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**SINTEF REPORT**

TITLE

**ALTERNATIVES TO SF<sub>6</sub>/SO<sub>2</sub> FOR MAGNESIUM MELT PROTECTION – FINAL REPORT OF THE IMA-SINTEF COLLABORATION PROJECT**

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**ABSTRACT**

Over the past decade, increasing global awareness of the greenhouse effect has resulted in an international push towards reduction of known greenhouse gases. For the magnesium industry, this push has involved minimizing and reconsidering the use of SF<sub>6</sub> – which is an extremely potent greenhouse gas – in the cover gas mixtures used to protect liquid magnesium from oxidation. In October 2000, the International Magnesium Association (IMA) commenced a collaborative research project with SINTEF Materials Technology in Trondheim, Norway, for the purpose of identifying and testing alternatives to SF<sub>6</sub>, a potent greenhouse gas, for magnesium melt protection. This report details the main findings of the IMA/SINTEF collaboration project. In short the research findings can be summarized as:

- Three promising SF<sub>6</sub> replacements, HFC 134-a, HFE 7100 and Novec™612, have been identified and tested in both laboratory and pilot scale for their relative technical and environmental performances.
- All three tested compounds (HFC 134-a, HFE 7100 and Novec™612) provide technically better melt protection than SF<sub>6</sub> under identical testing conditions.
- All three replacement compounds provide a lower total greenhouse gas impact than SF<sub>6</sub>.
- It is suggested that, for a site implementation of a new cover gas blend, a gas "optimization" - based on technical and environmental performance but with an element of economic consideration – is necessary

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## TABLE OF CONTENTS

<b>1</b>	<b>EXECUTIVE SUMMARY .....</b>	<b>3</b>
<b>2</b>	<b>INTRODUCTION.....</b>	<b>5</b>
<b>3</b>	<b>PROTECTION OF MOLTEN MAGNESIUM USING ALTERNATIVE COVER GASES .....</b>	<b>7</b>
	3.1 Summary - Protection of Molten Magnesium using Alternative Cover Gases .....	7
	3.2 Introduction .....	9
	3.3 Laboratory Scale Testing of Alternative Cover Gases .....	10
	3.3.1 Experimental .....	10
	3.3.2 Results .....	11
	3.4 Pilot Scale Testing of Alternative Cover Gases .....	24
	3.4.1 Experimental.....	24
	3.4.2 Results.....	25
	3.5 CFD Modelling of Gas Flow in Pilot Scale Furnace.....	34
	3.5.1 Problem description - injection of cover gas into a holding furnace.....	34
	3.5.2 Modeling of bath tub furnace system used in pilot scale campaign .....	35
	3.5.3 Short summary, CFD modeling study.....	39
<b>4</b>	<b>ALTERNATIVE MEANS OF MAGNESIUM MELT PROTECTION .....</b>	<b>40</b>
	4.1 Summary - Alternative Means of Magnesium Melt Protection .....	40
	4.2 Introduction .....	40
	4.3 Alternative Magnesium Melt Protection - Dissolved Fluorine .....	41
	4.3.1 Solubility of Fluorine in Magnesium and Its Alloys.....	41
	4.3.2 Testing the viability of oxidation protection through introducing Fluorine via the melt .....	42
	4.3.3 Is the measured fluorine solubility high enough to give melt protection? .....	43
<b>5</b>	<b>REGULATORY AND ECONOMIC ISSUES .....</b>	<b>47</b>
	<b>REFERENCES.....</b>	<b>49</b>

## 1. EXECUTIVE SUMMARY

Over the past decade, increasing global awareness of the greenhouse effect has resulted in an international push towards reduction of known greenhouse gases. For the magnesium industry, this push has involved minimizing and reconsidering the use of SF<sub>6</sub> – which is an extremely potent greenhouse gas – in the cover gas mixtures used to protect liquid magnesium from oxidation. In October 2000, the International Magnesium Association (IMA) commenced a collaborative research project with SINTEF Materials Technology in Trondheim, Norway, for the purpose of identifying and testing alternatives to SF<sub>6</sub> for magnesium melt protection. The research work was carried out during the period October 2000 to October 2002. Reports of the research status and results were provided during the duration of the project. A final project report was, however, not prepared as the project was cut short from a planned three, to two year duration. In spring 2004, the US Environmental Protection Agency took the initiative of funding the reporting of the un-published research. This report is a summary of all the research results obtained in the IMA/SINTEF project, which has not previously been fully reported.

In the IMA/SINTEF collaboration project, two parallel paths of finding suitable alternatives to SF<sub>6</sub> were followed:

1. Identifying and testing promising fluorinated (gaseous) compounds with low global warming potential as compared to SF<sub>6</sub>, which may be used as direct substitutes for SF<sub>6</sub> in cover gases.
2. Testing alternative means of magnesium melt protection, such as introducing fluorine to the melt rather than with a gas, or adding selected alloying elements which may prevent excessive oxidation (for example, beryllium).

From the testing of promising fluorinated cover gas alternatives (path 1), the results may be summarized as:

- Three promising SF<sub>6</sub> replacements, HFC 134-a, HFE 7100 and Novec™612, have been identified and tested in both laboratory and pilot scale for their relative technical and environmental performances.
- All three tested compounds (HFC 134-a, HFE 7100 and Novec™612) provide technically better melt protection than SF<sub>6</sub> under identical testing conditions.
- The overall compound ranking, in order from most to least amount of compound needed to protect a given magnesium melt surface was found to be; SF<sub>6</sub>, HFC 134-a, HFE 7100, Novec™612. Like SF<sub>6</sub>, all three compounds have significantly better melt protection properties in CO<sub>2</sub>/air than in air carrier gas.
- All of the three new active compounds – like SF<sub>6</sub> but unlike SO<sub>2</sub> – are effective magnesium fire quenchers.
- All three replacement compounds provide a lower total greenhouse gas impact than SF<sub>6</sub>.
- The alternate fluorinated compounds generally generate more hydrofluoric acid (HF) in the off-gas than SF<sub>6</sub>.
- It is suggested that, for a site implementation of a new cover gas blend, a gas "optimization study" – based on technical and environmental performance but with an element of economic consideration – is necessary.
- Proposed legislation may pose a threat to the use of HFC 134-a in Europe in the medium to long term. HFE7100 and Novec™ 612 are to date not covered by any proposed or active legislation.

From the research into alternative means of magnesium melt protection, the results may be summarized as:

- The solubility of fluorine in liquid pure magnesium and the alloys AM50 and RZ5 has successfully been determined in the temperature interval 650 to 950°C.
- At common magnesium processing temperatures around 700°C, the fluorine solubility in pure magnesium, AM50, and RZ5 is measured to approximately 10 ppm. This fluorine concentration is **theoretically** high enough to provide fluorine to a protective surface film in order to maintain its protection.

- It was, however, experimentally found that pure magnesium could not be effectively protected in air atmosphere purely by dissolved fluorine at the saturation level. Note that AM50 and RZ5 were not tested.

## 2. INTRODUCTION

Molten magnesium is rapidly oxidised in an oxygen-containing atmosphere – a strongly exothermic reaction which may cause burning if the liquid surface is left unprotected. In present industrial handling of molten magnesium (Mg), sulphur hexafluoride (SF<sub>6</sub>) or sulphur dioxide (SO<sub>2</sub>) – which inhibits the oxidation by facilitating the formation of a protective surface film – is thus commonly added to the atmosphere under which the liquid metal is kept.

The use of fluorine-containing compounds, such as SF<sub>6</sub>, for protection of molten magnesium was suggested and patented by Reimers in the early 1930s [1]. It was, however, not until the 1970s, following the work of Fruehling [2] and subsequently Couling [3,4], that SF<sub>6</sub> was introduced as an active compound in cover gases for magnesium melt protection. Prior to the introduction of SF<sub>6</sub>, magnesium was protected with alkali metal halide fluxes, sulphur dioxide (SO<sub>2</sub>), or even elemental sulphur. Although SF<sub>6</sub> has been used for more than two decades, it has only been recently that the mechanisms through which certain fluorine-containing gases protect liquid magnesium from uncontrolled oxidation were thoroughly investigated and partially revealed [5-7]. The key to its protective properties is partial decomposition/reaction between reactive fluorine and gaseous/liquid magnesium. Coupled to controlled oxidation, these reactions facilitate the formation of an elastic, non-porous protective surface film containing MgO and MgF<sub>2</sub> with a Pilling-Bedworth ratio larger than 1<sup>1</sup>. The mechanisms of fluorine-based melt protection were summarised and described by Tranell et. al [8].

Over the past decade, increasing global awareness of the greenhouse effect has resulted in an international push towards a reduction in the use of known greenhouse gases. For the magnesium industry, this push has involved minimizing and reconsidering the use of SF<sub>6</sub> – which is an extremely potent greenhouse gas – in the cover gas mixtures. In the United States, the Environmental Protection Agency (EPA) and the magnesium industry jointly launched a voluntary SF<sub>6</sub> Emissions Reduction Partnership in the late 1990's [9]. In Europe, the pressure to switch from SF<sub>6</sub> to alternative magnesium protection has increased with a recent proposal to the EU Parliament for regulation of a number of fluorinated greenhouse gases. With the passing of this proposal, the use of SF<sub>6</sub> in the magnesium industry will effectively\* be prohibited from January 1<sup>st</sup>, 2007 [10].

