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The behaviour of double oxide film defects in Al–4.5 wt% Mg melt

Fatemeh Najafzadeh Bakhtiarani · Ramin Raiszadeh

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Abstract The possibility of bonding of the two layers of a double oxide film defect when held in a liquid Al–4.5 wt% Mg alloy was investigated. The defect was modelled experimentally by maintaining two aluminium oxide layers in contact with each other in an Al–4.5 wt% Mg liquid alloy at 750 °C from 2 min to 16 h. Any changes in the composition and morphology of these layers were studied by SEM, EDX and XRD. The results showed that in contrast to previous studies reported in the literature on Al–0.3 wt% Mg in which the two layers bonded to each other after a holding time of 5 h, no bonding took place between the two oxide layers even after a holding time of 16 h. Based on the comparison between the two studies, it was concluded that a transformation involving rearrangement of atoms at the interface between the two oxide layers is essential for the bonding to take place between the two oxide layers. This criterion could be used to predict the bonding behaviour of oxide film defects when held in different liquid aluminium alloys, or when subjected to a HIPping process.

Introduction

The concept of the double oxide film defect, the most abundant but largely neglected defect in most reactive metals, such as Al and Mg, was first introduced by Campbell [1]. This defect forms when the surface of the liquid metal containing a surface oxide layer folds, by the action of a breaking wave or by droplets forming and falling back into the melt, as a doubled-over oxide film with some gas from the local atmosphere (presumably predominantly air) trapped between the two unwetted solid oxide layers [1]. The defect therefore necessarily resembles and acts as a crack that not only deteriorates the mechanical properties of the solidified casting, but also could act as an initiation site for the formation of other defects, such as hydrogen pores [2–5] and Fe-rich phases [6] before the solidification.

It was suggested, by Nyahumwa et al. [7, 8], that a double oxide film defect could consume its internal atmosphere of oxygen and nitrogen after an incubation time. The incubation time was suggested to be necessary for the transition of the amorphous to γ- or α-Al_2O_3, which would result in stresses in the film and the formation of cracks, bringing the internal atmosphere and the melt into contact.

The consumption of the internal atmosphere has been recently verified by Raiszadeh and Griffiths [9], who monitored the change over time of the volume of a trapped air bubble in different Al alloy melts, using real-time X-ray radiography. They found no incubation time before the start of the consumption of the internal atmosphere, and suggested that the cracks that formed on the oxide layers during its movement in the liquid metal (e.g. during the pouring) would provide the necessary paths for the contact of the internal atmosphere of the defect and the surrounding melt. Using a semi-empirical mathematical model [10], they suggested that the internal atmosphere of oxygen and nitrogen within a double oxide film defect should be consumed within a few seconds to 2 min, depending on assumptions about its initial size.

It was further speculated [7] that after the consumption of the oxygen and nitrogen, the surfaces of the film defect would be forced into contact. However, argon (of which air

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F. Najafzadeh Bakhtiarani · R. Raiszadeh (✉)
Department of Metallurgy and Materials Science and Research Centre for Mineral Industries, School of Engineering, Shahid Bahonar University of Kerman, Jomhoori Eslami Blvd., Kerman, Iran
e-mail: rraiszadeh@yahoo.com

contains approximately 1 vol%) is insoluble and nonreactive in Al, and would remain between the two oxide layers. Once the two unwetted sides of the double oxide film defect are in contact, there is a possibility that they could bond together, at least at some points, due to the changes that might occur in the nature of the oxide layers over time. The defect might then be partially deactivated, and its deleterious effect as a crack might be reduced.

The first evidence for this hypothesis was presented by Nyahumwa et al. [8], who studied the effect of Hot Isostatic Pressing (HIPping) on the fatigue life of an A356 alloy. They found that, in contrast to quiescently filled castings, which were relatively sound, extensive tangled networks of oxide films were distributed randomly in almost all polished sections of turbulently filled and non-HIPped castings. The oxide film defects in these networks constituted cracks, which showed that no bond had developed across the oxide–oxide interface. Test bars that were surface turbulently filled, and then subjected to a HIPping treatment, were also observed to contain networks of oxide films. However, the cracks and pores in the networks of these oxide films were partially or fully closed. Nyahumwa et al. suggested that when this alloy was subjected to a HIPping treatment, the applied pressure at a temperature close to its eutectic temperature caused the defects to collapse and their surfaces to be forced into contact. After an incubation period, the entrained Al_2O_3 film transformed to $MgAl_2O_4$. This transformation involved a volume change and atomic rearrangement of the crystal structure, which would be expected to encourage diffusion bonding across the oxide–oxide interface.

A more direct evidence for this hypothesis was presented by Aryafar and Raiszadeh [11] recently, who studied the possibility of the bonding of the two layers of a double oxide film defect when held in liquid A356 alloy (containing 0.3 wt% Mg). They modelled the defect experimentally by maintaining two aluminium oxide layers in contact with each other, with the atmosphere trapped between them in the A356 liquid alloy by varying time between 30 s and 48 h. Their results showed that the two layers of a double oxide film defect, when held in the A356 liquid alloy, might bond to each other by two different mechanisms: one during the transformation of Al_2O_3 to spinel ($MgAl_2O_4$) after relatively short holding times of a few minutes, which would cause the layers to bond at several points, and the other during the gradual transformation of spinel to MgO after longer times of 13 min to a few hours, which would cause strong bonding between the layers. It was shown that any bonding could take place essentially only after the oxygen and nitrogen of the atmosphere within the defect were consumed.

The kinetics of the oxidation is greatly enhanced by the increase in the Mg content of the alloy [12]. Impey [13], and also Tenorio [14], reported that the first oxide to form on the liquid of Al–(1–5 wt%) Mg alloys was an amorphous alumina layer. The presence of this amorphous layer was accompanied by an incubation period of about 5 min, after which, MgO crystals developed in the amorphous alumina–metal interface. Smaller secondary MgO crystals also nucleated within the amorphous film, due to the reduction of the amorphous alumina by Mg of the melt. The oxidation of Mg caused the local Mg concentration at the melt–oxide interface to fall below a critical value of 1.5 wt%, below which the formation of $MgAl_2O_4$ crystals is thermodynamically favoured [15].

According to Impey [13], breakaway oxidation occurs in the Mg-containing alloys when localised failure at the oxide–melt interface is initiated by the rapid growth of these large $MgAl_2O_4$ crystals, which generates considerable stress within the oxide film. They confirmed the nucleation and growth of $MgAl_2O_4$ to very large crystals at the metal–oxide interface by SEM and TEM techniques. Cochran et al. [16] also found crystalline $MgAl_2O_4$ on the surface of all samples oxidised after the incubation period, and suggested that this material initiated breakaway oxidation. However, Field et al. [17], who studied the oxidation of solid Al–4.2 wt% Mg at the elevated temperatures of 400–575 °C found no $MgAl_2O_4$ at the surface of the specimens. The SEM and TEM studies of these researchers showed that cracking of the amorphous oxide film was due to the nucleation and growth of MgO crystals at the metal–amorphous interface.

