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Effect of surface depletion of lithium on corrosion behaviour of aluminium alloy 8090 in a marine atmosphere

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Aluminium–lithium alloy 8090 is of great interest due to its low density and good mechanical properties. The high reactivity of lithium, however, makes it more prone to corrosion than other aluminium alloys, limiting its use in certain fields. In general, there is an intergranular attack with exfoliation in the most severely attacked sections of this alloy in marine and industrial environments. This attack also depends on the metallurgical history of the material, i.e. the part of the ingot from which the specimens are extracted. After one and two years' exposure to a moderately aggressive marine atmosphere, it was found that the materials taken from the centre of the ingot have a more widespread attack than specimens taken from the edges. This might be explained by the differing composition of the specimens according to their origin; more precisely, by the uneven distribution of the lithium, which tends to spread though the matrix of the ingot and form a lithium-impoverished layer several microns deep as a consequence of the series of thermal treatments applied.

1. Introduction

The development of new aluminium alloys has been influenced by the search for a compromise between mechanical properties (low density, high elastic modulus, high resistance) and corrosion resistance (enhance passivation, ability to generate protective anodic layers). Aluminium can form a wide range of alloys, and thus adapts very well to specific industrial requirements. Hence, aluminium alloys are used widely in many areas of technological development, one of the most important being the aerospace industry [1].

The aeronautical industry needs light, corrosion resistant materials, as this translates into considerable financial savings from reductions in both fuel consumption and aircraft maintenance. Aluminium–lithium alloys have arisen in this context as an alternative to conventional alloys (series 7 xxx i.e. Al-Zn-X alloys) or even carbon fibre series [2]. The addition of 1 % Li to the alloy permits a 3 % reduction in density and a 6 % increase in the elastic modulus. It is simple to obtain because of the high solubility of Li in Al (4.2 % at 600 °C in the Al–Li binary phase diagram). Most of these alloys, however, are of limited use because of their susceptibility to widespread and localized corrosion due to high Li reactivity. One type of attack is exfoliation.

Exfoliation is due to the tendency of the intermetallics formed in the alloy to segregate on grain edges [3]. When the material is subjected to an aggressive environment, they undergo an anodic dissolution. The large volume of corrosion products makes them tend to separate the grains above them in a pattern that is reminiscent of the leaves of an open book [4].

The present study uses samples that have undergone two years of natural exposure in a marine environment to try to determine the behaviour of an aluminium–lithium alloy and detect any differences in response to atmospheric action between samples taken from different parts of the original block.

2. Experimental procedure

The study material was an 8090 T81 aluminium–lithium alloy deformed by 6 % (see Table I for composition). Its microstructure was composed of a set of Al_3Li (δ′ phase) hardener precipitates lying on the edges of the grain and surrounding larger Al_3Zr (β′ phase) hardener precipitates. The iron precipitates, the preferential points of pitting nucleation, were also found in this zone. Fig. 1 shows a detail of each phase in the alloy studied. Finally, different Al–Cu–Li phases (phases T1 and T2) segregated within the grain. These do not pose problems in terms of intergranular corrosion as they are not on the edge of the grain [5, 6].

Three identical 50 mm × 190 mm × 10 mm specimens were cut from a single ingot. This enabled the performance of each specimen to be identified in terms of its position in the original block (specimens A, B and C), bearing in mind the face that was directly exposed (1 or 2 for upper or lower faces, respectively,

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TABLE I Composition of the 8090 alloy (wt %)

	Li	Cu	Mg	Zr	Fe	Si	Otros	Al
8090	2.4	1.15	0.67	0.11	0.05	0.02	0.07	bal.

