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By

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Since a research was carried out by G. Eger[1] at the first time on the alloy system of aluminium, magnesium and zinc, many authors have investigated on this system. Among them W. Köster[2] and M. Hamazumi[3] reported independently on the general diagram of this ternary system in the year 1936. Furthermore, the solid equilibrium relations on the aluminium corner of the diagram were studied in detail by W. L. Fink and L. A. Willey.[4]

These results being not in agreement in some points and the complete studies on the solid equilibrium relations lacking, we have taken up the present work to make these insufficient points in the diagram of Al–Zn–$MgZn_2$ more distinct with a relation of industrial alloys employed in our country.

Already, the binary systems[5] composing these ternary alloys were thoroughly investigated, and their results were almost in accordance with each other. However, the quasi-binary system of Al–$MgZn_2$ was not so complete that we have especially examined it at the beginning of this study.

Materials Used — The specimens employed were made from aluminium of 99.95% purity, electrolytic zinc of 99.98% purity and magnesium of 99.9% purity.

Preparation of Alloys — Aluminium was melted in a small graphite crucible lined with alumina in an electric resistance furnace under the cover of anhydrated mixtures composed of $MgCl_2$ 60% and KCl 40%. Zinc and magnesium were respectively added to the melted aluminium at about 700 °C. Thus the alloys desired were prepared. This alloying procedure was so effective that any loss of alloying elements could scarcely be recognized, judging from the results of chemical analyses of the specimens. The specimens to be used for the measurement of solid transformation were cast in a steel mould into a small ingot 8 mm in diameter and 40 mm long. They were annealed at temperatures from 320 °C to 350 °C, and then they were gradually cooled to the room temperature. The annealing more than one month was necessary for the specimens to attain equilibrium at the room temperature. The specimens to be used for the measurement of solidification changes and also for metallographic examination were respectively cast in cast iron mould 15 mm in diameter and 35 mm long from the same liquid alloys.

Chemical Analyses of the Specimens — Chemical analyses were not carried out for the specimens except some important ones, for the analytical compositions of the specimens were not so different from the charge compositions as above mentioned.

Methods of Investigations

Thermal Analyses — Differential thermal analyses as ordinary employed in our laboratory[6] were adopted for the determination of the solidification phenomena from liquid. As well known, the

Table 2 Chemical Analyses of the Specimens

Alloy No.	Weight Percentage %		
	Zn	Mg	Al
0502	93.76	1.73	remainder
0506	90.23	5.46	″
0513	82.53	12.84	″
1005	83.61	4.78	″
1013	78.77	13.02	″
1503	81.57	2.99	″
1504	82.07	3.72	″
1506	80.23	5.85	″
1512	74.56	12.58	″
2002	79.17	1.78	″
2006	73.17	6.68	″
2501	72.70	0.82	″
2505	71.45	4.30	″
2510	63.93	9.90	″
3002	67.12	1.20	″
3004	66.58	3.68	″
3504	62.30	4.12	″
3506	58.40	5.43	″
5006	45.13	5.29	″
6002	37.69	1.70	″
6502	33.44	1.96	″