Since the thermodynamics and kinetics of oxidation in Al–Mg alloys with high Mg contents are significantly different from those with low Mg content, the behaviour of double oxide film defects submerged in these two alloy groups (i.e. the bonding of the two oxide layers) might also differ. In this study, the experimental method used by Aryafar and Raiszadeh [11] was used to investigate the possibility of bonding between the two oxide layers of an oxide film defect in Al–4.5 wt% Mg alloy.

Experimental procedure

Al–4.5 wt% Mg alloy was prepared in a resistance-heated furnace by adding Al–50 wt% Mg master alloy to a commercial purity Al alloy. The composition of the resulting alloy is shown in Table 1. This alloy was then poured into

Table 1 The chemical analysis of the Al–4.5 wt% Mg alloy used in the experiments

Si	Fe	Cu	Mn	Mg	Zn	Cr	Pb	Al
0.02	0.07	0.001	0.005	4.45	0.005	0.009	0.02	Bal.

silica sand moulds with 5% sodium silicate and CO_2 gas as a binder in the shape of bars. The bars were machined to dimensions of 100 mm in length and 19 mm in diameter. Two bars were then put in a seamless extruded steel tube (which is made especially for gas industries) with dimensions of 210 mm in length and 20 mm in internal diameter (Fig. 1). The bases of the bars that were in contact with each other in the steel tube were polished to 9 µm before the bars were inserted in the tube, so that the oxide layers that naturally formed on them resembled the two layers of a newly formed double oxide film defect.

The steel tube was then transferred to a cylindrical electric furnace with a sliding door at the top. The temperature of the furnace was set to 750 °C before the start of the experiment. The temperature of the Al bars increased to 249, 408 and 566 °C after 1, 2 and 4 min, respectively (measured in a separate experiment using a K-type thermocouple inserted at the middle of the steel tube), and the bars finally melted in the tube in 390 s. The only possible leak path from the trapped atmosphere between the two oxide layers to the ambient atmosphere was through the gap between the oxide layer around the Al bars and the wall of the steel tube. To eliminate this leak path, the oxide layer around the top of the upper Al bar was removed with a sharp tool beneath the surface of the melt to remove the oxides that separated the melt from the steel tube, ensuring direct contact between the melt and the tube. The Al bars were held in the furnace by varying time between 2 min and 16 h, before the steel tube was raised in the furnace and held at the upper part of the heating chamber to let the liquid metal inside the tube solidify at a relatively slow rate (in about 40 s). The slow solidification of the metal was essential to prevent any thermal cracks from forming on the two oxide layers inside the melt.

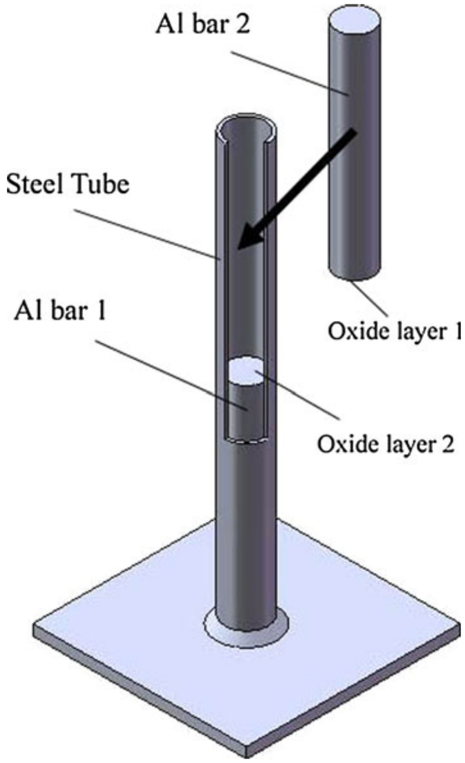


Fig. 1 Schematic illustration of the steel tube and the two Al bars inserted in it. After melting, the oxide layers 1 and 2 and the atmosphere trapped between them represented a double oxide film defect in a liquid Al alloy

After solidification, the steel tube was cut, and the Al bars were removed from it. The surfaces of the two oxide layers were then examined using optical microscopy, a Camscan Scanning Electron Microscope fitted with an Oxford Inca EDX for microanalysis and an Xpert X-ray diffraction (XRD) device.

Each experiment was repeated at least three times to confirm the repeatability of the results. More details of the experimental procedure can be found elsewhere [11].

Results

Before the melting of the bars

Figure 2 shows a photograph of the two oxide layers that were held in the furnace for 2 min. No apparent change has been detected in the surface of this specimen, compared to that of a polished surface of an Al–4.5 wt% sample, except for a change in the colour of the surface in some areas. However, the SEM micrograph of the surface of this specimen, which is shown in Fig. 3, showed some discontinuities in the oxide layer. A higher magnification picture of the area, denoted A in Fig. 3, is shown in Fig. 4. The EDX spectra obtained from the points denoted P1 and P4 on this micrograph are shown in Fig. 5, and the concentrations of Mg, O and the ratio of Mg to O at points P1 to P4 that were obtained by EDX are shown in Table 2.

The stoichiometric weight ratio of Mg to O in MgO and $MgAl_2O_4$ is 1.5 and 0.38, respectively. This ratio can be used to identify the presence of these two oxides in the oxide layers. The spinel and MgO oxide layers were distinguishable by XRD in the studies carried out by Aryafar and Raiszadeh [11]. The comparison between their XRD results and the Mg/O ratios that they obtained by EDX show that an Mg/O ratio smaller than 0.4 could be associated with an $MgAl_2O_4$ layer, a ratio between 0.4 and about 1 with a mixture of the two oxides, and a ratio larger than 1 to an almost pure MgO layer.

The crack visible in Fig. 4 probably formed during the expansion of the oxide layer during the heating. The material inside the crack (point P1) contained about 1.6 wt% O (see Table 2) and an Mg/O ratio of 3.3, suggesting the oxide layer to be very thin.

