ELECTRON-METALLOGRAPHIC STUDIES OF PRECIPITATION IN AN ALUMINIUM-ZINC-MAGNESIUM ALLOY

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I. Introduction

The phenomenon of precipitation hardening in aluminium alloys, containing zinc and magnesium, has been increasingly studied in recent years. Although Sander and Meissner[1] reported as early as in 1923 that aluminium-zinc-magnesium (Al-Zn-Mg) alloys could be hardened to high tensile strengths by decomposition of the supersaturated solid solution at low temperatures, development of commercial alloys was handicapped by the low ductility and high susceptibility to stress-corrosion cracking of the ternary alloys. The pressing demand for new alloys during the second World War and the observed improvement in resistance to stress-corrosion of these alloys on adding copper, manganese or chromium led eventually to the production of successful commercial alloys like 75 S, D.T.D. 5074, D.T.D. 687 and 7178 (Table I). Such alloys with a combined zinc-magnesium content of 7·5–9·5%

Table I

Typical compositions of some commercial alloys based on the aluminium-zinc-magnesium system

(All values are in weight percentages. Aluminium represents the balance in each case. Iron, Silicon and Titanium are impurities.)

Trade name of alloy	Zn	Mg	Cu	Mn	Cr	Fe	Si	Ti
75 S	5·40	2·40	1·35	0·16	0·22	0·28	0·16	0·05
D.T.D. 5074	5·80	2·38	1·37	0·31	0·12	0·25	0·17	0·05
D.T.D. 687	5·90	2·95	0·52	0·33	0·01	0·27	0·13	0·03
7178	6·65	2·70	1·96	0·06	0·24	0·26	0·14	0·05

acquire a tensile strength of over 80,000 psi on ageing and find wide application today as the strongest of aluminium alloys in the aircraft industry.

It has been realized for some years, however, that further improvements in the properties of Al-Zn-Mg alloys may be possible if the mechanism of sub-microscopic precipitation in them during the ageing period is clearly understood. The work of Polmear and Scott-Young,[2,3] Varley *et al.*[4] and the present authors[5] has thrown considerable light on the influence of composition, ageing temperature and time of ageing on the mechanical properties of these alloys. The X-ray investigations of Saulnier and Cabane,[6] Mondolfo *et al.*[7] and Graf[8] as well as the electron-microscopic studies of Nishimura and Murakami,[9] Varley *et al.*,[4] Nicholson *et al.*[10] and Thomas and Nutting[11] have shown that the precipitation process is complex in these alloys with formation of Guinier-Preston (G.P.) zones, transition phases and equilibrium precipitate in that order. Electron-metallographic studies have so far proved the most rewarding in this field and success in the development of better alloys seems to depend now on further investigations of the ageing sequence in these alloys under conditions leading to the highest hardness as well as tensile strength.

II. SCOPE OF PRESENT STUDIES

Aluminium alloys have generally been examined in the electron microscope through oxide replicas (250–500 Å thick) prepared by grinding, mechanical polishing, electropolishing and anodic oxidation of the specimen surfaces.[12,13] Although very successful in the case of other aluminium alloys, this method has been reported to be inadequate for the study of Al-Zn-Mg alloys,[4,11] especially in the early stages of ageing. The only reliable information obtained so far by this as well as the metal-shadowed carbon-replica technique[14] concerns the distribution and shape of the equilibrium precipitate plates in an advanced state of ageing. Unfortunately, full details regarding the preparation of these replicas and the resolving power of the electron microscope have not been given by the earlier investigators.

The thin-foil transmission technique has recently been applied with conspicuous success to Al-Zn-Mg alloys by the Cambridge metallographers.[10, 11] Thin strips (100–150 μ) of the alloys were aged at 120°, 160° and 300° C. respectively, electropolished to thin foils (200–2,000 Å) and examined directly in the high-resolution Siemens Elmiskop I. The ageing sequence in the D.T.D. 687 alloy and three experimental alloys with a combined zinc-magnesium content of 8·5–10·5% was thereby established as: Spherical G.P. Zones $\rightarrow$ Transition $MgZn_2$ platelets $\rightarrow$ Equilibrium $MgZn_2$ plates.

The present investigations were undertaken to explore, in the first instance, the limitations of the oxide-replica technique as applied to Al-Zn-Mg alloys with the aid of a 100 kV. Philips Electron Microscope capable of resolution up to 50 Å. The precipitation sequence was then studied with the aid of a standardized oxide-replica technique in an alloy whose composition and ageing temperature were chosen for maximum response to the precipitation treatment.

