The International Program to Identify Alternatives to SF_6 for Magnesium Melt Protection

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ABSTRACT:

Magnesium's combination of reactivity and significant vapor pressure in the molten state requires that film-forming inhibitors must be employed to limit metal losses due to oxidation and to prevent the oxide contamination of alloys prior to the production of cast parts. For more than 20 years the inhibitor of choice has been SF_6 at low levels in a blend with air or carbon dioxide. The use of SF_6 resulted in improved melt protection relative to SO_2 and simultaneously eliminated the toxicity and irritant issues associated with SO_2 storage and use. However due to the extreme global warming potential of the SF_6 molecule, first highlighted by environmental scientists in the 90's, the International Magnesium Association (IMA) recognized the need to identify new alternatives with both low environmental impact and low toxicity. A development program was initiated by the IMA in 2000 with US and Canadian government support. Several promising alternatives have been identified and tested over the past two years. The successful commercial implementation of one of these alternatives will allow the magnesium industry to significantly reduce its impact on the global warming issue in the near future.

INTRODUCTION:

Magnesium, unlike aluminum and zinc, possesses a significant vapor pressure at normal melt temperatures. At its melting point (650 °C) the pure material possesses a vapor pressure of 3 mm, which combined with the porous and non-protective character of the magnesium oxide film, results in active oxidation on melt surfaces exposed to air.[1] Initially, only oxide blooms (spotty, thick accumulations) may appear on the surface of an unprotected melt. But due to the liberated heat of reaction, active combustion with an intense white light soon begins. This excessive oxidation leads to increased costs due to metal losses and it degrades the quality and performance of components produced. Figure 1 illustrates the contrast in oxidation rates experienced in the production of hand cast ingots in the development foundry – with and without good melt protection. The melt protection of choice for more than 20 years has been SF_6 at 0.3 to 0.5% with air or air pus CO_2 in the high pressure die casting industry where magnesium use has grown at double digit rates for more than a decade.[2-9]

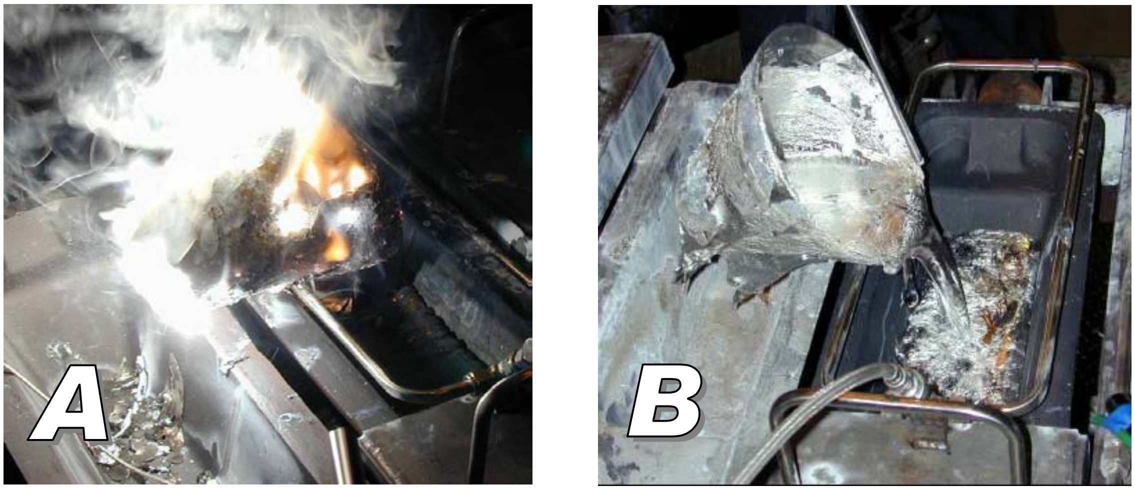

FIGURE 1: **Magnesium Ingot Casting Operation with alloy AM50A: A) Metal ladled from furnace with marginal melt protection *(left)*; B) Ladled form furnace with good melt protection *(right)*.** [photos – courtesy of D. Milbrath of 3M[16]]

This growth in magnesium die cast alloy volume has been primarily due to automotive demand for lightweight components.[10, 11] Magnesium is inherently 33% lower density than aluminum, which can lead to significant weight savings in automotive components produced in magnesium alloy. This in turn offers the potential for improved fuel economy to meet CAFÉ requirements in North America, or reduced CO_2 emissions over the life of a vehicle for lower environmental impact from the perspective of Global Warming.

