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Behaviour of Al–Mg alloys at high temperature

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The behaviour of a few Al–Mg alloys (up to 7.1 wt% Mg) has been studied on heating in air at 500° C for 8 h or more. The precipitation of a spinel phase, $MgAl_2O_4$, is found to take place on the surface and along the transverse section (depth) of the specimen. The alloys seem to be resistant to internal oxidation below 4.5% Mg and thereafter prone to it. Beryllium modification does not suppress the progress of internal oxidation taking place in the Al–Mg alloys. The results have been interpreted on the basis of anodized photomicrographs and X-ray diffraction data.

1. Introduction

The aluminium industry exists because of the universal presence of a protective layer of oxide 2 nm thick on the exposed surface of aluminium and its alloys. This impervious oxide layer prevents the diffusion of oxygen inside the aluminium matrix and also allows some deformation of the substrate without rupturing. However, the oxide film found on the surface of aluminium alloys is impervious, continuous and self-healing only at room temperature or at higher temperatures in the initial stages of oxidation. As the film thickness increases with temperature and time, cracks appear and further oxidation of aluminium alloys is possible [1]. In fact, aluminium alloys are highly resistant to oxidation at temperatures up to 200° C. At higher temperatures, the oxidation rate increases and when the temperature exceeds 350° C, internal oxidation of Al–Mg alloys containing appreciable amounts of magnesium may take place in an atmosphere containing both oxygen and water. This process is reported to be more significant at temperatures above 480° C [2]. Other alloys of aluminium are reportedly less susceptible to internal oxidation.

In the relevant literature, the internal oxidation of copper alloys [3–6], silver alloys [7, 8], Co–Cr alloys [9], Ni–Al alloys [10] and iron-based alloys [11], etc., and its mechanism have been reported. On the other hand, only possibilities are encountered for internal oxidation in Al–Mg alloys and microstructural evidence of the phenomenon is not available. It has been reported that in Al–Mg alloys containing up to 8 wt % Mg, progressive heating up to 400° C [12, 13] and at 500° C [14] can cause the formation of a duplex oxide film consisting of a thick outer layer of MgO over an inner compact layer of γ-Al_2O_3. Powder photographs of a stripped film formed at 500° C on an Al–3 wt % Mg alloy showed the presence of $MgAl_2O_4$ [1]. Leontis and Rhines [15] and Markworth [16] have also demonstrated the presence of $MgAl_2O_4$ in the surface oxide films on high Al–Mg alloys. The oxidation of Al–(1 to 14%)Mg alloys at temperatures of 600 to 1100° C revealed that a protective amorphous film on the metal surface crystallized to magnesium oxide and magnesium aluminate, accompanied by a sudden increase in the oxidation rate [17].

The process of internal oxidation is very interesting and can be studied in detail. It was considered undesirable in the beginning since it introduced inclusions into a clean material and unnecessarily precipitated solute inside the alloy [18]. Lately many potential uses of this phenomenon have been realized and partly achieved. The depth of internal oxidation can be utilized to measure the product of solubility and diffusivity of gases in metals and alloys. The diffusion coefficient of oxygen in iron has been determined in an Fe–0.1% Al alloy over a range of temperature by measuring the rate of internal oxidation and oxygen solubility [19, 20].

In addition to this, the process of internal oxidation is a very important means of introducing a controlled number of fine particles into a metal or an alloy for various studies. It is a powerful way of strengthening the material by means of dispersion-hardening, Ashby and co-workers [21–23] and Jones [24] studied the effect of dispersed particles on grain-boundary migration and on dispersion strengthening.

In this study, the behaviour of Al–Mg alloys on heating in air at 500° C was investigated to provide microstructural evidence supported by X-ray diffraction work regarding surface and internal oxidation.

2. Experimental procedure

2.1. Preparation of alloys

Five Al–Mg alloys were prepared from 99.99% Al and 99.9% Mg by melting in a graphite crucible under a flux. The temperature of the melt was not allowed to exceed 720° C. The cast alloys contained 2.0, 4.5, 5.0, 6.3 and 7.1 wt % Mg. Two more alloys were prepared by the addition of 0.0008% Be using a Cu–4% Be master alloy and contained 4.6 and 6.2 wt % Mg and traces of beryllium.

