

INTERACTION OF MAGNESIUM WITH GASES

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The purpose of this work was to select a protective atmosphere that would interact with magnesium to form a film on the surface of the molten metal preventing evaporation of magnesium. The concentration of the active gas in the protective atmosphere must be limited to exclude formation of a large quantity of non-metallic compounds and embrittlement of the film.

The same gases used in [1] were selected for these tests. The active components were sulfur hexafluoride (SF_6) and sulfur dioxide (SO_2), and nitrogen and carbon dioxide as diluents. The carbon dioxide must be obtained in a mildly active radical.

The rate of interaction between magnesium and the gases was determined by the weight method. Weighing was conducted every 0.5, 1, 2, and 4 h. Cylindrical samples 15 mm in diameter and 10 mm high on a corundum boat were placed in a quartz water-cooled container filled with the protective atmosphere, which was placed in a furnace (Fig. 1). The temperature was kept constant at 750° , at a pressure of 1 atm. The samples were prepared from a magnesium alloy of the Mg-Al-Zn system containing 8.2% Al, 0.72% Zn, 0.32% Mn, 0.055% Si, 0.021% Cu, and 0.038% Fe. The samples were polished with sand paper with a grain size of 20μ and washed in carbon tetrachloride.

The interaction of carbon dioxide with magnesium is described by the equation $2\text{Mg} + \text{CO}_2 = 2\text{MgO} + \text{C}$. Little research has been done on this reaction. Oxidation of magnesium in carbon dioxide proceeds much more slowly than in air [2], but the increase in weight is substantial. The film forming on magnesium in an atmosphere of CO_2 has no protective properties, which was explained in [3] by the presence of pores and cracks extending to the surface of the metal. It was stated in [4] that cracks can occur only in the stage preceding combustion. The existence of a thin film of MgO between the layer of scale and magnesium has been proposed, through which transfer of magnesium ions occurs by the Mott-Cabrer mechanism.

We investigated the oxidation of the magnesium alloy in pure nitrogen, carbon dioxide, and a mixture of these gases. The results obtained are shown in Fig. 2. Magnesium evaporates intensively in pure nitrogen,

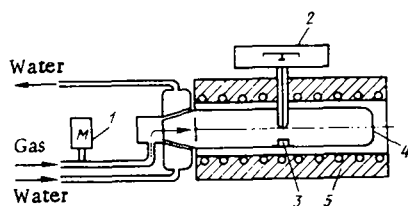


Fig. 1

Fig. 1. Schematic diagram of the apparatus: 1) manometer; 2) thermocouple; 3) sample; 4) reactor; 5) furnace.

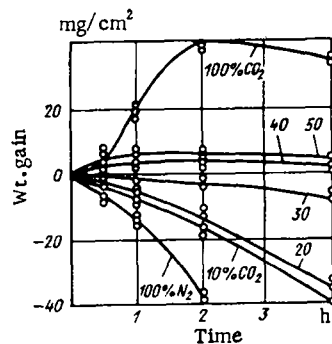


Fig. 2

Fig. 2. Kinetics of formation of a film on liquid metal in an atmosphere of $\text{N}_2 + \text{CO}_2$.

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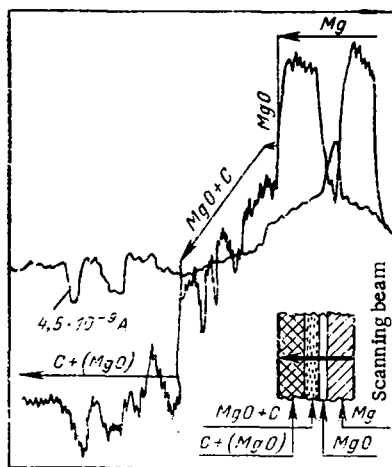


Fig. 3

Fig. 3. Change in the magnesium concentration in different layers of the film obtained in an atmosphere of 50 vol. % N_2 + 50 vol. % CO_2 at 750° .

