Effects of cover gases on melt protection of Mg alloys

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Abstract

Melt protection properties of inhibitor (SF_6, HFC-134a and SO_2)/air cover gas mixtures were investigated for different magnesium alloys, temperatures, gas concentrations and sealing conditions. Melt protection properties of the surface films formed in cover gas mixtures were also investigated for ambient atmosphere. The compositions of surface films formed in various cover gas mixtures were analyzed by X-ray photoelectron spectroscopy (XPS). For both under cover gas mixtures and ambient atmosphere, the surface film formed in HFC-134a with air cover gas mixtures provided effective melt protection properties for all test conditions. SO_2 showed the same melt protection properties as SF_6 for 680 °C whether the crucible is tightly sealed or not. XPS results revealed that the surface films formed under fluorine-bearing cover gas mixtures consist of MgO and MgF_2. Magnesium fluoride which has high Pilling–Bedworth ratio (PBR) can act as a barrier to further oxidation and evaporation of magnesium due to its dense and continuous structure.
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1. Introduction

Magnesium is the lightest of all structural metals and is thus very attractive for applications in transportation. The total vehicle weight can be reduced by using magnesium alloy components, such as seat frame, instrument panel, steering column, and transmission housing. Each 10% saving in dead weight of a motor vehicle corresponds to an increase in fuel economy of 5.5% [1]. This, in turn, means reduced exhaust emissions. However, sulfur hexafluoride (SF_6), which is one of the most potent greenhouse gases currently known, is commonly used during melting and casting of magnesium alloys to prevent the ignition of the melt. Its global warming potential is about 23,900 times worse than carbon dioxide (100-year time horizon), and for this reason it has come under intense environmental scrutiny [2]. The Kyoto Protocol calls for a reduction in SF_6 use. Environmental and economical concerns have caused the magnesium industry to look for possibilities to replace or reduce the outlets of SF_6 in the casting process.

Hydrofluorocarbon (CF_3CH_2F, HFC-134a) has been recently developed for magnesium melt protection by the Cooperative Research Center for Cast Metals Manufacturing in Australia [3]. Global warming potential of HFC-134a is 18 times lower than SF_6 and its atmospheric lifetime is only 0.46% of SF_6. Another candidate for the replacement of SF_6 is SO_2, which is the gas most commonly employed prior to the introduction of SF_6 in the 1970s. It is toxic, corrosive and can cause the acid rain, but it is cheap and easy to be extracted from gas mixtures by using its high solubility in water [4].

A lot of works, such as the oxidation nature of magnesium alloys [5–8] and investigation for the melt protection mechanism of inhibitor gases [9–12], has been carried out by many researchers. Considering the results of previous works and the practical aspect of using candidate gases, the selection of suitable candidate gases for the replacement of SF_6 and the investigation of melt protection properties of selected gas is required. In this study, the melt protection properties of HFC-134a and SO_2 were investigated and compared with that of SF_6. From the practical point of view, the investigations of melt protection properties of these gases were carried out under three different testing conditions:

1. Sealed condition: Standard condition for both cold and hot chamber die-castings. Furnace is tightly sealed. Molten magnesium alloy is under controlled atmosphere.

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2. Unsealed condition: Frequently happened condition. A certain area of furnace cover is opened to feed preheated ingots or to ladle melt into sleeve of cold chamber die-casting machine.

3. Atmospheric condition: Usually happened condition in permanent mold or sand casting for the production of ingots or parts in ambient atmosphere. The whole melt surface is exposed to an ambient atmosphere.

2. Experimental procedure

2.1. Melt protection properties of cover gas mixtures

A schematic illustration of melt protection property evaluation system is shown in Fig. 1. About 4 kg of AZ91D (or AM60B, hydro magnesium, Be content of the alloys is under 6 ppm) was melted in AISI 1020 mild steel crucible at 680 °C (or 720 °C) under 0.3% inhibitor (SF_6 or HFC-134a or SO_2)/air cover gas mixtures. Then, gas concentration was adjusted to a given value (0.02–0.3%). The initial oxide film was removed by steel scraper through the hole of steel cover to react the molten magnesium with controlled cover gas mixtures. Melt state was observed through the hole for 10 min in sealed condition (quartz window closed) or unsealed condition (quartz window opened). Carbon dioxide is commonly added for enhancing the melt protection properties of cover gas mixtures [13]. In this study, however, CO_2 was not added for the evaluation of melt protection properties of inhibitor gas only. Total amount of inhibitor/air cover gas mixture was 10 l/min. The area of melt surface and the hole of steel cover are 530.7 and 95 cm^2, respectively.