2.2. Polishing and etching

Samples 2 cm diameter, 1 cm thick were polished on a belt and with silicon carbide papers. The microstructures were revealed by the anodic etching technique

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developed by the author for aluminium and Al–Cu alloys [25] and Al–Mn and Al–Mg alloys [26]. The specimens were electrolysed for 5 min at 60 to 70° C under a constant current density of 15 A dm^{-2} in the following electrolyte:

H_2SO_4 = 40 ml
H_3PO_4 = 6 ml
HNO_3 = 1 ml
Distilled water = 88 ml

2.3. Oxidation treatment

The alloy samples were oxidized in air at 500° C for 8, 16 and 24 h respectively and anodized to reveal microstructures in all cases.

2.4. Extraction and identification of phases

Samples of all alloys under study from the as-cast and different oxidized conditions, containing various intermetallic compounds and non-metallic inclusions, were used for the extraction and identification of phases present. A 10% HCl solution in methanol was used to dissolve each alloy electrolytically by making it as an anode with platinum as the cathode. It took a minimum of two hours to dissolve the alloy matrix and to obtain sufficient insoluble residue which was centrifuged, washed three to four times with alcohol, dried and subjected to X-ray diffraction studies. From the diffraction patterns, *d* values were calculated and phases were identified by comparing with values in standard ASTM cards.

3. Results

The anodic etching technique developed for Al–Mg alloys successfully revealed minute details of morphology, such as dendritic cells, precipitation at cell boundaries, movement of cell boundaries and coring inside cells.

The appearance of numerous small precipitate particles mostly at cell boundaries for alloys oxidized in air at 500° C, except in the case of Al–2% Mg alloy, is of much interest. The precipitates appeared after 24 h of heating for Al–4.5% Mg alloy (Fig. 1) and Al–5.0% Mg alloy (Fig. 2), after 16 h of heating for Al–6.3% Mg alloy and after 8 h of heating only for higher magnesium alloys. The precipitate appeared mostly on cell boundaries, at junctions of cell boundaries and sometimes inside dendritic cells.

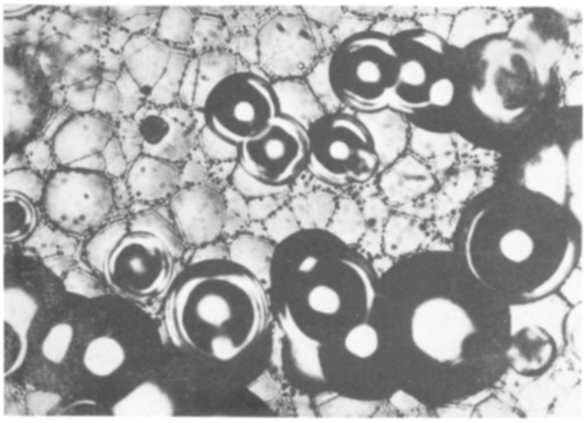

Figure 2 Al–5.0% Mg alloy, oxidized at 500° C for 24 h, showing small precipitates on cell boundaries (× 475).

Apart from this precipitate, photomicrographs of oxidized samples reveal the occurrence of coring inside the bigger dendritic cells. The peculiar microstructure of 5% Mg alloy oxidized at 500° C for 24 h deserves special mention here. A portion of the specimen showed coring in the bigger cells (Fig. 3) and another portion of the same specimen showed the appearance of small precipitate particles at the cell boundaries (Fig. 2). To check whether oxygen diffused inside the alloy and if internal oxidation of alloy actually took place, a transverse section of the same oxidized specimen, i.e. across the depth of the specimen, was cut and anodically etched. It showed maximum coring just below the top surface, which remained open to the atmosphere during heating. The coring decreased on moving away from the surface, but persisted up to one third of the depth from the surface. Small precipitates were found on cell boundaries throughout the depth of the transverse section (Fig. 4).