III. EXPERIMENTAL PROCEDURE

Materials.—The alloys for the preliminary ageing studies were prepared from INDAL aluminium of 99·0% purity and chemically pure zinc and magnesium. The alloy chosen for the detailed study was based on super-purity aluminium (99·996% pure). The method of preparation of the alloys has been described elsewhere.[5]

Heat treatment.—All specimens were of 0·5″ diameter and 0·4″ thickness in the homogenized and machined condition. They were solution-treated for 2 hours at 460 ± 5° C., quenched in water and aged in oil-baths at constant temperatures in the range of 50–200° C.

Mechanical testing.—The Vickers Pyramid Hardness Tester with a load of 5 kg. was used to determine hardness of the specimens after solution heat treatment as well as after ageing for different periods varying from a few minutes to a few months.

Electron-microscopic examination.—The oxide replicas were first prepared from a few test specimens by combining available electropolishing and anodizing techniques as well as by varying the experimental conditions. They were carefully examined in the electron microscope at magnifications varying from 5,000 to 50,000 with a view to arrive at the optimum conditions for production of satisfactory replicas.

IV. THE STANDARD OXIDE-REPLICA TECHNIQUE

The following factors were systematically varied in the initial study to evolve a standard oxide-replica technique for Al-Zn-Mg alloys:

(*a*) Composition of the electropolishing bath,

(*b*) Potential Difference and Current Density for the electropolishing operation,

(*c*) Time of electropolishing,

(*d*) Composition of the etching reagent and time of etching, (*e*) Composition of the anodizing bath,

(*f*) Potential Difference and Current Density for the anodizing operation,

(*g*) Temperature of the anodizing bath, and

(*h*) Technique for stripping the replicas.

After examining replicas obtained through different combinations of the above factors from alloys in the annealed, ageing, fully aged and softened conditions, the following standard procedure was evolved to obtain satisfactory oxide replicas:

The alloy specimens were carefully ground to 3/0 emery paper using paraffin dissolved in kerosene as lubricant and then prepared on the polishing wheel using coarse alumina as abrasive. Electropolishing was carried out in Jacquet's solution made up of 35 c.c. of 60% perchloric acid and 65 c.c. acetic anhydride at a potential difference of 15–20 volts and current densities of 0·02–0·03 amp./sq.cm. A stainless steel plate was used as cathode and the time of operation was 1–2 minutes at room temperature. The bright surface thus obtained was chemically etched for a few seconds in an aqueous solution of nitric acid (25%) and hydrofluoric acid (2%) to reveal the grain boundaries clearly. The anodic oxidation was then conducted in an aqueous 12% disodium hydrogen phosphate solution containing 0·5% sulphuric acid at a potential difference of about 15 volts at room temperature.

The stripping of the oxide replicas was achieved by first immersing the anodized specimens marked into squares with a scriber in a saturated solution of mercuric chloride in water for 30 seconds.[15] They were then transferred to a 3% solution of the chloride and left for 30–45 seconds for further amalgamation. A final immersion in a 1% solution of the chloride for 2–3 minutes led to the release of the oxide squares from the specimen surfaces. The floating squares were picked up carefully, washed in a 10% hydrochloric acid solution to get rid of any residual mercury and finally rinsed well with distilled water. The squares could then be mounted on specimen carriers, dried in desiccators and examined in the electron microscope.

Figures 1–10 show the electron-micrographs of Al-Zn-Mg alloys obtained by this standardised oxide-replica technique. It is possible to distinguish between grain-boundary precipitate (Fig. 1), matrix precipitate (Fig. 2), hexagonal and square etch pits (Figs. 3 and 4), precipitate-free matrix (Fig. 5), Guinier-Preston zones (Figs. 6–9), Widmanstaetten pattern of platelets (Fig. 10), partially or fully dissolved precipitate (Figs. 1 and 2) and preferentially nucleated precipitate (Fig. 4) in these electron-micrographs.

V. PRECIPITATION SEQUENCE IN AN AL-ZN-MG ALLOY

As earlier investigations[5] had shown that an aluminium alloy containing 6% zinc and 3% magnesium is the most satisfactory from the point of view of maximum response to precipitation hardening without the onset of brittleness, an alloy of this composition was prepared with superpurity aluminium and chemically pure zinc and magnesium. The Hardness/Ageing Time curves were obtained for this alloy at different temperatures (Fig. 11) and the ageing temperature of 100° C. was selected for the electron-metallographic study as leading to the highest hardness (192 V.P.N.) in a reasonable time (15–20 days). This temperature has not been chosen for study of the precipitation sequence by any of the earlier workers.

