SURFACE CHARACTERIZATION OF RAPIDLY SOLIDIFIED Al ALLOYS*

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Abstract

Rapidly solidified aluminium alloys with Mn, Fe and Mg were studied by depth profiling XPS and SIMS. Most of the Mn and Fe were found in deeper layers in metallic form while the Mg on the surface in oxide and carbonate state.

Introduction

Investigations have been rapidly increasing in the last 15 years [1] on new aluminium alloys solidification processes at high cooling rates (i.e. the well-known direct chill casting process). Activity is partly focused on the development of new technologies (strip and rod casting, atomisation, spray deposition and various forms of filament and ribbon casting) offering higher cooling rates. In addition extensive theoretical and experimental research is carried out concerning the properties of the rapidly solidified aluminium alloys [2].

The chemical properties of alloys having an excess of alloying elements in solid solution are different from the alloys made by conventional slow cooling casting techniques [3]. It was shown that the oxide layers developed at the surfaces of rapidly solidified powders make a definite impact on the mechanical properties of the final products [4]. For these reasons determination of the chemical state and composition of the surface and also of the near surface layers is of great theoretical and practical importance. In this work XPS together with Ar ion depth profiling and SIMS investigations were carried out on two sets of rapidly solidified Al-Mn and Al-Fe alloys.

Experimental

For the present study 60 μm thick (20 mm wide) ribbons were produced from the inductively heated melts by ejecting them onto a copper wheel rotating with 22 m/s equatorial velocity in air ambient. The estimated cooling

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* Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

rate was 10^6 K/s. Compositions are shown in Table 1. Heat treatment was carried out at 400°C for 2 h in air.

XPS measurements were performed on a Kratos XSAM 800 spectrometer using Mg K_α (1253.6 eV) and Al K_α (1486.6 eV) exaltation and FRR analyzer mode as described in detail elsewhere [5]. 2.5 keV Ar^+ ions were used for depth profiling.

Table 1

Composition of the Al alloys (atomic %)

Sample	Fe	Mn	Mg
1	—	5.5	—
2	7.2	—	—
3	—	9.8	0.9
4	4.5	—	1.34

Balzers QMG 511 type quadruple mass spectrometer was used for SIMS measurements with 3 keV Ar^+ ion sputtering and ionization. For reactive sputtering oxygen gas was also introduced.

Results and discussion

XPS investigations

Al-Mn alloys

For qualitative characterization of the surface wide scan spectra were recorded on both surfaces of the ribbons: on the one facing the wheel and on the other facing the air. The two spectra are essentially similar, only higher oxygen and carbon content is visible on the side facing the air. The constituent Mn shows up only with a very low intensity. Small amounts of Si, Ca, Na and S impurities can be detected. For detailed analysis the Mn *2p*, O *1s*, C *1s*, S *2p*, Al *2p* and the valence band were recorded on as the received samples and after five successive Ar ion etch steps of 2 min duration each. The most striking feature which can be deduced for the surface facing the air are the following:

- The Al appears in both oxide and elemental form [6], the oxide component being more intense (Fig. 1). This ratio turns to reverse after the second etch step but the oxide state is still present even after the 5th etch step.

