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THE DETERMINATION OF Mg SURFACE ENRICHMENT IN HEAT TREATED AlMgSi ALLOYS USING THE SXES METHOD

By

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Heat treatments result in Mg loss by diffusion from AlMgSi alloys. This was identified by many authors using different bulk measurements. Up to the present indirect methods have been applied to check the evaporation of Mg.

We studied this problem by soft X-ray emission spectroscopy (SXES) in the region of the $L_{2,3}$ emission peak of Al (approx. 17 nm) in a 150 nm thick layer. The heat treatment was made by electron beam, using the same beam also for the X-ray excitation, so the change of the Mg concentration in the surface layer was measured in vacuum undisturbedly.

Our results show that the Mg concentration essentially increases during the heat treatment near the surface. The bulk concentration of the Mg was 0,6 wt% and we recorded the same concentration in the initial state of the alloy on the surface too. After the heat treatment the concentration achieved a value of 70 wt% near the surface. The heat treatment was made at 480 ± 30 K.

It has been known for a long time that a prolonged heat treatment of AlMgSi alloys produces Mg enrichment on the surface [1].

In order to investigate this phenomenon resistance measurement [2], transmission electron microscopy [1], linear thermal expansion measurement [2], lattice parameter measurement [2], quadrupole mass spectrometric measurement [3], and microprobe [4] have been used.

The measurements unambiguously showed the surface enrichment or evaporation of Mg. Most of the investigations referring to this did not contain concrete data concerning the amount of Mg in the surface layer. Bulk type measurements were performed, with the exception of the measurement [4], extrapolating the Mg concentration on the surface.

In the following we summarize the main experiences of the research performed up to the present. Between the first heating and the heating cycles performed later, an essential difference was found. At the adequate temperature the process takes place in a relatively short time. The kinetics of the process can be expressed by the following relationship:

$$\frac{dc}{dt} = -M(c - c_\infty),$$

where c is the Mg concentration, c_∞ is its asymptotic value and M is a constant. Beside the effect of the diffusion processes certain oxidation processes take place. The equilibrium of the oxidation effect [5], and the evaporation [3], together with the diffusion process develop the Mg enrichment. That is why according to the measurements [4] the suitably measurable Mg enrichment develops only in the surface layer of a specimen heat-treated in air. A composite oxide structure is developing containing Mg and Al oxide [6]. The greater speed of oxidation is producing a Mg depleted zone beneath the Mg enriched surface layer.

In our present paper we attempt to determine the Mg concentration enriched in the 200 nm thick surface layer, preventing the oxidation of the specimen with heat treatment in vacuum.

Experimental equipment and conditions

For the investigation of the surface concentration of Mg we used the soft X-ray emission method (SXES). The main point of the method is that from the parameters of the characteristic soft X-ray radiation the electron density of states of the specimen can be determined. The scheme of the process is shown in Fig. 1 [7]. In our case for the relatively dilute solid solution, we performed most of our measurements on the transitions of the Al $L_{2,3}$ levels. According to the calculations of Segall [8] and Rooke [9] the density of

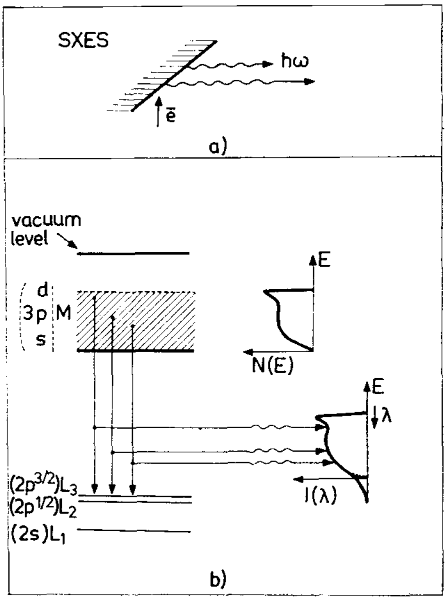

Fig. 1. The scheme of SXES process

states is given according to the relationship

$$I(E) \propto \nu^3 F(E)\ N(E)\ ,$$

where $I(E)$ is the X-ray intensity measured in arbitrary units, ν is the frequency of radiation, $N(E)$ is the part of the density of states involved, determined by quantum mechanical selection rules, $F(E)$ is the transition probability, and E is the energy.

On the above basis the Al $L_{2,3}$ SXES curve obtained by using the band structure calculation in [10] together with the first Brillouin zone, is shown in Fig. 2. The fine structure seen on the Al $L_{2,3}$ SXES curve, fitted at the gamma point 61.2 eV, exhibits a long wave tail with 1/2 power.