Table 1 Thermal Analyses of the Alloys

Alloy No.	Points of Change or Arrest °C								
	On Heating				On Cooling				
0501	276		338		371				343
0502	277		341		355			353	344
0503	278		342		344				343
0504	278		342		373		345		343
0505	275		345		415		349		343
0506	279			347	447	393	354		343
0507		317		350	473		359		344
0508		313		351	490		362		342
0509		313		349	513		372		344
0510		312		350	520		380		341
0511		309		347	535		381		335
0512				350	543	401	380		336
0513		313		350	547	412			336
0514					552	419			331
1000	277								
1001	276		340		419			353	344
1002	277		340		407				343
1003	277		341		403			357	342
1004	276	327	345		393			376	343
1005	276	314		350	399			376	342
1006		313		350	438	407	380		340
1007		313		350	450	411	384		342
1008		313		350	473	409	380		342
1009		313		350	489	414	380		342
1010		313		350	503	421	380		342
1011		313		350	515	430	383		342
1012		313			523	437	383		340
1013					527	446	381		340
1500	282								
1501	276		341						
1502	276		347		464				340
1503	276	329		350					
1504	276	325		350	465		380	355	339
1505	276	313		350					
1506		313		350	443		380		336
1507		313		351					
1508		313			469		380		338
1509		313							
1510		313							
1511		313							
1512		315							
1513									
2000									
2001	278		347						
2002	276			350	477			365	337
2003	276	331		350					
2004	276	321		350	491	393	381		340
2005		316		350					
2006		313			472	441	380		340
2007		317							
2008		317			465	453	381		338
2009		314							
2010		311							
2501	276		349	356					
2502	277			371					
2503	277	316		368					
2504		313		370					
2505		315		367					
2506		317		371					
2508		312		378					
2509		315		383					
2510		315		403					
3000	279			359					
3001	276				502			363	
3002	277	315			498		378		
3003	274	314			504		380		
3004	277	314			492		380		
3005		312			490				
3006		313							
3007		313			487	447			
3008		313			479	447			
3009					477	454			
3010					474	464			
3501	277	327		371					
3502	277	320		372					
3503	280	317		373					
3504		315							
3505		313		383					
3506		314							
3507		315		399					
4001	271	314							
4002	276	315		373					
4003	276	316		384					
4004		311		383					
4005		318		387					
4006		314		407					
4501	276	315		373					
4502	278	316		383					
4503	279	317		387					
4504	277	309		379					
5000	280								
5001	279	318							
5002	276	315							
5003	277	312							
5004		309							
6001	276								
6002	280	315							
6003		314							
6501	280	315							
6502	280	315							

Al-$MgZn_2$ Quasi-binary System

Alloy	Points of Change or Arrest °C	
$MgZn_2$ 95%	565	431
″ 90 ″	540	456
″ 85 ″	514	465
″ 80 ″	507	466
″ 75 ″	486	466
″ 70 ″	472	466
″ 60 ″	513	466
″ 50 ″	541	465
″ 40 ″	569	466

observation on cooling were not sufficient to determine the equilibrium, for solidification reactions do not always occur in equilibrium even on cooling with the very slow rate. Therefore, the solid transformations or some solidus points were determined with thermal analyses on heating. The arrests in solid transformation were too feeble to be detected with the usually employed couples. For that purpose we used a thrice folded 'differential couples to increase the sensitibity. Specimens were heated with the rate of 2 °C per minute.

Microscopic Methods — The results of the thermal analyses were checked on important specimens by microscopic examinations as described later.

Results of Experiments

Thermal Analyses — Thermal analyses were carried out for the alloys corresponding to the composition in 9 kinds of constitutional sections. The results of experiments are given in Table 1, and they are plotted in Fig. 1 to 9, in which the marks • and ○ indicate respectively the change points on heating and on cooling. The chemical analyses of some alloys are given in Table 2.

The composition of the alloys in Table 1 are represented by alloy numbers, in which the first two numerals indicate the weight percentage of aluminium and the next two that of magnesium. For example, alloy number 1513 indicates an