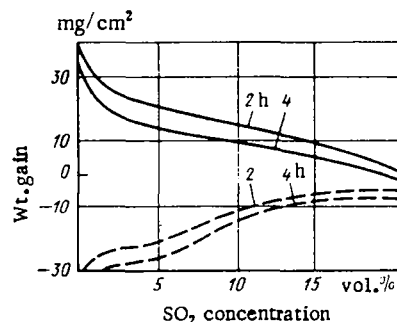


Fig. 4

Fig. 4. Effect of SO_2 concentration in atmospheres of CO_2 + SO_2 (solid lines) and N_2 + SO_2 (dashed lines) on the formation of nonmetallic compounds.

with almost no formation of Mg_3N_2 . The inertness of nitrogen is explained by the low ionization at the given temperature. Magnesium is intensively oxidized by a parabolic rule in pure carbon dioxide, with formation of nonmetallic compounds; the oxidation of magnesium in air obeys a linear rule. With a low concentration of CO_2 in a N_2 + CO_2 atmosphere a weak film is formed on the surface of the sample, slightly preventing evaporation of magnesium. Only with 40-50 vol. % CO_2 is the oxidation process stabilized, following a parabolic rule. A dense layer of carbon is observed on the surface of the sample. X-ray and local chemical analysis of the film showed magnesium oxide and carbon (soot). Evidently, the protective properties of the film formed in N_2 + 40-50 vol. % CO_2 are due to formation of a dense layer of soot covering the film, which consists of MgO .

Figure 3 shows the magnesium distribution through the section of the sample after 2 h in an atmosphere of 50 vol. % N_2 + 50 vol. % CO_2 . There is a thin film of MgO on the surface; thickening of the film is accompanied by formation of pores and cracks filled with soot, as is confirmed by the lower magnesium concentration. Finally, a dense layer of soot covers the entire film and the oxidation process ceases.

The reaction of sulfur dioxide with magnesium occurs as follows:



These reactions are observed at 600° ; the main products of the interaction at 700° are magnesium oxide and sulfur according to [5]. We found MgO and MgS at 750° . The stability of the process at this temperature occurring by Eq. (1) is also confirmed by the change in free energy, equal to 80,804 cal/g-atom.

Figure 4 shows the effect of the sulfur dioxide concentration in the atmosphere on the formation of nonmetallic compounds. Nitrogen and carbon dioxide were used as diluents. A small quantity of SO_2 (~1 vol. %) in the atmosphere* is sufficient for the formation of a dense protective film at temperatures near 700° . Our results indicate that no protective film is formed in an atmosphere of N_2 + SO_2 . The evaporation of magnesium is slowed down when the SO_2 concentration is raised to 20 vol. %, but this amount is insufficient for the formation of a strong film and healing of the defects formed. When nitrogen is replaced with carbon dioxide the sulfur dioxide slows down the oxidation process. In CO_2 + 20 vol. % SO_2 the oxidation is minimal. The formation of magnesium sulfide blocks defects in the film of magnesium oxide, thus creating a coating capable of protecting magnesium against evaporation. However, this coating is brittle and constant healing of the defects formed is necessary.

* French Patent No. 2047250, class B22d.

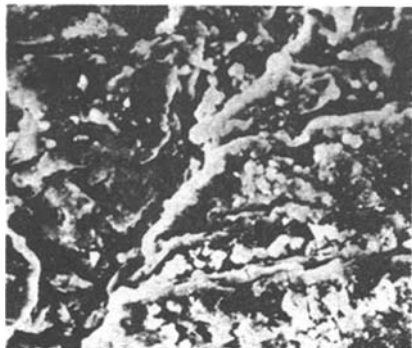


Fig. 5

Fig. 5. Cracks in a film obtained in 80 vol. % CO_2 + 20 vol. % SO_2 at 750° ($\times 1000$).

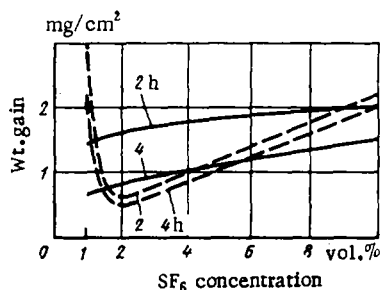


Fig. 6

Fig. 6. Effect of SF_6 concentration in atmospheres of $\text{CO}_2 + \text{SF}_6$ (solid lines) and $\text{N}_2 + \text{SF}_6$ (dashed lines) on formation of nonmetallic compounds.