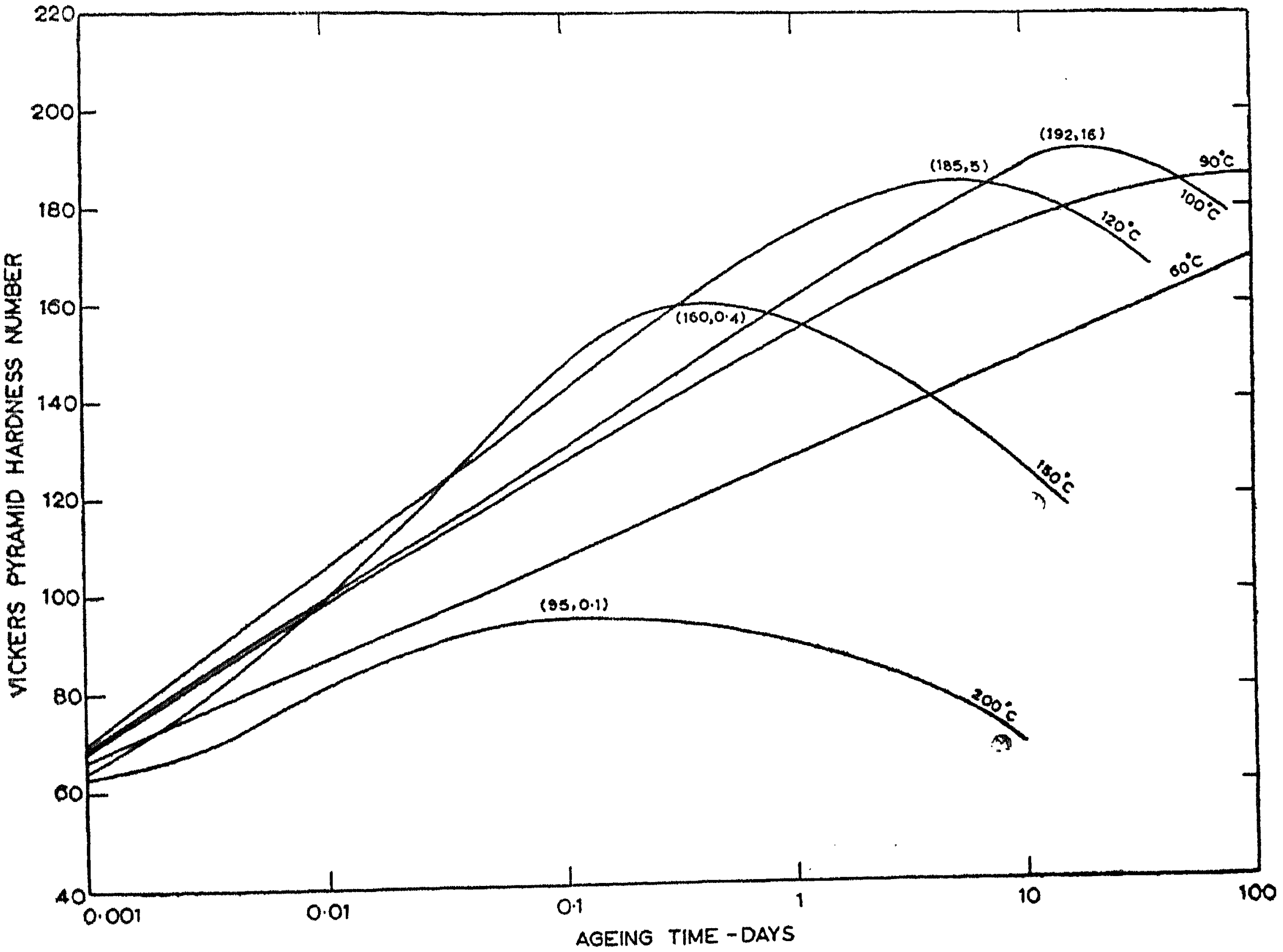

FIG. 11. Response to ageing at different temperatures of a high-purity Al–6% Zn–3% Mg. alloy.