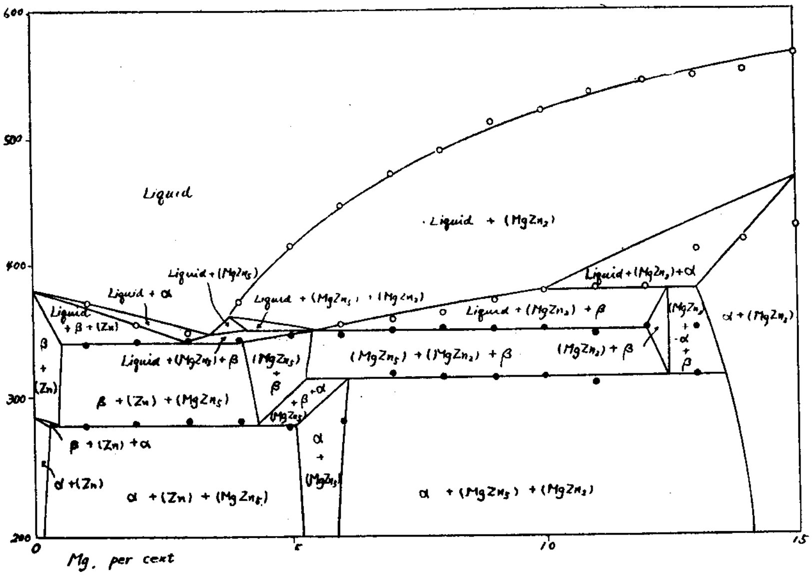


Fig. 1 Al 5% Series

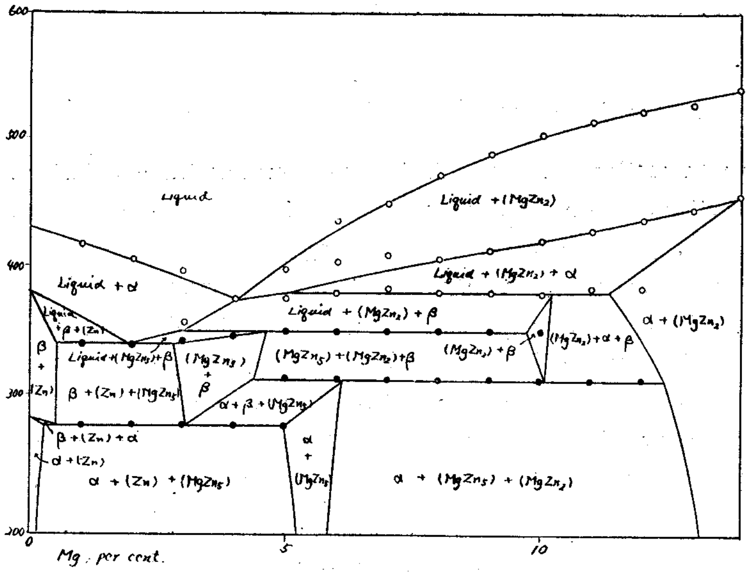


Fig. 2 Al 10% Series

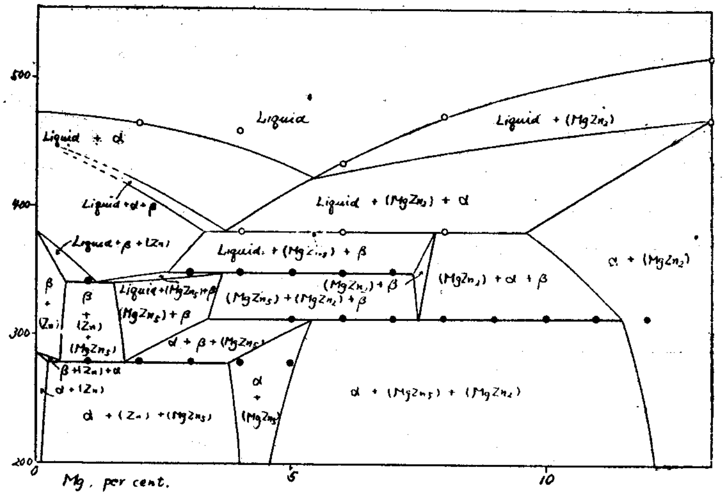