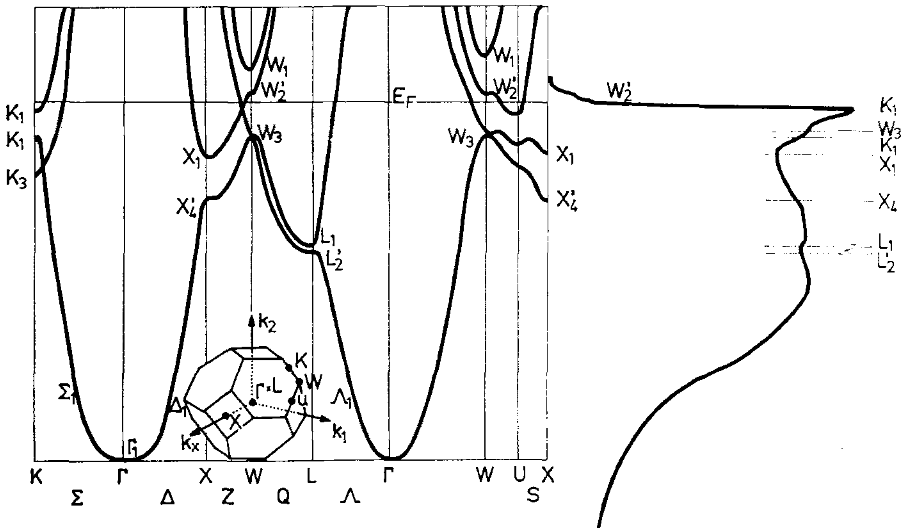

Fig. 2. Connection between a band structure and SXES curve for Al

The symmetry points of the Brillouin zone are: L_2'(68,6 eV), L_1(69,0 eV), X_4(70,1 eV), X_1(71,3 eV), K_1(71,4 eV) W_2(72 eV), K_1(72,7 eV) and W_2(73,9 eV). The emission edge characteristic of the Al Fermi surface appears at 72,8 eV.

The type of equipment was RSM 500 (Burewestnik, Leningrad), using a grating mirror, working in the 0,5—50 nm wavelength range, with photomultiplier detecting. The resolving power in the operating range was 0,07 nm (0,3 eV). The detailed description of the equipment may be found in the work of LUKIRSKII et al [11].

We performed the measurements using the transition of the Al $L_{2,3}$ levels. The specimens used were of $3 \times 10 \times 10$ mm^2, (15 mm long). The composition of the specimens was the following:

Al	matrix	
Mg	0,58 wt%	(0,65 at%)
Si	0,35 wt%	(0,34 at%)
Fe	0,14 wt%	(0,068 at%)
Cu	0,01 wt%	
Ti	0,03 wt%.	

The specimen was annealed for 45 min at 800 K in air and was quenched in water at room temperature.

The final treatment of the specimens was done "in situ" with an exciting electron beam (4 kV, 0.3 mA) in a vacuum not worse than 10^{-4} Pa. The temperature of the specimen during this heat treatment was 530 K ± 30 K, measured by the new method [12].

For the determination of the Mg concentration we used NEDDERMAYER's measurements, who has performed SXES measurements on AlMg alloys of different compositions [13].

Experimental results

As a starting point and for comparison we used the plot of AlMgSi taken after the annealing and quenching of the specimen (Fig. 3, curve a). The curve is essentially in agreement with the pure Al $L_{2,3}$ SXES curve, with the exception that the fine structure is less pronounced.

The plot shown in Fig. 3 curve b was taken after 9 min in situ heat treatment. Essential variation has not been found yet. The situation after

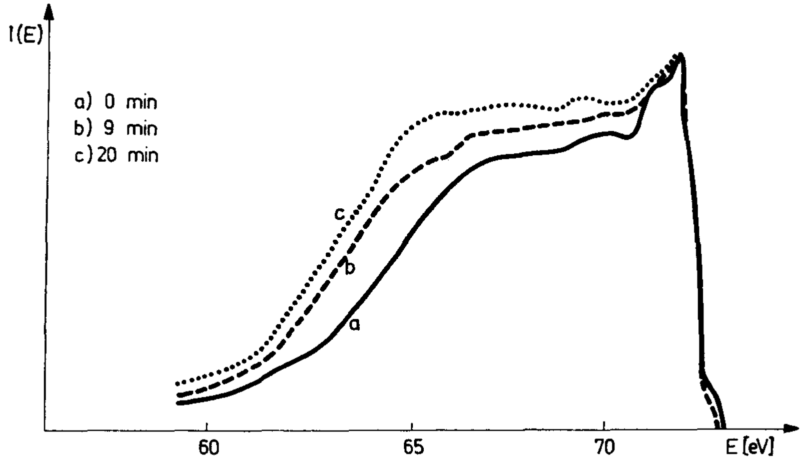

Fig. 3. SXES curves of AlMgSi alloys after annealing in vacuum. a) 0 min; b) 9 min; c) 20 min

20 min is shown by Fig. 3 curve c on which the appearance of a new local maximum can be observed at 66 eV.