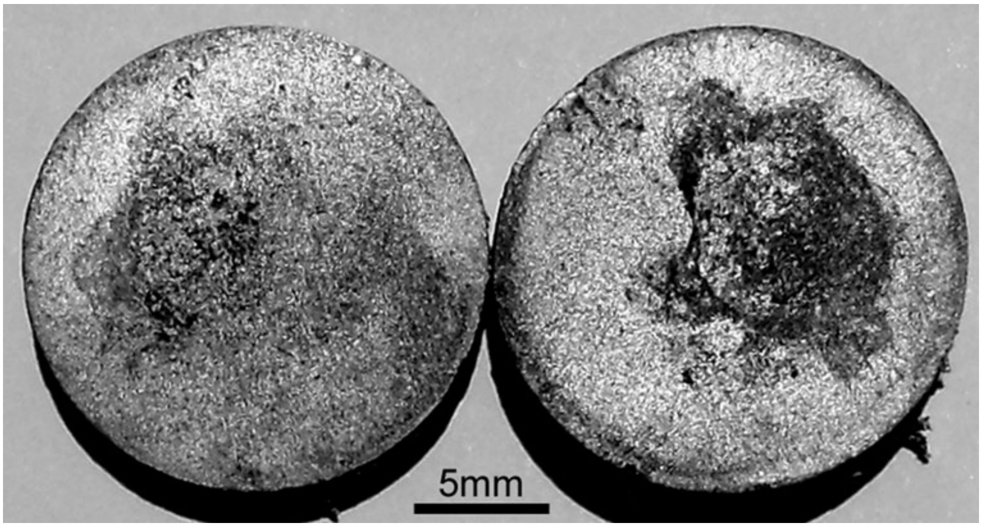


Fig. 2 Photograph of the oxide layers that were held in the furnace for 2 min

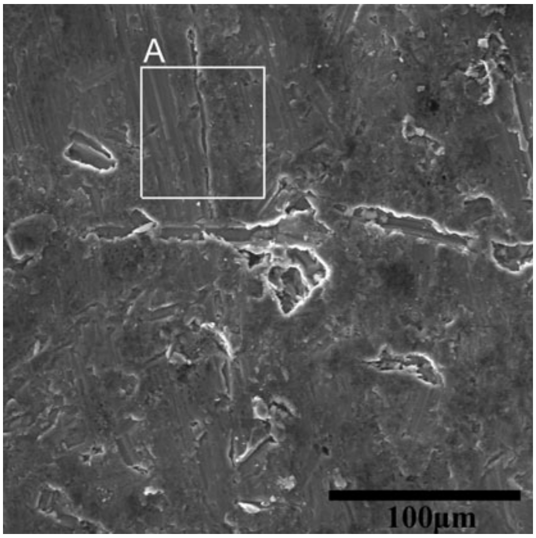


Fig. 3 SEM micrograph of the surface of the oxide layer shown in Fig. 2. Some discontinuities in the oxide layer are visible. A higher magnification micrograph of area (*A*) is shown in Fig. 4

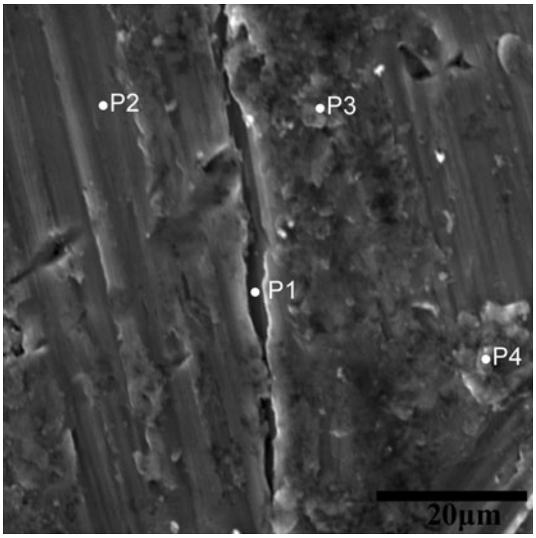


Fig. 4 A higher magnification SEM micrograph of the area denoted (*A*) in Fig. 3. The concentrations of the elements at points *P1* to *P4* are given in Table 2

This figure also shows that in some areas the flat oxide layer (point P2) grew to a rougher structure (points P3 and P4) which contained more Mg and O (see Table 2) and smaller Mg/O ratio. The decrease in the Mg/O ratio (from 0.92 on the flat structure to 0.49 and 0.33 on the rough surfaces) suggested that the spinel crystals nucleated and grew in the oxide microstructure.

The discontinuities in the oxide layer increased as the Al bars were held in the furnace for longer periods. Figure 6 shows the SEM micrograph of the oxide layer that was held in the furnace for 4 min. A higher magnification picture of this layer is also shown in Fig. 7. In contrast to the surface of the oxide layer shown in Fig. 3 which appeared to be fully oxidised, a localised accumulation of oxide with much thinner layer of oxide in between can be seen in Fig. 6. The EDX studies (see Fig. 8) revealed that the Mg/O ratio of the oxide layer generally decreased to 0.5 (point P1), an indication of the formation of spinel in the microstructure (probably beneath the MgO layer), and that the edge of the discontinuities observed in the microstructure contained a high concentration of Mg and O.

No $MgAl_2O_4$ peaks were observed in the XRD spectra obtained from any of the oxide layers that were held in the furnace for 2 min to 16 h, and the spectra showed only the presence of MgO in the microstructures (see Fig. 9). The absence of the $MgAl_2O_4$ peaks in the spectra could be attributed to the extreme thinness of this oxide. On the other hand, most of the diffraction peaks of MgO are very

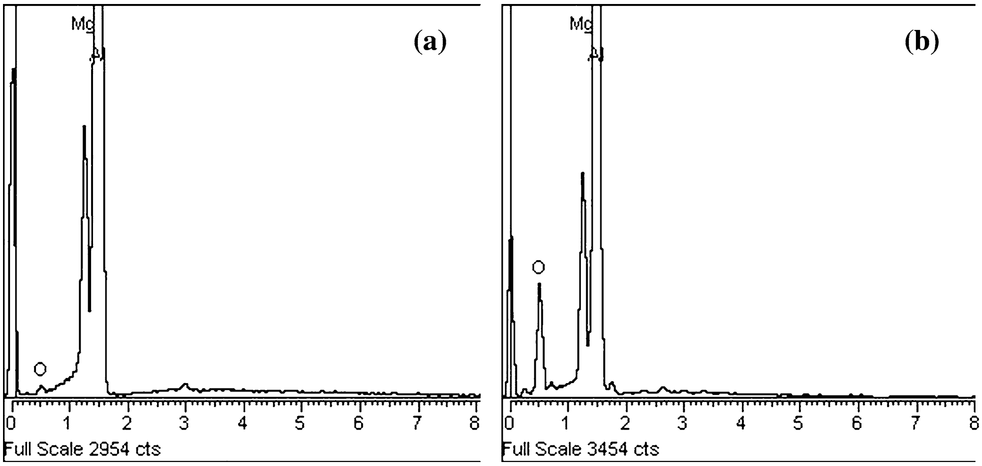


Fig. 5 EDX spectra obtained from points **a** *P1* and **b** *P4* given in Fig. 4. The concentrations of the elements are given in Table 2

Table 2 The composition of points P1 to P4 given in Fig. 4

Sample	Mg	O	Mg/O
P1	5.32	1.61	3.3
P2	3.11	3.37	0.92
P3	5.72	11.61	0.49
P4	8.4	25.36	0.33

