HYDROFLUOROCARBONS AS A REPLACEMENT FOR SULPHUR HEXAFLUORIDE IN MAGNESIUM PROCESSING

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Abstract

One of the major issues for users and potential users of magnesium is magnesium melt protection. This is particularly so with the use of sulphur hexafluoride (SF_6) coming under increased scrutiny, as it is now recognized as a very potent greenhouse gas. It has been demonstrated that SF_6 prevents molten magnesium from oxidation by adding fluorine into the unprotective magnesium oxide surface film. The hydrofluorocarbon gas 1,1,1,2-tetrafluoroethane (HFC-134a) has been recently developed for magnesium melt protection by the Cooperative Research Centre for Cast Metals Manufacturing (CAST) in Australia. This gas has a global warming potential 18 times lower than SF_6 and has been shown to be an effective replacement for SF_6 in many applications. HFC-134a has also been shown to have some unique properties resulting in more possible applications for magnesium melt protection than SF_6. Recent experience with HFC-134a in laboratory and plant trials is discussed as well as the global implications of replacing SF_6 with hydrofluorocarbons.

Introduction

Molten magnesium burns in contact with air and, in particular, moist air. Unlike many metals, the magnesium oxide film formed on molten magnesium in contact with air does not protect the metal from further oxidation. This is due to the fact that the molar volume of magnesium oxide is mismatched with the molar volume of the equivalent amount of magnesium (the Pilling-Bedworth ratio) [1]. When this is combined with the very high free energy of formation of magnesium oxide, molten magnesium will burn rapidly in air if not protected.

The use of fluorine-bearing gas atmospheres for protecting molten magnesium has been described as far back as the 1930s [2]. However, it was only in the 1970s that serious attempts were made to use this approach on a widespread basis, with the development of dilute SF_6 gas mixtures [3]. Although expensive, SF_6 is colorless, odorless, and nontoxic, and was a big improvement on the existing technologies based on fluxes and SF_6.

In the past 10 years, SF_6 has become recognized as a very potent greenhouse gas. It is about 23,900 times worse than carbon dioxide (100-year time horizon), and for this reason has come under intense environmental scrutiny [4,5]. The Kyoto Protocol calls for a reduction in SF_6 use. A recent paper has also linked SF_6 and a newly identified potent greenhouse gas trifluoromethyl sulphurpentafluoride [6].

A number of automotive companies are now stating that they will not accept magnesium components that have been processed using SF_6. Recent studies have been conducted on SF_6 minimisation in order to lessen the impact of magnesium processing on greenhouse gas emissions [7-9]. The U.S. Environmental Protection Agency has launched a voluntary partnership for SF_6 reduction [10]. Despite a number of companies stating that they can capture and reuse SF_6 in magnesium processing, there is still a strong drive to replace SF_6 completely [11,12].

SF_6 has been demonstrated to modify the magnesium oxide surface film in a way that makes the film more protective [13]. This was shown to be due to the fluorine component of the SF_6 only. This discovery led CAST researchers to investigate a range of chemicals that contain fluorine for possible use in magnesium melt protection applications. The most promising class of chemical investigated was the hydrofluorocarbons.

Hydrofluorocarbons as a replacement for SF_6

SF_6 is now considered an almost universal cover gas for most magnesium processing applications. The search for a "drop-in replacement for SF_6" has been ongoing for some years now. The requirements for a cover gas for magnesium melt protection are:

1. Must protect both pure magnesium and a range of magnesium alloys.
2. Low global warming potential.
3. Zero ozone depletion potential.
4. Safe and non-toxic at room temperature.
5. Nonflammable.
6. Minimal (or manageable) toxic thermal decomposition products.
7. Non-corrosive at room and molten metal temperatures.
8. Ideally cheaper than SF_6 to provide some financial incentive to change gases.
9. Readily available worldwide from more than one supplier.

Extensive searching of technical information yielded a number of candidate gases and these were tested for suitability for:

- Magnesium melt protection in a melting furnace.
- Single ingot casting of magnesium.