While the focus of climate change scientists was on carbon dioxide, nitrous oxide, and methane emissions as the greenhouse gases of concern, the Global Warming issue was a driver for continued growth in magnesium automotive applications. However, in a 1994 report environmental scientists of the International Panel on Climate Change added fully fluorinated chemicals to the list of greenhouse gases of concern. This included SF_6 along with a number of very stable fluorocarbon compounds, but the SF_6 molecule had the distinction of possessing the highest global warming potential (GWP) of any compound identified to-date.[12] On a 100 year time frame the GWP was reported to be 23,900 times that of CO_2, or 1 pound of SF_6 emissions would be roughly equivalent to 12 tons of CO_2. In a lifecycle analysis of vehicles this large GWP associated with the emissions from the melt protection used in the production and processing of magnesium negates much of the advantage of the magnesium weight saving. With this realization the Magnesium Industry recognized that continued growth in automotive applications would require that SF_6 be eliminated in both the production and processing of the alloys.

THE SEARCH FOR MELT PROTECTION ALTERNATIVES

As an interim step the Industry initially focused on communicating guidelines for the effective use of SF_6 in magnesium melt protection in order to minimize SF_6 emitted to the environment, while existing alternatives for melt protection were re-evaluated.[13] Unfortunately, the alternatives that existed were only those that had been generally abandoned with good reason when SF_6 was introduced in the early 70's. These were salt fluxes, which formed a barrier of molten salt over the melt surface, or SO_2 blends with air. The salt fluxes are undesirable due to the fact that in addition to evolving corrosive gas in the area of the die casting equipment and the operating personnel they also have a high propensity to randomly find their way into the die cast product, resulting in severely degraded corrosion performance. The SO_2-air mixtures are far less degrading to the foundry equipment and the cast product, but the hazards associated with storage handling and use of this highly toxic material, which is also an undesirable air pollutant, makes it a less than desirable option for most foundry managers. Consequently in 1998 the International Magnesium Association Board of Directors choose to appoint a committee to pursue an international program to identify new melt protection alternatives with low toxicity and limited environmental impact.

The committee organized in the spring of 1999 and first met at the Associations annual conference that year. Through a nine-month process proposals were solicited, reviewed and the best candidates interviewed. This lead to the selection of the Materials Technology Laboratory of SINTEF (The Norwegian Foundation for Scientific and Industrial Research) to pursue a research and development program to identify suitable melt protection alternatives. SINTEF is located on the campus of the Norwegian University of Science and Technology in Trondheim, Norway. It is the fourth largest independent scientific and research organization in Europe. The Laboratory personnel had valuable experience in the evaluation of magnesium processing technology through their association Norsk Hydro's magnesium operations in Porsgrunn, Norway. The selection and focus of the program was detailed in the first International Conference on SF_6 and the Environment held in San Diego in November of 2000.

The program employed a multifaceted approach in order to speed the process of identification of a new alternative without abandoning an orderly scientific approach to new insights into the mechanism by which known protective agents function. Part of the SINTEF team pursued a pragmatic evaluation of recently proposed alternatives such as BF_3 generated *in situ* from KBF_4, HFC-134, inert gas-CO_2 blends, and other new untested molecules containing fluorine and/or sulfur.[14] Other members of the team pursued a more disciplined approach to gain new insights into the mechanism involved in the formation and growth of protective films on the magnesium surface, employing advanced analytical methods to evaluate the films formed, as well as, evaluating the solubility and diffusivity of the active elements – sulfur and fluorine - in both the molten metal and the oxide. New data has been generated in these studies suggesting a soluble, or suspended, F-species in the molten metal may be involved with the "residual protective effect" associated with the fluorine containing agents. This effort continues and will be further documented at a later date.[14, 15]

In the early months of the program the pragmatic approach succeeded in identifying some promising candidates from among several commercial and developmental fluorine compounds. These included the HFC-134a, the automotive refrigerant adopted in the 80's as a replacement for the ozone depleting Freon-12, a chlorofluorocarbon (or CFC), and three compounds proposed as candidates by the Performance Material Division Laboratory of the 3M Company. Two of these were hydrofluoroethers HFE-7100 and HFE-7200 and the third a perfluoroketone (perfluorethyl, isopropylketone), a new patented compound under development at 3M for its reduced environmental impact in an unrelated application.[16] All four of these compounds were found to provide competitive performance, when compared to SF_6 mixtures for the protection of magnesium melts from oxidation. They are also attractive candidates because they are of low toxicity, non-flammable, non-ozone depleting, of short atmospheric lifetime, and possess a much-reduced global warming potential. Table 1 below compares the estimated GWP's of these compounds with SF_6 and several other compounds, which are greenhouse gases of environmental concern. Also included in Table 1 is sulfuryl fluoride, SO_2F_2, which possesses a low GWP and has also been found effective in melt protection. The compound is toxic, however. Its principal commercial use is as a termite fumigant. While somewhat less toxic than SO_2, the compound has no smell or irritant effect to provide adequate warning of its presence in the work environment, which could represent a significant industrial hygiene issue in the foundry work place.