With the further increase of the time of heat treatment, this peak emerges more vigorously and at the same time the maximum of the large peak below the emission edge gradually decreases. (Fig. 4 curves: a, b, c). After 80 and 90 min a new local peak appears at 63 eV (in Fig. 5 curves a, b). Curve c represents the emission spectrum after 200 min heat treatment, it does not change with further heating.

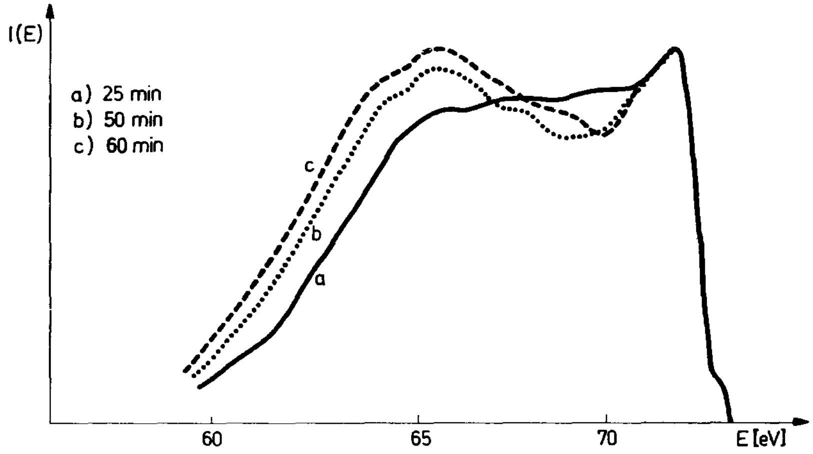

Fig. 4. SXES curves of AlMgSi alloys after annealing in vacuum a) 25 min; b) 50 min; c) 60 min

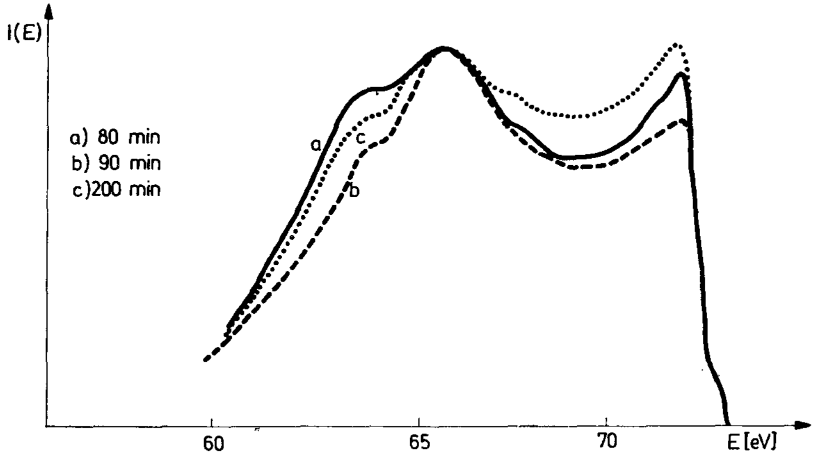

Fig. 5. SXES curves of AlMgSi alloys after annealing in vacuum. a) 80 min; b) 90 min; c) 200 min

Discussion

On the basis of NEDDERMAYER's work [13] on the various compositions of AlMg alloys, the spectra presented in Fig. 3 (curves a, b, c) correspond to 0.6 at%, 10 at% ± 5%, 20 at% ± 10% concentrations. Our experimental results in Fig. 4 (curves a, b, c) correspond to 30 at% ± 10%, 40 at% ± 10%, 50 at% ± 10% concentrations. The emission spectra in Fig. 5 (curves a, b, c) correspond to 60 at% ± 10%, 70 at% ± 10%, 40 at% ± 10% of Mg concentrations.

Thus the maximum Mg concentration in the surface layer under given conditions is 70%. It is most likely that the Mg atoms are outdiffusing from the matrix, and they evaporate from the surface during the same period.

From the measurements performed so far we can see that the enrichment of Mg concentration in the 200 nm thick surface layer significantly rearranges the density of states measured with the help of Al $L_{2,3}$.

This means that the density of states around 64 eV increases, and at the same time the density of states around the peak (72 eV) decreases significantly. These results are in adequate agreement with the modern theories (ATA, CPA) applied in the calculation of the density of states for alloys. The more detailed investigation of the problem is in progress.

In accordance with the results described above it can be ascertained that due to the effect of heat treatment for longer periods of time (90 min) at 500 K and higher temperatures, the Mg on the surface layer vigorously enriches and instead of the 24% obtained through extrapolation with the measurement [4], according to our measurements the concentration increases to 70%.

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