Fig. 3 Al 15% Series

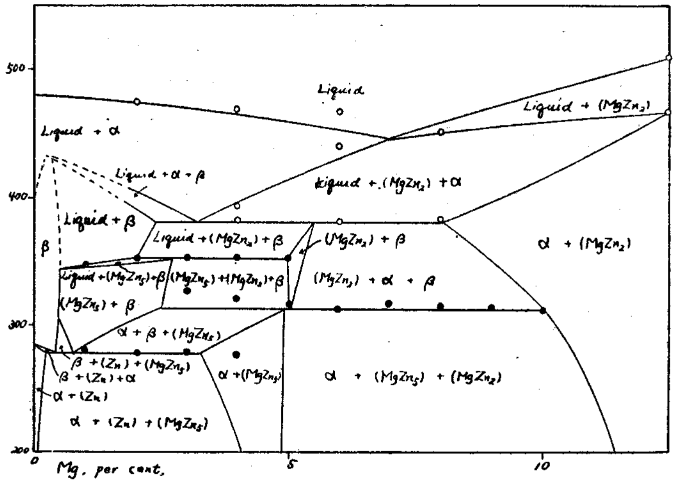


Fig. 4 Al 20% Series

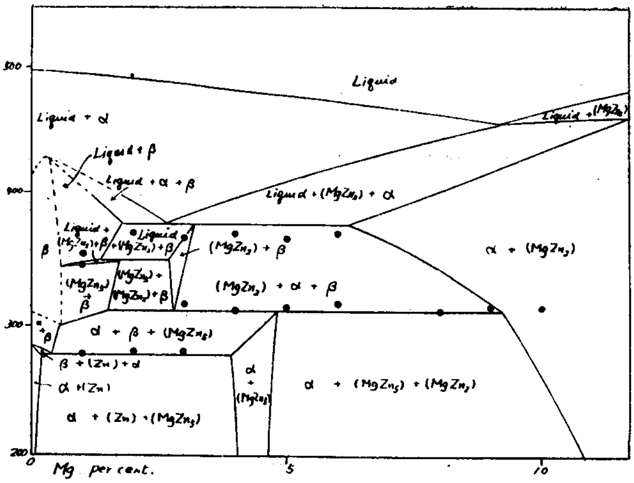
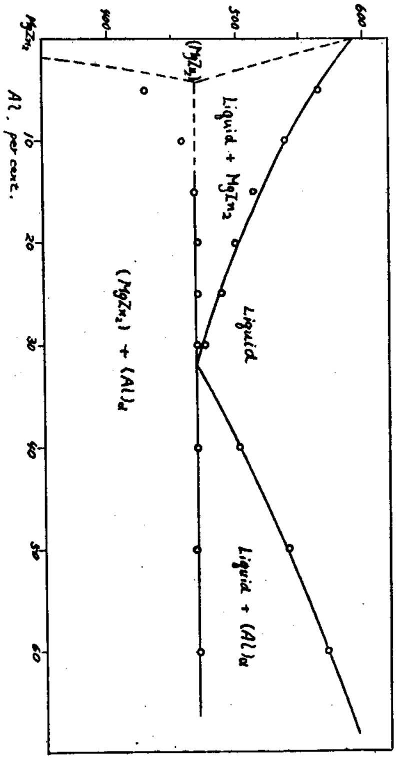