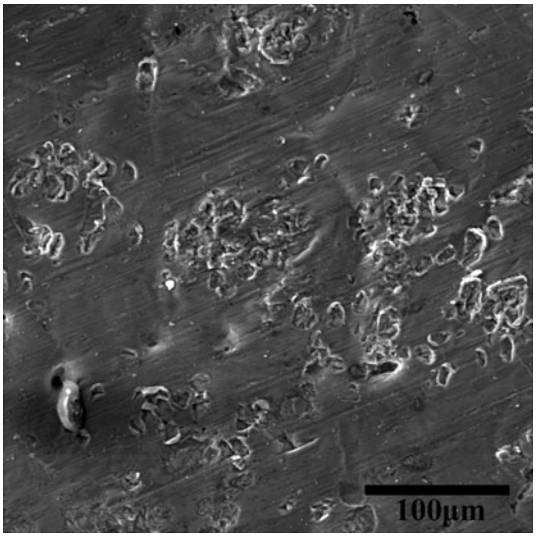


Fig. 6 SEM micrograph of the surface of an oxide layer that was held in the furnace for 4 min

close to those of Al. This, and the small thickness of the MgO layer, made the identification of this oxide difficult. However, as can be seen in Fig. 10 (the XRD spectrum obtained from the oxide layer that was held for 4 min), the peaks of these two materials that lay between $2\theta = 64°$ and 84^{o} were distinguishable, and this made the identification of the magnesium oxide possible.

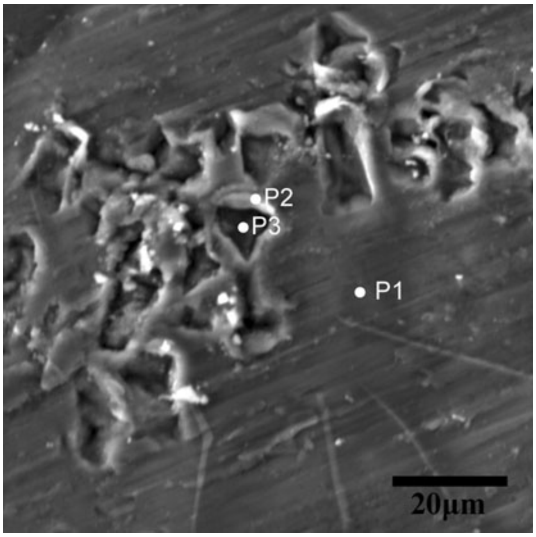


Fig. 7 A higher magnification of the SEM micrograph shown in Fig. 6. The EDX spectra obtained from points *P1* to *P3* are shown in Fig. 8

After the melting of the bars

Figure 11 shows a photograph of the two oxide layers that were held in the furnace for 7 min (i.e. 30 s after the complete melting of the bars). A dark patch appeared in the middle of the layer, which was attributed to the greater thickness of the oxide in this area [11]. Aside from a small leak of the liquid metal from the edge of the oxide layer on one side, no bonding took place between the two layers, and the layers were easily detached from each other.

The SEM micrograph obtained from this layer is shown in Fig. 12. The EDX spectra obtained from two areas on this figure, presented in Fig. 13, showed a relatively high concentration of 9.2 wt% Mg and 13.4 wt% O in most areas (e.g. the area denoted A in the figure), which increased to 21.6 wt% Mg and 29.3 wt% O in some

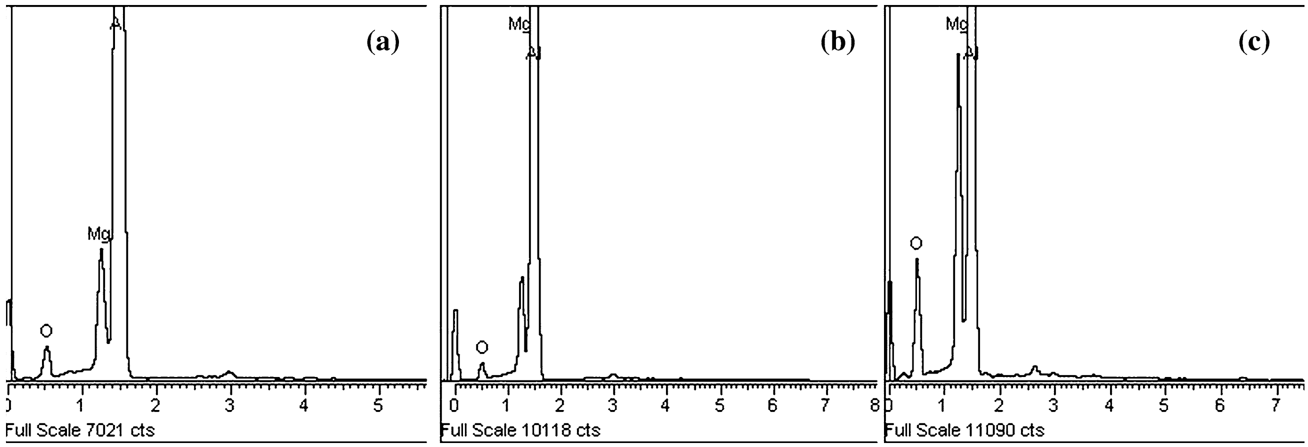


Fig. 8 EDX spectra obtained from points **a** *P1* (Mg = 4.6%, O = 9.0%, and Mg/O = 0.5), **b** *P2* (Mg = 10.3%, O = 21.0% and Mg/O = 0.5) and **c** *P3* (Mg = 5.5%, O = 8.8% and Mg/O = 0.63) given in Fig. 7. All concentrations are in weight percent

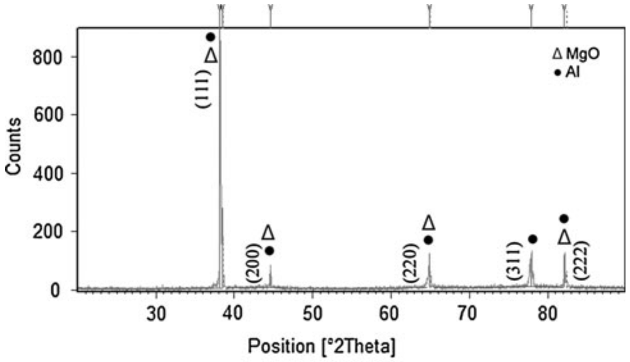


Fig. 9 XRD spectrum obtained from the surface of the oxide layer that was held in the furnace for 2 min

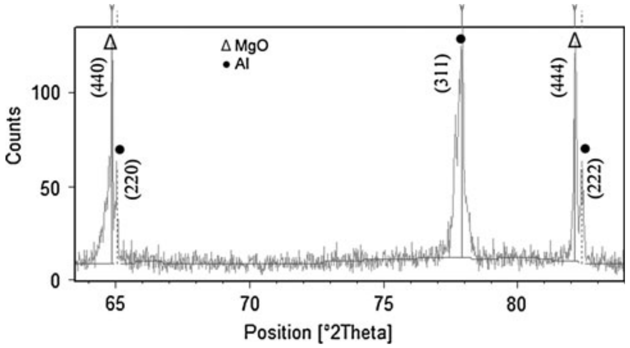


Fig. 10 XRD spectrum obtained from the surface of the oxide layer that was held in the furnace for 4 min, between $2\theta = 64^\circ$ to 84°

line-shaped areas (e.g. point B). The average Mg/O ratio of the oxide layer increased to 0.7, which revealed a reduction in the amount of spinel in the oxide layer.