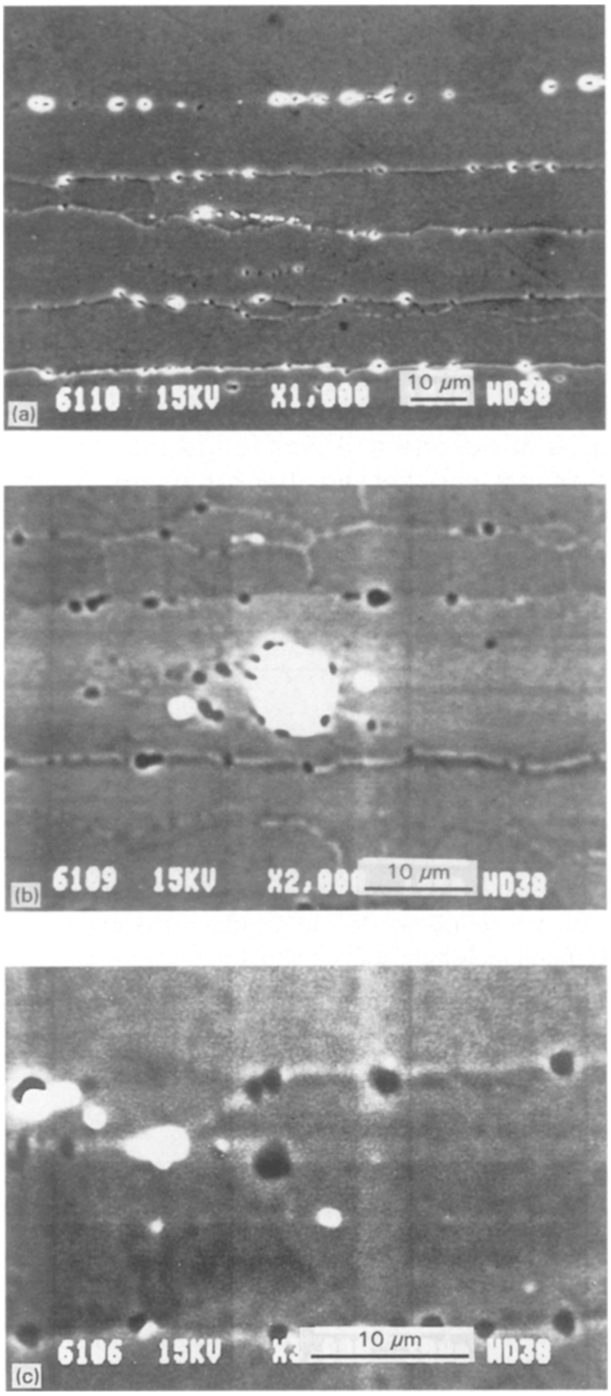

Figure 1 Microstructure of the Al–Li 8090 alloy, (a) δ′ precipitates (Al_3Li) situated on the edge of the grain, (b) β′ phase (Al_3Zr) is surrounded by δ′ phase, and (c) precipitates of Fe impurities on the edge of the grain.

see Fig. 2). After identification, they were set in an exposure panel on Txatxarramendi Island (Vizcaya, Basque Country).

The parameters used to typify the station were the NaCl and SO_2 concentrations. The amounts of each substance were determined by standard procedures [7, 8]. For SO_2, a concentration of 17 μg m^{-3} per day was found, indicating an unpolluted marine environment. The amount of NaCl was estimated to be 60 mg m^{-2} per day, classifying the station as moderately aggressive in accordance with literature data [9]. A nearby weather station facilitated access to meteorological data: hours of sunlight per month, temperature variations during the test period, rain fall during the year and relative air humidity.

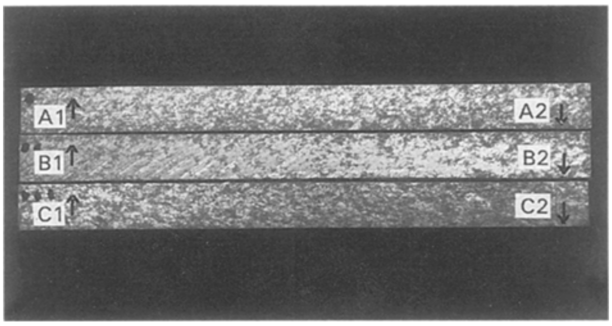

Figure 2 Layout of specimens in the original block (× 5).