2.2. Melt protection properties of surface films in ambient atmosphere

Melt protection properties of the surface films in ambient atmosphere were evaluated for AM60B alloy. About 4 kg of AM60B melt was exposed to 0.3% SF_6 (or HFC-134a or SO_2)/air cover gas mixtures to form oxide film for 10 min at 680 °C (or 720 °C). Subsequently, steel cover (4), gas-in tube (5), quartz window (6), and gas-out tube (7) were removed to expose the oxide film to atmospheric condition. The elapsed time until the film ignited was measured.
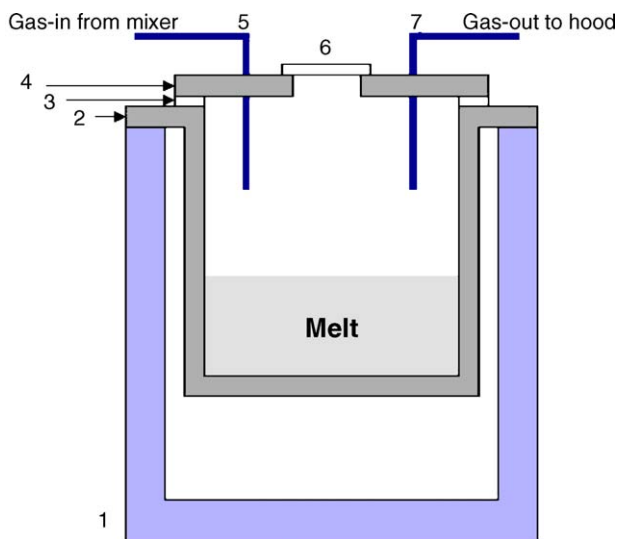

Fig. 1. Melt protection property experiment system: (1) furnace, (2) crucible, (3) ceramic wool, (4) steel cover, (5) gas-in tube, (6) quartz window, and (7) gas-out tube.
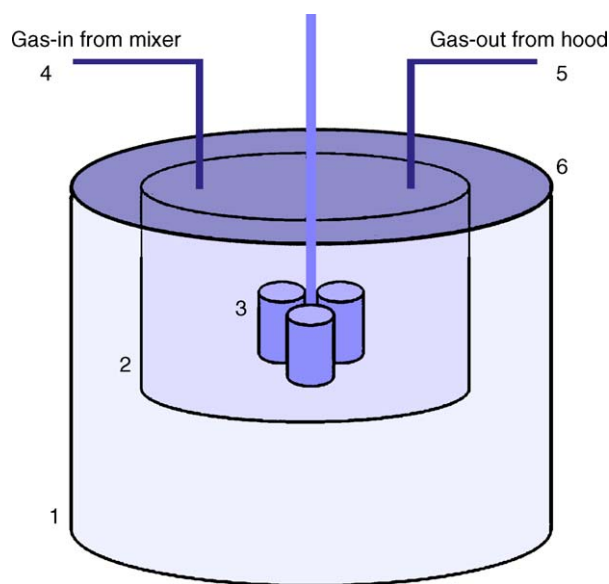

Fig. 2. Surface film formation system: (1) furnace, (2) steel chamber, (3) quartz crucibles, (4) gas-in tube, and (5) gas-out tube.

2.3. Surface film composition analysis

The surface film formation system is shown in Fig. 2. About 40 g of pure magnesium was melted in three different quartz crucibles under 0.5% (or 1.0%) SF_6 (or HFC-134a)/air gas mixtures at 720 °C. The initial oxide film was removed by steel scraper for the formation of a new surface film. Each quartz crucible was removed from the furnace after the film formation times of 100, 300, and 500 min. The melt in the quartz crucibles was rapidly and carefully solidified to get the surface films. The chemical characterization of the surface films was performed using X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA2000, 13 kV, 13 mA, Al Kα).

