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## Surface Corrosion of Mg-Containing Al-Based Alloys

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During heat-treatment of Mg-containing Al-based alloys, the Mg concentration changes considerably. As compared to the pure material significant surface corrosion is observed for the air heat-treated alloy. In vacuum heat treatment the Mg content of the surface layer increases considerably. Initially metallic Mg is detected on the surface which, however, becomes oxidized later on. On the basis of the investigations one has to assume that the process is not a simple diffusion mechanism only. A new conception is formed for the process according to which it is controlled by the breaking up of the  $Al_2O_3$  barrier layer by Mg.

Während einer Wärmebehandlung von Mg enthaltenden Al-Legierungen ändert sich die Mg-Konzentration beträchtlich. Im Vergleich zu dem reinen Material wird eine signifikante Oberflächenkorrosion für in Luft getemperte Legierungen beobachtet. Bei Vakuumtemperatur steigt der Mg-Gehalt der Oberflächenschicht beträchtlich an. Anfangs wird metallisches Mg auf der Oberfläche nachgewiesen, das jedoch später oxidiert wird. Auf der Grundlage der Untersuchungen muß angenommen werden, daß der Prozess nicht nur ein einfacher Diffusionsmechanismus ist. Eine neue Vorstellung für den Prozeß wird vorgeschlagen, derzufolge dieser Prozeß durch das Aufbrechen der  $Al_2O_3$ -Barrierschicht durch Mg gesteuert wird.

### 1. Introduction

The Mg concentration is changing in the Mg-containing Al alloys during heat treatments. This change may cause undesirable changes in the physical properties of the alloy.

Though the problem is widely referred to in the literature [1 to 5] there are still some questions unexplained. The dilatometric measurements [2] and mass spectrometry [3] indicated that the kinetics of the Mg loss is exponential. It has been concluded from this that the velocity of diffusion is higher than of the surface reactions: evaporation and oxidation. Inhomogeneous distribution of the Mg concentration is already demonstrated by microprobe studies [6] from which, however, a diffusion slower than the surface reactions could be expected. The above references deal first of all with the consequences and effects of heat treatment carried out in air in the temperature range from 300 to 600 °C. The vacuum heat treatment — according to the statements made in the literature so far — point to the evaporation of Mg only, whereas surface enrichment could not be detected.

### 2. Experimental Conditions

Composition of the investigated alloys: 1. AlMgSi (0.58 wt% Mg, 0.35 wt% Si, 0.14 wt% Fe), 2. AlMg (0.25 wt% Mg), 3. AlMg (4 wt% Mg).

The alloys were studied without any treatment and in heat-treated form, too. The heat treatments for the alloys were done at different conditions (in air and in vacuum) for 2 h at 500 °C.

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The investigations were made by soft X-ray emission spectroscopy (SXES) with the RSM-500 type device [7]. The samples of  $2 \times 8 \times 20 \text{ mm}^3$  size have been measured at room temperature under cooling.

The surface of the sample has been analyzed by the variation of the exciting electron energy to a depth ranging from 5 to 1000 nm. The spectra were studied in the vicinity of the soft X-ray Lee emission lines of Al and Mg.

Vacuum heat treatment has been carried out in situ by the help of exciting electron bombardment. The vacuum was in the range from 2 to  $4 \times 10^{-4} \text{ Pa}$  during the measurements.

### 3. Experimental Results

In comparison we plotted the curves of pure Al and Mg and their oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ) in Fig. 1.

The results may be summarized as follows:

1. On the surface of AlMgSi and AlMg alloys heat-treated in air the Mg enrichment occurs always in the form of MgO (as illustrated in Fig. 2).
2. On heat-treating the 4% AlMg alloy in air neither pure Al nor  $\text{Al}_2\text{O}_3$  could be detected [8] beside MgO in any depth up to 1000 nm.
3. The thickness of the oxide layer covering pure Al after the heat treatment is only about one third of that of the oxide layer covering the AlMg 0.25% alloy after the same heat treatment. Their SXES spectra are shown at various depths in Fig. 3 a and b.
4. Applying in situ vacuum heat treatment for the 4% Mg alloy the Mg enrichment in time is plotted in Fig. 4.
5. During vacuum heat treatment pure Mg diffuses first to the surface but oxidizes very soon (Fig. 5).

### 4. Discussion

On the basis of recent experimental results and previous data an hypothesis is presented about the evaporation of Mg and the mechanism of enrichment.

It is made use of the well-known fact that the surface oxide layer of the Al metal and its alloys have a special structure. There is an outer porous sponge-like  $\text{Al}_2\text{O}_3$

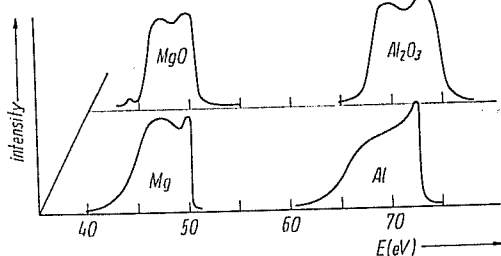


Fig. 1

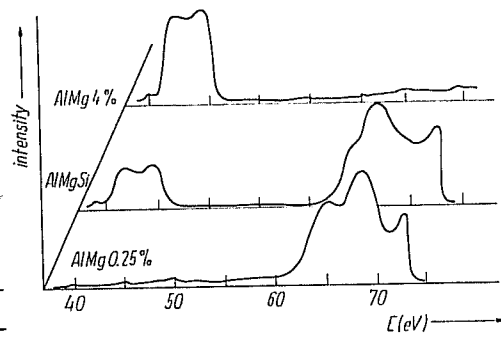


Fig. 2

Fig. 1. SXES  $L_{2,3}$  spectrum of pure Al and Mg  $\text{Al}_2\text{O}_3$ , and MgO