In the alloys modified with beryllium, the precipitate was present inside cells and concentrated in some regions in (Al–4.5% Mg–trace Be) alloy, oxidized at 500° C for 16 h (Fig. 5) and also appeared inside cells in (Al–6.2% Mg–trace Be) alloy, oxidized at 500° C for 16 h. Transverse sections of these alloys showed

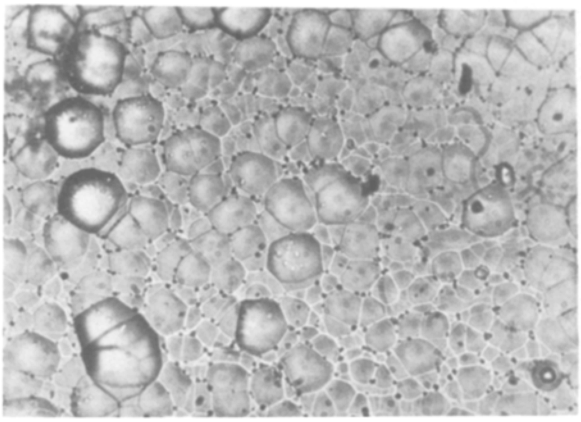

Figure 1 Al–4.5% Mg alloy, oxidized at 500° C for 24 h, showing small precipitates on cell boundaries (× 475).

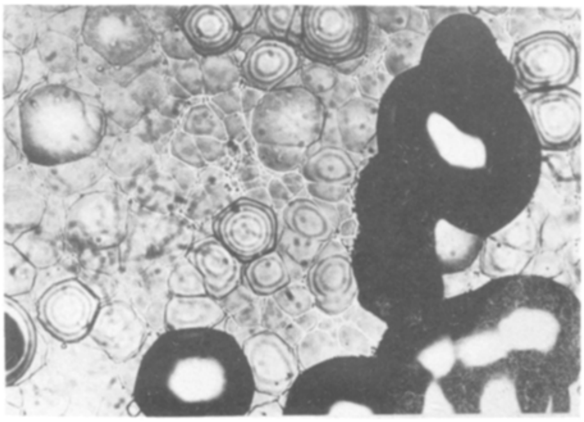

Figure 3 Another portion of Al–5.0% Mg alloy oxidized at 500° C for 24 h, showing coring in bigger cells (× 475).

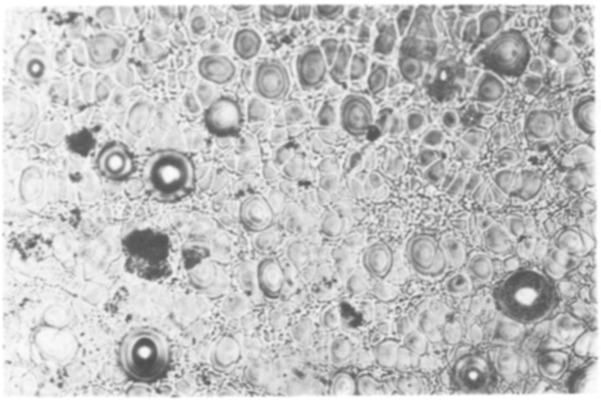

Figure 4 Transverse section of the above specimen, 1.5 mm below the top surface, showing coring as well as small precipitates on cell boundaries (× 475).

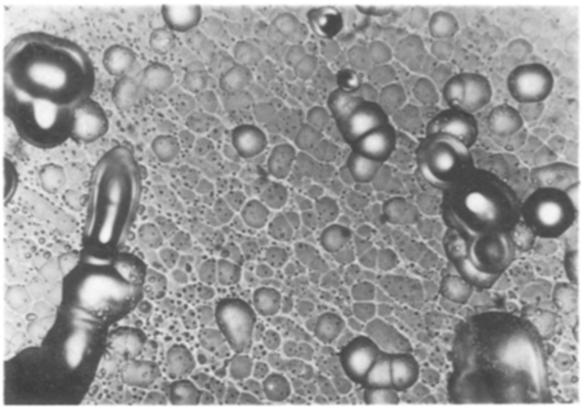

Figure 5 (Al–4.6% Mg–trace Be) alloy oxidized at 500° C for 16 h, showing precipitates concentrated in certain regions (× 475).

the precipitate occurring inside cells throughout the specimens.

The X-ray diffraction patterns of the extracted phases in the heat-treated samples provided the identification of the spinel phase, $MgAl_2O_4$, formed in the case of the following alloys:

Al–4.5% Mg oxidized at 500° C for 24 h

Al–5.0% Mg oxidized at 500° C for 24 h (Table I)

Al–7.1% Mg oxidized at 500° C for 8 and 16 h

Al–4.6% Mg–trace Be at 500° C for 16 h (Table II)

Al–6.2% Mg-trace Be at 500° C for 16 h

Spinel phase was not detected in Al–2% Mg alloy even after oxidizing at 500° C for 24 h.