In order to meet a new international environmental framework, the IMA initiated a three-year collaborative project in the year 2000 with the research institute SINTEF in Norway. The overall scope of the collaboration project was to identify and test feasible alternative(s) to SF<sub>6</sub>/SO<sub>2</sub> with regard to environment policies and workers health and safety, as well as economic considera-

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<sup>1</sup> For any given metal / metal oxide system, the "coverage" of the metal oxide on the corresponding metal surface – the ratio between the oxide and metal molar volumes – may be described by the *Pilling-Bedworth Ratio* (PBR) [9], as defined by equation (1):

$$PBR = \frac{m_{oxide} / \rho_{oxide}}{n m_{metal} / \rho_{metal}}$$

where  $m_{oxide}$  is molar mass of oxide,  $\rho_{oxide}$  is the density of oxide,  $m_{metal}$  is molar mass of the metal,  $\rho_{metal}$  is the density of the metal, and  $n$  is the number of metal atoms needed to form an oxide molecule. With PBR values <1, the oxide layer is porous, providing poor metal surface coverage. For systems with  $1 < PBR < 2$ , the oxide layer is generally dense, giving good coverage (as with for example Al<sub>2</sub>O<sub>3</sub>). For a PBR > 2; the large difference between the molar volume of oxide and that of the metal creates tensions which may give cracks in the oxide layer (e.g., Fe<sub>2</sub>O<sub>3</sub>). For magnesium oxide (MgO), the PBR equals 0.81, i.e., the oxide provides poor coverage of the metal surface. In combination with the strongly exothermic nature of the Mg oxidation reaction, un-controlled oxidation and subsequent fire will take place if Mg metal is left unprotected in oxygen containing atmospheres at temperatures above its melting point.

\* Facilities consuming < 500kg/annum will be exempt

tions. After 2 years of collaboration between the IMA and SINTEF, the project was terminated and the results of the research were hence not fully reported. In spring 2004, the US Environmental Protection Agency (EPA) took the initiative of getting the research reported and thus contracted ICF Consulting to find a suitable party to report the research. ICF Consulting subsequently selected SINTEF to report the research in the form of four separate deliverables: 1) A publication at the IMA Conference in New Orleans, May 2004; 2) A journal publication; 3) A full report of all research carried out in the IMA project that has previously not been reported; and 4) Samples and media material produced during the collaboration project. This report is deliverable number 3.

With the identification of fluorine as the active ingredient in magnesium protection, a number of fluorinated gases have been suggested as replacements for SF<sub>6</sub>. In the IMA/SINTEF collaboration project and through independent work outside the project, three promising fluorine-based replacements; HFC 134-a, HFE 7100 and Novec™612, were identified and extensively tested in both small laboratory tests and pilot industrial scale tests during the last year of the project. The results of this testing, as well as modelling of gas flow inside a magnesium holding furnace, are detailed in Section 3. In Section 4, results from experimental work on “alternative” (to gas) protection of magnesium are reported. Section 5 contains some concluding remarks from the study.

### 3. PROTECTION OF MOLTEN MAGNESIUM USING ALTERNATIVE COVER GASES

#### 3.1 Summary – Protection of Molten Magnesium using Alternative Cover Gases

Three fluorinated compounds; HFC 134-a, HFE 7100 and Novec™612, have been tested for their suitability as SF<sub>6</sub> replacements in cover gases for magnesium melt protection. The compounds respective performances under different conditions were compared to each other and to SF<sub>6</sub>. The testing was carried out both through laboratory scale experiments and through a pilot scale campaign at Norsk Hydro's research laboratories in Porsgrunn, Norway. The evaluation of the different compounds' technical and environmental performances was based on visual observations during melt exposure to cover gas, as well as analysis of the gases generated over the exposed melt surface. The different conditions / parameters tested were:

- **Carrier gas mixtures;** CO<sub>2</sub>, Ar/Air (**lab. scale**); and 100 % dry air, CO<sub>2</sub>+5% dry air (**lab. and pilot scale**)
- **Total gas flow rates / active compound concentration;** 1.0, 0.5 and 0.25 l/min with 0.05-1% active compound (**lab. scale**); 20, 10, 5 and 2.5 l/min, each gas mixture containing 500±30ppm active compound (**pilot scale**)
- **Alloys;** Pure Mg (**lab. scale**); the die casting alloy AM50 (5-5.8% Al) and the sand casting alloy RZ5 (3.5-5% Zn, 0.8-1.7% RE (rare earth metals) and 0.4-1% Zr) (**lab. and pilot scale**)
- **Temperatures;** 670, 700 and 800°C (**all alloys, lab. scale**); 680°C (only AM50) and 710°C (AM50 and RZ5) (**pilot scale**)

In addition, the respective compounds' abilities to quench magnesium fires were tested.

Results of the technical and environmental performance evaluation as well as fire quench testing, may be summarized as:

- All three active compounds give better melt protection than SF<sub>6</sub> under each of the tested conditions. The general, overall ranking, in order of most to least amount of active compound needed to protect a given magnesium melt surface, was found to be: SF<sub>6</sub>, HFC 134-a, HFE 7100, Novec™612.
- All three compounds have significantly better protection properties in CO<sub>2</sub>-rich carrier gases than in air.
- "Diluting" air with Argon as a carrier gas led to very bad melt protection.
- It is significantly more difficult to protect both pure magnesium and its alloys at high temperatures than at lower temperatures. Pure magnesium is particularly difficult to protect at high temperatures. Air is not a suitable carrier gas at temperatures above 700°C for any Mg alloy.
- More fluorine per unit time is generally needed to protect the RZ5 alloy than the AM50 alloy.
- While their relative performances were not compared, all of the three new active compounds – like SF<sub>6</sub> – are effective magnesium fire quenchers.
- All three replacement compounds provide a lower total greenhouse gas impact than SF<sub>6</sub>.
- The relative CO<sub>2</sub>-equivalent emission of the three compounds, under technically optimal conditions, was from best to worst; HFE 7100, Novec™612, HFC 134-a and SF<sub>6</sub>. It should however be noted that Novec™612 had not reached its protective limit in these measurements and therefore, its relative rating may be questionable.
- CO was the principal off-gas specie produced in the furnace gas with CO<sub>2</sub> as carrier for each of the tested active compounds HFC 134-a, HFE 7100 and Novec™612.

- HF was generated in the furnace off gas mainly when synthetic air (a mixture of 79% N<sub>2</sub> and 21% O<sub>2</sub>) or even more so, Argon/synthetic air mixtures, were used as carrier gases. This may be due to elevated moisture levels carried in these gases and/or different gas-magnesium reactions occurring compared to the CO<sub>2</sub> carriers. HF levels were highest when using Novec™612 as the active compound in the cover gas.

In addition, it was shown that Computational Fluid Dynamics modelling may be applied to evaluate design parameters of a closed Mg furnace in order to obtain a desired cover gas flow in the furnace. Important parameters to the overall furnace cover gas flow include the distance between gas inlet pipe and metal, gas inlet hole diameter, temperature difference between furnace temperature and metal surface as well as gas velocity.

### 3.2 Introduction

Three fluorinated gas (or liquid at room temperature) compounds - Novec™612, HFE7100 and HFC 134-a - were selected to be extensively tested for their suitability as active components in cover gases for magnesium melt protection.

- **HFC 134-a (CF<sub>3</sub>CH<sub>2</sub>F)**. A hydrofluorocarbon commonly used as a refrigerant in vehicle air conditioners. The estimated GWP of HFC 134-a is 1300. The compound has several manufacturers but its use as a magnesium protectant is patented by the Australian Magnesium Corporation (AMC). The patent is at the time of the report writing under dispute in the US.
- **HFE 7100 (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>)**. A fluorinated ether currently used as a precision cleaning solvent. The compound is liquid at room temperature (BP=60°C) and the estimated GWP of HFE 7100 is 390. The compound is manufactured by 3M but its use as a magnesium protectant is patented by AMC. The patent is at the time of the report writing under dispute in the US.
- **Novec™612 (C<sub>3</sub>F<sub>7</sub>C(O)C<sub>2</sub>F<sub>5</sub>)**. A fluorinated ketone which is liquid at room temperature (BP= 49°C). The estimated GWP of Novec™612 is ~1. The compound is mainly targeted at fire fighting applications but manufactured and licensed for use as a magnesium protectant by 3M.

The selection of the three active compounds was based on previous testing carried out in the first year of the IMA/SINTEF collaborative project. In a first round of laboratory experiments, a large matrix style parameter test campaign was carried out, as described in Section 3.3. Using the results of the laboratory tests, a subsequent pilot plant scale testing campaign was designed and carried out at Norsk Hydro's research laboratories in Porsgrunn, Norway. This campaign is further described in Section 3.4. In conjunction with the pilot scale campaign, a Computational Fluid Dynamics study was carried out to describe the cover gas flow in the pilot scale furnace. This modelling study is detailed in Section 3.5.