2.4. Comparison of crucible damage for various cover gas mixtures

Crucible damage by corrosive characteristics of inhibitor gas or its thermal decomposition products was evaluated by exposing mild steel crucible (AISI 1020) to ambient air (0% inhibitor/air), 0.3% SF_6 (or SO_2 or HFC-134a)/air cover gas mixtures at 720 °C for 5 h.

3. Results and discussion

3.1. Melt protection properties of cover gas mixtures

Required inhibitor concentrations for magnesium melt protection in various inhibitors, test temperatures and sealing conditions are shown in Fig. 3. HFC-134a/air cover gas mixtures provided excellent melt protection properties for all test temperatures, sealing conditions and alloys. Required inhibitor concentration of HFC-134a/air cover gas mixture for melt protection was only 0.03% for most stable state of low melt temperature (680 °C) and sealed condition. HFC-134a/air cover gas mixtures also protected the melt effectively at concentration as low as 0.1% even in severe state of high melt temperature (720 °C) and unsealed condition. SF_6 and SO_2 gas mixtures showed the same melt protection properties at low melt temperature whether the crucible was tightly sealed or not, even though the required inhibitor concentration of SF_6 was lower than that of SO_2 at high
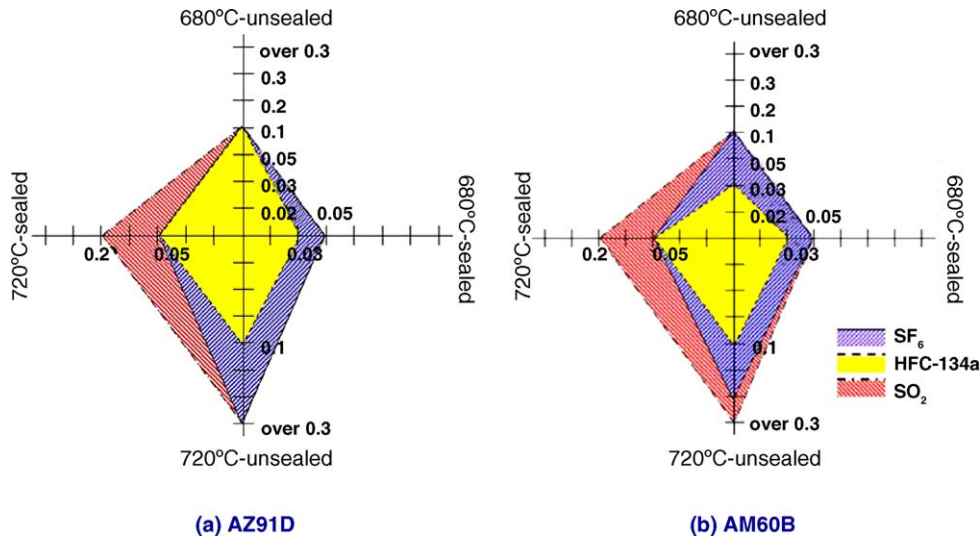
Fig. 3. Required inhibitor concentrations of HFC-134a, SF$_6$, SO$_2$/air cover gas mixtures for different alloys, test temperatures, and sealing conditions (unit: vol%).

melt temperature. SF$_6$ and SO$_2$/air cover gas mixtures could not protect AZ91D melt at high concentration of 0.3% for high melt temperature and unsealed condition. For AM60B melt, 0.3% SF$_6$/air cover gas mixtures protected the melt while the melt ignited under SO$_2$/air cover gas mixture of the same concentration. Required inhibitor concentrations for the protection of AM60B were the same or lower than that of AZ91D because the addition of aluminum to magnesium increases the rate of oxidation progressively, up to the limit of the solid solubility of aluminum in magnesium [5]. HFC-134a can be used as a replacement of SF$_6$ due to its excellent melt protection property and SO$_2$ also can be a good candidate because the typical die-casting temperatures of AZ91D and AM60B alloys are under 680 °C [14].