The first specimens were assessed after one year of exposure, and the rest were recovered after two.

3. Results and discussion

The specimens revealed performance differences according to their zone of extraction from the original block. After the first few months of testing, it was clear that the specimens from the upper and lower faces of the original block (A1 and C2) retained their original shine and had a much better aspect than those from the inner part of the ingot (A2, B1, B2 and C1). At the end of the first year, a more uniform attack could be seen macroscopically in those samples as shown in Fig. 3. This tendency held until the end of the experiment (two years). After microscopic examination, the attack was similar in all cases: intergranular with a tendency for exfoliation to occur in areas with a more severe attack as can be seen in Fig. 4. However this was not to be the same extent on different faces. Again samples coming from the inner part of the ingot showed loss of grains relating to the greater extent of the attack than those from the outer surface. The depth of the attack was similar on exposed faces (118 μm for specimens exposed for one year and 140 μm for the two year test); they were obtained independently. The corrosion kinetics appear to follow a parabolic law of growth, with a greater depth in the first year that attenuates with time. This deceleration of the kinetics may be due to the accumulation of the corrosion products which hinders subsequent attack [10]. The earthward surfaces of the exposed samples had a predictably worse aspect since these did not benefit from the washing effect of rain that eliminates the Cl$^-$ ions and other aggressive agents that might be deposited. The result is the appearance of bubbles and a more widespread attack as shown in Fig. 5.

There may be a double mechanism to explain the heavier general attack on the specimens from the ingot core. Firstly, it might be due to the larger size of the