The photograph of the two oxide layers that were held in the furnace for 30 min, presented in Fig. 14, shows no bonding formed between the two layers. The increase in the extent of the dark patch at the middle of the layers reveals that the layers are still growing in thickness at this stage. This figure also shows many cracks that formed on the layers. The cracks are clearly visible in the SEM micrograph obtained from the surface of this specimen (see Fig. 15). However, no liquid metal passed through these cracks to bond the two oxide layers to each other. The EDX spectra obtained from point P1 (not presented here, for brevity) showed that the oxide layer contained 20.1 wt% Mg and 25.5 wt% O (Mg/O ratio of 0.8). The presence of a relatively high concentration of oxygen on the surface of the dendrites in the crack (determined by the EDX spectrum obtained from point P2 to be 7.6 wt%) showed that the oxygen was still present in the atmosphere trapped between the two oxide layers.

The extent of the dark patch on the oxide layer increased greatly when the oxide layers were held in the furnace for 1 h (see Fig. 16). The SEM micrograph of this specimen, shown in Fig. 17, revealed that the number and extent of the cracks in the microstructure were increased, compared to those of the specimen that was held in the furnace for 30 min (Fig. 15). However, no evidence for the formation of bonding between the two layers was found. The EDX studies of the surface of the dendrites inside the cracks showed that oxygen was still present in the trapped atmosphere. The oxygen peak disappeared from the EDX spectrum obtained from the dendrites inside the cracks when the oxide layers were held in the furnace for 5 h or longer (see Figs. 18, 19).

No bonding formed between the two oxide layers, even when the Al bars were held in the furnace for 16 h (see Fig. 20). A detachment between the oxide layer and the edge of the test bar (shown by an arrow in Fig. 20) was observed in all the test bars that were held in the furnace for 5 h or longer. This detachment, which probably occurred due to a slight movement of the mould during its removal from the furnace after the experiment, implied an increase in the brittleness of the oxide layers as the layers

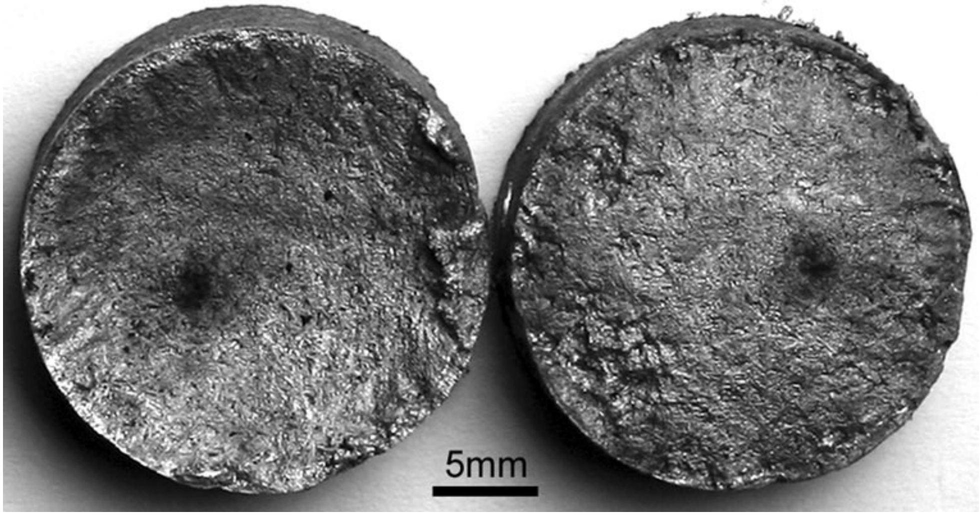


Fig. 11 Photograph of the oxide layers that were held in the furnace for 7 min (30 s after complete melting of the bars)

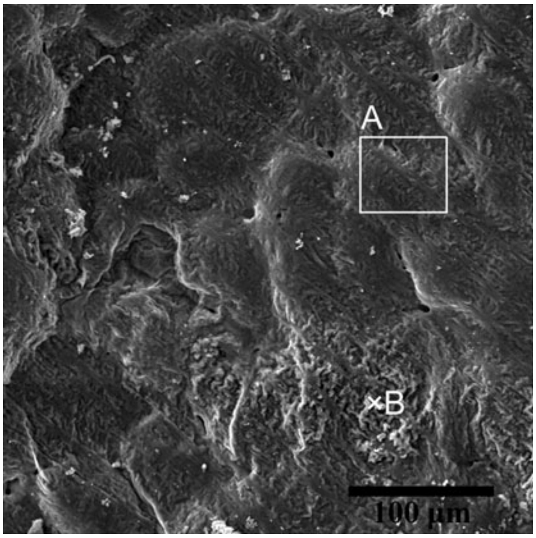


Fig. 12 SEM micrograph of the surface of the oxide layer shown in Fig. 13. The EDX spectra obtained from area (*A*) and point (*B*) are shown in Fig. 13

grew in thickness over time. Comparing the number of cracks that formed during solidification in the microstructure of the oxide layers that were held in the furnace for different time periods (Figs. 12, 15 and 17) also suggested an increase in the brittleness of the layers over time.

The variation in the average concentration of O and Mg, as well as the ratio of Mg/O, in the oxide layers (measured by EDX) over holding time is shown in Fig. 21. It can be seen that the concentration of oxygen increased gradually in the oxide layer up to a holding time of 1 h, after which it remained almost constant. This implied that the oxygen was present in the trapped atmosphere up to a holding time of about 1 h and was gradually consumed by the reaction with the liquid metal during this time.

The rate of the increase in the concentration of oxygen in the oxide layer was at first high (about 1.6% per min at the holding time of 2 min, see Fig. 22), which gradually decreased to almost zero at a holding time of 60 min. A temporary increase in the rate of the addition of oxygen to the oxide layer was observed at the holding time of 4 min.