3.2. Melt protection properties of the surface films in ambient atmosphere

The average elapsed times, which the surface films keep their surface stable until ignition, are shown in Fig. 4. The
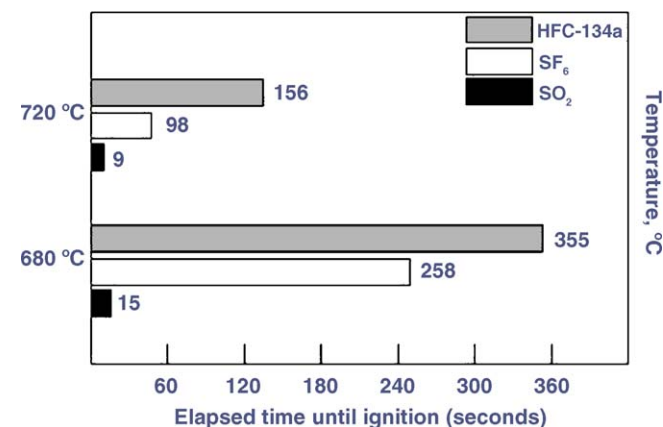

Fig. 4. Average elapsed times which the surface films keep their surface stable until ignition.

main reaction in the experiment under cover gas mixtures occurs between liquid metal and cover gas mixture because the initial oxide film is removed and fresh liquid metal react with controlled atmosphere. However, there is the solid surface film which formed in 0.3% inhibitor/air atmosphere for 10 min between metal and cover gas mixture for the experiment in ambient atmosphere. The property of surface film may be a major factor that has an influence on the melt protection property because the pre-existing solid surface film is exposed to ambient atmosphere. Another important factor is relative densities of the inhibitor gases because inhibitor/air cover gas mixture is exhausted from the crucible and ambient air is incorporated after the steel cover, gas tube and quartz window are removed. The surface films formed in HFC-134a/air cover gas mixture also showed excellent melt protection properties in ambient atmosphere for both 680 and 720 °C. The surface films formed in HFC-134a/air cover gas mixture protect the melt for 355 and 156 s, while that formed in SF$_6$/air cover gas mixture began to burn after 258 and 98 s, at 680 and 720 °C, respectively. Relative densities of the inhibitor gases are 5.1 (SF$_6$, air = 1), 3.5 (HFC-134a), and 2.3 (SO$_2$) [15–17]. SF$_6$ can offer better blanketing effect than other gases due to its high vapor density. However, the surface film formed in HFC-134a/air cover gas mixtures showed relatively good melt protection property in spite of poor blanketing effect. SO$_2$ is 2.3 times heavier than air though it is the lightest one among the three tested gases. Moreover, SO$_2$ and SF$_6$ showed the same melt protection property at 680 °C, sealed and unsealed condition for the experiment in protective atmosphere. However, the surface film formed in SO$_2$/air cover gas mixtures kept its surface stable only for 15 s for the experiment in ambient atmosphere. These mean that the melt protection properties of the surface films formed in HFC-134a or SF$_6$ cover gas mixture have dominantly originated from the surface film's own characteristics but that formed in SO$_2$/air cover gas mixture depends on the cover gas mixtures.

Table 1
Peak positions (in eV) of the surface film elements, for the surface films produced under SF_6 or HFC-134a/air atmosphere with various inhibitor concentrations and exposure time

	Exposure conditions					
	100 min		300 min		500 min	
	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
Under SF_6/air atmosphere						
O (1s)	532	530.81	530.8	531.28	531.66	531.3
Mg (2p)	50	50.8	50.8	50.28	50.66	51.3
F (1s)	686	685.8	685.8	685.28	685.66	685.3
Under HFC-134a/air atmosphere						
O (1s)	531.52	531.4	531.33	531.11	531.03	531.35
Mg (2p)	50.52	50.4	50.33	50.11	50.03	50.35
F (1s)	685.52	686.4	685.33	685.11	685.03	685.35

