The behaviour of entrainment defects formed in commercial purity Mg alloy cast under a cover gas of SF$_6$

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Abstract. In the casting of light alloys, the oxidised film on the melt surface can be folded due to surface turbulence, thus forming entrainment defects that have a significant negative effect on the mechanical properties of castings. Previous researchers reported that the surface film of Mg alloys formed in an atmosphere containing SF$_6$ had a complicated structure composed of MgO and MgF$_2$. The work reported here aims to investigate the behaviour of entrainment defects formed in magnesium alloys protected by SF$_6$-containing atmospheres. Tensile test bars of commercial purity Mg were cast in an unsealed environment under a cover gas of pure SF$_6$. Scanning electron microscopy (SEM) of the fracture surface of the test bars indicated entrainment defects that consisted of symmetrical films containing MgO, but also sulphur and fluorine. The results of these examinations of the symmetrical films were used to infer the potential formation and development of entrainment defects in commercial purity Mg alloy.

1. Introduction

Due to the rapid oxidation of liquid magnesium in air, a cover gas is used to protect Mg alloys in the casting process. The melt surface is generally covered by a continuous solid protective film formed due to the reaction between the molten Mg and the cover gas. Surface turbulence, (e.g. a splash or a vortex), which is common in casting operations, can lead to a folding action of the surface film, entraining a small amount of the surrounding atmosphere. When the folded structure is submerged into the bulk liquid, it becomes an entrainment defect. This kind of defect has been widely recognized as a major factor in the poor quality and lack of reproducibility of the properties of both Al and Mg alloy castings [1, 2].

Currently sulphur hexafluoride (SF$_6$) is one of the most widely used cover gases in industry [3], but its protective mechanism was not clear for decades. Cashion et al. [4] suggested that MgO particles could form a cohesive “raft” on the Mg melt surface in a SF$_6$ atmosphere, halting the rapid oxidation. Pettersen et al. [5] partly supported Cashion’s process, and suggested that SF$_6$ could dissociate to provide atomic fluorine, which would diffuse into the porous MgO layer, forming MgF$_2$. Xiong and Liu [6] found MgF$_2$ particles between the film and the Mg alloy substrate, giving support to Pettersen’s process. The sulphur contents in the surface films were reported to be very low (0.01%–0.02%) [5], or not detected [4].

So far, research into entrainment defects in Mg alloys has been limited [1]. The work reported here was aimed at trying to understand the behaviour of entrainment defects by investigating the surface films of entrainment defects formed in a SF$_6$ atmosphere.
2. Experiment procedure
Castings were produced using PEPSET resin-bonded sand mold, cast with commercial purity magnesium. The sand contained 2% Na$_2$SiF$_6$ as an inhibitor. The casting process was carried out in an unsealed environment with a cover gas of pure SF$_6$.

After solidification, the castings were machined into test bars, (of 37mm gauge length and 6.75mm diameter in the gauge length), and tested using a Zwick 1484 tensile test machine, at a strain rate of 1mm/min. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) were then carried out, using a Philips JEOL6060 SEM and Philips JEOL7000 SEM with Oxford INCA EDS, to investigate the nature of the defect found on the fracture surfaces of the broken test bars.

![Figure 1](image)

**Figure 1.** (a) Fracture surfaces of a broken tensile test bar (the diameter of the test bar was 6.75 mm); (b) The boundary between the black and the bright regions shown in (a).

|                | C   | O   | Mg  | Si  | F   | S   |
|----------------|-----|-----|-----|-----|-----|-----|
| **Bright area**|     |     |     |     |     |     |
| Sample size    | 15  | 15  | 15  | 15  | 15  | 15  |
| Mean           | 1.784 | 0.476 | 97.655 | 0.0727 | Nd. | Nd. |
| Standard Deviation | 0.821 | 0.159 | 0.967 | 0.0562 | Nd. | Nd. |
|                |     |     |     |     |     |     |
| **Black area** |     |     |     |     |     |     |
| Sample size    | 15  | 15  | 15  | 15  | 15  | 15  |
| Mean           | 5.08 | 10.36 | 83.13 | 0.25 | 0.49 | 0.09 |
| Standard Deviation | 1.94 | 3.62 | 5.13 | 0.10 | 0.15 | 0.06 |

