Using SO2/Air/N2 Atmosphere as Melting Protection for Pure Magnesium and AZ91D Alloy: Post-Print

Authors: Wang Xianfei, Xiong Shoumei

Date: 2016-11-04T00:00:00+00:00

Abstract

Using three experimental methods, the protective behavior of SO2/Air/N2 atmosphere on pure magnesium and AZ91D alloy melts was investigated. The phase composition, microstructural morphology, and growth process of the formed surface film were analyzed using X-ray diffractometer (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), Auger electron spectrometer (AES), and X-ray photoelectron spectrometer (XPS). The growth and protection mechanism of the surface film was discussed in combination with thermodynamic calculations, and the stability of the surface film was finally examined. The results show that in the SO2/Air/N2 atmosphere, the protective surface film is composed of a mixture of MgO, MgS, and MgSO4. MgSO4 is a thermodynamically stable phase, and its formation is crucial. When using SO2/Air/N2 atmosphere as the protective atmosphere with a fixed SO2 content, the Air content cannot be too high or too low.

Full Text

Use of SO /Air/N Cover Gases for the Protection of Molten Magnesium and AZ91D Alloy

WANG Xianfei, XIONG Shoumei
State Key Laboratory of Automotive Safety and Energy, School of Materials Science and Engineering, Tsinghua University, Beijing 100084

Correspondent: XIONG Shoumei, professor, Tel: (010)62773793, E-mail: smxiong@tsinghua.edu.cn

Supported by National Natural Science Foundation of China (No.51275269), National Key Technologies R&D Program (No.2011BAE22B02) and Ministry of Science and Technology International S&T Cooperation Program of China (No.2010DFA72760)

Manuscript received 200—, *in revised form 200–**–*

Abstract

Molten magnesium and AZ91D alloy oxidize rapidly during the casting process. Sulfur dioxide (SO) mixed with carrier gases can be used to protect the melt by reacting with the surface to form a coherent protective film. In this paper, the films formed in SO /Air/N cover gases were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The formation process and protective mechanism of the surface film were also discussed. The results show that the protective film is composed of MgO, MgS and MgSO . MgS increases the Pilling-Bedworth Ratio of the surface film and enhances its protective capability. MgSO is the thermodynamically stable phase and its formation is important for the development of the protective film. When SO /Air/N cover gases are used to protect the melt and the SO content is fixed, the air content should be controlled within a certain range.

KEY WORDS magnesium and magnesium alloys, gas protection, SO , surface film

Introduction

Magnesium and its alloys are extremely susceptible to oxidation in the molten state [1]. For decades, SF gas has been used as a protective atmosphere during the melting of pure magnesium and magnesium alloys [2]. However, due to its severe greenhouse effect (23,900 times that of CO) and long atmospheric lifetime (3,200 years), the gradual restriction and eventual prohibition of SF has become inevitable [3,4]. Researchers worldwide have been investigating the protection mechanisms of various gases on molten magnesium and magnesium alloys to identify suitable alternatives.

While new protective gases and technologies are still under development, SO gas has been applied industrially as a temporary substitute. However, SO is toxic and the protective effect of SO -containing atmospheres is unstable. Consequently, numerous studies [5-9] have examined the protective effects and process parameters of SO -containing atmospheres on molten magnesium, finding that SO /air mixtures containing 0.5–2.0% SO can provide effective protection, with a certain amount of O being essential. Schubert [10] and Cashion et al. [11,12] further revealed that surface films formed in SO /air atmospheres consist primarily of MgO with small amounts of sulfur, with XPS analysis detecting sulfur present as MgSO and MgS. The surface film exhibits a two-layer structure: an inner MgO/MgS layer and an outer MgSO layer.

Despite these findings, the protective effects of SO -containing atmospheres, the structure of protective surface films, and their growth mechanisms remain incompletely understood, particularly regarding the role of oxygen. Therefore, this work employs multiple experimental methods to investigate the protection mechanisms and film growth kinetics of SO -containing atmospheres on molten magnesium and magnesium alloys, aiming to clarify the roles of sulfur and oxygen and provide theoretical guidance for developing more effective protective gases.