Fig. 5 Al 25% Series

Fig. 10 Al-MgZn₂ Quasi-binary System



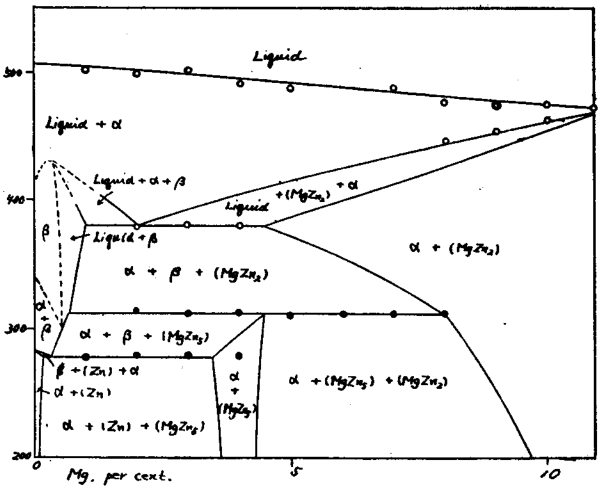


Fig. 6 Al 30% Series

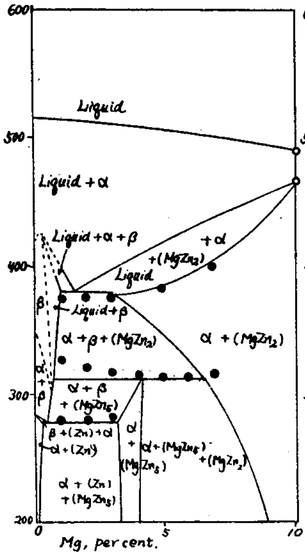


Fig. 7 Al 35% Series

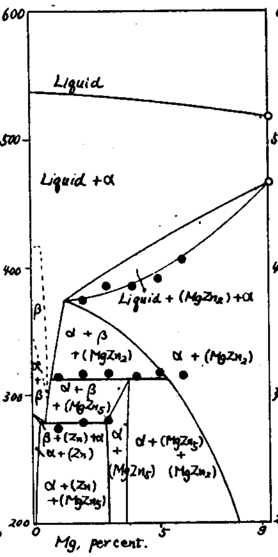


Fig. 8 Al 40% Series

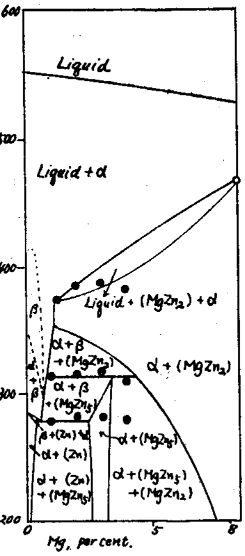


Fig. 9 Al 45% Series

alloy containing 15% Al, 13% Mg and the remainder Zn. In Table 1, the results of the thermal analyses of quasi-binary Al-$MgZn_2$ are also given, and they are plotted in Fig. 10. From these results, the exsistence of five non-variant reactions were observed as follows.

The invariant halting at 380 °C was recognized to be a peritecto-monotectic reaction,

$$\text{Liquid}+(\text{Al})_\alpha \rightleftarrows (\text{MgZn}_2)+(\text{Al})_\beta,$$

which was not found by W. Köster, but by M. Hamazumi as a peritecto-eutectic reaction at 370 °C. In this reaction formula, the parentheses show a solid solution of the phase indicated in it.

Similarly as given by W. Köster and M. Hamazumi, the points of arrest at 350 °C and 340 °C were observed on heating curves. They belong to the invariant reactions,

$$\text{Liquid}+(\text{MgZn}_2) \rightleftarrows (\text{Al})_\beta+(\text{MgZn}_5)$$

in the point of Al 11%, Mg 4% and Zn 85%, and

$$\text{Liquid} \rightleftarrows (\text{Al})_\beta+(\text{MgZn}_5)+(\text{Zn})$$

in the point of Al 4%, Mg 3% and Zn 93%.

In addition to the invariant arrests above mentioned, the two more invariant arrests, which were not clearly given by the both authors, were found to be at 313 °C and 276 °C on heating curves. One is a peritecto-eutectoid reaction,

$$(\text{Al})_\beta+(\text{MgZn}_2) \rightleftarrows (\text{Al})_\alpha+(\text{MgZn}_5)$$

and the other is a ternary eutectoid reaction,

$$(\text{Al})_\beta \rightleftarrows (\text{Al})_\alpha+(\text{MgZn}_5)+(\text{Zn}).$$

The invariant points of these two reactions could not accurately be estimated, but will be respectively near the points of 29.5% Al, 0.5% Mg, 70% Zn and 21% Al, 0.2% Mg, 78.8% Zn judging from the general equilibrium diagram which is obtained by our experiments.

Microscopical Study — For microscopical study, slowly-cooled or heat-treated specimens were taken and some typical ones are given in Photo. 1 to 14. Especially the etching reagent introduced by J. Schramm [7] was employed to distinguish $(\text{Al})_\alpha$ from $(\text{Al})_\beta$.

Photo. 1 represents the microstructure of the slowly cooled alloy 0501 etched by nitric acid, in which (Al_α) and (Zn) are present respectively as white and