P value: <0.0001 <0.0001 - <0.0001 - -
Nd. = Not detected

3. Results

3.1. Entrainment defects formed in pure Mg under a cover gas of pure SF$_6$
Three different types of entrainment defects, formed under the same conditions, (casting of commercial purity Mg protected by pure SF$_6$), were found.
Figure 1(a) shows the fracture surfaces of a broken tensile test bar. Two symmetrical macroscopic black areas were seen on both fracture surfaces. Figure 1(b) shows a SEM image of the boundary between the black and bright areas shown in figure 1(a). Slip planes were seen in the bright area, and the black region had a comparatively smooth surface.

Table 1 shows the EDS results corresponding to both regions and it can be seen that sulphur and fluorine were only detected in the black region. The oxygen content of the black region was significantly higher than that of the bright area, and indicated the oxygen in the black region was not produced by oxidation after tensile testing, and that the black regions were entrainment defects with a surface film that contained oxygen, fluorine, and sulphur.

Figure 2(a) shows another entrainment defect formed in the same casting, (commercial purity Mg cast under pure SF₆). EDS analysis (see figure 2(b)), corresponding to the black region shown in figure 2(a), revealed that the surface film contained oxygen and fluorine, but no sulphur.

Figure 3(a) shows an entrained bubble (around 0.48 cm³) captured in a tensile test bar. A SEM examination, using a backscattered electron beam, was carried out to observe the surface film of the trapped bubble (figure 3(b)), indicating dark spot-like regions distributed on the film surface. In addition, a wrinkled track was also found. An observation at higher magnification (figure 3(c)) showed
cracks in the surface of the dark region. The EDS results (table 2) revealed that the dark spots had higher contents of sulphur and oxygen than the surrounding white areas. However, fluorine could not be clearly recognized by EDS in both regions, indicating that MgS or MgSO₄ might be the active species making the film protective. Thus it can be suggested that S₂(g) or SO₂ also existed in the final residual entrained gas of the bubble.

**Table 2.** A comparison of the EDS results of the element contents in both regions shown in figure 3(b), by Student’s T test.

|          | C  | O  | Mg | S  |
|----------|----|----|----|----|
| **Sample size** | 15 | 15 | 15 | 15 |
| **Mean**  | 36.6 | 14.24 | 46.6 | 1.04 |
| **Standard Deviation** | 10.4 | 5.54 | 17.5 | 1.04 |
| **Sample size** | 15 | 15 | 15 | 15 |
| **Mean**  | 8.96 | 4.05 | 86.61 | 0.07 |
| **Standard Deviation** | 3.51 | 1.54 | 4.89 | 0.08 |

**P value**

<0.001  <0.001  -  0.001

**Figure 4.** Equilibrium diagram for the reaction between 1e-8 kg 90%SF₆/Air and different amounts of Mg. To make it clear, the amounts of residual reactants in the cover gas and products present by logarithm (base 10) in Y-axis.

3.2. **Thermodynamic calculation to approximate the evolution of gas occurring inside entrainment defects**

A hypothetical thermodynamic calculation (figure 4) was carried out, using HSC software from Outokumpu, HSC Chemistry for Windows (http://www.hsc-chemistry.net/), in order to explore what might occur to the atmosphere inside an entrainment defect as the entrained gas reacted with the surrounding melt. This software can suggest which products are most likely to occur, based on
thermodynamic calculations. Since the casting process was carried out in an unsealed environment, the cover gas inevitably contained some air. The entrained gas for the calculation was assumed to be 1e-08 kg 90%SF$_6$/Air ($\approx 1.67$ mm$^3$) in contact with sufficient Mg for any reaction to go to completion. The temperature was set to 700 $^\circ$C, the pressure to 1 atm, and the decomposition products of SF$_6$ were assumed to be SF$_5$, SF$_4$, SF$_2$, F$_2$, and F(g) [7, 8]. In addition, according to the EDS results shown in table 2, S$_2$(g) and SO$_2$ were assumed to also exist in the entrained gas.