Experimental Materials and Methods

The experimental materials consisted of commercial AZ91D alloy and pure magnesium (99.95% purity). The chemical composition of AZ91D (mass fraction, %) was: Al 8.7, Zn 0.56, Mn 0.2034, Cu 0.0005, Fe 0.001, Ni 0.0007, Si 0.031, with Mg as the balance. Prior to experiments, both AZ91D and pure Mg were cut into 80 mm × 50 mm × 20 mm blocks, cleaned with ethanol, and reserved for use. The experimental gases included high-purity SO (99.9%) and N (99.999%), with synthetic air containing 20.0% O and 80.0% N (denoted as "Air" throughout this paper).

The experimental apparatus comprised three main systems: a heating and insulation system, a gas supply system, and a temperature control system, equipped with a surface film removal device. Three experimental methods were employed: sealed melting, open melting, and oxidation weight gain. The sealed melting method was used to investigate the effect of Air (O) content on protection effectiveness. The open melting method was used to study the growth process of surface films in SO -containing atmospheres. The oxidation weight gain method was used to evaluate the long-term stability of surface films.

In sealed melting experiments, prepared AZ91D or pure Mg samples were placed in a stainless steel crucible inside the furnace, which was then sealed and evacuated to 50 Pa using a vacuum pump. A mixed gas of specific composition was introduced via mass flow controllers until the furnace pressure reached 0.08 MPa. The crucible was heated to the set temperature, held for a specified duration, and then cooled with the furnace. In open melting experiments, the crucible was not sealed, and a continuous flow of SO +N mixture (total flow rate: 1 L/min) was maintained. After heating to the set temperature and melting the sample, the old surface film was removed, timing commenced, and after different holding periods, the sample and crucible were raised to the cooling zone above the furnace for rapid cooling. The oxidation weight gain method was similar to open melting, but samples were polished with 100, 600, and 1000-grit SiC paper to a smooth finish, the old surface film was not removed after melting, and sample mass was continuously measured using an electronic balance during the experiment. The melting temperature was 680 °C for AZ91D and 700 °C or

730 °C for pure Mg.

The surface films were analyzed using SEM for morphology, EDS for chemical composition, and XRD for phase structure. AES combined with Ar ion sputtering was used to analyze compositional depth profiles. XPS was employed to determine the valence states of elements in the surface and near-surface regions to identify the phase composition.

Results and Discussion

2.1 Protection Effect Figure 1 [Figure 1: see original paper] shows the macroscopic surface morphologies of AZ91D and pure Mg after holding in sealed conditions under SO /Air/N atmospheres with different Air contents. For AZ91D, when the Air content was 20%, the surface was covered with uniform cauliflower-like oxides, indicating no protection. At 40% Air content, only a few large cauliflower-like oxides formed, with most of the surface being protected. At 90% Air content, AZ91D was completely protected with no cauliflower-like oxides. Pure Mg exhibited similar dependence on Air content. These results demonstrate that a certain amount of air is necessary for SO -containing atmospheres to achieve complete protection of molten AZ91D and pure Mg.

2.2 Surface Film Structure Figure 2 [Figure 2: see original paper] presents cross-sectional and high-magnification surface SEM images of the film formed on AZ91D in a sealed furnace at 680 °C for 20 min in 0.5%SO /90%Air/9.5%N atmosphere (completely protected sample). A dense surface film formed with strong adhesion to the substrate, with thickness ranging from 0.5 to 1.5 m. The high-magnification image reveals granular oxides on the film surface and what appears to be a thin outer layer. XRD and EDS analysis results (Mg 55.0, O 38.2, S 2.5, Al 4.3, at%) indicate the film consists primarily of MgO with small amounts of S (Al originates from the substrate).