4. Discussion

An interesting and little-known phenomenon appeared to be manifesting itself in Al–Mg alloys in the present investigation. The technique of anodic etching, which was developed specially for these alloys, provides us with clear microstructural evidence of the occurrence of numerous small precipitates. These were distributed mostly on dendritic cell boundaries or at the junctions of cell boundaries and sometimes inside cells. On looking through the microscope at higher magnification (1200 ×) these precipitates looked like octahedral particles. On extraction and identification by X-rays, the precipitate turned out to be the spinel $MgAl_2O_4$. It is to be noted that this phase never occurred in as-cast specimens and formed only when Al–Mg alloys having a magnesium content of more than 2% were oxidized at 500° C for 8 h or more.

TABLE I The observed *d* values of Al–5.0% Mg alloy oxidized in air at 500° C for 24 h*

Serial No.	Observed values of alloy		Standard *d* values from ASTM cards for phase $MgAl_2O_4$	
	d (nm)	I/I_0 (visual)	*d* (nm)	I/I_0
1	0.2428	10	0.2436	100
2	0.2300	100	0.2333	3
3	0.2047	50	–	–
4	0.1991	80	0.2021	58
5	0.1425	90	0.1429	58
6	0.1274	20	0.1278	2
7	0.1223	100	0.1232	9
8	0.1172	50	0.1166	7
9	0.1088	30	0.1079	4
10	0.1042	10	0.1052	12
11	0.1018	30	0.1010	5
12	0.0943	50	0.0952	3
13	0.0935	80	0.0933	10

*The strongest lines are underlined.

The anodized photomicrographs of oxidized samples also point to the existence of coring at a few places. The coring, which occurred inside the bigger cells of oxidized samples, could not be due to the segregation of solute inside cells, which if present in the as-cast stage anneals out completely or partially during long homogenizing periods. Coring may be due to the diffusion of oxygen from the atmosphere while oxidizing the alloy samples in air.

Combining the presence of the precipitate $MgAl_2O_4$ and coring in oxidized samples, it may be concluded that oxygen diffuses through the surface pores and along its path combines with the less noble metal magnesium, and consequently leads to internal oxidation in alloys having Mg > 2% with the formation of $MgAl_2O_4$. The precipitation at cell boundaries or at the junctions of cell boundaries is due to the cell boundaries containing higher concentrations of oxidizable solute elements (because of segregation in

TABLE II The observed *d* values for (Al–4.6% Mg–trace Be) alloy, oxidized in air at 500° C for 16 h*

Serial No.	Observed values of alloy		Standard *d* values from ASTM cards for phase $MgAl_2O_4$	
	d (nm)	I/I_0 (visual)	*d* (nm)	I/I_0
1	0.2433	10	0.2436	100
2	0.2329	100	0.2333	3
3	0.2024	80	0.2021	58
4	0.1432	80	0.1429	58
5	0.1223	80	0.1232	9
6	0.1175	30	0.1166	7
7	0.1016	10	0.1010	12
8	0.0934	70	0.0933	10
9	0.0909	60	0.0903	6
10	0.0832	70	0.0825	20

*The strongest lines are underlined.

the alloy) and also having more activation energy, so that they are preferred nucleation sites for oxidation. Sometimes oxidation takes place inside cells due to inclusions, dislocations etc.

The beryllium modification does not suppress the internal oxidation of Al–Mg alloys. It suppresses only oxidation during melting by strengthening the protective properties of oxide films of aluminium and its alloys.

Though the process of internal oxidation is generally considered undesirable, it can be used for dispersion strengthening and for measuring the product of solubility and diffusivity of gases in metals and alloys.

5. Conclusions

1. The occurrence of internal oxidation in Al–Mg alloys has been demonstrated with the help of an anodic etching technique and X-ray diffraction work.

2. Al–Mg alloys when oxidized at 500° C seem to be resistant to internal oxidation below 4.5% Mg and are thereafter prone to internal oxidation.

3. The process manifests itself in the form of precipitates appearing mostly on cell boundaries while oxidizing the specimen in air at 500° C for 8 h or more. The precipitate appears after 24, 16 and 8 h for alloys containing 4.5%, 6% and 7% Mg.

4. The precipitate was identified by X-ray diffraction to be $MgAl_2O_4$.

5. Beryllium modification does not suppress the process of internal oxidation taking place in Al–Mg alloys.

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