In figure 4, the horizontal X-axis denotes the amount of liquid magnesium in contact with the entrained gas, and the vertical Y-axis denotes the logarithm (base 10) of the amounts of residual reactants and products. The whole process could be divided into three periods: (i) in period 1, liquid Mg preferentially consumes fluorides in the cover gas, forming MgF$_2$, while S$_2$(g) accumulates in the residual gas. A portion of S$_2$(g) reacts with oxygen, forming SO$_2$, MgO, MgS, and MgSO$_4$. They are theoretically produced, but they can be neglected in a practical process since their amounts are too small (less than $10^{-20}$ kg, while MgF$_2$ occurs at more than $10^{-10}$ kg); (ii) in period 2, nearly all fluorides in the entrained gas have been consumed, and liquid Mg reacts with S$_2$(g) and SO$_2$, forming MgO and MgS. The existence of MgSO$_4$ can also be practically neglected, due to its small amount (less than $10^{-15}$ kg, while both MgO and MgS occurs at more than $10^{-10}$ kg); (iii) in period 3, S$_2$(g) and SO$_2$ have been depleted, and liquid Mg reacts with nitrogen, forming Mg$_3$N$_2$.

Therefore, the detected sulphur shown in table 1 and 2 might mainly exist as MgS, consistent with the suggestions of [8, 9], and the existence of MgS in the surface film can be suggested to depend on the F:S ratio in the cover gas.

4. Discussion

Sulphur and fluorine were not found in all of the films formed in the commercial purity Mg castings protected by pure SF$_6$; sulphur was only found in two films and fluorine in two other different films. The thermodynamic calculation shown in figure 4 suggested that the existence of MgF$_2$ and MgS in the surface film was determined by the F:S ratio in the cover gas. Therefore, the evolution process for an entrainment defect can be suggested to be as shown in figure 5.

**Figure 5.** Formation and evolution process of the observed entrainment defects. (a) a surface film formation; (b) original entrainment defect; (c) cracks caused by melt flow; (d ~ f) final entrainment defects.
In stage 1, figure 5(a), a protective film has been formed on the melt surface due to the reaction between liquid Mg and the cover gas. The protective film might contain MgF$_2$ but not MgS, based on [4, 5] and the observation shown in figure 2. Moreover, according to Xiong and Wang [10], who found that the film formed on the surface of Mg melt had a high content of oxygen under a cover gas of 0.1%SF$_6$/air, MgO can be contained in the surface film shown in figure 5(a), resulting from $\text{2Mg} + \text{O}_2 = \text{MgO}$, when the surrounding atmosphere of the Mg melt has a high concentration of air, especially during the pouring process.

In stage 2, figure 5(b), the protective film can be folded over onto itself due to surface turbulence, forming entrainment defects. The original entrainment defect would be covered by the initial surface film, consisting of MgF$_2$ and MgO. The entrained gas may originally consist of SF$_6$ and air.

In stage 3, figure 5(c), the initial surface film can be cracked or even partly removed, by the movement of the melt. Thus fresh liquid Mg can come into contact with the interior of the defect through the cracks, reacting with the trapped gas and forming new surface films. In conjunction with the calculation shown in figure 4, the formation of the new surface film can reduce the total fluorine content in the trapped gas, but the sulphur content might not decrease. Simultaneously, hydrogen might diffuse into the entrained gas [2], through the cracks and the permeable film.

Therefore in stage 4, three types of final entrainment defects might exist, as shown in figure 5(d) ~ (f), and the different observed defects on the fracture surfaces have given evidence of different types of entrainment defects:

Firstly, if the amount of the liquid Mg that comes into contact with the entrained gas, was not enough to consume the fluorides in the trapped gas, corresponding to period 1 shown in figure 4, the surface film can only contain MgF$_2$ and MgO, as shown in figure 5(d), consistent with the results shown in figure 2. The residual entrained gas might contain SF$_6$, hydrogen, air and the decomposition products of SF$_6$.

Secondly, if the liquid Mg, in contact with the entrained gas, consumed nearly all of the fluorides in the trapped gas, but did not deplete sulphur, corresponding to the period 2 shown in figure 4, the final surface film can contain MgS, MgF$_2$, and MgO, as shown in figure 5(e), consistent with the observation shown in figure 1. The residual entrained gas therefore mainly contains sulphur, air and hydrogen at this stage. In addition, if the initial surface film containing MgF$_2$ was removed, the final surface film would only contain MgS and MgO as shown in figure 3 and table 2.

