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Development of 3M™ Novec™ 612 Magnesium Protection Fluid as a Substitute for SF_6 over Molten Magnesium

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Abstract:

Fluorinated ketones are a new class of materials that have been shown to be useful in protecting molten magnesium and its alloys from burning. A cover gas can be easily formulated from these volatile liquids with carrier gases such as dry air, CO_2, N_2 or their mixtures. Concentrations of fluorinated ketones as low as 0.010% can be effective in preventing fires by producing a thin protective film on the melt surface.

This performance makes fluorinated ketones attractive potential replacements for SF_6 in this application. However, differences in molecular stability translate into modifications of cover gas formulation and cover gas use. SF_6 is thermally very stable and does not undergo a significant thermal degradation at Mg melt temperatures, while fluorinated ketones degrade at surface temperatures above 550°C. This means that SF_6 needs to be used at relatively high concentrations (to get sufficient protection) and is not completely consumed by the Mg (excess SF_6 is emitted). Fluorinated ketone will be effective at low concentrations (due more complete reaction and more available F content) but can produce undesirable products (by thermal degradation) if used in large excess. This translates into optimal fluorinated ketone use at low concentrations with higher cover gas flow rates and an optimized gas distribution over the melt.

One fluorinated ketone is being commercialized as 3M™ Novec™ 612 Magnesium Protection Fluid. It is a very volatile, nonflammable liquid that will evaporate into a carrier gas stream as needed for molten magnesium protection. It is safe and environmentally friendly since it has an atmospheric lifetime of about 5 days, does not remove atmospheric ozone, and has a Global Warming Potential (GWP) about the same as CO_2. It is projected to have lower operating cost than SF_6 in many applications as well as virtually eliminating global warming emissions from molten magnesium processes presently using SF_6.

Introduction:

Magnesium and its alloys are becoming important materials of construction for a number of products. Fabrication with these materials generally requires heating the metal to near melting for extrusion or casting from a melt. At these temperatures magnesium is highly reactive with atmospheric oxygen due to the volatility of the metal and exothermic formation of MgO. Traditionally fluxes have been be used to float a layer of molten salts over the melt to separate the metal from air. However, fluxes have a tendency to be mixed into the melt and resulting occlusions accelerate corrosion due to chlorine content. In many cases there is also unacceptable metal loss in the dross and flux sludge. The alternative to fluxes has been the use of an atmosphere containing SO_2 (from oxidation sulfur powder spread on the melt surface or direct addition of the gas). This has been common practice for several decades, but has required care since SO_2 is toxic, corrosive and environmentally unacceptable today.

A number of fluorine containing materials such as NF_3, BF_3, SO_2F_2, IF_5, PF_5, SbF_5, and SF_6 were suggested for melt protection [1,2] as early as the 1930's, but were not extensively tested until the '70s. This may have been due to limited commercial availability as well as the high toxicity of most of the suggested compounds. Fruehling [3] and Couling4, 5 showed that SF_6 not only protected the molten magnesium, but it was safe to use since it was nonflammable and of low toxicity. It could also be used in lower concentrations than SO_2. In the intervening years SF_6 has become the dominate cover gas agent for operations using molten magnesium. It is easily used in holding furnaces and nearly all casting operations with pure magnesium and most of its alloys.

Studies by Cashion [6] and Pettersen, et.al. [7] have shown that SF_6 works by forming a tight non-porous film on the surface of the melt. The film is a mixture of MgO crystals and MgF_2 in an amorphous form. Long-term exposure to SF_6 increases the film thickness with an increased concentration of MgF_2. Eventually MgF_2 crystals are produced.

Due to the very stable nature of SF_6 only a small portion of the SF_6 in the cover gas mixture actually reacts with the Mg and a significant amount is emitted unchanged. With increased concerns about global warming this emission of SF_6 is no longer acceptable environmentally. Table 1 shows that 1 pound of SF_6 is equivalent to over 22,000 pounds of CO_2 in its impact on global warming. The International Magnesium Association (IMA) published guidelines [8] for the efficient use of SF6 in response. The trade organization also initiated an independent study of replacement cover gases to evaluate replacements.

Fluorinated Ketone Agents:

While the other fluorinated materials previously suggested are highly toxic, others such as perfluorocarbons (PFCs) are safe and nearly as stable as SF_6. Unfortunately, this stability translates into high GWP, which eliminates them as replacements. Hydrofluorocarbons (HFCs), introduced as replacements for CFCs to eliminate ozone destruction, are safe and they have been shown to be useful in protecting magnesium [9], but they also have significant GWP. Most recently another class of fluorinated materials, ketones, have been introduced with a global warming impact similar to that of CO_2.