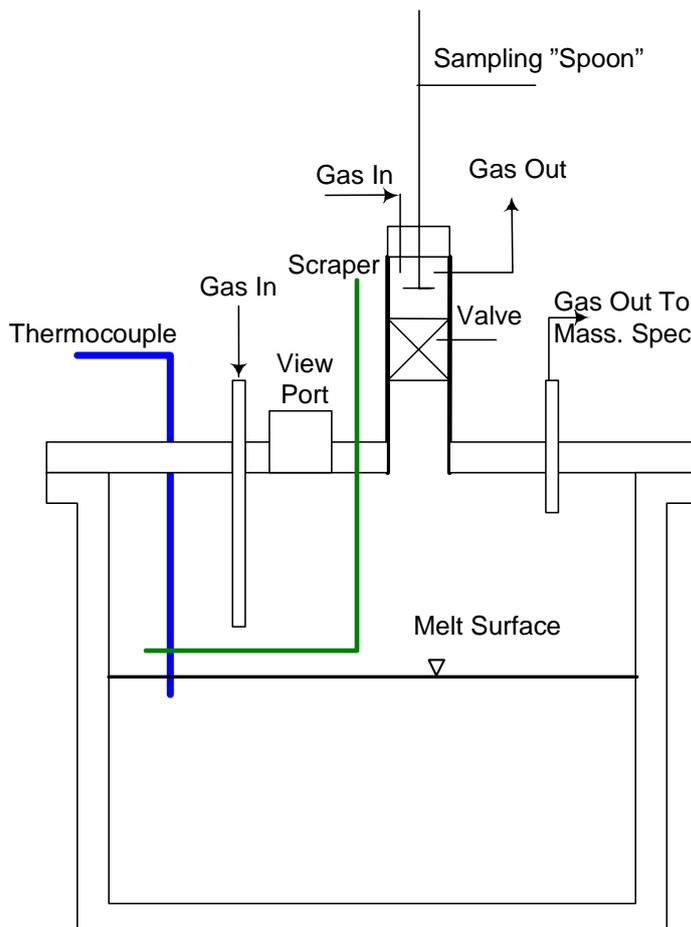
### 3.3 Laboratory Scale Testing of Alternative Cover Gases

As mentioned in Section 3.2, a first exploratory laboratory scale campaign was carried out in order to get an appreciation of how the three new compounds performed - compared to each other and to  $\text{SF}_6$  – under different conditions. Well aware of its limitations in terms of giving reliable absolute values of, for example off-gas products, translatable to real life conditions, this investigation was designed to give indications of trends of how the different compounds behave under comparable conditions.

#### 3.3.1 Experimental

All testing was carried out in a closed crucible with in-built viewing, raking, sampling and gas analysis system (shown in Figure 3.1). The crucible was heated in a Kanthal element "open pot" furnace. In these experiments, a matrix of different test parameters was investigated. The full experimental test matrix is laid out in Appendix 1. The main experimental parameters were:

- **Active components:** Novec™612, HFE7100, HFC134a,  $\text{SF}_6$
- **Carrier gas:** Air,  $\text{CO}_2/5\%\text{air}$ ,  $\text{CO}_2$ ,  $\text{Ar}/5\%\text{Air}$ ,  $\text{Ar}/\text{CO}_2$ ,  $\text{CO}_2/\text{N}_2$
- **Alloy:** Pure Mg, AM50, RZ5
- **Temperature:**  $670^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $800^\circ\text{C}$
- **Flow rate ( $Q_{\text{tot}}$ ):** 1.0, 0.5 and 0.25 l/min
- **Active compound concentration:** Ranging between 0.05% and 1.0%



**Fig. 3.1.** Schematic drawing of the test furnace. The internal diameter of the crucible is 210 mm, i.e. the melt surface area  $\sim 0.03 \text{ m}^2$

For each new parameter combination, the investigated gas composition was purged over the melt surface until stable conditions were obtained (~10 minutes for new active compound concentration, ~30 minutes for new temperature). The surface was then raked and the off-gas (Mass Spectrometer) analysis started. Although this procedure may result in minor traces of fluorine remaining in the melt, it was considered the best practical approach.

Each off-gas was analysed with 6 mass sweeps, each taking approximately 2 minutes. The magnesium melt surface was observed for 10 minutes before film sampling. For each new active component and carrier gas, the magnesium (or alloy) metal was replaced.

The protection suitability for each of the different tested parameter combinations was evaluated on the basis of visual observations of protection efficiency (excessive oxidation, surface film characteristics etc) as well as off-gas composition. These observations are presented in a summarised version in the following section. Observations for each set of conditions are tabulated in Appendix 1.

### 3.3.2 Results

#### Visual Observations of the Performance of the Cover Gases

If not otherwise stated, observations refer to a total gas (active compound + carrier) flow ( $Q_{tot}$ ) of 0.5 l/min. "Effective" or "adequate" protection is here defined as a metal surface after exposure which is shiny or dull metallic (with or without coloured lustre), without spotfires/smoke and oxide build-up.

#### **Novec™612**

##### Pure magnesium

- *Novec™612 and air*: Dull metallic at the higher concentrations, more shiny at low concentrations. Protection effective at 0.05% (limit to test). All in all, Novec™612 in air produces a comparatively thick surface film. When protection fails (700°C/0.05%, all tests at 800°C) the film grows thick and crusty. Smoke not observed at 670°C. At 700°C, smoke is observed at 0.05% active compound, while at 800°C smoke is always observed (1.0%, 0.5% and 0.2%). Spot fire is observed at sampling at 670°C, not observed at 700°C, and continuous smoulder/fire at 800°C
- *Novec™612 and CO<sub>2</sub>/5%air*: Generally brilliant shiny, elastic but thin film. Slightly coloured at lower Novec™612 concentrations (due to light refraction: film thickness ~0.5 µm). Protection effective at 0.05% active compound but it is likely that lower concentrations, although not tested, would be effective at temperatures around 700°C. At 800°C, the film is still thin, but with a dull, cracked layer on top. No smoke observed at 670°C and 700°C. At 800°C smoke is observed at 0.1% Novec™612. No spot fires observed at 670 and 700°C. Continuous fire is observed at 800°C with 0.1% active component gas but no fire observed with 0.2%.
- *Novec™612 and 100% CO<sub>2</sub> (only tested at 700°C)*: Thin, blackened or coloured surface but no smoke or spot fires observed.

##### AM50

- *Novec™612 and air*: Satin film at 670°C, more shiny at 700°C. Protection effective at 0.05% (lower limit for test) at both temperatures. Crusty layer at 800°C No smoke observed at 670°C and 700°C. At 800°C smoke is observed at 0.5% Novec™612. Spot fires observed at sampling at 670°C, 700°C and 800°C for lower Novec concentrations.
- *Novec™612 and CO<sub>2</sub>/5%air*: Satin grey film with 0.1% Novec™612 concentration at 670°C. 0.05% concentration (lower limit for test) protects effectively with a shiny elastic surface film. At 700°C, shiny thin and more (relatively) brittle film. At 800°C satin dull film at higher Novec

concentrations. Effective protection at 0.05% (lower limit to test) at both 700°C and 800°C. No smoke or spot fires at all at 670°C, 700°C and 800°C.

#### RZ5

- *Novec™612 and air*: At 670°C satin grey/dull metallic (thick surface film) when high concentration, shiny at low concentrations. At 700°C shiny metallic. Effective protection at 0.05% (limit to test) at both 670°C and 700°C. At 800°C, satin at low concentrations, crusty dark at high concentrations. Smoke is not observed at 670°C and 700°C, but at 800°C. Spot fires observed stochastically during sampling.
- *Novec™612 and CO<sub>2</sub>/5%air*: At 670°C dull metallic film with the higher Novec concentrations, shiny metallic film at lower concentrations. At 700°C shiny metallic film. Protection effective at 0.05% (limit to test) at both temperatures. At 800°C, satin brittle and cracked film at all concentrations, but protects at 0.075%. Smoke is not observed at 670°C and 700°C. At 800°C, smoke is observed only at 1% active compound. Spot fire observed at lower Novec concentration for 670°C but not at 700°C and 800°C.

Interestingly, the RZ5 alloy was left in CO<sub>2</sub>/5%Air (without active component) for 20 minutes following the experiments, without signs of oxidation products building up. The melt was also raked after 20 minutes without any effect other than small spot fires.

#### **HFE 7100**

##### Pure magnesium

- *HFE 7100 and air*: At 670°C, shiny surface film with effective protection at 0.05% (limit to test). Generally very elastic films (i.e., at most temperatures/concentrations). At 700°C/0.2% HFE, crusted, thick film. No smoke observed at 670°C. At 700°C, smoke was observed. Spot fires observed during sampling at 670°C. 700°C unable to observe due to smoke. 800°C not tested.
- *HFE 7100 and CO<sub>2</sub>/5%air*: At 670°C, brilliant shiny thin surface film with effective protection at 0.05% (limit to test). Extremely elastic films. 700°C/0.2% also effective protection. 800°C crusted thick. No smoke or spot fires observed at any temperatures and concentrations.