Finally, if all fluorides and sulphur in the entrained gas were consumed by the Mg melt, corresponding to period 3 shown in figure 4, the surface film might contain MgS, MgO, MgF$_2$ and Mg$_3$N$_2$, as shown in figure 5(f). The residual entrained gas might only contain N$_2$ and H$_2$. If the process continued further, making more liquid Mg come into contact with the entrained gas, N$_2$ can be depleted, so that the final entrained gas might only contain H$_2$. However, Mg$_3$N$_2$ has not been found in the samples of the experiment. Thus there may not be enough time for the entrained gas to react with liquid Mg, forming Mg$_3$N$_2$, before solidification.

The evolution process and results revealed that entrainment defects can exist with a trapped gas in Mg castings, acting as a crack initiator, similar to the entrainment defects in Al castings [2]. In addition, the evolution process also indicated that all the components of the initial entrained gas can be consumed by reaction with liquid Mg. Thus the effect of entrainment defects in Mg casting might be effectively reduced, by increasing the holding time before solidification [13], so that the reproducibility of the properties of Mg castings can be improved. Compared with aluminum alloy, which cannot efficiently consume nitrogen (78% volume of the initial trapped gas) in the entrained gas [11, 12], Mg alloy castings might achieve a better reproducibility through this technique.

5. Conclusion

The surface films of three typical entrainment defects formed in commercial purity Mg cast under a cover gas of pure SF$_6$ have been observed. The surface films contained different combinations of compounds: (1) MgS and MgO; (2) MgF$_2$ and MgO; (3) MgS, MgF$_2$ and MgO. In addition, a thermodynamic prediction revealed that fluorides in the entrained gas could be preferentially
consumed compared to air. An evolution process of the entrainment defects formed in pure Mg/pure SF$_6$ was suggested, and the composition of the surface film depended on which stage the defect was in.

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**References**
[1] Griffiths W D and Lai N W 2007 Double oxide film defects in cast magnesium alloy *Metall Mater Trans A-Phys Metall Mater Sci* **38A** 190-196
[2] Campbell J 2004 *Castings* (Oxford: Butterworth-Heinemann)
[3] Polmear I J 2006 *Light alloys: metallurgy of the light metals* (Oxford: Butterworth-Heinemann)
[4] Cashion S P, Ricketts N J and Hayes P C 2002 The mechanism of protection of molten magnesium by cover gas mixtures containing sulphur hexafluoride *Journal of Light Metals* **2** 43-47
[5] Pettersen G, Ovrelid E, Tranell G, Fenstad J and Gjestland H 2002 Characterisation of the surface films formed on molten magnesium in different protective atmospheres *Mater Sci Eng A-Struct Mater Prop Microstruct Process* **332** 285-294
[6] Xiong S M and Liu X L 2007 Microstructure, composition, and depth analysis of surface films formed on molten AZ91D alloy under protection of SF6 mixtures *Metall Mater Trans A-Phys Metall Mater Sci* **38A** 428-434
[7] Kubaschewski O and Hesselemam K 1991 *Thermo-chemical properties of Inorganic Substances* (Belin: Springer-Verlag)
[8] Aarstad K 2004 Protective Films on Molten Magnesium PhD Thesis Norwegian University of Science and Technology
[9] Shih T S, Liu J B and Wei P S 2007 Oxide films on magnesium and magnesium alloys *Mater Chem Phys* **104** 497-504
[10] Xiong S M and Wang X F 2010 Protection behavior of fluorine-containing cover gases on molten magnesium alloys *Trans Nonferrous Met Soc China* **20** 1228-1234
[11] Kumari S S S, Pillai U T S and Pai B C 2011 Synthesis and characterization of in situ Al-AlN composite by nitrogen gas bubbling method *J Alloy Compd* **509** 2503-2509
[12] Swaminathan S, Rao B S and Jayaram V 2002 The influence of oxygen impurities on the formation of AlN-Al composites by infiltration of molten Al-Mg *Mater Sci Eng A-Struct Mater Prop Microstruct Process* **337** 134-139