Table 1
Atmospheric Lifetimes and Global Warming Potentials of SF6 Replacements

Compound	Lifetime (yrs)	GWP (100 Yr ITH)	
CO_2	100-150	1	
SF_6	3200	22,200	
C_3F_8	2600	8,600	PFCs
C_4F_{10}	2600	8,600	
C_6F_{14}	3200	9,000	
CF_3CH_2F	13.6	1,600	HFCs
CF_3CHF_2	32.6	3,800	
CHF_3	243	14,800	
$C_3F_7C(O)C_2F_5$	**0.014**	**~1**	**FKs**

Fluorinated ketones (FKs) are low boiling liquids that are nonflammable, of low toxicity, and high volatility (see Table 2). Environmentally they have short atmospheric lifetimes and thus have negligible global warming impact. They are safe and stable materials in most applications, much like PFCs. The difference is that they are readily decomposed by sunlight to ultimate products of CO_2, HF and some trifluoroacetic acid.

Unlike SF_6, FKs are liquids at room temperature. They are easily evaporated into a carrier gas stream by a number of methods. One system makes use of the high FK vapor pressure to produce a saturated gas stream (about 5-7%) in a pressure vessel and then dilute it into the carrier gas stream. This method has the advantage of having no moving parts and promises to be very reliable. Other methods of pumping liquid into the gas stream where it quickly evaporates have also been shown to be useful.

Table 2
Fluoroketone $C_6F_{12}O$ Properties

Physical Properties	
Boiling Point °C	49
Freezing Point °C	-108
Viscosity, liquid @ 20°C, cSt	0.042
Vapor Pressure @ 20°C, kPa	32.6
Liquid Density @ 20°C, g/mL	1.61
Gas Density @ 80°C - 1 Atm, g/mL	0.011

EHS Properties	
Atmospheric lifetime, days	<10
Global Warming Poteintial	~1
Flash Point	None
PEL, ppmV	150
Acute LC50, ppmV	>100,000

When compared to SF_6, FKs are much less stable and readily will react with Mg to form MgF_2. In addition, the FKs contain significantly more F atoms per molecule than SF_6 or lower HFCs. This translates to more available F per molecule to form a protective film on the melt surface. Potentially the FKs will be more efficient to use (lower use rates for equivalent protection) than other agents.

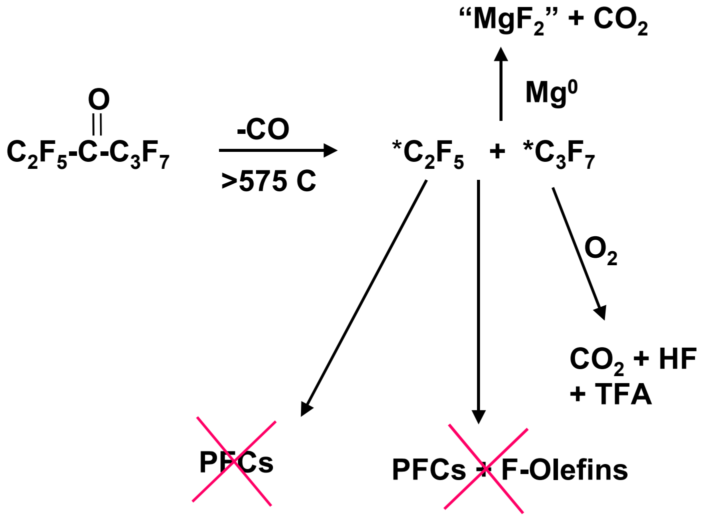
Melt Protection Performance:

Testing to date has proved this to be true by protecting melts of pure magnesium and all of the alloys tested. The FKs generally have provided protection at significantly lower concentrations than SF_6. Some differences between the protection efficiency due to different carrier gases have been seen. Testing was done with melts at temperatures from 680 to 790 °C in laboratory furnaces and pilot scale melts where large surface areas need to be protected. Casting operations such as ingot, sand and die with either pure or alloyed magnesium have also been successfully protected. As with furnace protection, significantly lower concentrations of FKs are needed for protection. The concentration difference, however, is generally greater in open casting operations than for furnace operations.