Fractographic studies showed that cracks are the most characteristic defects (Fig. 5).

Sulfur hexafluoride interacts with magnesium by the reaction: $4\text{Mg} + \text{SF}_6 = 3\text{MgF}_2 + \text{MgS}$

Figure 6 shows the effect of the SF_6 concentration in the atmosphere on the formation of nonmetallic compounds. In atmospheres of $\text{CO}_2 + \text{SF}_6$ there is a monotonic increase in the weight of the samples, varying little with the SF_6 concentration. In $\text{N}_2 + \text{SF}_6$ atmospheres the weight gain is lowest with 1.5-3 vol. % SF_6 . The weight gain increases by a linear rule with increasing amounts of SF_6 . Insufficient SF_6 (~1 vol. %) leads to formation of a thick brittle film.

X-ray analysis showed that the film formed in atmospheres of $\text{CO}_2 + \text{SF}_6$ and $\text{N}_2 + \text{SF}_6$ consists of MgF_2 and MgO , with the intensity of the lines much weaker after holding in $\text{N}_2 + \text{SF}_6$. Nitrogen slows down the formation of MgF_2 . The phenomenon of so-called nonferrous cabbages is not observed in this atmosphere; in an atmosphere of $\text{CO}_2 + \text{SF}_6$ this process occurs with as little as 5 vol. % SF_6 (Fig. 7).

Figure 8 shows the film formed in 98 vol. % CO_2 + 2 vol. % SF_6 . It should be noted that the thickness of the film differs in polished and unpolished sections of the samples. Growths occur on sharp angles, and the film is thicker and more brittle, with greater likelihood of cracks forming.

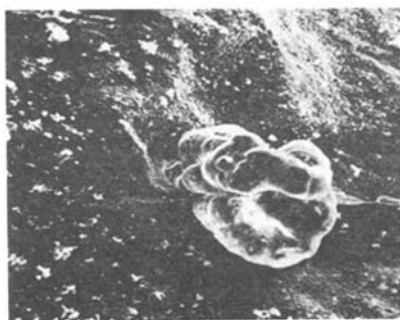


Fig. 7

Fig. 7. Nucleation and growth of a nonferrous cabbage on the surface of the film obtained in 90 vol. % CO_2 + 10 vol. % SF_6 at 750° ($\times 100$).

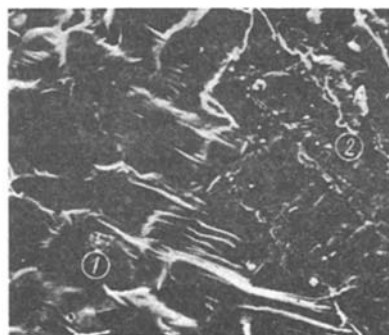


Fig. 8

Fig. 8. General view of the film obtained in 98 vol. % CO_2 + 2 vol. % SF_6 at 750° ($\times 3000$): 1) polished section; 2) unpolished section.

CONCLUSIONS

1. At 750° no protective film preventing evaporation of magnesium is formed on the surface of a molten magnesium alloy of the Mg-Al-Zn system in an atmosphere of nitrogen or N₂ + 1-20 vol. % SO₂
2. In an atmosphere of 40-50 vol. % N₂ + 60-50 vol. % CO₂ a coating of soot is formed on the surface of the molten magnesium alloy, preventing evaporation of magnesium.
3. Sulfur dioxide slows down the oxidation of magnesium in an atmosphere of CO₂, and 20 vol % SO₂ is sufficient to block defects in the MgO film.
4. In an atmosphere of CO₂ with 1-10 vol. % SF₆ a dense protective film is formed on the surface of magnesium, the thickness of the film changing little with the SF₆ concentration.
5. The optimal quantity of SF₆ in a nitrogen atmosphere is 1.5-3 vol. %; the thickest and densest protective film is formed on the surface of the molten magnesium alloy under these conditions.

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