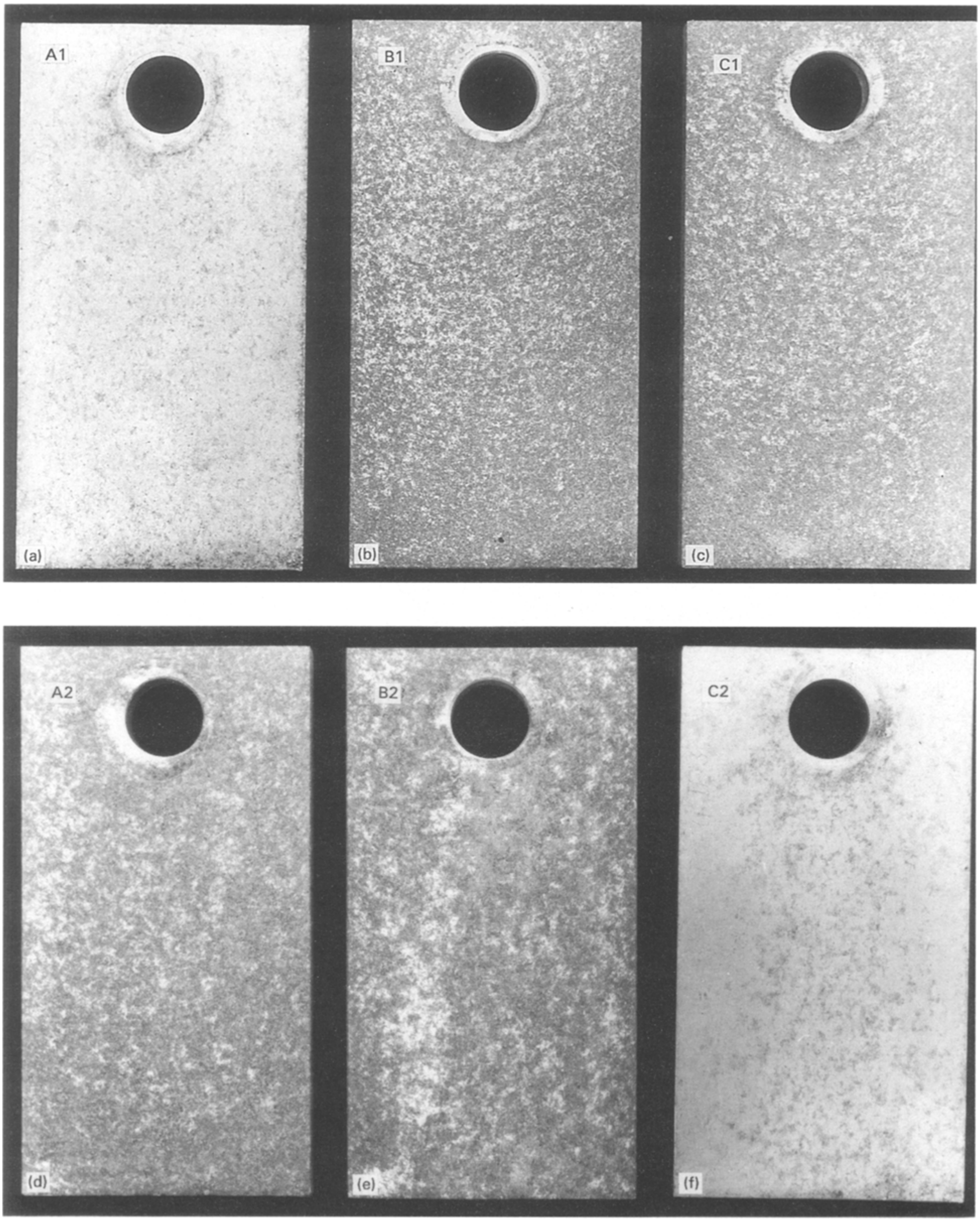

Figure 3 Aspect of differing degree of attack on specimen faces after one year of exposure. External faces of the original block retain their shiny appearance whilst internal faces have a worse appearance: (a) sample A1; (b) sample B1; (c) sample C1; (d) sample A2; (e) sample B2; and (f) sample C2.

grain produced during sample manufacture (rolling). The ingot core cools much more slowly, producing a larger grain size (Fig. 6) and thus favouring precipitation and swelling in several phases increasing the paths for the corrosive attack [11]. These results agree with literature findings that try to relate the Al–Li alloy production process to the appearance of micropiles that initiates the corrosion process [12–14]. Secondly, the attack on outer faces also might be mitigated by the depletion of Li on the surface as a consequence of the same lamination process. According to Ramamurty *et al.* [15], the range of heat treatments undergone by the alloy during manufacture produce a diffusion of Li in the aluminium matrix. Although the release of the Li from the alloy is mainly controlled by this diffusion, it is also related to the proportion of this element that is eliminated from the free surface. This is because the depletion rate is linked

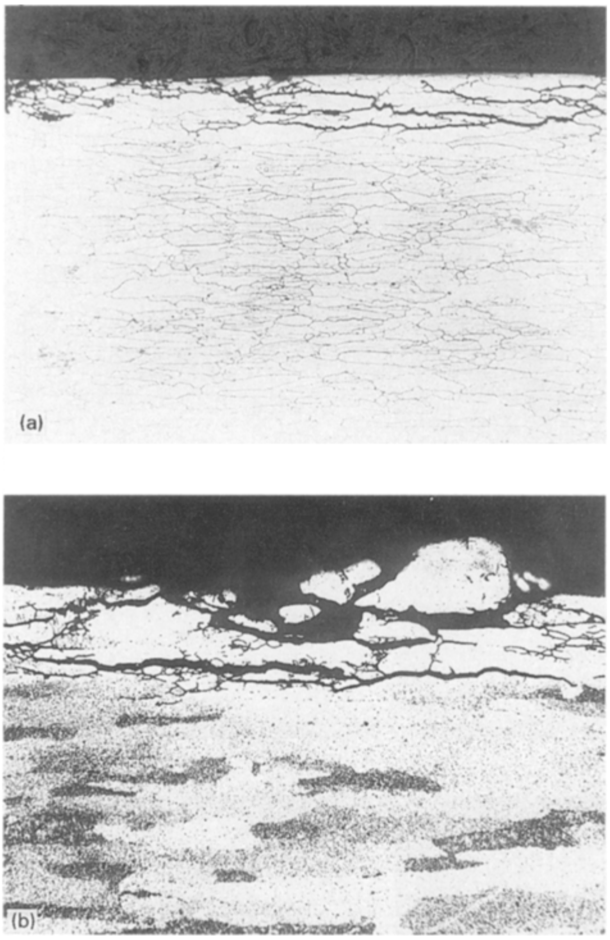

Figure 4 Morphology of the attack; (a) intergranular attack after 1 year of exposure (× 700), and (b) exfoliation after two years of exposure (× 140).