From these "screening tests", one candidate gas stood out from the others tested [14]. This gas is 1,1,1,2-tetrafluoroethane (also known as HFC-134a) and it has the following characteristics:

a) It protects pure magnesium and has been successfully tested with a range of alloys.
b) It has a global warming potential of only 1,300 compared to 23,900 for SF_6.
c) It has zero ozone depletion potential.
d) It is safe and non-toxic at room temperature and is non-flammable.
e) There are only minor toxic thermal decomposition products.
f) It is non-corrosive at room temperature, but some corrosion issues are present at molten magnesium temperatures.
g) It is only about one-third the cost of SF_6 and is readily available worldwide.

HFC-134a as a gas for magnesium melt protection

Since the first public release of information on this new patented gas system, the main questions asked of the CAST research team have been:

- How does it work?
- What concentration should be used?
- What diluent gases should be used?
- In what applications can the gas be used?

This paper addresses some of these issues, but more detail will be supplied in forthcoming publications.

How does HFC-134a work?

Fluorine-bearing cover gas mixtures protect molten magnesium by adding magnesium fluoride to the magnesium oxide layer on the melt surface. With SF_6/dry air mixtures, Cashion [13] found that the surface film was composed of magnesium oxide and up to 13% magnesium fluoride. When using cover gas mixtures containing HFC-134a, surface films on magnesium may contain up to 50% magnesium fluoride. When the Pilling-Bedworth ratio of magnesium fluoride is combined with magnesium oxide, the addition of magnesium fluoride increases the ratio closer to unity. Basically, the molecular volume of the mixed oxide/fluoride approaches the molecular volume of the magnesium used to make it. Therefore, the oxide film does not crack and acts as a barrier to further oxidation.

What concentration should be used?

This is highly dependent on:

- The alloy used, particularly the beryllium and aluminum contents.
- How well the containment vessel is sealed.
- What diluent gas is used.
- The moisture content of the diluent gas.
- The time of exposure to the gas.
- Temperature.

The starting point for calculating consumption rates should be the same composition and flow rates as used for SF_6. However, in some cases, it has been shown that 3 times less HFC-134a than SF_6 was able to be used in a well-sealed furnace [14].

What diluent gas should be used?

HFC-134a has been tested using dry air, carbon dioxide, and nitrogen as diluent gases. All diluent gases tested have been shown to be effective. Further work in this area is being conducted to determine the optimum combinations for various applications.

In what applications can the gas be used?

The use of HFC-134a has been tested in a range of applications including:

- Melt protection in a melting/holding furnace (Figure 1).
- Magnesium squeeze casting.
- Open mould ingot casting (Figure 2).
- Magnesium sand casting.
- Magnesium investment casting.
- Magnesium high-pressure die casting.
- Fire prevention/extinguishing in a dross container.

The last application on the list is not possible with SF_6. Magnesium fires cannot be extinguished with SF_6, but HFC-134a has been shown to be able to control magnesium fires. This has useful application in dross containers where burning magnesium can create a lot of fumes, posing a hygiene problem in magnesium foundries.

To date, HFC-134a has been successfully used on the alloys AM60, AZ91, AZ31, pure magnesium, and an experimental rare earth containing magnesium alloy. Applications to be tested in the future will include direct chill casting operations.

Because of differences in the rate of reaction and flow characteristics between SF_6 and HFC-134a, modifications to the gas delivery system to the melt surface need to be considered along with possible materials substitution for some areas. It is recommended that CAST be contacted if assessment trials of this new gas are to be undertaken.

Figure 1: Pure magnesium protected with an HFC-134a/dry air cover gas

Figure 2: Ingots of pure magnesium cast using HFC-134a/dry air cover gas (photo courtesy of AMC)

How does HFC-134a compare to other new gas developments?

There are a number of new developments in magnesium cover gases. This is quite encouraging, as it would appear that many organizations are now concerned with the greenhouse gas emissions from SF_6 use.

The Magshield system developed by Hatch produces boron trifluoride by thermal decomposition of a fluorine-bearing powder [15]. As boron trifluoride is very toxic, its use would appear limited to those systems that are tightly sealed.