3.3. Surface film composition

The peak positions from XPS spectra are used to determine the chemical bonding between the elements in the surface film. Table 1 shows peak positions of the surface film elements produced under SF_6 or HFC-134a/air atmosphere. Mea-
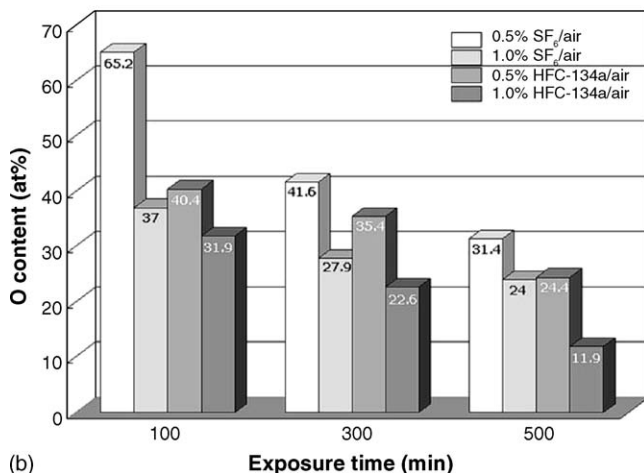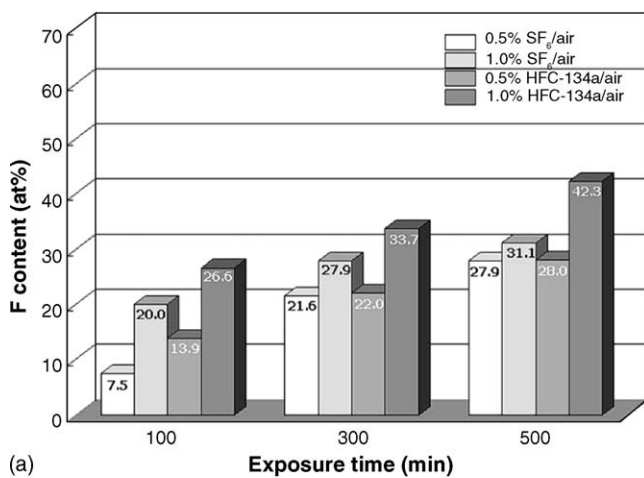
sured values correspond to the peak position ranges for MgO (530.0–532.1 eV) and MgF_2 (685.4–685.75 eV) [18,19]. Fig. 5 shows fluorine (Fig. 5a) and oxygen (Fig. 5b) content of the surface film determined by XPS spectra. There is no significant trend in the content of magnesium for changes in inhibitor concentration and exposure time. Fluorine content increases with increasing inhibitor concentration and exposure time while oxygen content decreases. Cashion et al. [19] reported that the fluorine content of the surface film increased with increasing inhibitor concentration (0.1–1% SF_6) in the cover gas mixtures but the exposure time (1–100 min) has no significant effect on the content of magnesium, oxygen and fluorine in the surface film for the melt temperature of 700 °C. It is impossible to compare Cashion's and our results because experimental conditions have some differences in the range of exposure time, inhibitor concentration, melt temperature and total gas flow rate. However, fluorine content of the surface film with increasing inhibitor concentration shows the same tendency. Higher fluorine content was detected for the surface film formed in HFC-134a/air cover gas mixture compared with the film formed in SF_6/air cover gas mixture of the same inhibitor concentration and exposure time. SF_6 is more stable than HFC-134a. Atmospheric lifetime of SF_6 is 200 times longer than that of HFC-134a [2]. Thermal decomposition of SF_6 starts from 800 °C but that of HFC-134a starts from 250 °C, although decomposition tendency depends on the moisture content of inhibitor or carrier gas and presence of catalytic materials [15,20,24]. It is assumed that thermally unstable HFC-134a provides fluorine easier than SF_6 as a thermal decomposition product and molten magnesium forms more magnesium fluoride under HFC-134a/air cover gas mixture.

Table 2 shows the equilibrium vapor pressure of magnesium and several metals [21]. Vapor pressure of magnesium is extremely higher than other metals, which shows stable melt state and cast usually in ambient atmosphere. Liquid magnesium evaporates easily due to its high vapor pressure and oxidizes rapidly with the generation of large amount of heat. The surface film should cover the molten magnesium to prevent further evaporation and oxidation of magnesium. The Pilling–Bedworth ratio (PBR), the ratio of oxide volume produced to metal volume consumed, of magnesium is 0.73, and the oxide tends to be porous and non-protective because it cannot cover the whole melt surface [22]. However, the surface film which consists of magnesium oxide (PBR = 0.73) and magnesium fluoride (PBR = 1.29) is fine-grained and dense layer as reported by Pettersen et al. [11], and thus it can cover the larger area of the melt surface and act as a barrier to further oxidation because magnesium fluoride increases PBR of the surface film closer to unity. From the facts that HFC-134a provides fluorine easier than SF_6 and fluorine content of the surface film increases with increasing inhibitor concentration, the superior melt protection property of HFC-134a/air cover gas mixture comes from high proportion of magnesium fluoride in the surface film.