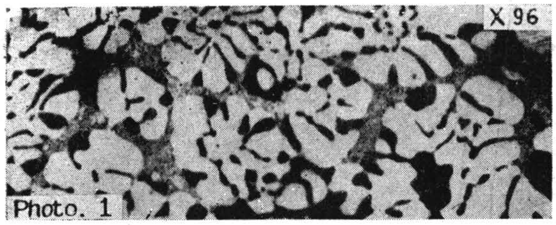


Photo. 1

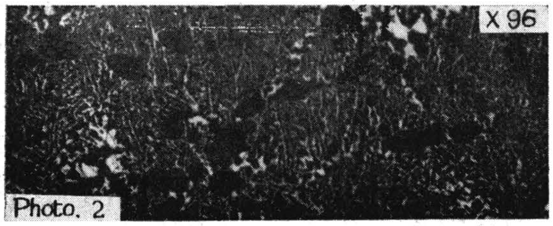


Photo. 2

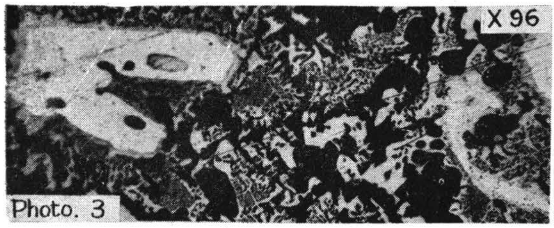


Photo. 3

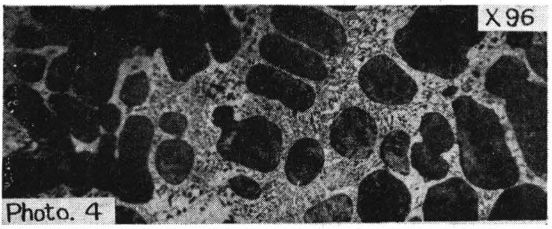


Photo. 4

Photo. 5

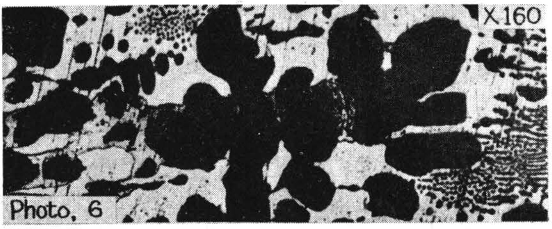


Photo. 6

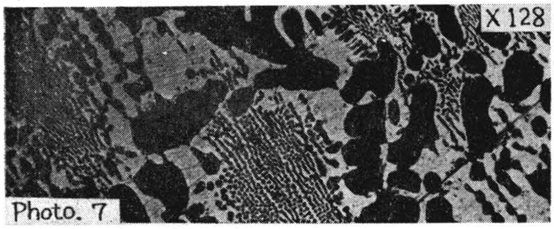


Photo. 7

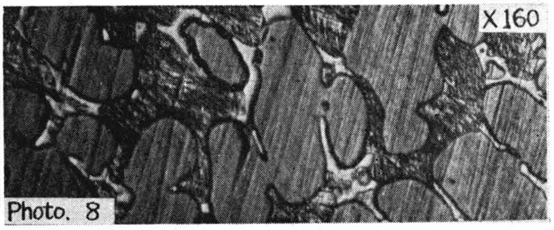


Photo. 8

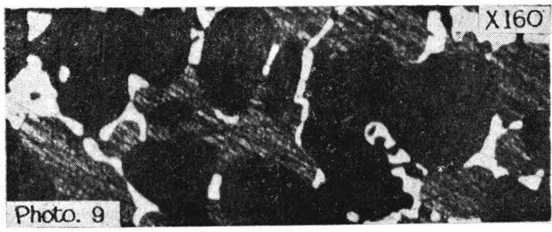


Photo. 9