##### AM50

- *HFE 7100 and air*: 670°C at 0.2% and to some extent 1.0% HFE is OK, otherwise satin grey or discoloured surface film at all temperatures. Smoke is observed in all tests. No spot fires observed at 670°C and 700°C. At 800°C unable to observe due to smoke.
- *HFE 7100 and CO<sub>2</sub>/5%air*: Shiny, brittle somewhat uneven surface film, although effective protection at 0.05% (limit to test) at both 670°C and 700°C. At 800°C, satin cracked film at 0.1%. No smoke or spot fires observed at any temperature.
- *HFE 7100 and Ar/5%CO<sub>2</sub>*: Somewhat brittle surface film, protective at 670°C and 700°C (not tested at 800°C). Traces of smoke development during raking. The oxide colour was grey for low HFE 7100 concentration and turned black for higher concentrations.

##### RZ5

- *HFE 7100 and air*: Thin viscous oxide layer. Thinner with lower concentration active compound. Protective at 670°C and 700°C down to 0.05% cover gas concentration. A lot of smoke at 800°C, 0.5 l/min, and 0.5% cover gas concentration.
- *HFE 7100 and CO<sub>2</sub>/5%air*: Viscous, thin oxide. Protective at 670°C, 0.5 l/min cover gas flow rate and at least down to 0.05% concentration. At 800°C, development of nodular oxide build-up at 0.05%, protective oxide with 0.1%.

- *HFE 7100 and Ar/5%CO<sub>2</sub>*: Dark, thin, and viscous oxide. Protective at 670°C with 0.5 l/min and 0.2% active compound concentration in cover gas. Some smoke during raking for lower concentration or higher temperatures.

### **HFC 134a**

#### Pure magnesium

- *HFC 134a and air*: Shiny brittle surface film. Sample with severe spot fire (670°C/0.2%-1l/min) discoloured with white powder. Protection effective at 0.12% HFC. 700°C/0.2% is also effective, but protection fails at 800°C (thin, crusted). Smoke is not observed at 670°C and 700°C, but severe at 800°C. Spot fires observed at 670°C/0.06% HFC for cover gas flow rate,  $Q_{tot} = 1.0$  l/min (severe, discolouring the sample), and at 700°C. At 800°C impossible to observe due to smoke.
- *HFC 134a and CO<sub>2</sub>/5%air*: Brilliantly shiny less brittle film (compared to pure air). Protection effective at 0.06% - 1.0 l/min at 670°C and at 0.2% - 1 l/min at 700°C. Protection fails at 800°C (thin, black, crusted). No smoke or spot fires observed at any temperature.

#### AM50

- *HFC 134a and air*: Shiny, brittle surface film. Protection effective at 0.06% with  $Q_{tot} = 1.0$  l/min at 670°C, and 0.12% at 700°C. Protection fails at 800°C (thin, dull white). No smoke observed at 670°C and 700°C. At 800°C smoke is observed at 0.12% but not at 0.24%. Spot fires observed at all temperatures.
- *HFC 134a and CO<sub>2</sub>/5%air*: Shiny oxide less brittle surface film. Protection effective at 0.075% with  $Q_{tot} = 0.74$  l/min at 670°C, and 0.12% at 700°C. Protection fails at 800°C (satin cracked). No smoke or spot fires observed at any temperature.

#### RZ5

- *HFC 134a and air*: Relatively poor protection. Thin greenish, reddish, or violet oxide on the melt. Spot fires at sampling for all cover gas concentration and flow rates. Increased fire intensity at 800°C.
- *HFC 134a and CO<sub>2</sub>/5%air*: Thin greenish oxide layer, viscous to some extent. Protective (no spot fires or smoke) at all cover gas flow rates, active compound concentrations and temperatures.

### **SF<sub>6</sub>**

#### Pure magnesium

- *SF<sub>6</sub> and air*: At 670°C, protective during sampling for highest concentration (1.6% and 0.5 NI/min). Spot fires during sampling for lower concentration. At higher temperature (up to 800°C; gas flow 0.5 l/min, SF<sub>6</sub> concentration 1%) there were fire and smoke during both raking and sampling.
- *SF<sub>6</sub> and CO<sub>2</sub>/5%air*: Thin, viscous, and protective oxide layer with various colours. At 670° protective at least down to 0.2% SF<sub>6</sub> at 0.5 l/min cover gas flow rate. Protective also at 800°C with 1% SF<sub>6</sub> at 0.5 l/min cover gas flow rate.

#### AM50

- *SF<sub>6</sub> and air*: Relatively poor protection at all cover gas flow rates and concentrations. Thin, viscous, greyish oxide on the melt. Spot fires at sampling for all cover gas concentration and flow rates. Increased fire intensity at 800°C.

- *SF<sub>6</sub>* and *CO<sub>2</sub>/5%air*: Protective (no spot fires or smoke) at all cover gas flow rates, active compound concentrations and temperatures. Thin greyish/colourized oxide layer, somewhat brittle.

#### RZ5

- *SF<sub>6</sub>* and *air*: Poor protection at all cover gas flow rates and concentrations. Thin, viscous, greyish oxide on the melt. Spot fires at sampling for all cover gas flow rates and active compound concentrations. Increased fire intensity at 800°C.
- *SF<sub>6</sub>* and *CO<sub>2</sub>/5%air*: Protective (no spot fires or smoke) at all flow rates, active compound concentrations and temperatures. Thin, viscous (more than in air) greyish oxide layer.

### Summary, Visual Observations

#### General Observations

- *CO<sub>2</sub>/5%* air carrier gas generally provides better protection than pure air. It also is regarded as safer than air, with generally far less smoke and fire observed. Air does not appear to be an effective carrier at temperatures above 700°C.
- The effect of "diluting" air with Argon as a carrier gas led to very bad melt protection (and in some cases the formation of black oxide). It was found that not even Ar/20%air (+ for example Novec™612) was an effective cover gas. If diluted with Argon, the carrier needed as much as 50% air to be protective with Novec™612. HFC 134a combines better with Argon than Novec™612 and HFE7100. However, both air and *CO<sub>2</sub>/5%* air gives far better results than carriers containing Argon.
- Pure magnesium is more vulnerable to temperature changes than the alloys. This is shown in the results as excellent protection of pure magnesium at any cover gas concentration at 670°C, and less effective protection at 700°C and especially 800°C. The alloys generally behave better at elevated temperatures due to their lower Mg content.

#### Novec™612

Novec™612 protected all alloys tested well at 670°C and 700°C. It tends to over-protect at high concentrations, producing satin, moderately thick (~1 µm) oxide layers. At low concentrations, oxide appearance is shiny metallic. At 800°C, Novec™612 protects pure Mg in *CO<sub>2</sub>/air* in 1.0% concentration; AM50 in *CO<sub>2</sub>/air* (0.05%), while RZ5 is protected both in air (0.2%) and *CO<sub>2</sub>/air* (0.075%), although the oxide appearance is cracked dull metallic. With 100% *CO<sub>2</sub>* (700°C), a dull black cracked coating forms.

When Novec™612 protects effectively, the general impression is that it produces a thin, flexible, shiny metallic oxide film (flexible also when over-protecting).

#### HFE 7100

HFE7100 shows higher dependency on carrier gas than the other active compounds, as is it more efficient in *CO<sub>2</sub>/5%* air compared to 100% air. In 100% air, it protects pure Mg only at 670°C (down to 0.05%), while it fails to protect AM50 well at any temperature. In *CO<sub>2</sub>/5%* air, pure Mg is protected at 670°C (down to 0.05%) and at 700°C (0.2%), while protection fails at 800°C. AM50 is protected both at 670°C and 700°C at 0.05%, although the oxide film is somewhat uneven. At 800°C the film turns satin brittle metallic, although no smoke or fires was observed. No tendencies of over-protection were observed.

When HFE7100 protects effectively the general impression is that it produces a very thin, brilliant shiny oxide film, very elastic (with pure Mg), quite elastic (RZ5) and brittle (with AM50).

### HFC 134a

HFC 134a protects both pure magnesium, AM50 and RZ5 at 670°C and 700°C (0.06% - 0.08%) carried with both air and CO<sub>2</sub>/5% air to some extent but generally not as well as either HFE 7100 or Novec™612. At 800°C, protection has a tendency to fail with spot fires and excessive oxidation.

When HFC 134a protects effectively, the general impression is that it produces a very thin, shiny metallic oxide film, which is brittle with 100% air carrier gas. The film is brilliantly shining with pure Mg in combination with CO<sub>2</sub>/5% air, and AM50 carried with 100% air. For RZ5, films seem to be slightly coloured HFC134a is to some extent more prone to “serious” spot fires at sampling than the other active compounds.

### SF<sub>6</sub>

Again, a mixture of CO<sub>2</sub> and 5% air as carrier gas gave better protection than a carrier gas of 100% air.