Figures 5–10 and Table II illustrate the precipitation process in the chosen alloy at 100° C. as revealed by the oxide-replica technique in the 100 kV. Philips Electron Microscope. It has to be emphasized in this connection that the precipitation was found to proceed at different rates in different grains of the same specimen and only a general over-all picture of

TABLE II

Growth of Guinier-Preston zones and Widmanstaetten platelets on ageing an Al-6% Zn-3% Mg alloy at 100° *C.*

Ageing time (Days)	Hardness (V.P.N.)	G.P. Zones diameter (Å)	Size of platelets	
			Length (Å)	Width (Å)
0	72	..	..	..
2	167	75–125	..	..
4	176	200–300	..	..
7	183	300–450	..	..
10	187	400–600		
15	191	500–750	250–750	50–150
20	192	600–800	250–1000	50–150
25	191	600–800	250–1000	50–200
30	190	600–800	250–1000	50–200
45	190	600–800	250–1000	50–200

the precipitation sequence is given by Figs. 5–10 and Table II. Grain-boundary precipitation was invariably detected after solution treatment and quenching (Figs. 3 and 4). This precipitate was often revealed by square as well as hexagonal etch pits along the grain boundary. The super-saturated solid solution obtained on quenching did not reveal, however, any pre-precipitation zones (Fig. 5). The first evidence of any structure was obtained only after about two days' ageing with the appearance of circular regions about 75 Å in diameter (Fig. 6).

The reported clustering of the zinc and magnesium atoms into spherical Guinier-Preston zones and their steady growth with increase in hardness[11] are well brought out by Figs. 6–8. As the zones reach the critical size of about 600 Å in diameter, platelets (250–500 Å long and 50–100 Å wide) are nucleated from within the zones themselves (Figs. 8 and 9). The onset of maximum hardness in the alloy seems thus to be associated with the maximum number of zones approaching the critical size and disintegrating into platelets. The nucleation and growth of platelets take place rather slowly, keeping the alloy in the fully hardened condition for a reasonably long time

(15–30 days). The platelets grow more than 1,000 Å in length and 200 Å in width before softening sets in (Table II). The growth of the platelets is generally in one preferred direction (Figs. 8 and 9), although a Widmanstaetten pattern is occasionally obtained in over-aged specimens (Fig. 10). There is evidence for the reported tendency for preferential precipitation on dislocations or sub-grain boundaries (Fig. 4). Precipitate-free regions[4,11] near the grain boundaries have not, however, been observed.

VI. DISCUSSION OF RESULTS

The present investigations have clearly shown that the oxide-replica technique, when suitably standardized, is capable of giving much useful information on the precipitation mechanism in Al-Zn-Mg alloys. The results obtained for some of these alloys by the thin-foil transmission method have been confirmed here, for the first time, with the aid of a replica technique. The G.P. zones became visible at diameters of 75 Å in the present work, whereas zone diameters of 30 Å were detected by the thin-foil transmission technique. This may be due to either the lack of fidelity of the oxide replica or the slightly lower resolution of the electron microscope used in the present studies. In spite of this possible limitation, the oxide-replica method has its unique place in such investigations as information obtained from thin foils (200–2,000 Å thick) may not always be valid for massive specimens, as generally employed for precipitation hardening in practice.

The formation of spherical zones in Al-Zn-Mg as well as Al-Ag alloys has been noticed earlier[10] and explained on the basis of the relative sizes of the solute and solvent atoms.[8,16] The atomic diameter (3·20 Å) of magnesium is 12% larger than that of aluminium (2·86 Å), but the small atoms (2·75 Å) of zinc are supposed to relieve the strain around magnesium atoms in the G.P. zones. The actual mechanism of zone nucleation is not very clear, although vacancies quenched-in from the solution-treatment temperature have been generally held responsible for the rapid diffusion rates and low activation energies associated with the formation of zones. Preferential precipitation along dislocation lines and sub-grain boundaries, occasionally observed in such studies, may then be understood as due to preferential migration of vacancies and solute atoms to dislocations after quenching.

The platelets have been shown here, for the first time, to nucleate from within the zones, as envisaged by Guinier.[8,16] Earlier workers have not observed this slow disintegration of zones into platelets at the somewhat higher ageing temperatures employed by them and hence have concluded that the zones dissolve into the matrix while the platelets get nucleated by a different mechanism, *e.g.*, segregation of solute atoms along stacking faults. The present work strongly suggests that the structural changes on precipitation are at least partly allotropic in nature and the following sequence may be a continuous one:

G.P. Zones → Transition Precipitate → Equilibrium Precipitate.