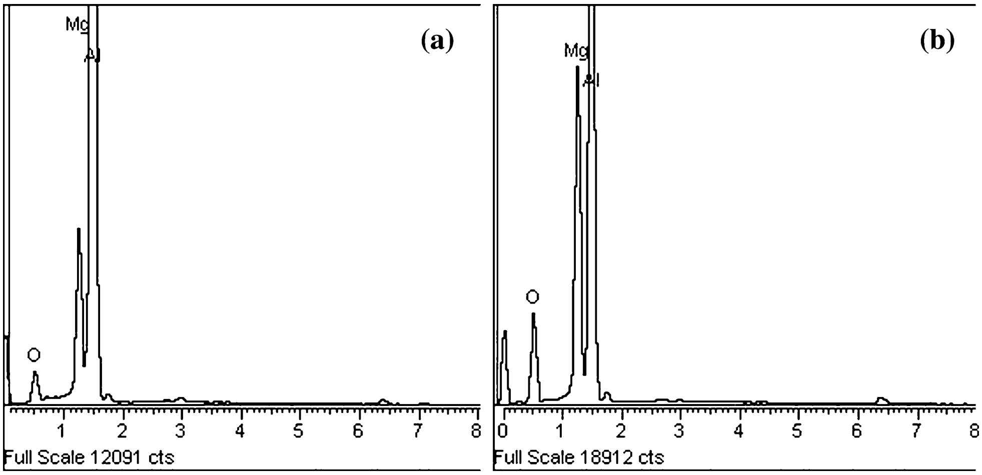
Figure 21 also shows that the concentration of Mg, as well as the Mg/O ratio, slightly increased during the first 2 min of holding, then decreased up to a holding time of 4 min (which was coincident with the temporary increase in the rate of the addition of oxygen to the oxide layer), and then increased afterwards up to a holding time of 5 h, after which it remained almost constant.

Discussion

Comparing the Mg/O ratio of the freshly formed oxide layer in the crack shown in Fig. 4 (point P1) and that of the flat oxide layer at the background of the picture (point P2) (3.3 and 0.92, respectively) showed a fundamental change in the oxide layer during the first 2 min of heating in the furnace. The type of the oxides could not be detected directly in this research; however, considering the above Mg/O ratios and the results reported in the literature [13, 14], it can be suggested that whole of the oxide layer transformed from amorphous alumina to crystalline MgO during this holding time.

Considering the low diffusion coefficient of Mg in solid Al (2.08×10^{-10} cm^2 s^{-1} [18], for Al–5 wt% Mg at 673 K, the temperature of the Al bars at the holding time of 2 min), it can be assumed that the transformation of alumina to MgO caused the local concentration of Mg at the melt–oxide interface to decrease locally below the critical

Fig. 13 EDX spectra obtained from **a** the area denoted (*A*) (9.2 wt% Mg and 13.4 wt% O) and **b** the point denoted (*B*) (21.6 wt% Mg and 29.3 wt% O) on Fig. 12



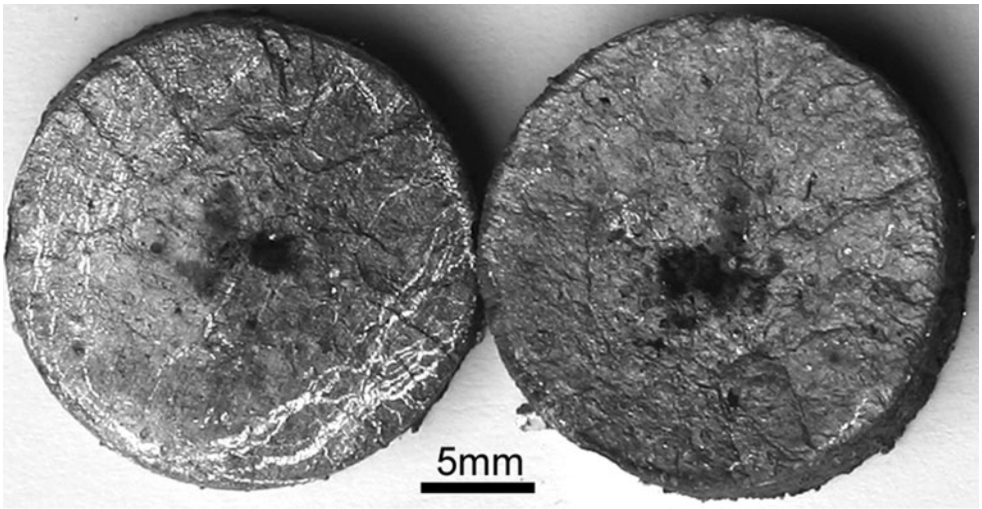


Fig. 14 Photograph of the oxide layers that were held in the furnace for 30 min. Many cracks are visible on the layers

value of 1.5 wt%, below which the formation of spinel crystals is thermodynamically favoured [15]. The growth of the rough structure with a low Mg/O ratio (0.49 and 0.33, at points P3 and P4, respectively, see Table 2) within the oxide layer shown in Fig. 4 confirmed the nucleation and growth of the spinel in the MgO oxide layer at a holding time of about 2 min. This, with the further decrease in the average Mg/O ratio of the oxide layers from 0.55 to 0.47 (see Fig. 22), was shown to continue the holding time of 4 min.

The nucleation and growth of the spinel in the oxide layer was coincident with the appearance of the discontinuities in the oxide layer (Figs. 3, 6) and an increase in the rate of addition of oxygen to the layer (at the holding time of 4 min, Fig. 22). These observations supported the breakaway mechanism proposed by Impey [13], who considered the nucleation of large $MgAl_2O_4$ crystals in the MgO oxide layer responsible for the generation of considerable stress within the oxide film and the localised failure of the film, which exposes the fresh metal to the atmosphere and increases the rate of oxidation.

The increase in the Mg/O ratio after the melting of the bars (from 0.47 at the holding time of 4 min to 0.72 at the holding time of 7 min, see Fig. 21) suggested that the spinel that formed before the solidification started to transform to MgO. The gradual transformation of the $MgAl_2O_4$ oxide layer to MgO in Al–0.3 wt% Mg has also been reported by Aryafar and Raiszadeh [11].

The Mg/O ratio between the holding times of 7 min and 1 h, when the oxygen was still present in the atmosphere trapped between the two layers, remained almost constant. A simple mass balance reveals that this is only possible when the spinel and MgO grow in thickness with equal rates. The exact mechanism of this growth is not clear. However, one can speculate that the stress associated with the nucleation and growth of spinel (as was suggested by Impey [13], at the oxide–melt interface) would cause the

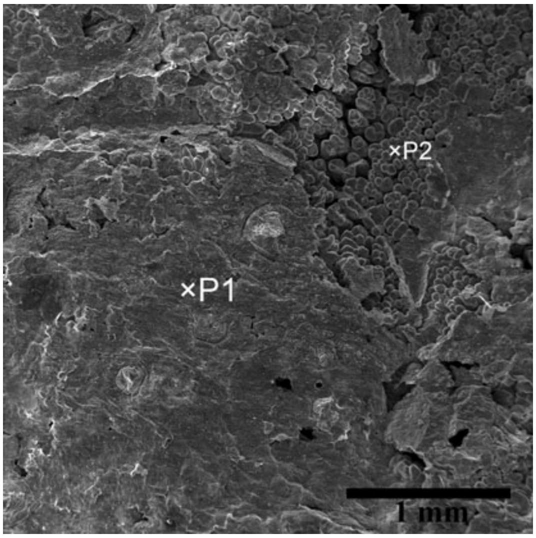


Fig. 15 SEM micrograph of the surface of the oxide layer shown in Fig. 14. The concentration of the elements (all in wt%) are determined by EDX to be 20.1% Mg and 25.5% O, at point *P1*, and 5.4% Mg and 7.6% O at point *P2*