For a well-sealed furnace, German researchers have been examining the use of argon in a furnace attached to a die casting machine [16]. This would seem to have merit, but could cause problems with burning during cleaning of the furnace. It relies on direct chill cast feed material, which is available only from a limited number of suppliers at a cost well above ingot prices.

Brochot has been marketing a new cover gas system for magnesium ingot casting [17]. Few details have been publicly released, but the gas is known to contain xenon. It is not clear whether this gas blend has applications other than ingot casting.

Environmental implications

The environmental implications of switching from SF_6 to HFC-134a in primary magnesium production are complicated. For example, a magnesium smelter operating on hydroelectric power can expect carbon dioxide emissions in the vicinity of 7 tonnes of carbon dioxide per tonne of magnesium cast [5]. However, a magnesium smelter using coal for electricity production can expect figures up to an order of magnitude higher than this. In the former case, the greenhouse gas emissions from using SF_6 in primary magnesium production are two-thirds of total emissions. In the latter they would only be 17% of total greenhouse emissions. Although this may be important locally, global adoption of HFC-134a as a replacement for SF_6 would have major implications.

The annual usage for cover gas is difficult to determine because most companies are reticent to release consumption figures. However, a potential market for SF_6 of about 255,000 kg per year can be conservatively estimated assuming the following figures:

- 375,000 tonnes of primary magnesium production (of this, not all will have been produced using SF_6).
- 135,000 tonnes of magnesium used in casting applications (again, of this, not all will have been processed using SF_6).
- 0.5 kg SF_6/tonne of magnesium produced in primary magnesium production [19].
- 0.5 kg/tonne of magnesium casting via casting processes (some estimates are as high as 4 kg/tonne) [5].

At current prices of about $13 per kg for SF_6 and $5 per kg of HFC-134a, global adoption of HFC-134a would result in savings for the magnesium industry of just more than $2 million per year and a greenhouse gas savings of 5.8 million tonnes of carbon dioxide equivalent. EPA estimated that in 1997, the magnesium industry released 3 million tonnes of carbon dioxide equivalent through the use of SF_6 in the U.S. alone.

Primary magnesium production is growing at a rate of about 3% per year, and the magnesium casting sector is growing at a rate of 13% per year (this is a conservative estimate - it could be as high as 20%). The latter might grow even faster once the use of SF_6 for magnesium casting is eliminated and a major environmental impediment for widespread adoption of magnesium in automotive use has been removed.

It could be argued that current users of magnesium in the automotive industry would pay a small amount for a reduction in greenhouse gas emissions from elimination of SF_6. However, this is probably true only in the western world where environmental pressures are greatest. What is more realistic is that at the present time organizations will switch to a new gas in a serious manner only if it is cheaper. The lower greenhouse gas emissions would be a bonus.

The true impact of the widespread introduction of magnesium into automotive applications is a complex issue. Many organizations claim that reducing the mass of a vehicle reduces fuel consumption and then go on to claim a reduction in carbon dioxide emissions as a result. However, one must take into account the greenhouse gas emissions emitted in the primary magnesium or aluminum production process. This will be a function of the energy source used to produce the electrical energy, which is a large proportion of the energy cost of the primary production process of these two metals.

A recent paper has detailed that if SF_6 is used in the production process for magnesium castings for automotive use, it is not possible to reach the break-even point on greenhouse gas emissions if the vehicle is driven for less than 200,000 km [20]. If the greenhouse gas emissions from the use of SF_6 are eliminated in the production process, then the authors estimated a break-even point of 67,000-109,000 km.

Conclusions

The use of HFC-134a as a magnesium cover gas to replace SF_6 for a range of magnesium processing applications would appear to be possible. In addition, it has also been shown to have benefits that are not possible with SF_6-containing gas mixtures.

The global replacement of SF_6 by HFC-134a could result in global greenhouse gas savings of more than 5 million tonnes of carbon dioxide equivalent per year. This is equivalent to the yearly greenhouse gas emissions of more than 1 million automobiles. At the same time, switching from SF_6 to HFC-134a could result in significant cost savings to magnesium processing operations.

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