### **Analysis of Off-gas Products**

Although mass spectrometry is not an ideal method of quantitatively measuring the off-gas composition of a relatively unknown reaction products, an indication of relative amounts of the same gas specie under various process conditions can be estimated. Such comparisons are presented below from the obtained mass spectra for the pure magnesium and the AM50 alloy. The off-gases over the RZ5 alloy were not analyzed. The different off-gas species identified through the mass spectra are listed in Table 3.1.

**Table 3.1** List of potential off-gas species and their associated highest MS peaks. The bold face numbers are used for identification.

<b>Decomp. Product</b>	<b>Name</b>	<b>Associated Characteristic</b>	<b>MS peaks (Mass number)</b>	<b>CAS (Chemical Abstracts Services) Registry No.</b>
CO	Carbon monoxide	Toxic (LTEL=50ppm)	28, <b>12</b>	630-08-0
CO <sub>2</sub>	Carbon dioxide	Carrier (GWP = 1)	<b>44</b>	124-38-9
COF <sub>2</sub>	Carbonic difluoride	Toxic (LTEL=5ppm)	<b>47</b> , 66	353-50-4
CF <sub>3</sub> CO <sub>2</sub> H	Trifluoro acetic acid	Toxic (No safe exp. limit)	<b>45</b> , 69	76-05-1
CF <sub>4</sub>	Carbon tetrafluoride	High GWP (= 6900)	<b>69</b> , 50	75-73-0
C <sub>2</sub> F <sub>6</sub>	Hexafluoro ethane	High GWP (= 9200)	<b>69</b> , 119	76-16-4
HF	Hydrofluoric acid	Corrosive, (no safe exp limit)	<b>20</b>	7667-39-3
C <sub>2</sub> F <sub>4</sub>	Tetrafluoro ethene	High GWP (~ 8000)	31, <b>81</b>	116-14-3
C <sub>4</sub> F <sub>10</sub>	Decafluoro butane	High GWP (= 7000)	<b>69</b> , 119	355-25-9
C <sub>3</sub> F <sub>6</sub>	Hexafluoro propene	High GWP (~ 8000)	31, <b>69</b>	116-15-4
CHF <sub>3</sub>	Trifluoro methane	High GWP (= 11700)	<b>69</b> , 51	75-46-7
HFC 134a	1,1,1,2-tetrafluoroethane	High GWP (= 3800)	33, <b>69</b>	811-97-2
SF <sub>6</sub>	Sulfur hexafluoride	High GWP (= 24000)	<b>127</b> , 89	2251-62-4

In order to identify the various off-gases, the database “Spectra online” ([www.galactic.com/SpcOnline](http://www.galactic.com/SpcOnline)) was consulted. Since most of the gas species show multiple peaks on a mass spectra, some of the peaks will overlap with peaks from other gas species. The most common example is CO and N<sub>2</sub> which both have the largest peak on M = 28. Table 3.1 also shows the peaks used for identifying the gas species. It is important to point out that neither

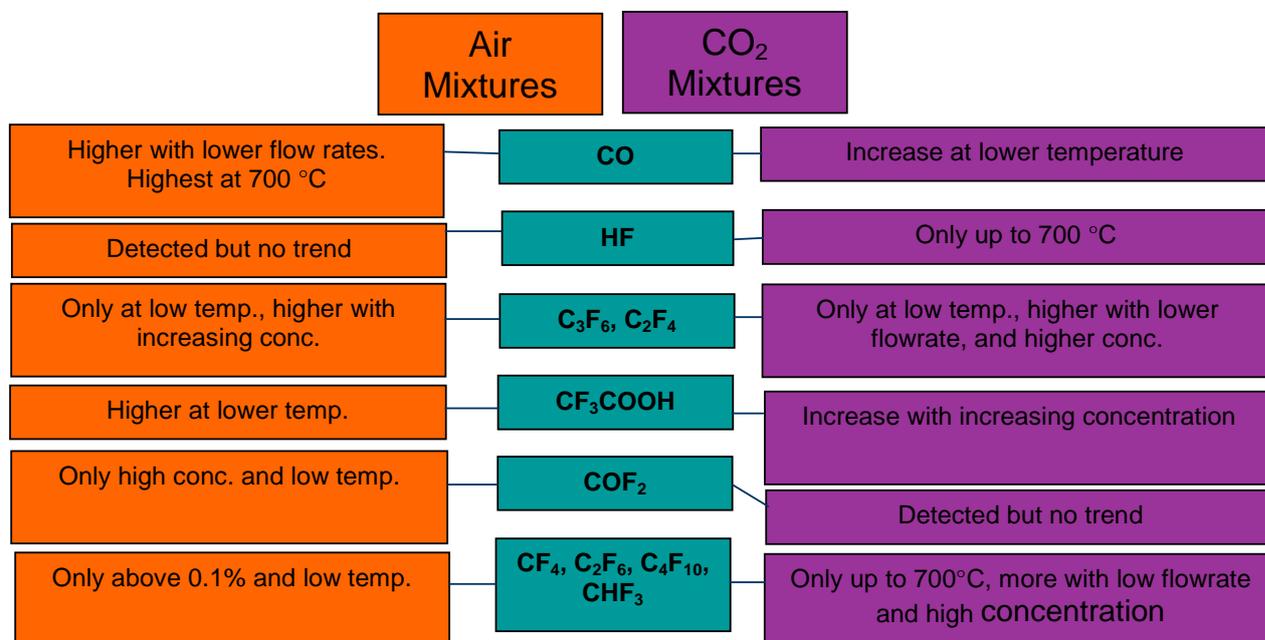
gaseous HFE7100 nor Novec™612 have well documented (in public databases) peaks and thus, un-destructed HFE7100 or Novec™612 could not be determined.

It must be kept in mind that the peak at  $M = 45$  was used to identify the  $\text{CF}_3\text{CO}_2\text{H}$  gas. When  $\text{CO}_2$  ( $M = 44$ ) is used as part of the carrier gas, this will also contribute to the 45 peak. The reason for this is that carbon (and all matter containing carbon) contains a fraction of 1.1%  $^{13}\text{C}$ .

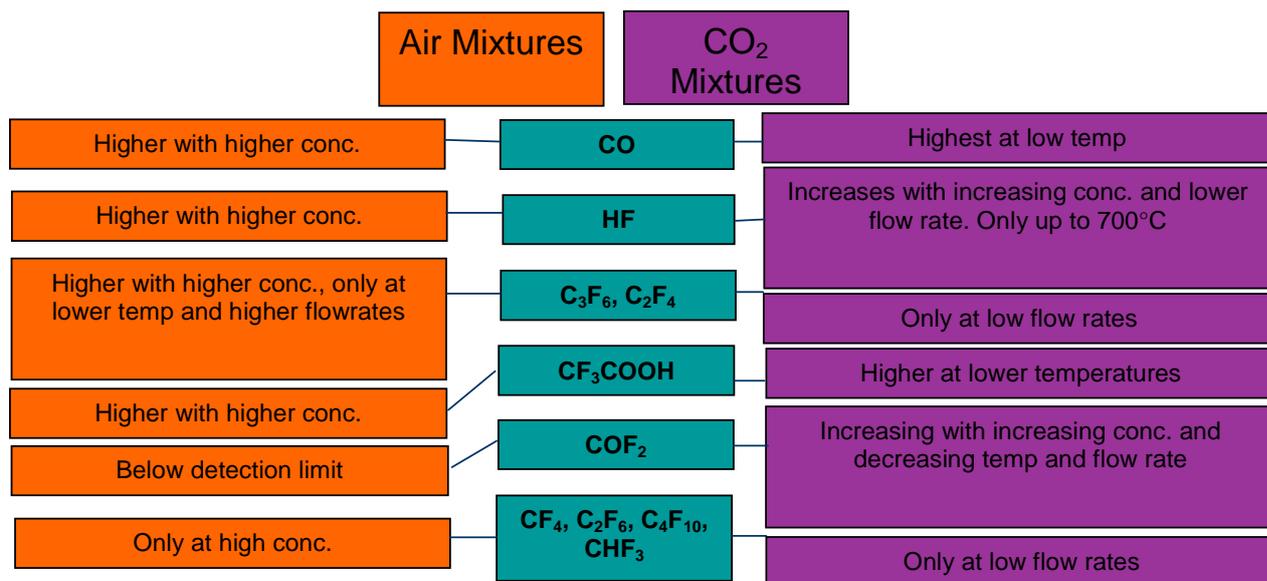
All the off-gas species with high GWP (except  $\text{SF}_6$ ) are for simplicity grouped together. The reason for this is that they have many common peaks and their separation through MS techniques thus not straight forward, and from an environmental point of view, their “GWP impact” are not substantially (orders of magnitude) dissimilar.