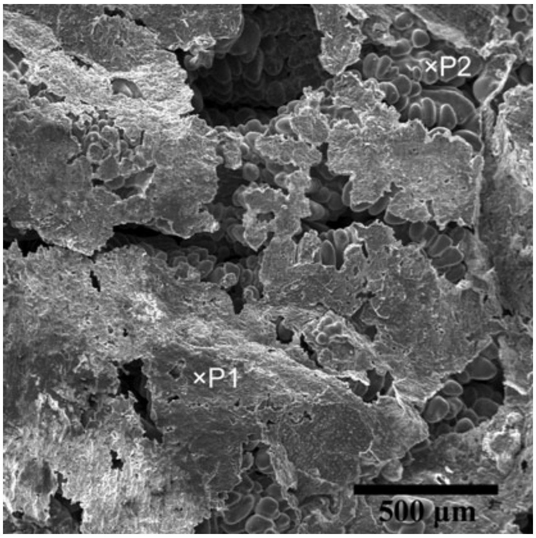


Fig. 17 SEM micrograph of the surface of the oxide layer shown in Fig. 16. The concentration of the elements at point *P1* (all in wt%) are determined by EDX to be 31.5% Mg and 35.7% O and at point *P2* to be 4.5% Mg and 6.4% O

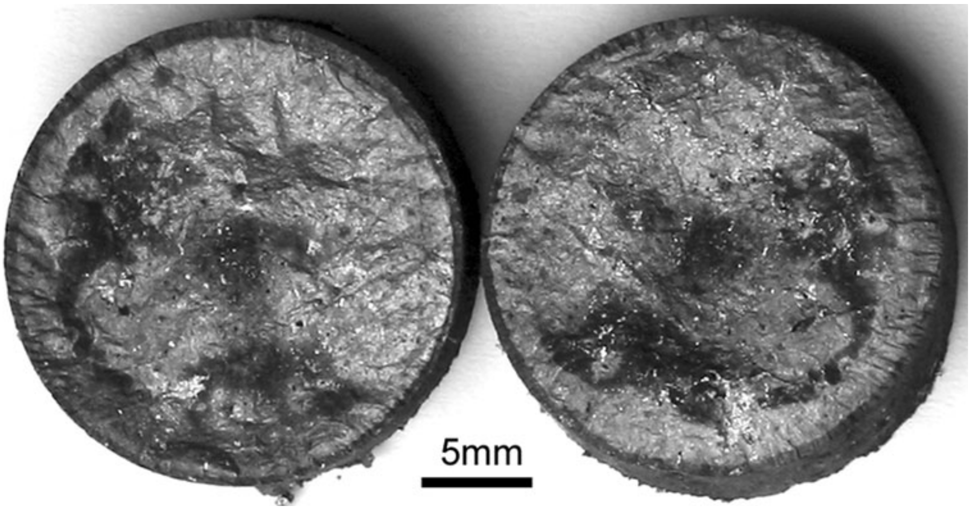


Fig. 16 Photograph of the oxide layers that were held in the furnace for 60 min

oxide layer to crack, which would expose the fresh liquid metal to the trapped atmosphere. The oxidation of the liquid metal to amorphous alumina and its later transformation to MgO would cause a local depletion of Mg in the liquid metal adjacent to the interface, which would provide the required thermodynamic condition for the nucleation of spinel. This cycle would continue until all of the oxygen in the trapped atmosphere is consumed at a holding time of 1 h.

After this time, at the absence of oxygen in the trapped atmosphere, the spinel would transform to MgO by the reaction with the Mg of the liquid alloy [11] (see Eq. 1). This caused the Mg/O ratio to increase from 0.76 at the holding time of 1 h to 1.02 at the holding time of 5 h. This ratio remained almost constant after this holding time, which showed that almost all of the spinel has transformed to MgO by the holding time of 5 h.

$$\{\mathrm{Mg}\} + \frac{1}{3}\,\langle \mathrm{MgAl_2O_4}\rangle = \frac{4}{3}\,\langle \mathrm{MgO}\rangle + \frac{2}{3}\,\{\mathrm{Al}\} \qquad (1)$$

Figures 14, 15, 16, 17 and 18 showed that no liquid metal passed through the cracks that formed on the oxide layers to bond the two layers to each other. This could be due to the surface tension of the melt, or perhaps due to the low fluidity of the liquid metal, if the cracks formed during the advanced stages of the solidification.

Aryafar and Raiszadeh [11] showed that any bonding can take place between the two layers essentially only after

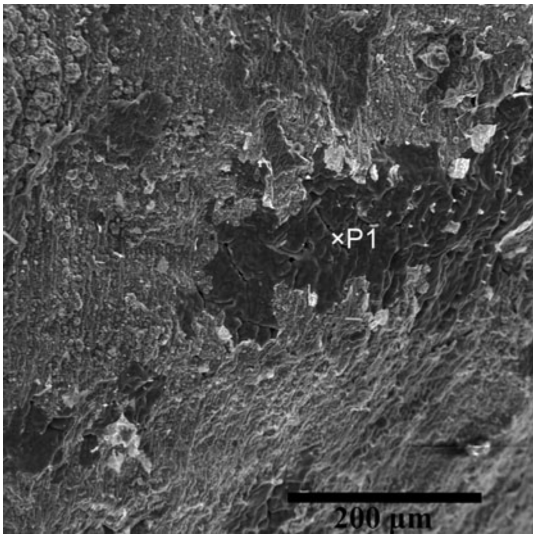


Fig. 18 SEM micrograph of the surface of the oxide layer that was held in the furnace for 5 h. The EDX spectrum obtained from point *P1* is shown in Fig. 19

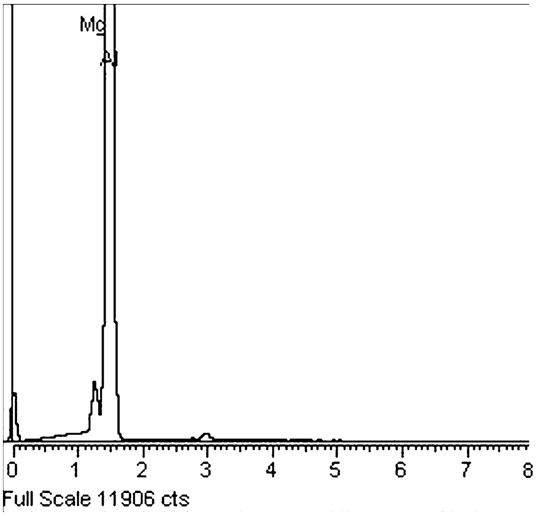


Fig. 19 EDX spectrum obtained from point *P1* on Fig. 18. No oxygen peak is detected in the spectrum

the oxygen and nitrogen of the atmosphere within the defect are consumed. The EDX studies (Fig. 21) showed that the oxygen within the trapped atmosphere completed at a holding time of about 1 h. Comparing this time to the consumption rates obtained by Raiszadeh and Griffiths [9, 10] suggests that the nitrogen within the trapped atmosphere would be consumed in about 2.5 h. However, no bonding between the two layers was observed even after 16 h of holding the Al bars in the furnace.

