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Magnesium Melt Protection

NORBERT Hort^{a,*}, BÖRN Wiese^b, HAJO Dieringa^c, KARL Ulrich Kainer^d

Magnesium Innovation Centre, Helmholtz-Zentrum Geesthacht
D-21502 Geesthacht, Germany

^anorbert.hort@hzg.de, ^bboern.wiese@hzg.de, ^chajo.dieringa@hzg.de,
^dkarl.kainer@hzg.de

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Abstract. Mg especially in the molten state is well known for its high affinity to O₂. When O₂ content of the atmosphere is larger than 4%, molten Mg will burn! To avoid this, melt protection is necessary. At present mostly SF₆ is used during primary production and processing of Mg and its alloys. Unfortunately SF₆ is a very potent greenhouse gas that is > 23,000 times more effective than CO₂. This also affects life cycle considerations e.g. for the use of Mg alloys in transportation. However, other protective gases like SO₂ or fluorinated hydrocarbons like HFC134a, Novec 612, or AMCover (=HFC134a) have been suggested to replace SF₆. Additionally fluxes mixed from different salts may be used again as well to protect molten Mg. But fluxes and feasible replacements of SF₆ also have disadvantages. Moreover SF₆ and other fluorinated hydrocarbons are under discussion especially in Europe. There is an existing EU legislation that will ban SF₆ from 2018 and there are similar discussions regarding all other fluorinated hydrocarbons. Due to this, new innovative ways have to be found or old methods have to be renewed to allow Mg industries further safe processing of molten magnesium. This contribution will report the state of the art in protecting molten Mg and alternatives to the use of SF₆.

Introduction

Like other metals Mg forms an oxide film during melting operations. But unlike other metal and alloy oxide films MgO does not stick to the melt surface, it is not dense and it will get thicker over time. Basically the film that forms on molten Mg has a Pilling-Bedworth ratio (PBR) < 1 [1]. This allows steady access of O₂ to the melt surface and therefore continuous oxidation (= burning melt). Additionally the vapour pressure of molten Mg and its alloys is very high and allows Mg to evaporate easily. Deposits of extremely fine powder will form at colder areas around the Mg melt. Due to the high ratio of surface to volume this Mg dust can also easily ignite [2]. Therefore it is absolutely necessary to avoid oxidation and also to control evaporation of Mg from the melt. To achieve this, some opportunities are available like the use of fluxes, protective gases, alloying elements etc. The following text will discuss the different ways of melt protection and consequences.

Fluxes. The use of fluxes is very traditional since the early days of Mg industries [3,4]. Fluxes have been used for refining as well as for melt protection and they consist mainly of different fluorides and chlorides. They can prevent molten Mg effectively from burning but they also can be incorporated into components during casting. The flux contamination of melts during casting can negatively affect mechanical properties as well as corrosion behaviour. However, two major techniques have been in use:

Dow Technique [4]: Melting in a bath of protective flux containing a few percent of CaF_2 is recommended for small castings. In this process the melt for the castings is poured from below the melt surface. The ladle used has a blade at the lower side to cut the film of the flux covering the melt surface. For larger casting the use of an inspissated flux is recommended. Before pouring the melt for casting, the covering flux is completely removed.

Elektron Technique [4]: This two-step process resembles the older I.G. Farbenindustrie process. A fluid flux (Melrasal Z) was used for melting the ingots or scrap and after melting a more inspissated flux (Melrasal E) was used for casting and stirred into the melt. Prior to pouring the pasty viscous cover of the inspissated flux was drawn away from the lip of the crucible.

Sulphur and SO_2 . S powder was already in use in the early days of Mg castings at the beginning of the 20th century [3]. It reacts with oxygen to SO_2 and basically SO_2 is then responsible for the protection of molten Mg. This idea was further developed to the direct use of SO_2 together with carrier gases (dry air, CO_2 , or $\text{N}_2 + 0.5\text{-}1.0\% \text{SO}_2$) to effectively protect molten Mg. However, SO_2 itself is toxic and maximum allowable concentrations at the working place have to be respected. In combination with H_2O SO_2 will react to sulphurous acid H_2SO_3 . Sulphurous acid attacks especially all steel crucibles and tools that are used to handle molten Mg [4,6]. However, today SO_2 is often recommended as a suitable SF_6 replacement in the EU [7].

SF_6 and Fluorinated Hydrocarbons. At present mostly SF_6 is used during primary production, processing and recycling of Mg and its alloys. SF_6 is a stable, non-toxic, odour-less gas. It was first mentioned in 1934 and got introduced for melt protection almost 30 years ago [8,10]. Unfortunately SF_6 is a very potent greenhouse gas with a global warming potential (GWP) of $> 23,000$ compared to CO_2 [5]. This also affects life cycle considerations e.g. for the use of Mg alloys in transportation [11]. However, the full mechanism of how SF_6 protects molten Mg still is not fully understood. But there is evidence that SF_6 reacts together with Mg and O_2 and is able to form a stable and sticking film on Mg with a PBR > 1 [9]. To achieve this, minor concentrations in the range of 0.2-0.5 % SF_6 in a carrier gas are used. Carrier gases can be Ar, CO_2 , N_2 , dry air etc. However, the presence of O_2 also seems to be necessary.