### Pure Magnesium

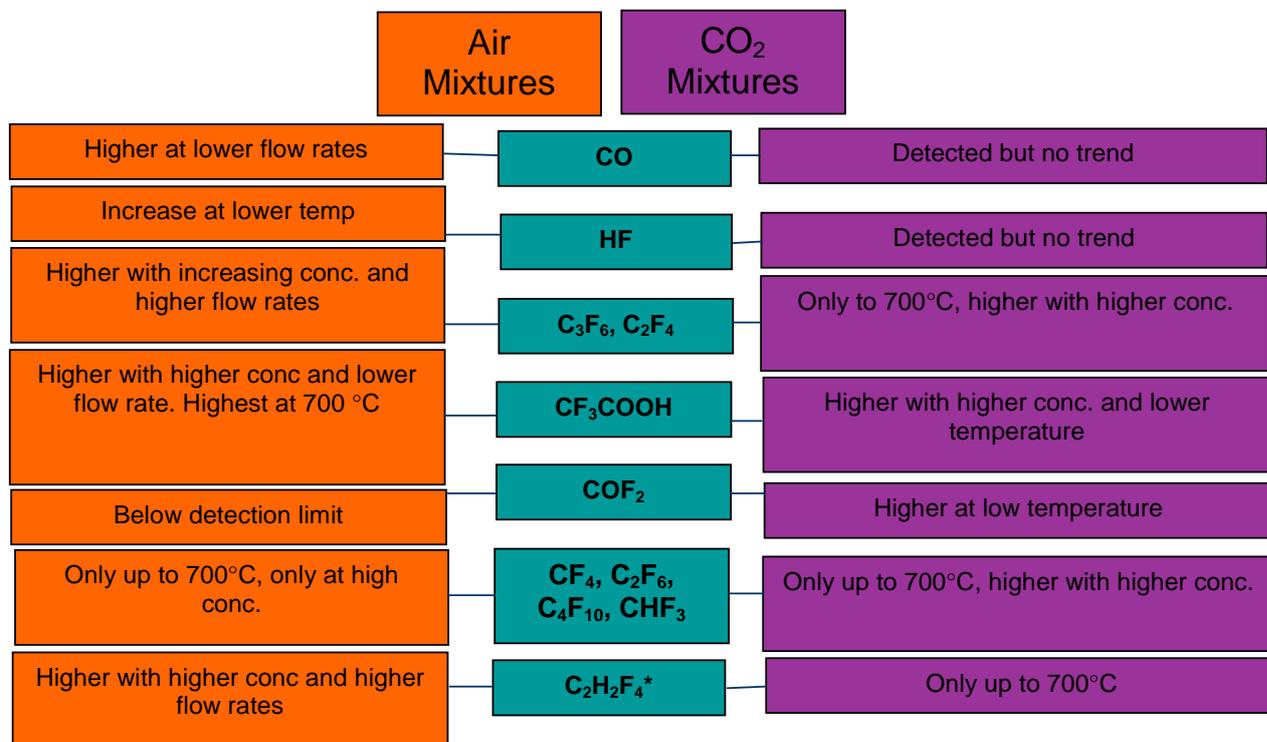
Figures 3.2 to 3.4 are schematics of the trends observed in the quantities of each off-gas specie (or groups thereof) for the two carrier gases containing Novec™612, HFE7100 or HFC134-a respectively. Figure 3.5 is a schematic comparison of the relative amounts of off-gas species observed for the different active components in 100% air and  $\text{CO}_2/5\%\text{Air}$  respectively under equal conditions (standard condition  $670^\circ\text{C}$ ,  $Q_{\text{tot}}=0,5$  l/min, Active component = 0.2%)



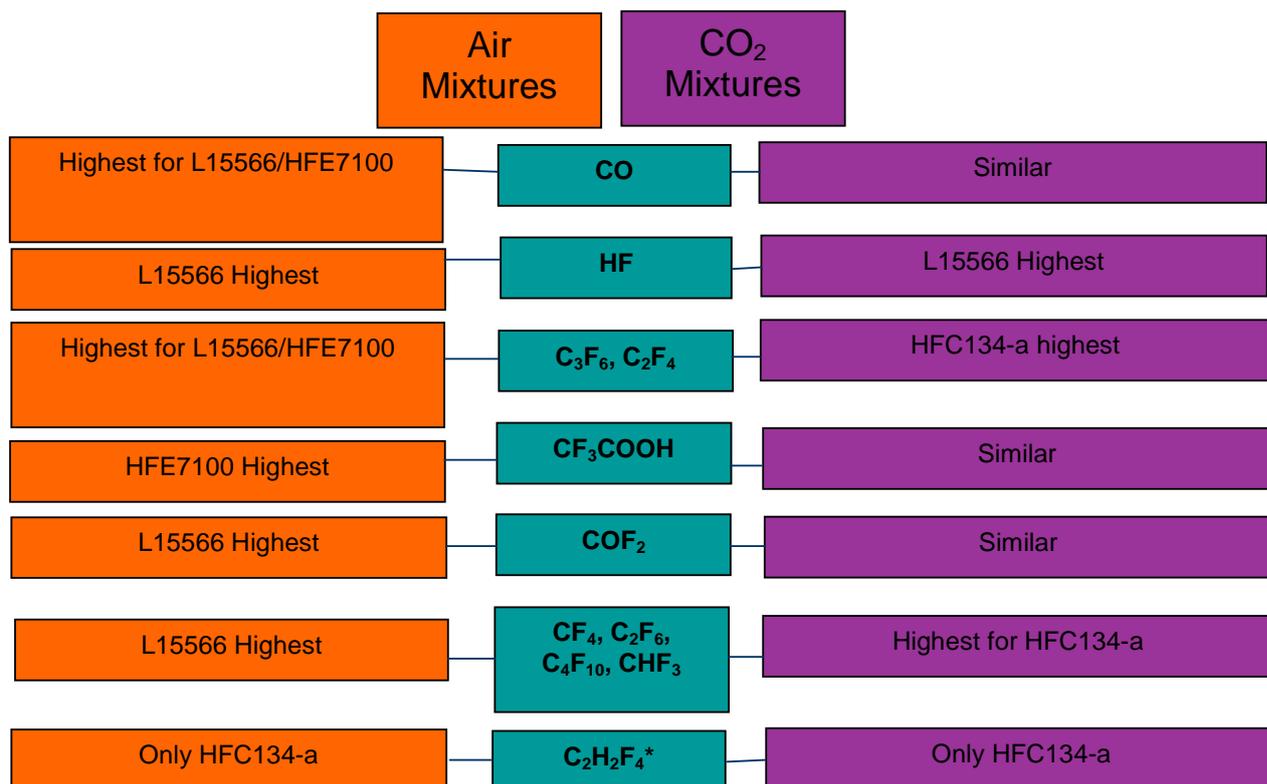
**Figure 3.2.** Schematic of the trends observed in the quantities of each off-gas specie (or groups thereof) under the two carrier gases (100% Air or  $\text{CO}_2/5\%\text{Air}$ ) containing Novec™612



**Figure 3.3.** Schematic of the trends observed in the quantities of each off-gas specie (or groups thereof) under the two carrier gases (100% Air or CO<sub>2</sub>/5%Air) containing HFE7100



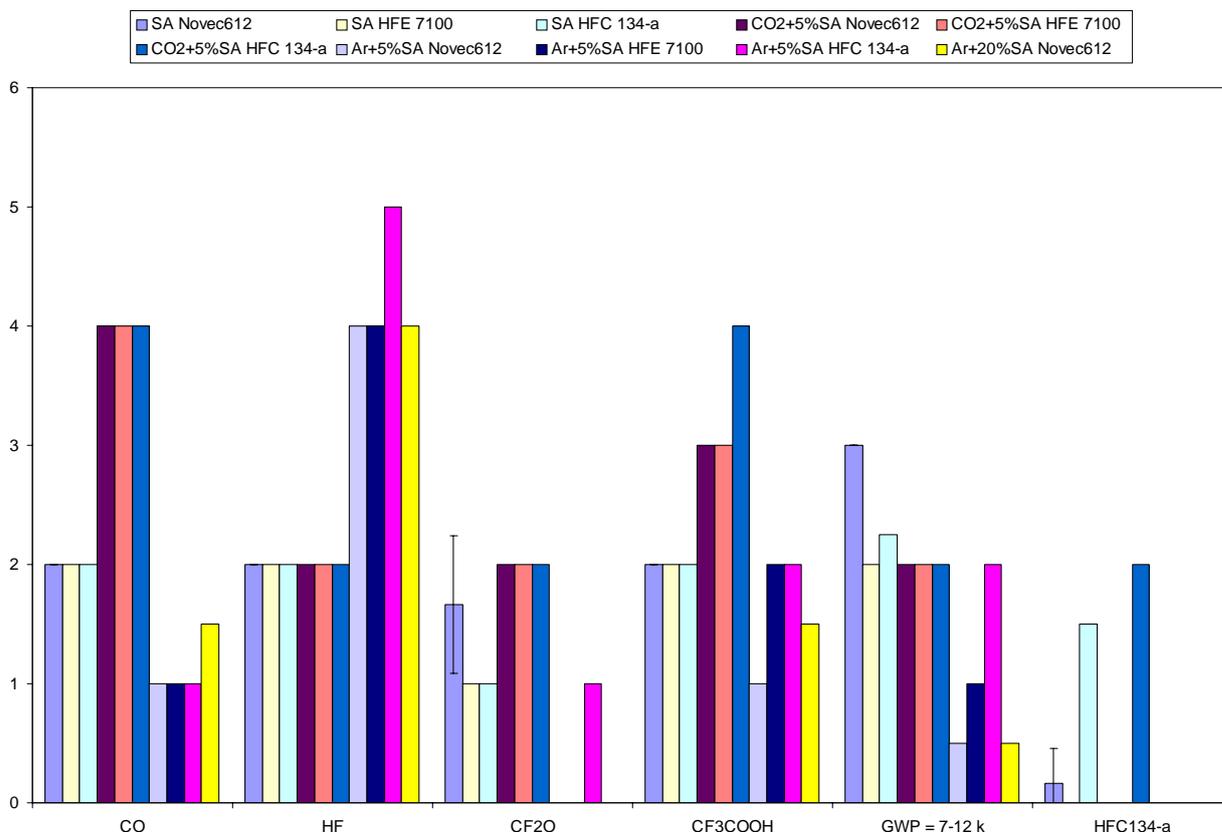
**Figure 3.4.** Schematic of the trends observed in the quantities of each off-gas specie (or groups thereof) under the two carrier gases (100% Air or CO<sub>2</sub>/5%Air) containing HFC134-a