Aryafar and Raiszadeh [11] also showed that the two oxide layers held in a liquid Al alloy containing 0.3 wt% Mg started to bond to each other after 13 min of holding, and that the bonding became almost complete after about 5 h. They realised that the main bonding took place when the spinel started to transform to MgO, and associated the bonding to the penetration of liquid metal through the porous MgO layer. If true, the oxide layers in the present experiments should have bonded to each other after 5 h, when almost all of the spinel had transformed to MgO.

From this difference in the results, it could be concluded that the cause of the bonding of the layers in the Aryafar and Raiszadeh experiments with Al–0.3 wt% Mg was the transformation that took place at the surface of the two oxide layers. After the oxygen and nitrogen of the trapped atmosphere were consumed, the two unwetted sides of the oxide layers would be in contact. The spinel molecules from both sides would get involved in the reaction at the same location and bond the two oxide layers at that location. In contrast, in the present experiments with Al–4.5 wt% Mg, the spinel layer formed beneath the MgO layer [13], and, therefore, no transformation that could bond the two layers to each other took place at the surface of the oxide layers.

This criterion for the bonding of oxide layers in an oxide film defect, i.e. the presence of a transformation involving rearrangement of molecules at the surface of oxide layers, could be used to predict the bonding behaviour of double oxide film defects when held in different liquid aluminium alloys, or when subjected to a HIPping process. The findings of this research, therefore, suggest that in contrast to Al–7%Si–0.3%Mg (A356) alloy [8], HIPping process would not cause the two layers of an oxide film defect to bond to each other. Further investigation, however, is needed to verify this suggestion.

Conclusions

This study showed that no bonding took place between the two oxide layers that were held in the liquid Al–4.5 wt% Mg alloy for 16 h. The comparison between the results obtained in this study and the previous studies on Al–0.3 wt% Mg alloy (in which the two layers bonded to each other almost completely after a holding time of 5 h) revealed that for the two layers to bond to each other, not only must the oxygen and nitrogen trapped within its atmosphere be consumed, but also a transformation which involves the rearranging of the atoms must take place at the surface of the oxide layers. These two criteria could be used to predict the bonding behaviour of oxide film defects when held in different liquid aluminium alloys, or when subjected to a HIPping process.

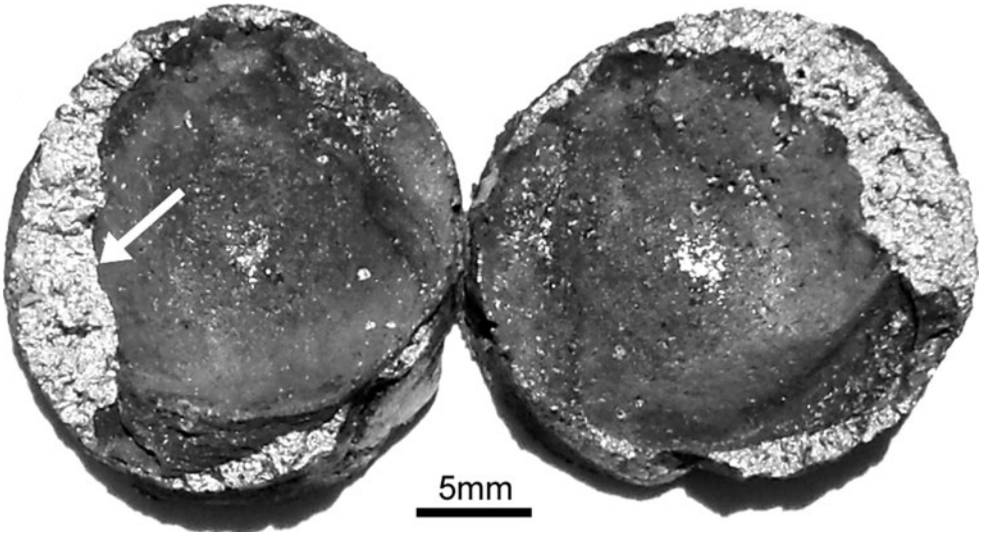


Fig. 20 Photograph of the oxide layers that were held in the furnace for 16 h. The detachment of the oxide layer from the edge of the test bar is shown by an *arrow*

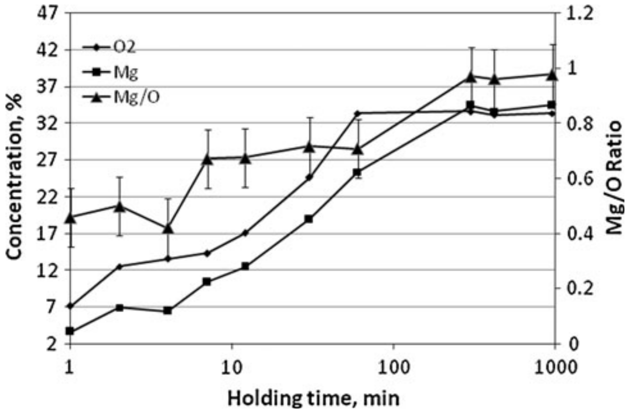


Fig. 21 The average concentrations of O, Mg and Mg/O ratio in the oxide layers that were held in the furnace for different time periods

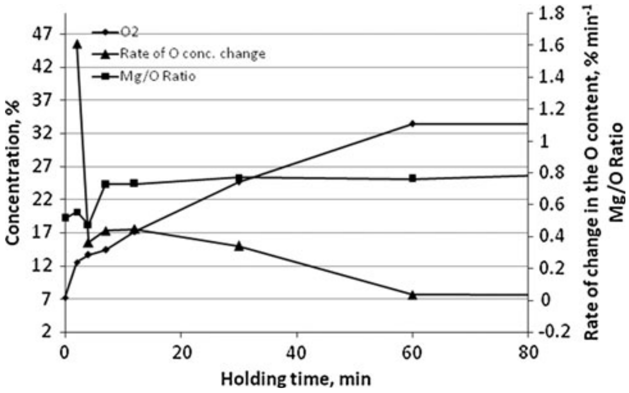


Fig. 22 The average concentration of O, the rate of change in the average concentration of O and the Mg/O ratio in the oxide layers held in the furnace for different time periods

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