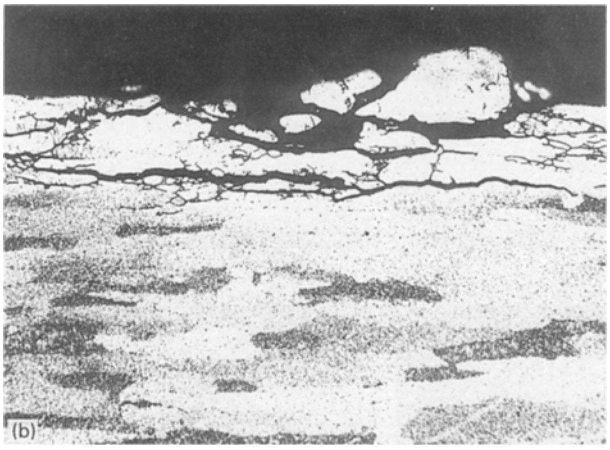

Figure 5 Detail of blistering on faces not exposed directly during the atmospheric test (× 5).

to the Li concentration gradient: the greater this is, the greater the loss of the element.

On certain occasions, the heat treatment applied to the alloy creates an oxide layer that acts as a barrier to the spread of lithium. The diffusion gradient thus diminishes and losses of the element are minimized. Normally, however, this treatment takes place in protective atmospheres, and the oxide layer does not form on the surface. This causes a steeper concentration gradient and thus enables more Li to rise to the