**Figure 3.5.** Schematic of the trends observed in the relative quantities of each off-gas specie (or groups thereof) under the two carrier gases (100% Air or CO<sub>2</sub>/5%Air) as a comparison between the three active gas components at 670°C, Q<sub>tot</sub> = 0,5l/min and concentration. (L15566 was the laboratory name of Novec™612 prior to commercialization when these tests were run)

In Figure 3.6, the off-gas products over pure magnesium have been grouped for various conditions but at a constant **total** amount of active compound per unit time (active compound concentration\*Q<sub>tot</sub>=constant).

**Pure Mg: Category values for constant gas flow, cover gas concentration and temperature.**

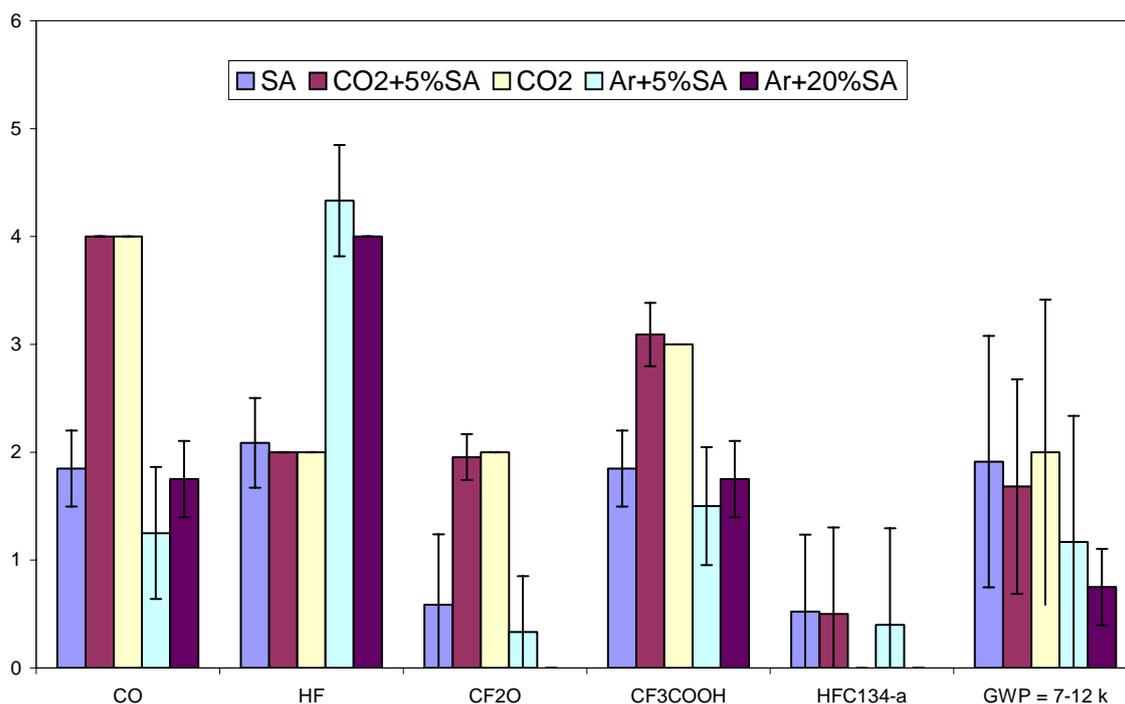


**Figure 3.6.** Relative amounts of selected off-gas products over pure magnesium at 670°C. The Y-axis is a measure of off-gas product intensity ( $\approx$  amount) on a relative scale. The height of each peak may be compared to another for the same gas species but the relative heights between species cannot be compared.

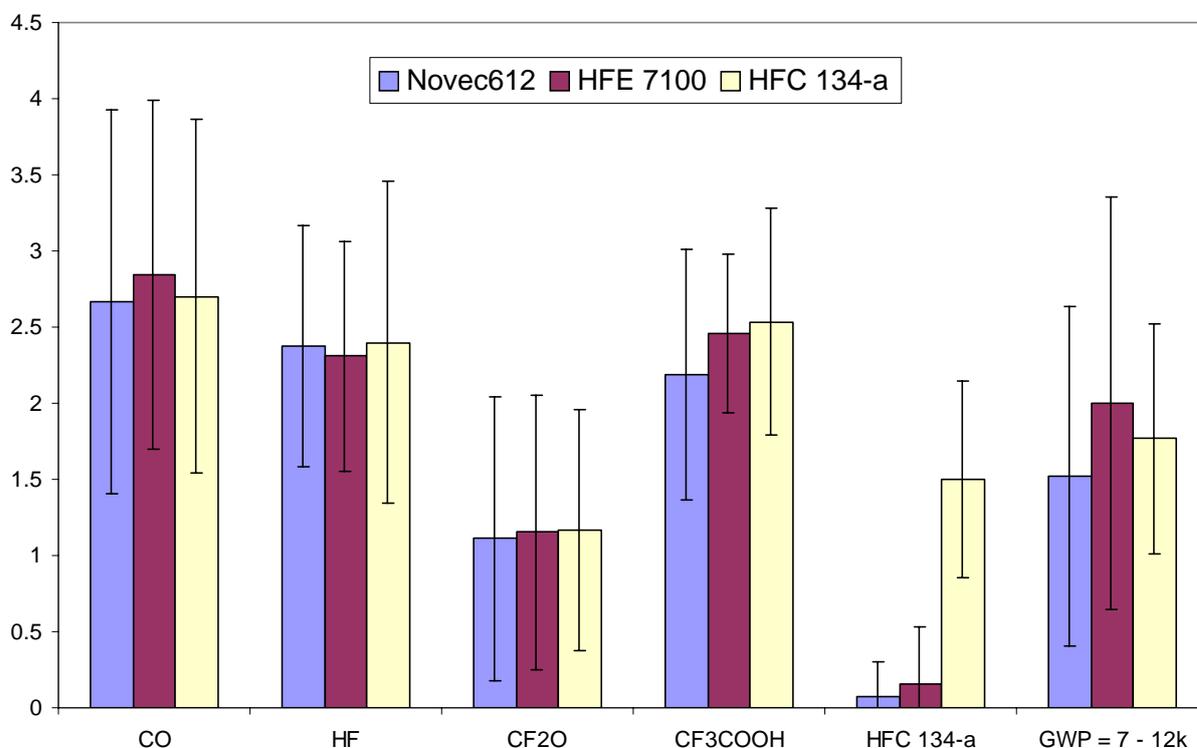
In Figure 3.7, the relative average concentration of the different off-gas products for the three different active compounds for all experiments (concentrations,  $Q_{tot}$ , carrier gases and temperatures) have been compared.

In Figure 3.8, the same comparison as in Figure 3.7 has been done but for the different carrier gases.

As apparent from Figures 3.6 to 3.8, the  $CO_2$ -containing carrier gases produce overall higher concentrations of the carbonic difluoride ( $COF_2$ ) and the trifluoro acetic acid ( $CF_3COOH$ ) than the non- $CO_2$ -containing carrier gases. The type of carrier gas, however, does not seem to greatly influence the total amount of high GWP by-product gas species generated. It is also seen that although there are differences in relative amounts of off-gas species for the three active compounds under different conditions, the relative **average** concentrations of off-gas species are not remarkably different (compare Figures 3.6 and 3.8).



**Figure 3.7.** Relative amounts of selected (and grouped) off-gas products over pure magnesium. Values are averages for the different active components and their concentrations, flow-rates, and temperatures for the different carrier gases.



**Figure 3.8.** Relative amounts of selected (and grouped) off-gas products over pure magnesium. Values are averages for the different carrier gas flow-rates, temperatures and carriers for the different active compounds

### AM50

For the AM50 alloy, the analogous plots to Figures 3.6 to 3.8 (for pure magnesium) were made. These are numbered Figure 3.9 to 3.11.