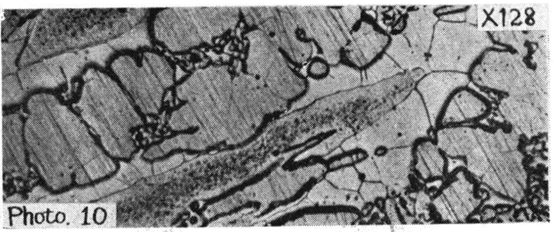


Photo. 10

Photo. 11

Photo. 12

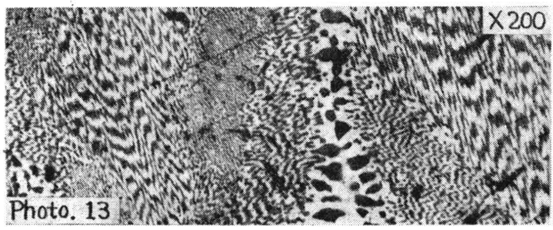


Photo. 13

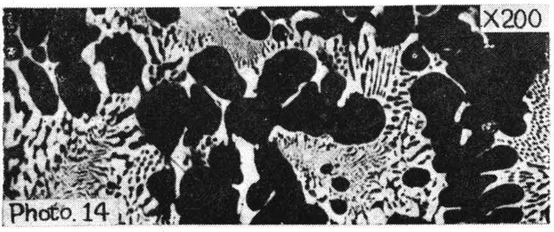


Photo. 14

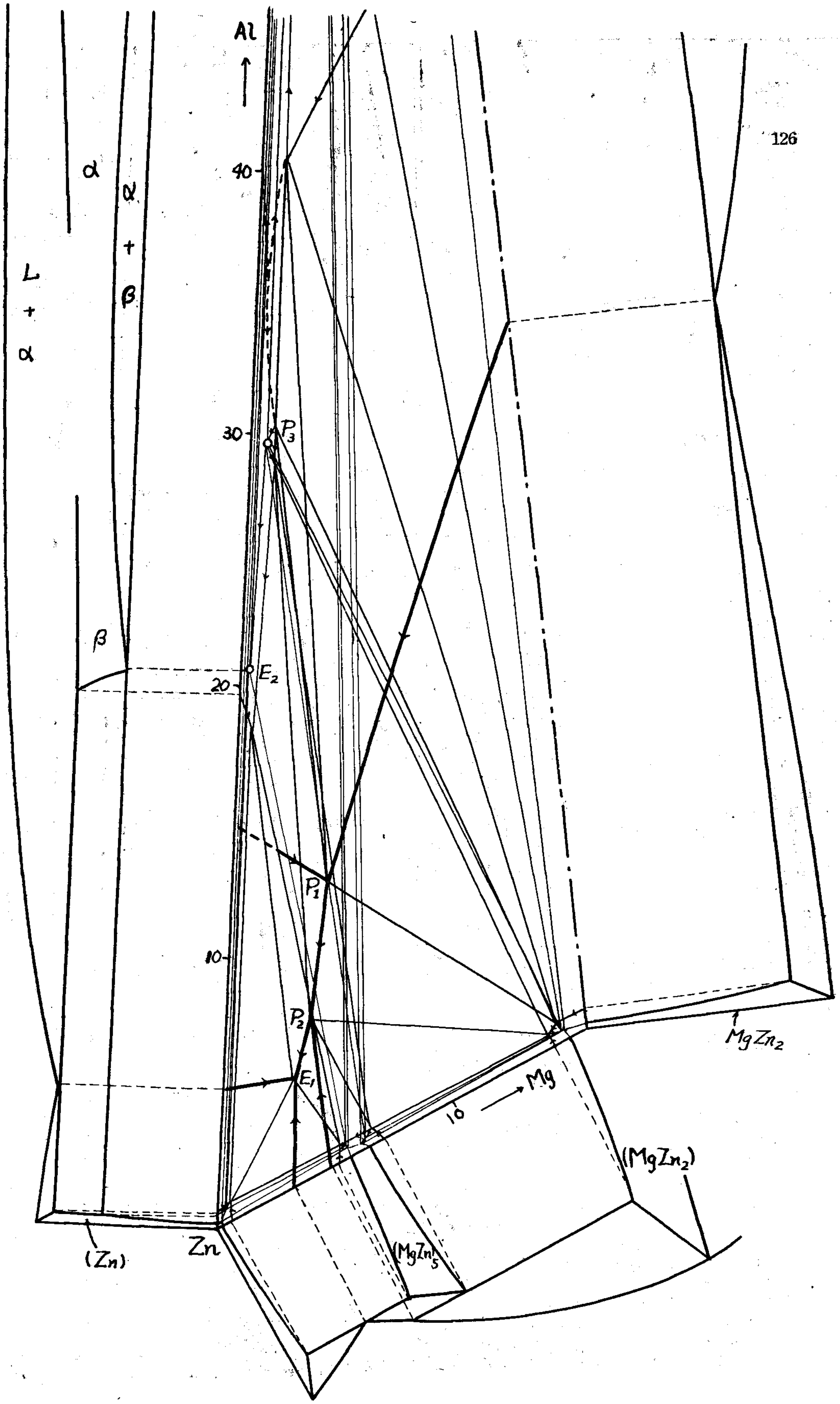


Fig. 11 General Equilibrium Diagram

black crystallites in the ground of the ternary eutectic $(Al)_{\beta}+(Zn)+(MgZn_5)$, and Photo. 2 (Alloy 0502) shows $(Al)_{\alpha}$ in the matrix of the ternary eutectic mixture.