The nature of the transition and equilibrium precipitates could not be established by the oxide-replica technique with the same certainty as by the thin-foil transmission method. Etch pits formed by the grain-boundary precipitate were, however, found to be hexagonal or square in shape, suggesting that both the cubic $(Al, Zn)_{49}Mg_{32}$ and the hexagonal $MgZn_2$ phases are precipitated during quenching. The former is perhaps precipitated at a higher temperature and the latter at lower temperatures, as suggested by the Al-Zn-Mg ternary equilibrium diagram. The structures of the transition and equilibrium precipitate have already been established for ageing temperatures lower than 160° C.[11]

The present work confirms the earlier conclusion that the increase in hardness in Al-Zn-Mg alloys is due only to a fine dispersion of the precipitating phases, unlike in aluminium-copper alloys. The formation of precipitate-free zones having considerable influence on the resistance to stress-corrosion of these alloys has not, however, been confirmed.

VIII. SUMMARY

The mechanism of sub-microscopic precipitation in an Al-Zn-Mg alloy selected for its maximum response to ageing has been studied by a standardized oxide-replica technique in a 100 kV. Philips Electron Microscope. Contrary to earlier conclusions, examination of the oxide replicas has been shown to reveal details of the precipitation process almost as clearly as the thin-foil transmission technique. The reported formation of spherical Guinier-Preston zones followed by the development of a Widmanstaetten pattern of precipitated platelets has been confirmed. The zones have, however, been shown to grow into the platelets and *not* to dissolve in the matrix as reported earlier. The precipitation process has been correlated with the Hardness/Ageing Time curve and the structure of the precipitates has also been discussed.

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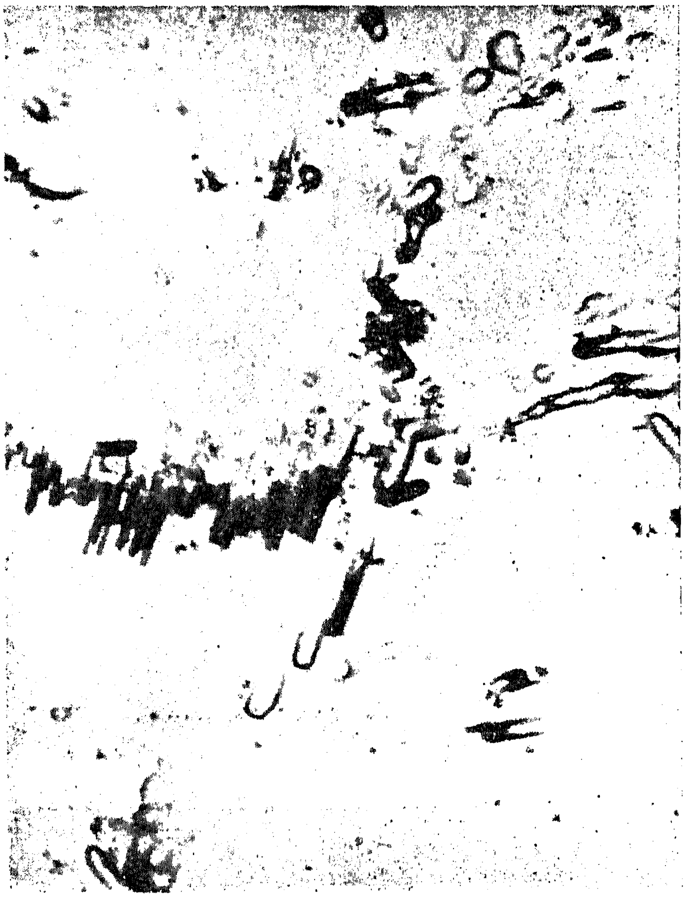