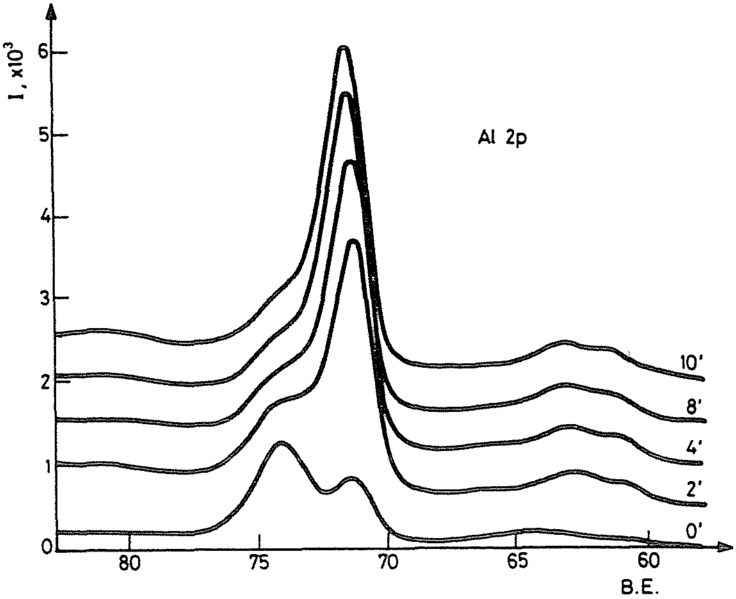

Fig. 1. Changing of the Al *2p* line shape during ion etch of the Al-Mn alloy (surface to the air)

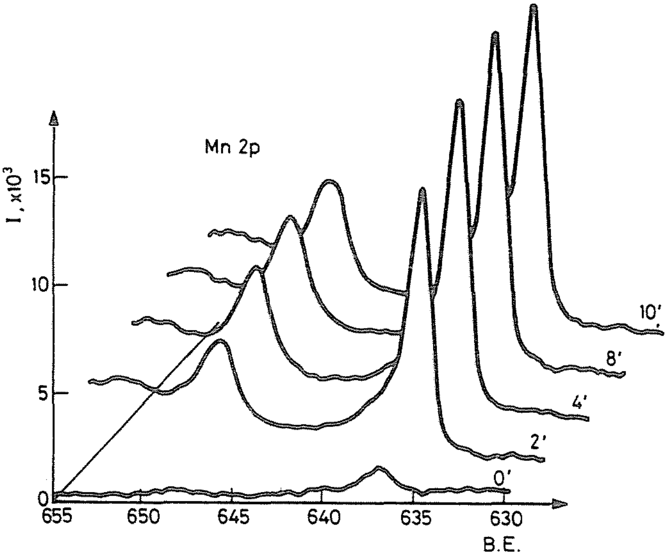

Fig. 2. Changing of the Mn *2p* line during ion etch (surface to the air)

— The Mn can hardly be detected before etching and its intensity does not change considerably even after the first etch step (Fig. 2). The valence state of the Mn proved to be essentially metallic with a very tiny amount of oxide component.

- The O *1s* line is asymmetric and its intensity decreases steadily in the successive etch steps.
- The C *1s* peak essentially represents carbon in (—CH_X—) state; its intensity drops to a quarter of the starting value after the first etch step and does not change significantly during the following ones.

The state of the ribbon surface facing the rotating copper wheel is qualitatively similar to the opposite side. However the aluminium is less oxidized, more Mn is present even in the outermost layers, and the carbon contaminate is also smaller.

Al-Fe alloys

The wide scan spectra show the presence of a large amount of oxygen and carbon impurities, however, Fe can hardly be detected on the as produced samples (Fig. 3). The presence of sulphur, silicon and calcium contaminants was also evaluated. The Ar ion etch experiments show that the surface is covered by a large amount of carbon contaminate (50 at%), but the majority of it can be etched away in 2 min. The oxygen content (about 32 at%) on the surface is the same as for the Al-Mn alloys. Most of the iron were in metallic form with a small amount of oxide.