From own experience it can be reported, that after the consumption of O_2 mixtures of N_2 - SF_6 mixtures could lead to an exothermic reaction as well. In this case Mg reacts exothermically with N_2 and Mg_2N_3 can form. Regardless of the efficiency of SF_6 it is having impact as a climate gas. Compared to CO_2 the GWP of SF_6 is $> 23,000$. And basically this is one of the reasons why in EU SF_6 will be banned from 2018 on [13]. There are similar considerations regarding all other fluorinated hydrocarbons (FHC).

FHC like HFC134a, HFE7100, Novec 612 etc. are regarded as a candidate to protect molten Mg and to replace SF_6 [12]. Their reaction mechanism seems to be similar to that of SF_6 and is based on reactions of F with Mg and O_2 . However, the GWP of most FHC is much less than that of SF_6 [13]. Their use is not as easy as the use of SF_6 . Generally the feeding has to be adjusted to the geometry and service parameters of the melting and casting devices. But FHC can effectively protect molten Mg.

However, SF_6 and FHC contain fluorine and they react with molten Mg. F is set free, reacts with Mg vapour and Mg melt surfaces and the MgF contributes to the film formation. But when set free in an excess amount, free fluorine can react with humidity ($=\text{H}_2\text{O}$) and forms HF. HF is highly toxic and its maximum allowable concentration at working places must not be exceeded. The toxicity is one reason why the EU tries to ban SF_6 and other fluorine containing gases besides their GWP [5, 13].

Ar, N₂, CO₂. As a noble gas Ar can protect molten Mg to a certain extent. It is heavier than air and could replace it, avoiding oxidation of melts. However, this would be only working well in a fully closed environment, where Ar cannot diffuse and mix with the atmosphere. Additionally Ar is not very effective in suppressing the evaporation of Mg from the melt and compared to other gases it is rather expensive.

Quite often N₂ is also regarded as an inert gas. However, in the case of Mg and its alloys it reacts with the melt forming Mg₂N₃. This nitride can form ammonia in the presence of humidity. To a certain extent this can be controlled [14]. But basically N₂ is a carrier gas for SF₆ or other FHC.

CO₂ snow or solid CO₂ are also used for Mg melt protection [15]. It cools the top of the Mg melt, lowers vapour pressure and inhibits air making contact with the molten Mg. The GWP of solid CO₂ is 1, provided that the production of solid CO₂ snow is not considered. The disadvantage is the generation of highly toxic carbon monoxide and solid carbon on the interface between melt and CO₂. This technology is patented but not currently used commercially.

Be, Ca/CaO. Be is an element, that is present in almost any pure Mg or Mg alloy. In contents lower than 4 ppm it reduces flammability [3,6]. It is added to pure Mg directly after primary production by Al-Be master alloys. In an investigation from 1953 [HUDDLE1953], Mg-Al-Be and Mg-Al-Ca-Be can be molten in air without ignition. However, in amounts > 10 ppm, Be coarsens the microstructure of Mg castings and deteriorates mechanical properties [4,6].

Ca and CaO can form protective films with a PBR > 1, but providing protection in binary alloys. The effect of Ca on the oxidation resistance was known for a long time [3, 4]. However, the explanation on how CaO is incorporated in to the oxide layer of Mg-Ca has not been completely clarified. Studies show an improvement of the ignition resistance, but often also the formation of Mg₂Ca or Al₂Ca. These intermetallic compounds reduce the ductility of Mg alloys. Recently the idea came up to replace Ca by CaO to achieve similar results on the ignition resistance in the processing of Mg [16-19]. The effects of Ca and CaO in comparison are showing that CaO is a cost efficient way to substitute Ca for this purpose [18].

Summary

SF₆ and several FHC will be banned in the EU from 2018 on. For further successful production and processing replacements for SF₆ and FHC have to be established in Europe until 2018. Additionally the REACH legislation also affects other countries who want to export Mg and its alloys or products made from these materials. Therefore the world outside the EU will also be affected and has to use Mg melt protection that is in agreement with European legislation as long as the EU is a target market.

Actually the use of fluxes or SO₂ might be an alternative. While the first still may incorporate impurities to the melt, the latter is connected with strict maximum concentrations at work places due to its toxicity. Both alternatives perhaps will limit future Mg applications at least in Europe.

The use of Ca/CaO can be a solution for some alloys. It effectively can reduce the flammability of Mg alloys. But Ca is also an effective alloying element that influences mechanical properties, corrosion behaviour etc. However, while Ca is well known to improve properties of some creep resistant alloys, it also causes problems with castability in high pressure die casting when used in the range of 2%.

If it is not possible to use alternatives to fluorinated gases or to improve flammability by alloying the last chance might be fully tight melting units and closed transportation tubes, feeding nozzles etc. In this case Ar and to some extend N₂ could provide a basic protection within the areas where molten Mg is present. However, it would be recommended to use a slight overpressure, to allow protective gases to leak out rather than standard atmosphere to enter the Mg containing areas.

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