Fig. 5. Fluorine (a) and oxygen (b) content of the surface film determined by XPS spectra.

3.4. Mild steel crucible damage by cover gas mixtures

Anhydrous SO_2, SF_6, HFC-134a gases are non-corrosive at room temperature. However, some corrosion issues are present

Table 2
Equilibrium vapor pressure of liquid metals as a function of temperature

	Equilibrium vapor pressure at melting point (mmHg)	Equilibrium vapor pressure at 680 °C (mmHg)	Equilibrium vapor pressure at 720 °C (mmHg)	Melting point (°C)
Magnesium	2.69	4.65	9.14	650
Aluminum	6×10^{-9}	1.4×10^{-8}	6.7×10^{-8}	660
Tin	3.44×10^{-23}	9×10^{-9}	4.1×10^{-8}	232
Gold	6.17×10^{-6}	–	–	1063
Lead	3.6×10^{-9}	3.98×10^{-3}	2.8×10^{-2}	328

at molten magnesium temperatures [3]. Fig. 6 shows the inside of the crucible exposed to ambient atmosphere (Fig. 6b), 0.3% SF$_6$/air (Fig. 6c), 0.3% SO$_2$/air (Fig. 6d), and 0.3% HFC-134a/air (Fig. 6e and f), at 720 °C for 5 h. There are no significant differences between the surface morphology of the crucibles, which were exposed to ambient air, SO$_2$/air, and SF$_6$/air cover gas mixtures. The surface of mild steel crucible was slightly

damaged. However, the crucible, which was exposed to HFC-134a/air cover gas mixture, was seriously damaged. The oxide layers of 2–3 mm thickness were buckled and peeled. This result on the corrosive property of HFC-134a/air cover gas mixtures at molten magnesium temperature is well matched with Ricketts and Cashion's recent works [23,24]. They showed that the corrosion is severe when using dry air as the diluent gas for
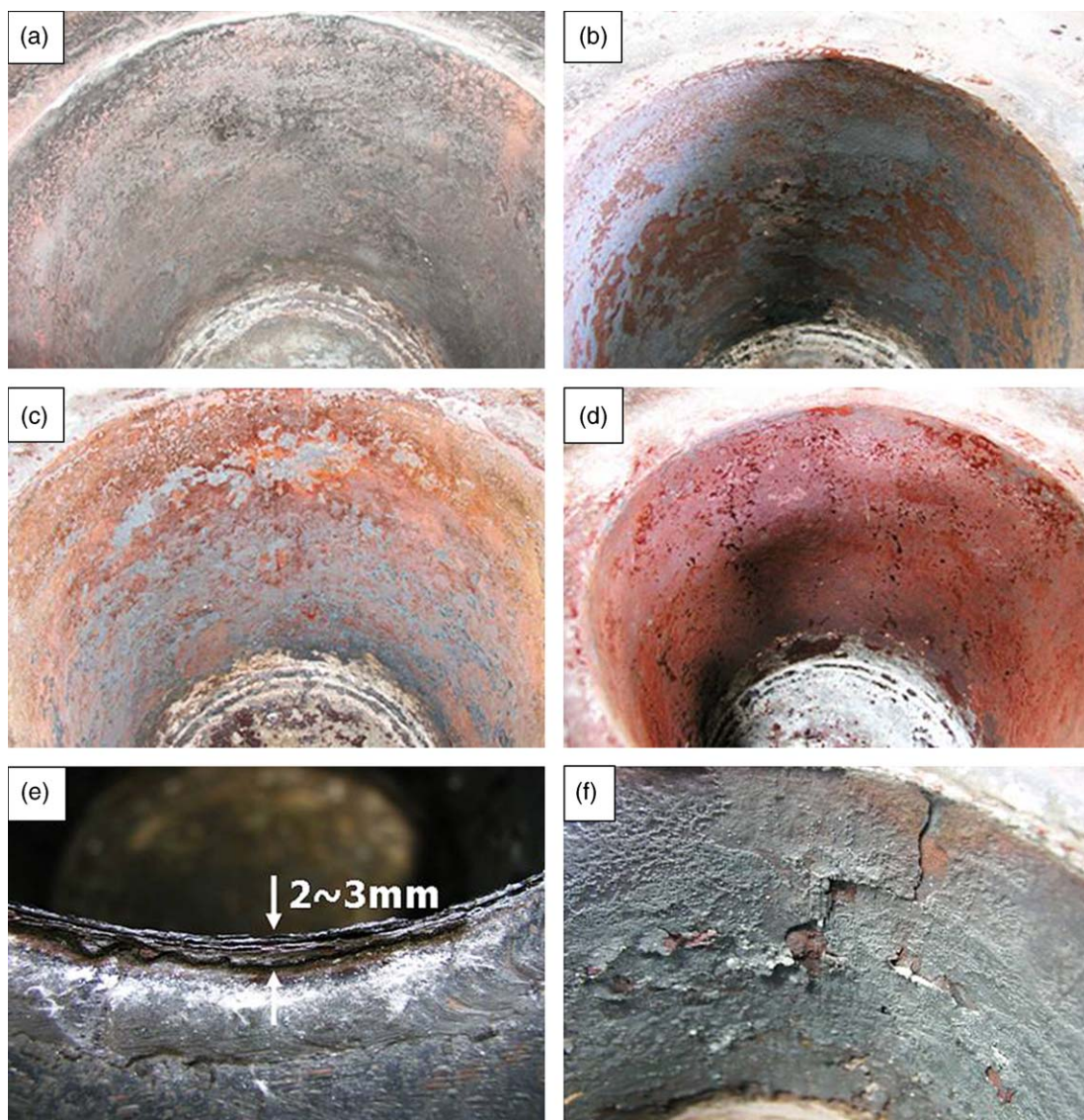