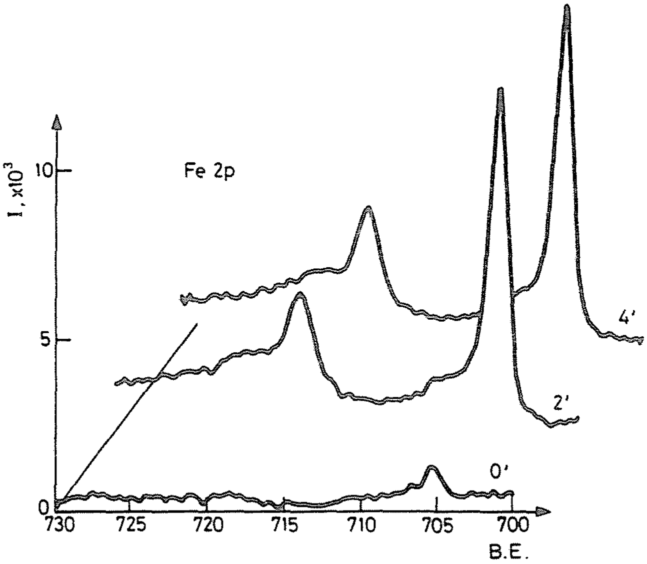

Fig. 3. Changing of the Fe *2p* line during ion etch (surface to the air)

Alloys containing Mg

In spite of the Mn and Fe the magnesium can be found on the surface of the samples in oxidized and carbonate form. After heat treatment a thick $MgCO_3$ layer was formed while the other alloying elements were migrated deeply into the sample, and the could be detected after long etching only.

A simple two layer model, consisting of an Al_2O_3 layer covering the alloy and a hydrocarbon outer layer, was applied for all of the sample, but without success. This means that the structure is more complicated: in addition to the observed graded distribution of carbon and oxygen impurities, lateral inhomogenities can also not be excluded.

SIMS investigations

Because of the high surface sensitivity of SIMS impurities present in very small quantities could also be detected on the samples: i.e. Li, K, Mg, Cl on both sides and Cu on the side facing the wheel. The sensitivity and sampling depth of the SIMS and XPS methods are different still the results of the depth profiling are comparable. Consequently various degree of enrichment of Al and oxygen as well as the relative depletion of alloying elements were determined (Fig. 4). This surface segregation is extended over a depth of 20 nm on the side facing the wheel and of 50 nm on the other side.

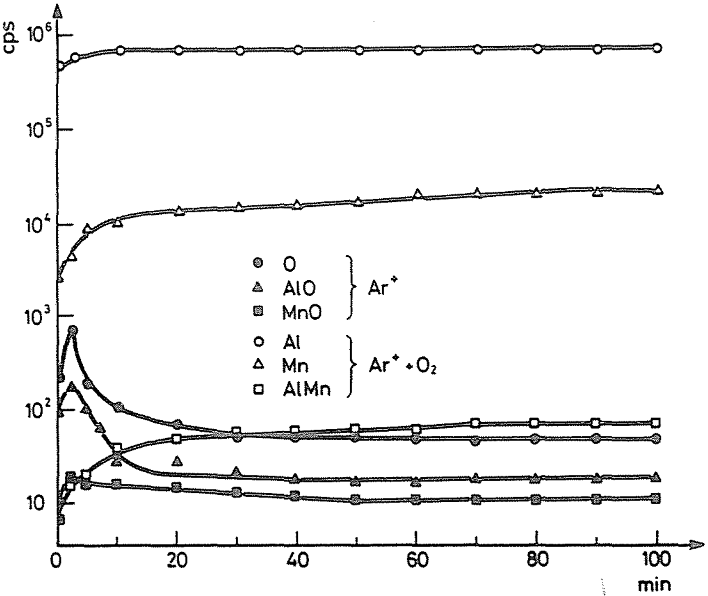

Fig. 4. SIMS profile of the Al-Mn alloy (surface to the air)

Conclusions

XPS chemical analysis combined with Ar ion depth profiling revealed characteristic surface segregation: enrichment of the outermost layers in aluminium, oxygen and carbon, partial oxidation of aluminium and though depletion but presence of the alloying elements in the surface and near-surface layers. Front side of the ribbons facing the copper wheel cools down faster, consequently, it exhibits a smaller degree of oxidation and less pronounced segregation but copper impurity from the wheel can also be detected.

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