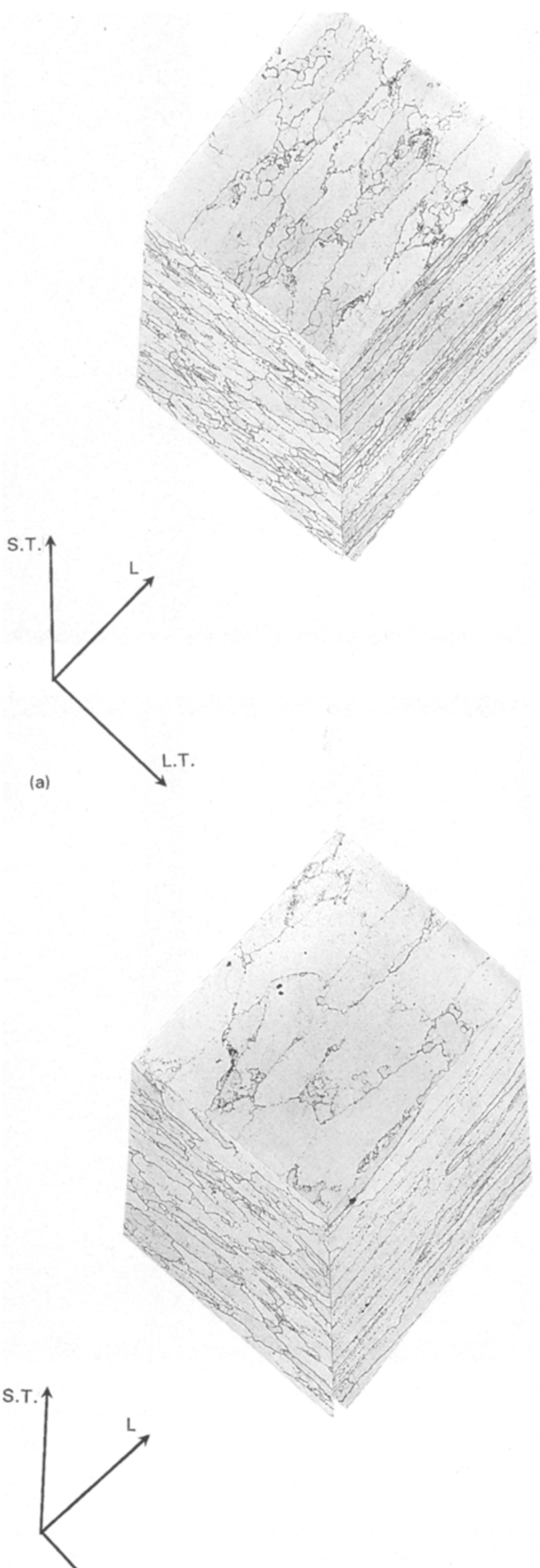

Figure 6 Three-dimensional optical micrograph illustrating grain size and morphology of aluminium alloy 8090: (a) size and shape of specimen A1 grain; (b) size and shape of specimen B1 grain; and (c) size and shape of specimen C2 grain (all × 116).

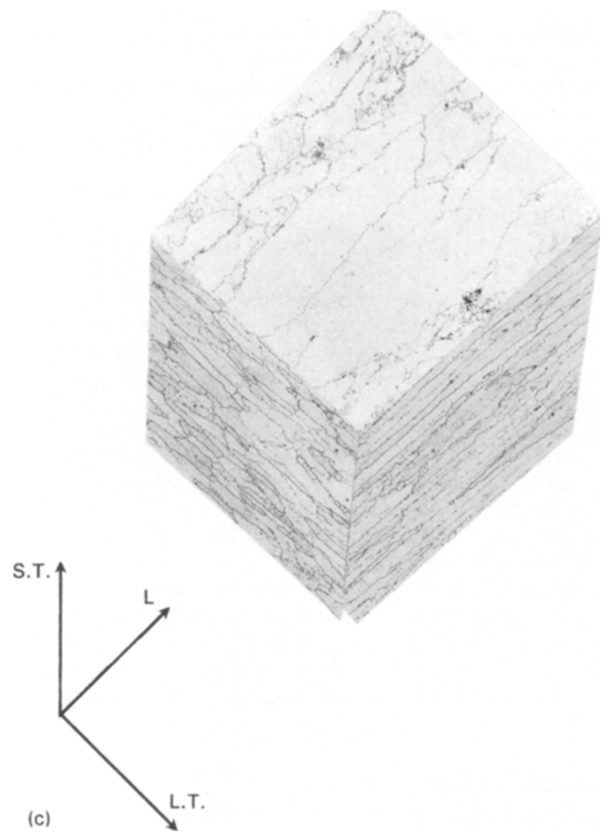

Figure 6 Continued.

surface. For all of the above reasons, the specimens from the bulk of the ingot are not deficient in Li concentration on any of their faces, while the samples from the surface have one face with a lower amount of lithium. This makes the external faces different and less susceptible to widespread corrosion than the rest.

Microhardness profiles were produced for a qualitative assessment of this phenomenon. After an ageing process, the hardness of the aluminium–lithium alloys increases in comparison with pure Al because of the presence of δ′ hardener intermetallics. If there were a loss of Li during the thermal treatments, it would be perceived as a change in hardness as these precipitates would not be able to form. The corresponding levels of hardness are thus low on the surface and increase until the constant level of the bulk of the material is reached [16]. These tests revealed an approximately 1000 μm thick depleted layer which, according to literature information, may occur in treatments with prolonged annealing over a long period [17] when the face is taken from the outside of the bulk, while its levels stay constant and above the others in the inner faces (Fig. 7). This can be explained as a consequence of the low concentration of δ′ hardener intermetallics (Al_3Li) which can form in this zone. This analysis of microhardnesses can explain the differing corrosion behaviours, which is thus a consequence of the different compositions of the faces: those with less Li have a better appearance due to their lower susceptibility to corrosion produced by the release of Li.