With melt protection proven competitive with SF_6 in the laboratory, the three alternative compounds in bold type in TABLE 1 were selected for full scale foundry testing this September (2002) to confirm their performance relative to SF_6 in real commercial scale equipment and under identical conditions of concentration, carrier gas flow, metal temperature, and alloy composition. The three compounds were selected because the

TABLE 1: GWP's of Potential Alternative Agents Compared to Existing Protective Agents and Greenhouse Gases of Concern

	COMPOUND	***LIFETIME, Yr***	***GWP (100Yr)***
Benchmarks	CO_2	100 – 150	1
	N_2O	120	360
	CH_4	12	24
	SO_2 (health & safety hazard)	---	---
	SF_6	3,200	23,900
Alternatives	***CF_3CH_2F – F134A***	***13.6***	***1,600***
	$C_4F_9OCH_3$ – HFE7100	***4.1***	***320***
	$C_4H_9OC_2H_5$ – HFE7200	0.8	55
	$C_3F_7COC_2F_5$ – FK (NOVEC-612™)	***0.014***	***~1***
	SO_2F_2 (health & safety hazard)	---	~1

F134a is a known commercial product, readily available worldwide as the refrigerant most commonly used in automotive and household appliances. Although it possesses a significant GWP compared to the other candidates, it is small when compared to SF_6 and it offers the potential to immediately and economically reduce the greenhouse gas emissions for magnesium applications by at least 95%. The HFE 7100 and 7200 are industrial cleaning solvents produced by 3M and available at reasonable costs. Although the GWP for 7100 is higher than that of the 7200, it was selected for large scale testing because it produced less HF in laboratory testing and it was found to be more effective in extinguishing burning metal. The perfluoroketone was selected because it possesses the lowest GWP and provides the ultimate opportunity for reduction of greenhouse gas emissions without the health and safety issues associated with the SO_2 or SO_2F_2 alternatives. While the compound is not widely available at present, the compound is currently in commercial development by 3M as a replacement for Halon used in electrical fire extinguishers and fire protection systems. Thus it is expected to be widely available soon and based on its performance in laboratory and foundry trials 3M has announced commercial development of the compound for magnesium melt protection under the trade name – Novec 612™. (It should be noted that the melt protection used in Figure 1B was 3M's Novec 612.)

The trial was conducted in Hydro Magnesium's development foundry in Porsgrunn, Norway in September of 2002. Each of the three melt protection agents was evaluated in a 500 Kg holding furnace in the die casting foundry with a melt surface area of 0.5 square meters. Melts used in each case were AM50A and ZE41A (or RZ5, buy European designation). The melt temperatures were 680 ºC and 710 ºC. The carrier gases used were either "dry air" or "CO2 + 5%Air" with the protective agent at 500 ppm in all experiments. The delivery rate of the protective agent was controlled by the carrier flow, which was varied step-wise from a low of 2.5 liters/minute to a maximum of 20 liters/minute. The relative performance was judged based on the minimum flow rate required to prevent active oxidation of the melt surface for a period of 10 minutes, following a period of 30 minutes to allow the furnace atmosphere to equilibrate with the protective gas mixture. This performance was documented using digital images and video.

Numerous samples were collected throughout the trial for latter analysis to verify that the alloy chemistry and die cast mechanical properties were not altered. The gas mixtures were analyzed at the inlet to the furnace, within the furnace as well in the ambient air. On-site the analyses were made by Fourier Transform Infrared analysis. Samples were also collected for latter analysis off-site by gas chromatography and mass spectroscopy. This data is currently being generated and collected for latter communication in a final report targeted to issue in June of 2003.

CONCLUSIONS & CURRENT STATUS

From the observations and data collected in the trial the following conclusions were reported.

- All three alternative agents provided better melt protection than SF6 at the same operating conditions.
- All protective gas mixtures provided significantly better protection in CO_2-5%Air than in Dry Air alone. This was true for SF_6 as well as the alternative agents.
- At 710 ºC melt protection is a much greater challenge than at the lower melt temperature and the CO_2-Air is the preferred carrier.
- Since the new agents are less stable thermally than SF_6, gas distribution is believed to be of greater importance.
- With these agents the governing factor in performance appears to be the amount of fluorine delivered per unit time, per unit area of melt surface. Under the conditions used in the present trials then the order of performance form least to best then was F134, HFE7100, and Novec 612™ with 4, 9, & 12 F atoms, respectively.
- Use of these gases in magnesium processing offers the potential to reduce greenhouse gas emissions by greater than 99 %, relative to current practices using SF6 mixtures.

Commercial development trials of both the F134A and the Novec 612™ have begun with promising results to date.[17, 18] The final report for this IMA program is anticipated by June of 2003 with summary presentations and training sessions targeted to follow.

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