Fig. 2. The total SXES spectrum of heat-treated alloys in air (300 nm)

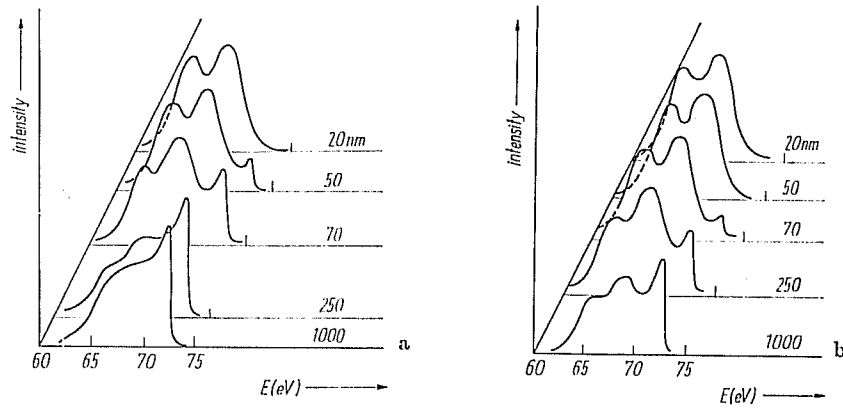


Fig. 3. The Al  $L_{2,3}$  spectrum of oxidized a) Al 99.99% and b) AlMg 0.25% samples as a function of the measuring depth

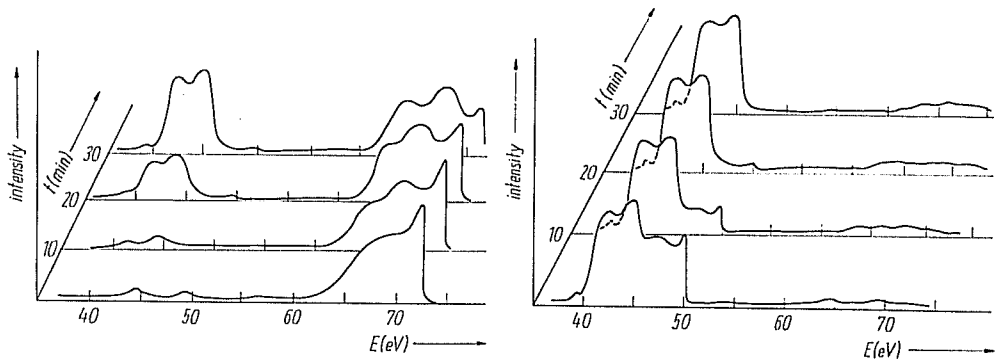


Fig. 4

Fig. 5

Fig. 4. The total SXES spectrum of the (in situ, vacuum) heat-treated AlMg 4% alloys at the power 8 W of electron bombardment (depth 250 nm)

Fig. 5. The total SXES spectrum of the (in situ, vacuum) heat-treated AlMg 4% alloys at power 320 W of electron bombardment (depth 250 nm)

layer and a compact closed barrier layer below it [5]. This layer in the Mg-containing Al alloys is of the spinel structure. Mg in the course of its evaporation has to pass through this layer. This diffusion cannot take place directly because even the oxygen ion which is smaller than Mg cannot permeate through this compact layer.

According to our assumption at high temperatures (200 to 600 °C) Mg, due to its higher affinity forms a complex oxide, and breaks up the barrier layer because the lattice parameters of the complex are larger than those of the  $Al_2O_3$ . Then the outward diffusion of the Mg atoms takes place easily through the broken barrier layer and at the same time the oxygen atoms penetrate deeper and deeper into the bulk, consequently the thickness of the oxide layer is also growing. This mechanism will give rise to a mixed layer, consisting of the broken-up spinel-type MgO and  $Al_2O_3$  phases.

The most important results derived from the hypothesis are that with its help the exponential kinetics of the evaporation of Mg [2], the enrichment of Mg [6], and

the existence of a layer depleted in Mg below the enriched layer [6] can be explained simultaneously.

Obviously, the diffusion velocity of Mg is higher in the porous  $\text{Al}_2\text{O}_3$ -type layer than in the bulk, thus a layer is formed with a smaller Mg concentration. The Mg atoms become oxidized during their diffusion, promoting thereby the drift of Mg. This process causes the enrichment of Mg.

So it may be assumed that not the diffusion within the bulk is the rate-governing process, but the break-up mechanism of the transitional mixed layer by the Mg atoms.

It can be assumed that the rate of the breaking mechanism at low Mg concentrations is proportional to the concentration. From this the exponential kinetics follows.

The breaking mechanism depends above all on temperature in the same manner as the reduction of the  $\text{Al}_2\text{O}_3$  by Mg. The starting of the evaporation of Mg depends on the activation energy of the breaking process. According to experience the evaporation starts in the range from 200 to 250 °C. It is in agreement with other results [3].

By the help of this theory our measured data can be easily explained.

1. The reason of the larger thickness of mixed oxide layer on the surface of Mg-containing Al alloys is that the breaking-passing mechanism promotes the deeper penetration of the oxygen.

2. Mg during vacuum heat treatment comes to the surface by the breaking mechanism, too (the transition layer develops even at  $10^{-4}$  Pa). The diffusing Mg becomes oxidized, controlled by the diffusion rate, so the oxidation is slower than in the air heat-treated case. This explains the fact of finding metallic Mg in the surface during the first stage of the in-situ heat treatment.

3. During the heat treating in air the transition layer has been drastically changed in the case of the high concentrated (Al 4% Mg) alloy, so the surface oxide layer has become thicker than the depth accessible to the study, so merely MgO superimposed over  $\text{Al}_2\text{O}_3$  could be detected.

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