In the slowly cooled alloy 0506, the primary separation is $(MgZn_2)$ which is enveloped by $(MgZn_5)$ in the ground of the binary eutectic $(Al)_{\beta}+(MgZn_5)$ as shown in Photo. 3. Both Photo. 2 and 3 were etched by the special etching reagent.[7]

Photo. 4 and 5 show the microstructures of the slowly cooled alloys 1502 and 1504, in which are observed a black dendritic $(Al)_{\alpha}$ being peripherally transformed into $(Al)_{\beta}$ with the binary peritectic reaction $Liquid+(Al)_{\alpha}\rightarrow(Al)_{\beta}$, and in the latter the binary eutectic $(Al)_{\beta}+(MgZn_5)$ is observed, it being different from the former.

The annealed alloys 3009 and 3010 show almost similar structures in which the primary $(Al)_{\alpha}$ is surrounded by the matrix of the binary eutectic $(Al)_{\alpha}+(MgZn_2)$, but only in 3009 alloy a small amount of $(MgZn_5)$ is seen. The difference between them is shown in Photo. 6 and 7.

Photo. 8 to 11 show the microstructures of the alloys in the Al 10% constitutional section quenched from 330 °C after 30 hours annealing. The alloy 1002, etched either by a nitric acid or by the special reagent, shows the structure in equilibrium of $(Al)_{\beta}+(MgZn_5)+(Zn)$ at this temperature. It is recognized in Photo. 8 and 9. Photo. 10 (alloy 1006) and Photo. 11 (alloy 1010) represent respectively $(MgZn_2)+(MgZn_5)+(Al)_{\beta}$ and $(MgZn_2)+(Al)_{\alpha}+(Al)_{\beta}$.

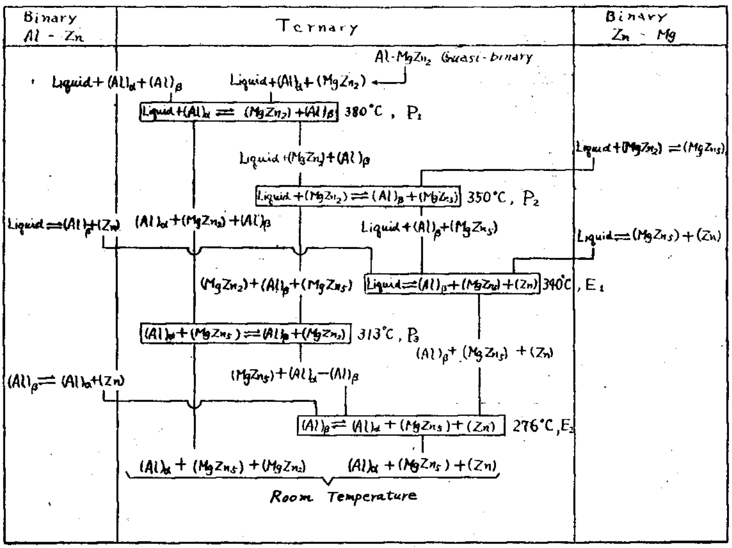


Table 3 General View of Transformation Process

Photo. 12 to 14 are the microstructures of alloys of the quasi-binary Al-$MgZn_2$ containing respectively Al 15%, 30% and 40%. From these microphotographs these alloys are observed to make a quasi-binary system.

Summary

The constitutions of the alloys of aluminium, zinc and $MgZn_2$ were investigated, and the equilibriums on the side of zinc and aluminium were determined. From these experimental results, we obtained a general diagram as shown in Fig. 11. Table 3 shows the solidification and transformation process of this system considered from this diagram.

Acknowledgement

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