4. Conclusions

The present study has detected the same corrosion behaviour in all samples in the atmospheric corrosion test: intergranular attack with exfoliation in the zones where the attack is greatest. However, general corrosion varies according to the origin of the specimens. Faces taken from the bulk of the original block have a worse aspect and undergo widespread attack, while

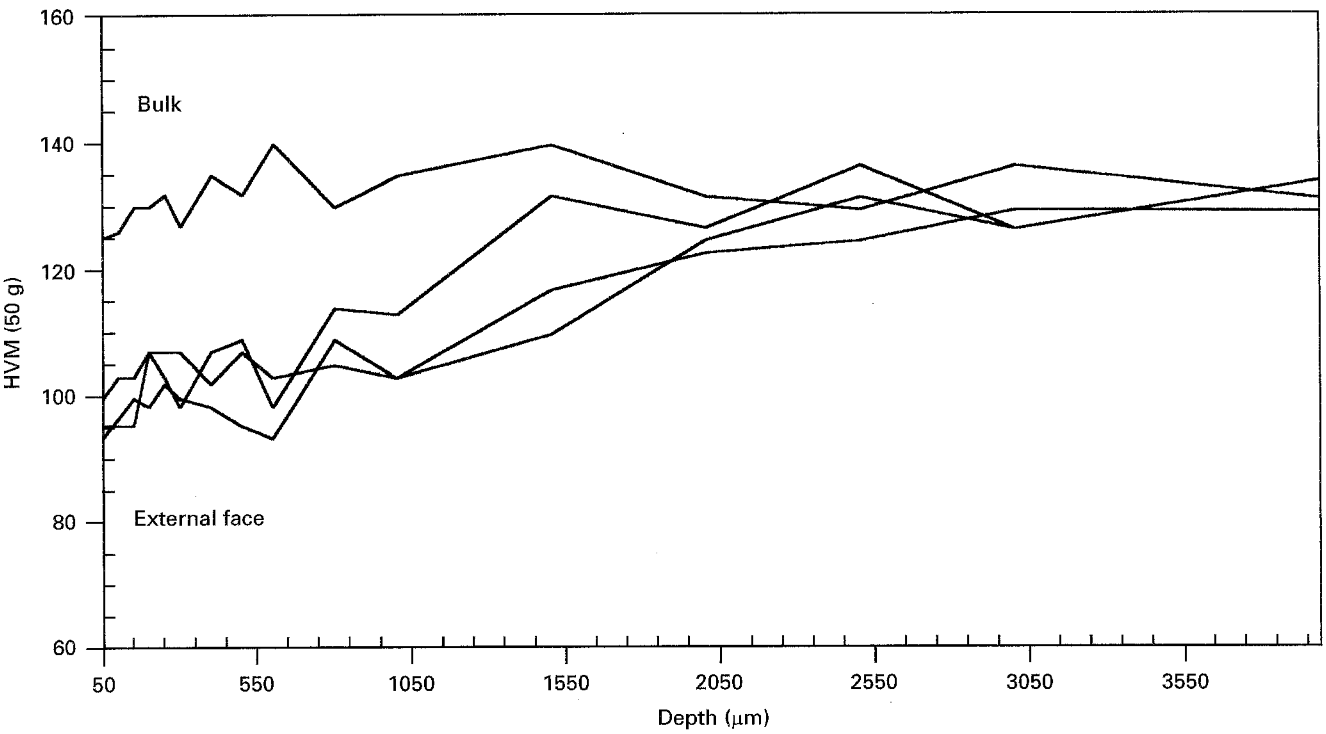

Figure 7 Microhardness profile with 50 g load for 15 s. This variation in hardness levels indicates the existence of an Li-depleted layer 1000 μm deep.

the aspect of those taken from an outer part of the original block is much better and maintains its original shine. This preferential behaviour is confirmed by the distinct composition and microstructure of each face as a consequence of Li depletion during the heat treatment applied in the 8090 alloy manufacturing process.

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