Figure 3 [Figure 3: see original paper] shows cross-sectional SEM images of films formed on pure Mg at 700 °C for 60 min in sealed conditions under 1.0%SO /20%Air/79%N (partially protected) and 1.0%SO /60%Air/39%N (completely protected) atmospheres. Figure 4 [Figure 4: see original paper] displays AES elemental depth profiles for these films. The partially protected sample exhibited a continuous but non-uniform film consisting of a single layer primarily composed of MgO, with only trace S at the film/substrate interface (Figure 4a). The completely protected sample showed a continuous, uniform film with a two-layer structure: a bright outer thin layer and a dense inner layer. Correspondingly, the AES profile reveals two main layers (Figure 4b): an inner layer containing Mg, O, and S with uniform compositional variation, and an outer layer containing only Mg and O. Since XRD analysis confirmed the presence of MgO and MgS, and the elemental atomic fractions in the inner layer approximately satisfy xS + xO = xMg (where xS(O,Mg) represents the atomic fraction of element S(O,Mg)), it can be concluded that the inner layer consists of MgO and MgS, while the outer layer is primarily MgO.

2.3 Surface Film Growth Process As established in Sections 2.1 and 2.2, protection of molten Mg and magnesium alloys by SO -containing atmospheres requires a certain amount of air. Therefore, studying film growth under open conditions (where air is present) is crucial for understanding the protection mechanism. Figure 5 [Figure 5: see original paper] shows AES elemental depth profiles for films formed on AZ91D at 680 °C in 0.5%SO +N atmosphere under open conditions for different holding times. After 60 min (Figure 5a), the film contains Mg, O, and S. Al does not participate in film formation but exists as Al O at the film/substrate interface. The film exhibits a two-layer structure: an outer layer of MgO and an inner layer containing Mg, O, and S (MgO + MgS). After 150 min (Figure 5b), the film contains only Mg, O, and S (MgO + MgS) without layered structure, though O content rises rapidly near the outermost surface, suggesting a thin layer of a new phase.

Figure 6 [Figure 6: see original paper] presents AES depth profiles and cross-sectional morphologies for films formed on pure Mg at 700 °C in 0.5%SO +N atmosphere under open conditions. After 3 min (Figure 6a), the film shows a two-layer structure: an inner layer containing only Mg and O, and an outer layer containing Mg, O, and S with O content slightly higher than Mg. After 10 min (Figure 6b), a similar two-layer structure exists, but the inner layer now also contains S. At 30 min (Figure 6c), a three-layer structure develops: an inner layer with uniform variation of Mg, O, and S; a middle layer where O content exceeds Mg; and an outer layer with high S content. After 90 min (Figure 6d), the film maintains a three-layer structure: a fine-grained inner layer with few pores, a dense middle layer with columnar grains, and a fine-grained outer layer.

2.4 Surface Film Surface Phase Composition The structural analysis suggests that AZ91D surface films may contain a thin surface layer of a new phase. For pure Mg, elemental depth profiles show significant variations: the inner layer satisfies xS + xO xMg and consists mainly of MgO and MgS, while the middle layer has O $>$ Mg and the surface layer has high S content, indicating possible new phases in the outer layers. XPS analysis was performed to determine element valence states in the surface region. Figure 7 [Figure 7: see original paper] shows high-resolution XPS spectra from the surface and at approximately 50 nm depth for a film formed on pure Mg at 730 °C in 0.5%SO +N for 10 min. Binding energies were calibrated using the C 1s standard (284.8 eV) [13].

The Mg 2p spectra (Figures 7a and 7b) show three peaks: at (49.3 ± 0.2) eV corresponding to Mg [13], at (50.3 ± 0.2) eV to MgO [14,15], and at (50.9 ± 0.2) eV to MgSO [14]. The O 1s spectra (Figures 7c and 7d) reveal three forms: at (529.4 ± 0.2) eV for MgO [15], at (531.9 ± 0.2) eV for MgSO [14], and at (532.8 ± 0.2) eV for MgCO [13] (from contamination). The S 2p spectra (Figures 7e and 7f) show a single peak at (169.3 ± 0.2) eV, corresponding to MgSO , indicating sulfur exists as MgSO in both the surface and at 50 nm depth. Therefore, the new phase formed in the surface film is MgSO .