FIG. 1

FIG. 2

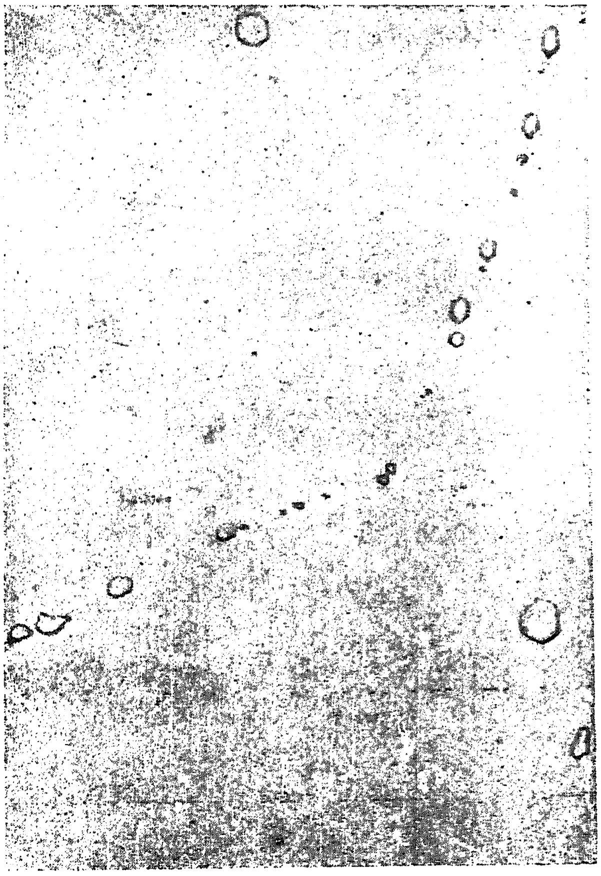


FIG. 3

FIG. 4

FIGS. 1–4

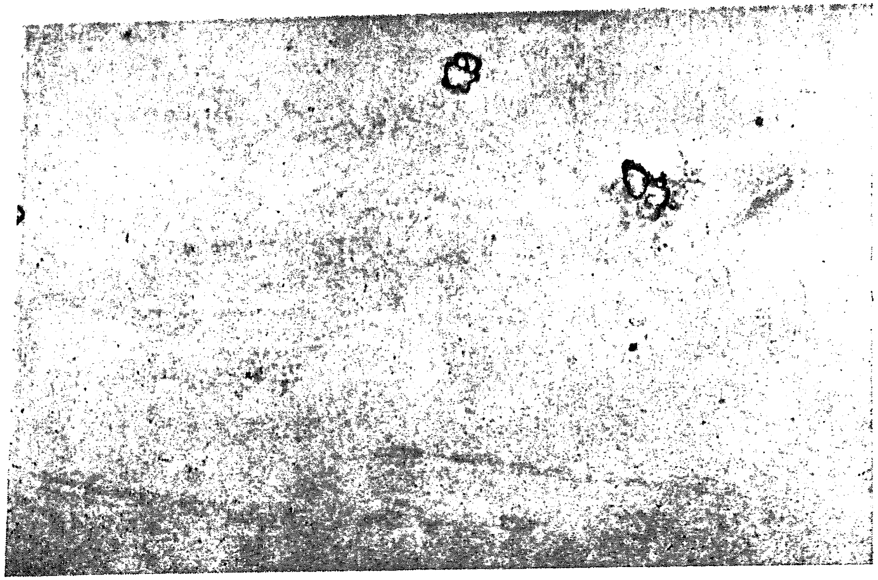