Emissions:

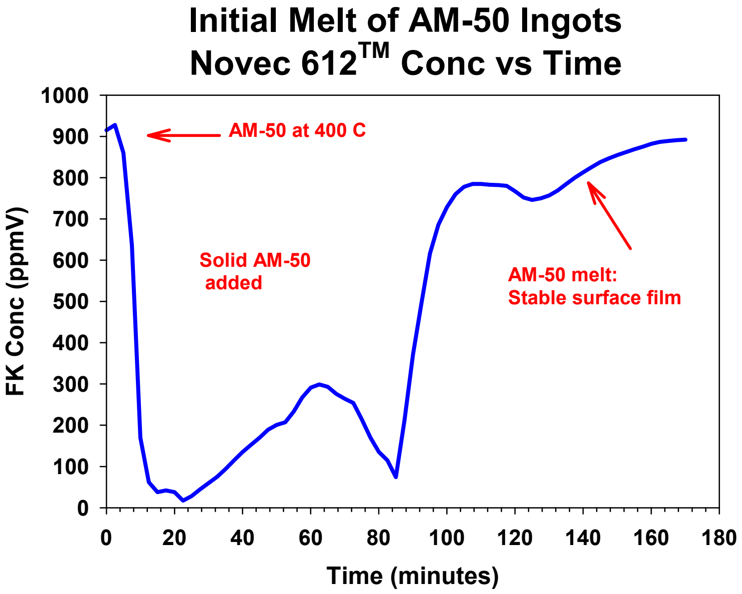
The chemical reactions that occur in a cover gas environment have yet to be examined in detail for nearly all agents (including SF_6, SO_2, and the new fluorochemicals). For FK cover gases analyses of products formed by thermal degradation and of the off gases during testing has lead to a general understanding of which reaction pathways are available (See Scheme 1). The FK will begin to thermally degrade at temperatures of about 550 to 575°C producing carbon monoxide. The fluorochemical fragments remaining (fluoroalkyl radicals) are very reactive and are totally consumed by unprotected magnesium surfaces and magnesium vapors producing MgF_2 and CO_2. During open casting operations or when a fresh metal surface is exposed to cover gas the FKs appear to be completely consumed by these reactions. Once the protective film forms less Mg is available for reaction and the fluorochemical radicals can undergo additional reactions that produce perfluorocarbons (PFCs) and fluoro-olefins (F-olefins). Neither of these products is desirable due to environmental (high GWP of PFCs) or worker safety (some F-olefins are toxic) concerns. However, if there is sufficient O_2 present in the cover gas mixture, the radicals appear to oxidize to form HF, CO_2, and possibly some trifluoroacetic acid (TFA). These reactions with oxygen consume the radicals so that PFCs or F-olefins are virtually eliminated from off gases.

Scheme 1
Reactions of FK over Molten Magnesium



Protection of a typical melt of magnesium is a dynamic situation where all of the reactions from Scheme 1 can be seen. Figure 1 illustrates this. The incoming concentration of FK of 1000 ppmV in pure CO_2 rapidly decreases to nearly zero as the solid metal melts. Fresh surfaces of AM-50 are produced as liquid metal is produced on the surface of the ingots. Once the melt pool engulfs the remaining solid metal, a stable surface begins to form. The FK concentration increases since there is less reactive surface to react with. When the melting is complete the final FK concentration recovers to 90% of the incoming cover gas agent. Normal operations were metal ingots are added to replace metal consumed in casting operations will go through a similar cycling of cover gas agent concentration.

Figure 1



This means that all of the reactions shown in Scheme 1 are possible and the products associated with them have been observed in various trials. Emissions from ingot casting (see Table 3) contained a small amount of FK despite a relatively high concentration in the cover gas. The large amount of available Mg virtually consumes all the FK. As a result PFCs and F-olefins were undetected, but a small amount of HF was found (possibly due to ambient moisture being drawn into the process).

Table 3
Emissions from Casting Trials

	Conditions			Gas Analysis			
Alloy	**FK Conc (ppmV)**	**Flow Rate (CFH)**	**Ingot Quality**	**FK found ppmV**	**PFIB Found ppbV**	**PFC Found ppmV**	**HF Found ppmV**
AM-50	500	30	Good	4	Not Det	-	10
AM-50	250	30	Marginal	1	Not Det	-	-
Pure Mg	750	90	Good	4	Not Det	Not Det	-
Pure Mg	1000	90	Good	14	Not Det	Not Det	-
Pure Mg	500	20	Poor	9	Not Det	Not Det	-

ppmV, ppbV refer to parts per million, billion by volume

Cover gases in a furnace have a different composition (Table 4). Much less FK is consumed and significant amounts of PFC and F-olefin in the form of perfluoroisobutylene (PFIB) were found over AM-50 and pure Mg. These experiments were done with CO_2 as the carrier gas and very little O_2 was present. It important to note that skimming an established surface film generating fresh Mg surface virtually eliminated these products.