Peak intensities in XPS reflect relative elemental concentrations. At the surface, the Mg 2p peak for MgSO (50.9 ± 0.2 eV) is stronger than those for Mg (49.3 ± 0.2 eV) and MgO (50.3 ± 0.2 eV), and the O 1s spectrum shows only the MgSO peak (531.9 ± 0.2 eV), indicating the surface layer (high S content) consists mainly of MgSO with minor MgO and Mg. At 50 nm depth, the Mg 2p peak for MgO (50.3 ± 0.2 eV) is stronger than those for Mg and MgSO , and the O 1s spectrum contains both MgO (529.4 ± 0.2 eV) and MgSO (531.9 ± 0.2 eV) peaks, suggesting the film at this depth consists primarily of MgO and MgSO with minor Mg. Combining AES and XPS results, the surface film formed on pure Mg under open conditions has a three-layer structure: an inner layer of MgO + MgS, a middle layer of MgO + MgSO , and an outer thin layer of MgSO .

2.5 Surface Film Growth and Protection Mechanism To understand the film growth and protection mechanism, thermodynamic analysis of Mg oxidation in SO - and O -containing atmospheres was performed. Figure 8 [Figure 8: see original paper] shows the Mg-O-S two-dimensional equilibrium diagram at 680 °C [16], including the isobaric line for SO at 5.0×10^{2} Pa and the state point for pure SO atmosphere. Points 1–4 correspond to actual atmosphere state points (considering only the equilibrium of SO decomposition to S and O).

The diagram indicates that at 680 °C, all atmosphere state points fall within the MgSO stability region (even at 0.1% Air), suggesting MgSO should be the final oxidation product, while MgO and MgS should not form. This contradicts experimental observations, indicating that MgO and MgS formation cannot be explained by the Mg-O-S equilibrium diagram alone and requires consideration of changing thermodynamic conditions during film growth. Additionally, increasing Air content moves the state point deeper into the MgSO stability region, enhancing MgSO stability.

Based on these results, the film formation process is proposed as follows: Due to abundant O in open atmospheres and the high reactivity of Mg with O , a rapid initial MgO film forms on the molten Mg and AZ91D surface. Since MgSO is thermodynamically stable, it subsequently forms on the outer side of the initial film (Figure 6a). Meanwhile, the porous MgO structure [17] allows SO molecules to penetrate through macro- and micro-pores between MgO grains, reacting with Mg vapor to form MgS within the film (Figures 5a and 6b). MgS has a Pilling-Bedworth ratio of 1.4 [7,18] and can form a dense, effective protective film with MgO.

With a Pilling-Bedworth ratio of 3.2 [7], MgSO formation on the film exterior is crucial for protective film development. Thermodynamic calculations show MgSO is the stable phase, while MgO and MgS should not form. However, once MgSO forms on the film exterior, it creates a dense protective layer with MgO that significantly impedes SO and O transport into the film. This reduces gas pressure within the film, altering the thermodynamic state such that MgSO is no longer stable, allowing MgO and MgS to form and exist stably (Figures 5b, 6c, and 6d).

Under sealed conditions, increasing Air (O) content enhances MgSO stability and promotes its formation in the outer film layer, facilitating development of the protective MgO + MgS film (Figures 2, 3b, and 4b) and achieving complete protection of molten Mg and AZ91D (Figures 1e and 1f). At low Air (O) content, combined with O consumption by reaction, the state points in Figure 8 (e.g., points 1-3) shift into the MgO stability region where MgSO is no longer stable and cannot form in the outer layer. The film then forms primarily through Mg-O reaction, with limited SO transport to the substrate-film interface producing minor MgS (Figures 3a and 4a). Cauliflower-like oxides form where MgS cannot develop, resulting in only partial protection (Figures 1c and 1d). At very low Air (O) content, only MgO forms, providing no protection (Figures 1a and 1b).

2.6 Surface Film Stability Although MgSO formation is crucial for protective film development, its high Pilling-Bedworth ratio of 3.2 can cause film cracking and loss of protection if excessive MgSO forms within the film [18]. Therefore, protective film stability is equally important. Figure 9 [Figure 9: see original paper] shows oxidation weight gain curves for AZ91D at 700 °C in various atmospheres. In SO /Air atmospheres (Figure 9a), at 0.03%, 0.1%, and 0.3% SO , AZ91D mass increased rapidly within 15–20 min, indicating violent oxidation and ignition. At 0.4% and 0.5% SO , mass gain was slow during the first 60 min (~3 mg/cm^2), then increased rapidly until ignition. This suggests a protective film forms initially but gradually loses effectiveness. At 1.0% and 2.0% SO , mass gain remained slow throughout, indicating formation of a stable protective film that grows without cracking. Thus, when using SO /Air atmospheres, SO concentration must be adjusted based on operating conditions, with higher concentrations improving protection.