FIG. 5

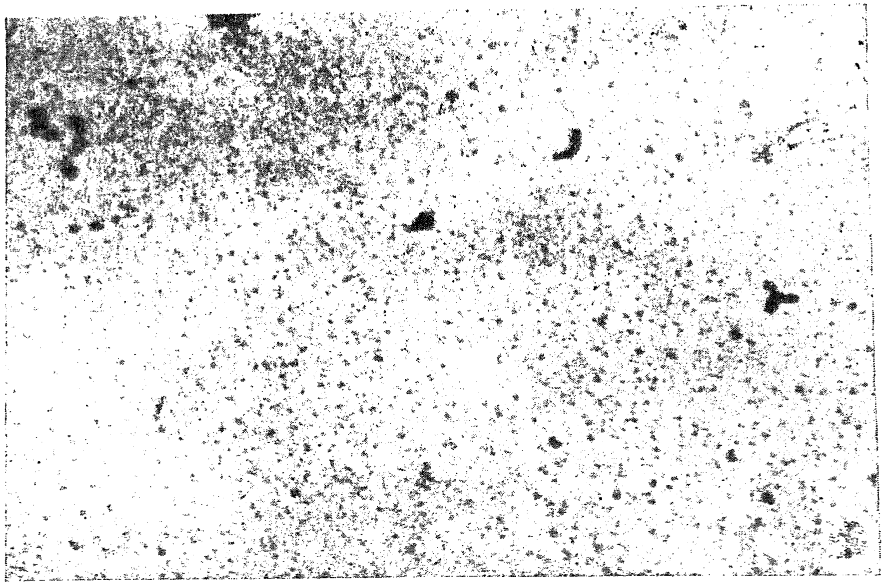
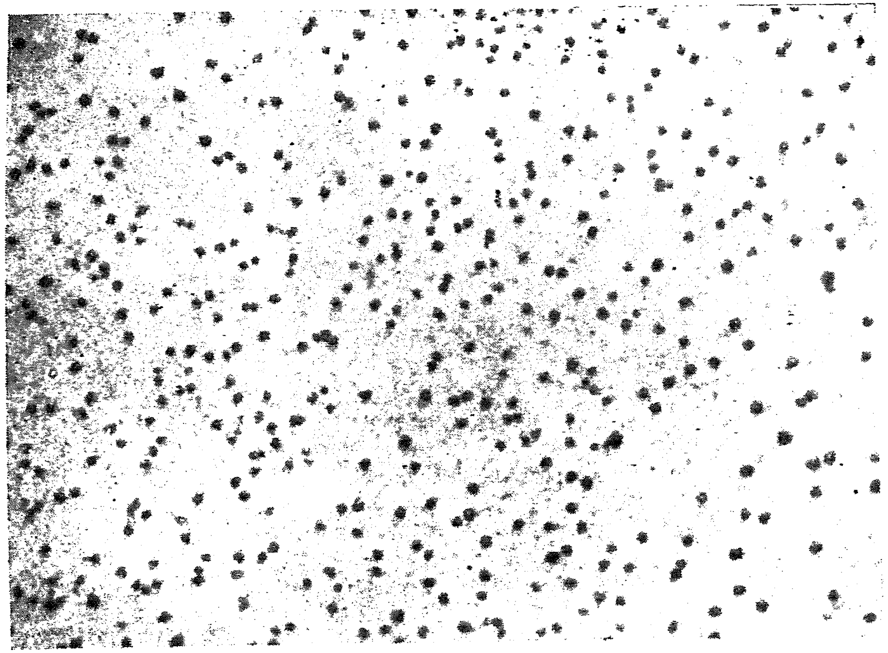
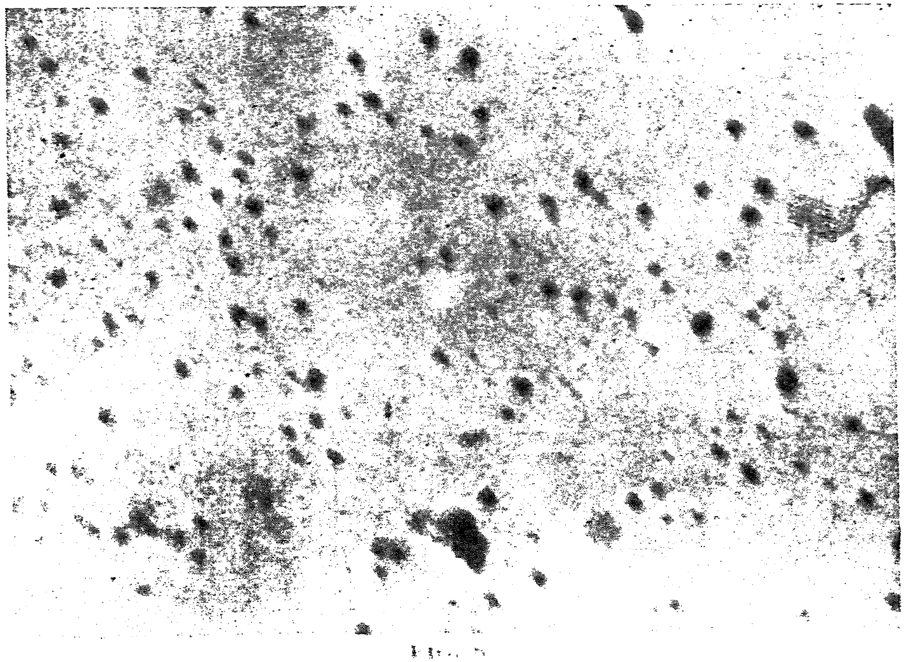