Fig. 6. AISI 1020 mild steel crucible surface: (a) before exposure, (b) exposed to ambient atmosphere-720 °C-5 h, (c) exposed to 0.3% SF$_6$/air-720 °C-5 h, (d) exposed to 0.3% SO$_2$/air-720 °C-5 h, (e) and (f) exposed to 0.3% HFC-134a/air-720 °C-5 h.

HFC-134a due to the formation of highly corrosive hydrogen fluoride, the thermal decomposition product of HFC-134a and the formation of hydrogen fluoride can be inhibited dramatically when using nitrogen or carbon dioxide as the diluent gas. In this study, high purity synthetic air was used as the diluent gas to evaluate melts protection or chemical properties of inhibitor gas only. However, considering the corrosive property of HFC-134a shown in this study and Ricketts and Cashion's work, it seems that single air should not be used as the diluent gas for practical use of HFC-134a as a replacement of SF_6.

4. Conclusions

Melt protection properties of environmentally conscious HFC-134a/air and SO_2/air cover gas mixtures were investigated and compared with that of SF_6/air cover gas mixtures for protective and ambient atmosphere. The surface film formed in fluorine bearing gases, HFC-134a and SF_6, showed better melt protection properties than that formed in fluorine free gas, SO_2, for both protective and ambient atmosphere. SO_2 showed acceptable melt protection property only for protective atmosphere. Fluorine bearing gases provide fluorine as a thermal decomposition product and the fluorine forms magnesium fluoride, which prevents further evaporation and oxidation of magnesium. HFC-134a provided fluorine easier than SF_6 due to its relatively low thermal stability at molten magnesium temperature and the surface film, which formed in HFC-134a/air cover gas mixtures, contains more magnesium fluoride than that formed in SF_6 cover gas mixtures. In case of using air as a diluent gas for HFC-134a, highly corrosive hydrogen fluoride can be formed as a thermal decomposition product and can cause severe corrosion problem for magnesium melting devices. Suitable diluent gases, such as nitrogen or carbon dioxide should be used for the use of HFC-134a as an inhibitor gas.

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