In 0.4%SO /Air/N atmospheres (Figure 9b), at 20% Air, AZ91D showed slow mass gain for 60 min before rapid oxidation and ignition. At 50% Air, violent oxidation began around 110 min. At 80% Air, mass gain remained slow throughout the test. However, at 90% Air, violent oxidation occurred at 60 min. Therefore, when using SO /Air/N atmospheres with fixed SO content, Air content must be neither too high (which promotes excessive MgSO formation, causing film cracking and protection loss) nor too low. Stable protection requires an appropriate Air content.

Conclusions

(1) Under sealed conditions in SO /Air/N atmospheres with fixed SO content, increasing Air content improves protection of AZ91D and pure Mg. When Air content exceeds the critical value for MgSO formation, complete protection is achieved.

(2) In SO /Air/N atmospheres, an initial MgO layer forms on the melt surface, followed by sequential formation of MgSO and MgS within the film. AZ91D protective films consist mainly of MgO and MgS with minor MgSO in the outermost layer. Pure Mg protective films comprise MgO, MgS, and MgSO with different layer structures under open and sealed conditions.

(3) During Mg oxidation in SO - and O -containing atmospheres, MgSO is the thermodynamically stable phase. Its formation on the film exterior facilitates MgS formation inside the film, thereby enhancing the protectiveness of the MgO film.

(4) For melting of pure Mg and magnesium alloys, SO /Air atmospheres can be used as protective gases, with increased SO concentration improving protection. SO /Air/N atmospheres can also be used, but when SO content is fixed, Air content must be neither too high nor too low to maintain stable protection.

References

[1] Jafari H, Idris M H, Ourdjini A. Corros Sci, 2011; 53: 655

[2] Bartos S C. In: Hryn J ed., Magnesium Technology 2001, Warrendale, PA: TMS, 2001: 43

[3] Ricketts N J, Cashion S P, Bailey R. In: Dahle A ed., Proc 1st Int Light Metals Technology Conference, Brisbane, Australia: CAST, 2003: 275

[4] Mirak A, Davidson C J, Taylor J A. Corros Sci, 2010; 52: 1992

[5] Fruehling J W. PhD Dissertation, University of Michigan, America, 1970

[6] Pettersen G, Øvrelid E, Tranell G, Fenstad J, Gjestland H. Mater Sci Eng, 2002; A332: 285

[7] Aarstad K. PhD Dissertation, Norwegian Universtity of Science and Technology, Norway, 2004

[8] Ha W, Kim Y J. J Alloys Compd, 2006; 422: 208

[9] Argo D, Lefebvre M. In: Kaplan H I ed., Magnesium Technology 2003, San Diego, USA: TMS, 2003: 15

[10] Schubert W, Gjestland H. In: Kainer K U ed., Magnesium Alloy and Their Applications, Weinheim, Chichester: Wiley, 2000: 761

[11] Cashion S P. PhD Dissertation, University of Queensland, Australia, 1998

[12] Cashion S P, Ricketts N J. In: Kaplan H, Hym J, Clow B eds., Magnesium Technology 2000, Warrendale, PA: TMS, 2000: 77

[13] Moulder J F, Stickle W F, Sobol P E, Bomben K D. Handbook of X-ray Photoelectron Spectroscopy, Eden Prairie, MN: Perkin-Elmer, 1992

[14] Ardizzone S, Bianchi C L, Fadoni, M, Vercelli B. Appl Surf Sci, 1997; 119: 253

[15] Wang X M, Zeng X Q, Zhou Y, Wu G S, Yao S S, Lai Y J. J Alloys Compd, 2008; 460: 368

[16] Barin J, Knacke O. Thermochemical Properties of Inorganic Substances. Berlin: Springer Verlag, 1973, Suppl 1977

[17] Liu M, Shih D S, Parish C, Atrens A. Corros Sci, 2012; 54: 139

[18] Pilling N B, Bedworth R E. J Inst Met, 1923; 28: 534

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv –Machine translation. Verify with original.