FIG. 6





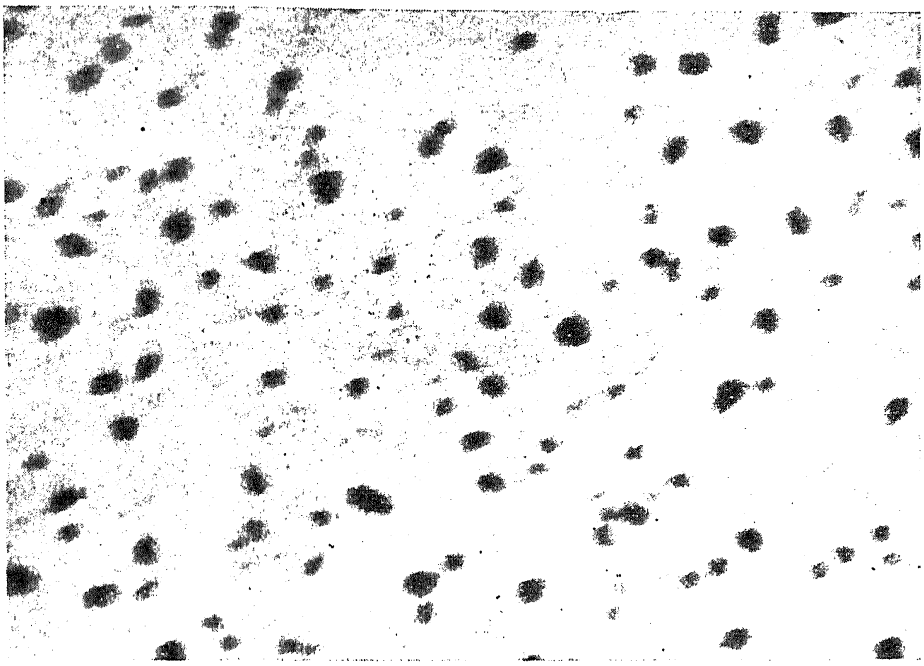


FIG. 9

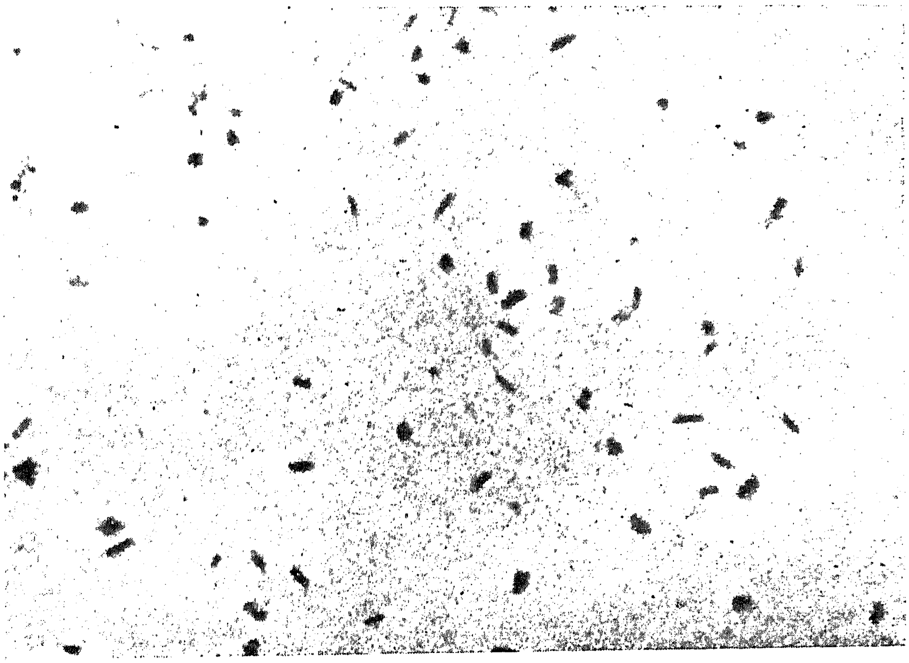


FIG. 10

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EXPLANATION OF PLATES

FIGS. 1–10. Structure of a high-purity Al–6% Zn–3% Mg alloy after different heat treatments.

PLATE XIV

FIG. 1. Annealed, × 10,000.
FIG. 2. Annealed, × 10,000.
FIG. 3. Aged for 30 hours at 100° C., × 6,000.
FIG. 4. Aged for 5 days at 100° C., × 10,000.

PLATE XV

FIG. 5. Solution heat treated and quenched, × 10,000.
FIG. 6. Aged for 2 days at 100° C., × 40,000.
FIG. 7. Aged for 10 days at 100° C., × 20,000.
FIG. 8. Aged for 20 days at 100° C., × 40,000.

PLATE XVI

FIG. 9. Aged for 25 days at 100° C., × 40,000.
FIG. 10. Over-aged and softened, × 4,500.