segregation of α from β.

5 The field–$nw'E'n'$: the structure $\beta'+\theta$

The alloy in this field begins to separate β at the liquidus surface *BFGEDB* and solidifies at its solidus surface, which on the temperature being lowered, segregates θ due to the decrease in solubility. The curve *cf* in the sectional diagram 5 shows the segregation of θ in β. As to the segregation of θ from β, an alloy with 56.6% Ag, 0 4% Al, and 43% Zn, when quenched at 600°, shows the β structure (Photo 6), but when quenched at 400° it turns heterogeneous (Photo 7 : $\beta'+\theta$). The transformation of $\beta\rightarrow\beta'$ takes place also in this field. The curve *cf* in the sectional diagram 5 corresponds to the segregation of θ from β.

6 The field–$P'C'F'G'$: the structure Eutec.$(\beta'+\text{Al})+\beta'$

The horizontal *RCX* shows the binary eutectic reaction, Liq.$\rightarrow AlAg_2+Al$ at 565°. The temperature is lowered by the addition of the zinc. This relation is represented by the curve *CP* along which β, Al and the melt are in equilibrium. As the binary compound $AlAg_2$ dissolves zinc, Ag_2Zn_3 and Ag_2Zn_5 the curve *CP* corresponds to the equilibrium existing between Al, the melt and β but not the compound $AlAg_2$. The melt of the alloys in this field begins to separate out the β crystals at temperatures below those of the liquidus surface *FCPGF* and continue till the eutectical surface *RCPs* is attained. At this stage Al begins to be separated symmetrically with β, and thus the melt comes to solidify. The curve *CD* in the sectional diagrams 1 and 2 and the liquidus curve *BC* in the sectional diagrams 3—6 show the separation of β. The curve *cD* in the sectional diagrams 1 and 2, and the curve *Cc* in the sectional diagrams 3—6 are due to the separation of the binary eutectic (β+Al). Comp. Photo 8 and 9.

7 The field–$P'C'X'T'$: the structure Al+Eutec.(β'+Al)

The alloys in this field show the eutectic structure as described in the previous field. The melt begins to separate out the Al crystals at temperatures below those of the liquidus surface *CKTP* and continues till the eutectical surface *CXVP* is reached. At this surface it completely solidifies separating the binary eutectic Al+β. The curve *ED* in the sectional diagrams 1 and 2 and the curve *CD* show the primary separation of Al, and the curve *Dd* in the sectional diagrams 1 and 2 and the curve *Cd* in the sectional diagrams 3—6 show the separation of binary eutectic (Al + β).

The author wishes to express his thanks to Professor M. Chikashige for his valuable suggestions and kindly help throughout the course of the investigation.

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Plate I

Photo 1. 92% Ag. 3% Al and 5% Zn. ×150.

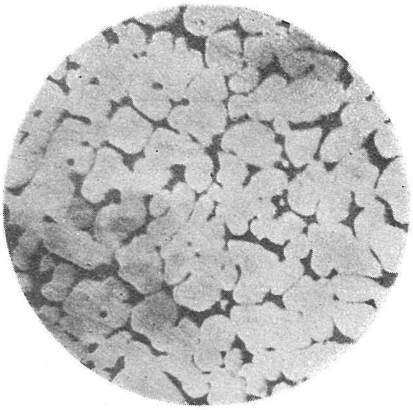

Photo 2. 85% Ag. 6.5% Al and 8.5% Zn. ×150.

Photo 3. 75% Ag, 1% Al and 24% Zn. ×150.

Photo 4. 69.5% Ag, 0.5% Al and 30% Zn. Quenched at 400°. ×150.

Photo 5. The same alloy quenched at 600°. ×150.

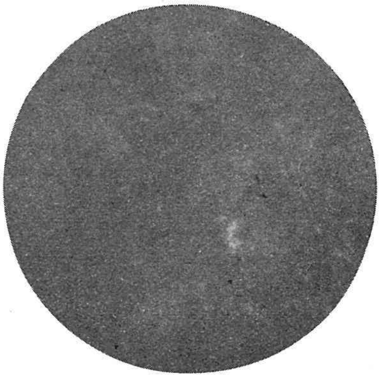

Photo 6. 56.6% Ag, 0.5% Al and 43% Zn. Quenched at 600°. ×150.

Plate II

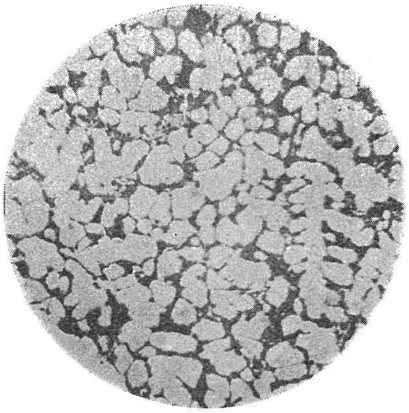

Photo 7. The same alloy quenched at 400°. ×150.

Photo 8. 50% Ag, 20% Al and 30% Zn. ×150.

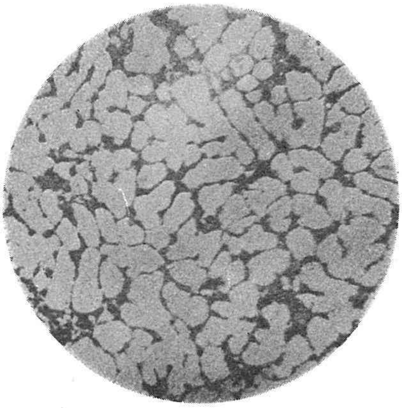

Photo 9. 58% Ag, 20% Al and 22% Zn. ×150.

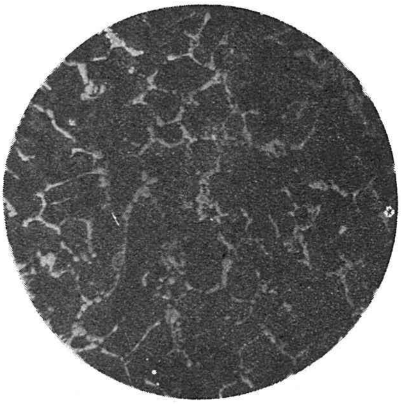

Photo 10. 70% Ag, 25% Al and 5% Zn. ×150.

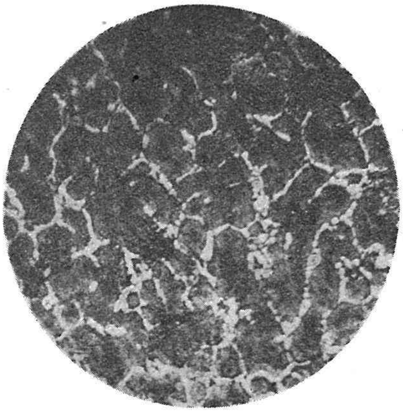

Photo 11. 45% Ag, 45% Al and 10% Zn. ×150.

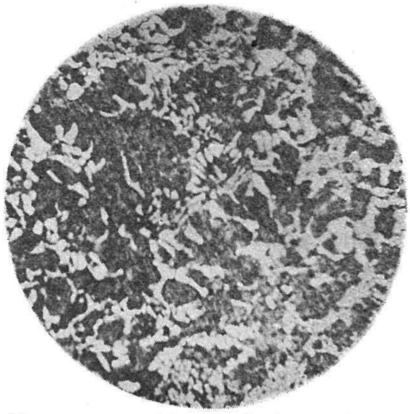

Photo 12. 47% Ag, 35% Al and 18% Zn. ×150.