Table 4
Composition of Furnace Gases

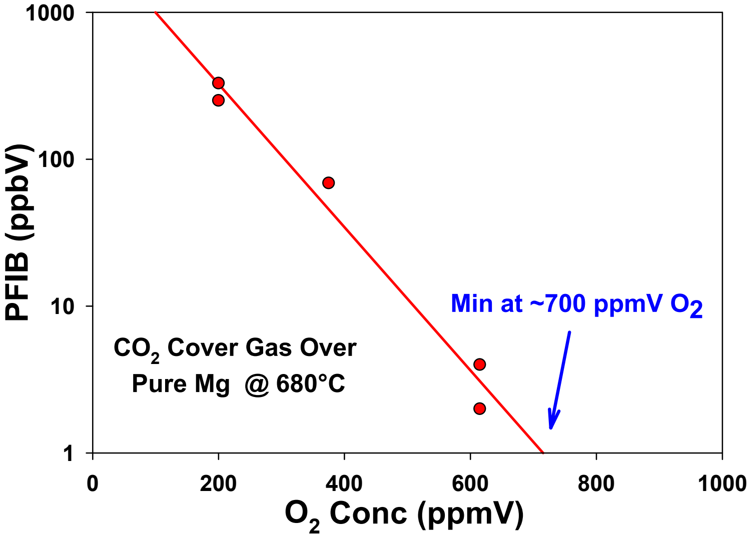
	Conditions				Gas Analysis		
Alloy	**Melt Temp (°C)**	**FK Conc (ppmV)**	**Flow Rate (CFH)**	**Furnace Protection**	**FK found ppmV**	**PFIB Found ppbV**	**PFC Found ppmV**
AM-50	680	1000	20	Good	894	204	-
AJ-52	720	1000	10	Good	164	26	322
Pure Mg	680	1000	20	Good	23	23	380
Pure Mg skimmed	680	1000	20	Good	1	Not Det	Not Det

Use Guidelines for Safe and Effective Use:

A strategy has evolved to control the production and emission of PFCs and F-olefins as a result of these development studies. The presence of oxygen in the cover gas mixture minimizes the production of PFCs and F-olefins. This can be seen in Figure 2 where increasing amounts of O_2 rapidly decreases the amount of PFIB found in a closed furnace. Additions of a small percentage of dry air (1-5%) to the CO_2 carrier gas are sufficient to ensure oxygen concentrations high enough (2000 to 10,000 ppmV) to inhibit F-olefin production.

Figure 2

Effect of O_2 Content of Cover Gas



The use of low concentrations of FK agent also decreases production of unwanted fluorochemicals. Lower concentrations can be accommodated since the mass of reactive F delivered to the melt is the critical parameter for protection. The product of agent concentration and the flow rate determines the mass of F delivered. Lower concentrations can be used if the flow is increased. In a recent study 2.5 L/min flow of 500 ppmV FK was equivalent to 110 ppmV FK delivered at 10 L/min in protecting AM50.

Flow rate rather than concentration can also be used to alter protection so that more agent is available when the amount of fresh Mg surface is increased during drossing or ingot addition. This is actually more effective in providing good protection. The more reactive FK does not have the "carry" of SF_6 over the melt. Use of higher concentrations may only serve to produce unwanted off gases while a higher flow rate will get sufficient agent to all of the melt surface.

The final part of this strategy is not to overprotect the melt. It was difficult to have too much SF_6 since what didn't react was emitted unchanged. Any of the newer fluorochemical agents will react and excess agent can produce materials that are not acceptable. Better control of the agent also makes their use more economical as well.

The recently completed pilot scale test by SINTEF as a part of the IMA study of replacement cover gases indicated that these strategies work. The CO_2 carrier gas contained a small percentage of dry air to provide O_2 levels to minimize PFC and F-olefin production. The study partially optimized the amount of FK used over an AM-50 melt. The resulting cover gas composition contains only a small amount of unchanged agent, a very small amount of PFC, and no detectable F-olefin or COF_2. The level of HF higher than was expected and is being further examined.

Table 5
Novec 612 Furnace Emissions

AM-50 @ 680°C with 500 ppmV in CO2-5%air

Gas Flow rate	Novec 612 Conc	PFC Conc	F-Olefin Conc	COF2 Conc	HF Conc
2.5	22 ± 5	25 ± 7	ND	ND	84 ± 19
L/min	ppmV	ppmV			ppmV

from IMA-SINTEF Study of SF$_6$ Replacement Cover Gases

Availability of FK:

Beta-site testing of the FK as 3M^{TM} Novec^{TM} 612 Magnesium Protection Fluid is underway with a number of commercial-scale tests in progress or being planned for the remainder of 2002 and early 2003. Specifically, ingot casting trials will be completed at Noranda's Magnola production facility and are planned for Norsk Hydro's Becancour facility. Testing with die castors and recyclers early in 2003 will follow these tests. This work is intended to verify the protection, economics and worker environment in real operations. These results will enable efficient conversions later in 2003.

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