It can be seen that, similarly to pure magnesium, the CO<sub>2</sub> containing carrier gases produce overall higher concentrations of, especially, the trifluoro acetic acid (CF<sub>3</sub>COOH) but also of the carbonic difluoride (COF<sub>2</sub>). In these experiments, it was also shown that the amount of high GWP species goes radically up if no air goes into the carrier gas. Like pure magnesium, it was also seen that although there are differences in relative amounts of off-gas species for the three active components under different conditions, the **average** concentrations of off-gas species are not remarkably different (compare Figures 3.9 and 3.11). The only difference to pure Mg appears to be that the HFE7100 component generates relatively higher concentrations of the high GWP products.

AM50; category values of off-products for gas mixtures with T = 670 °C and constant amount cover gas

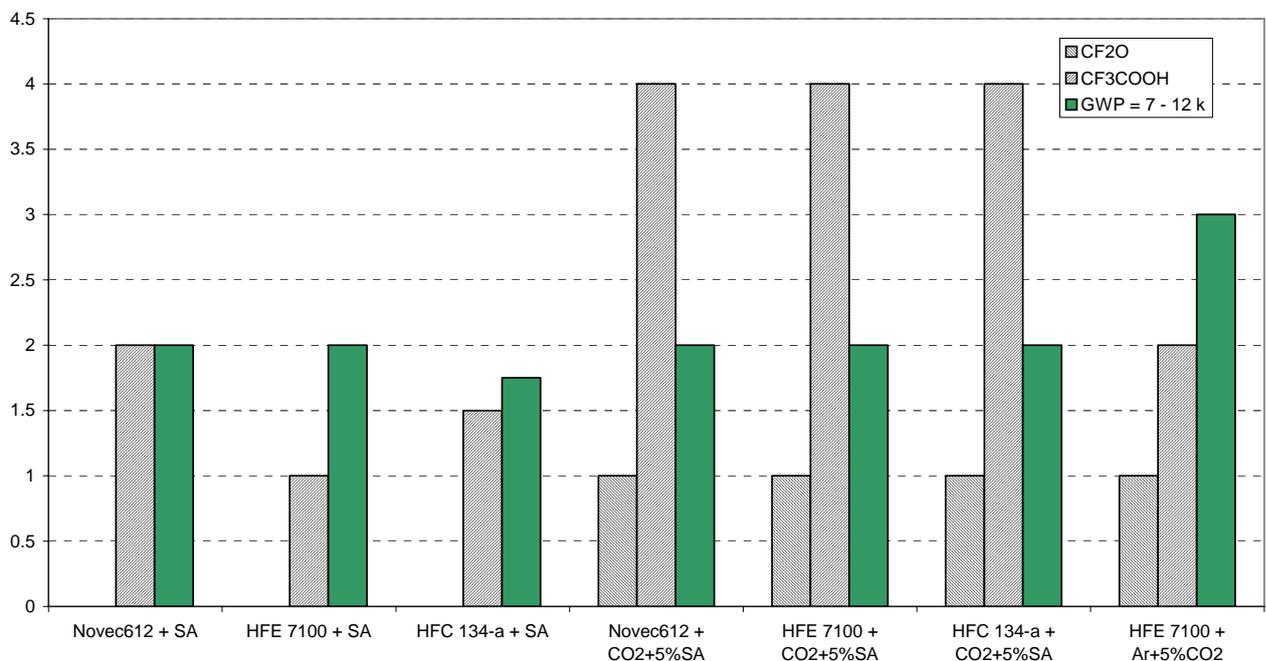
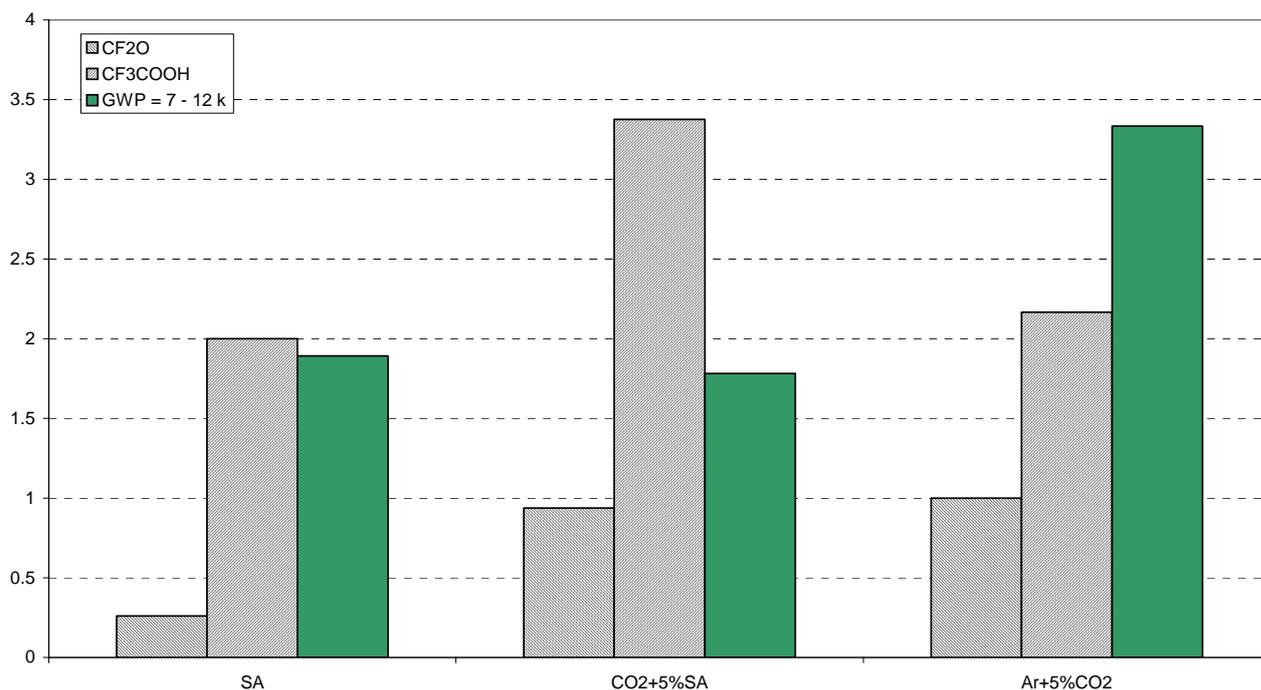
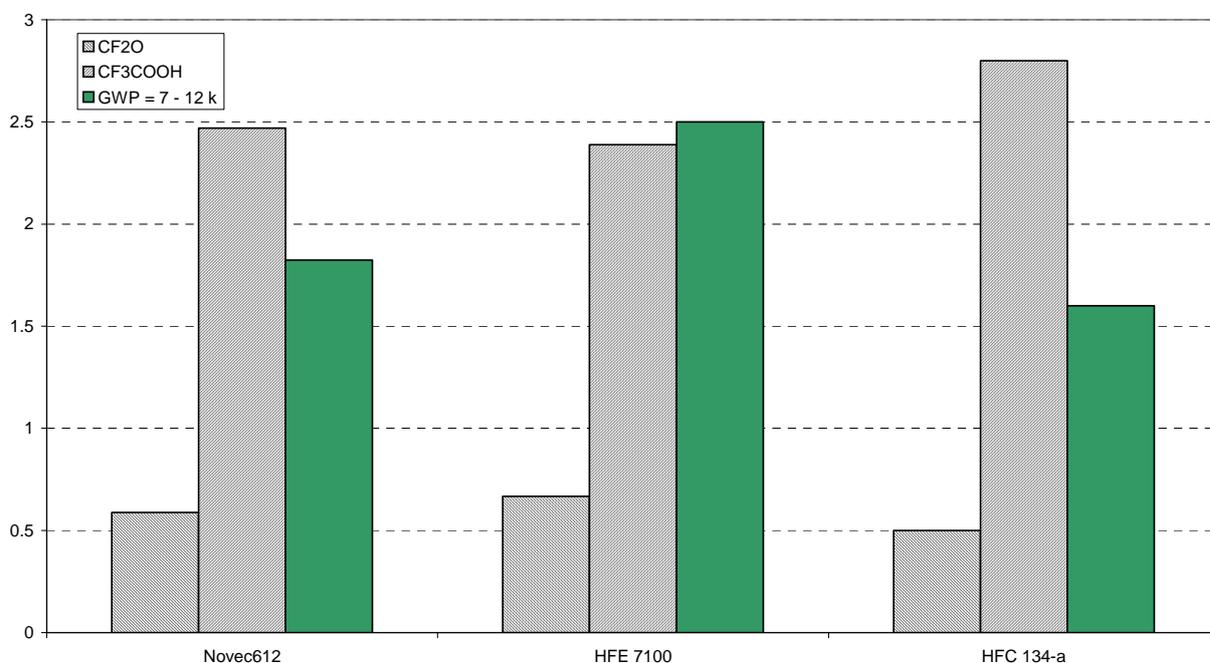


Figure 3.9. Relative amounts of selected (and grouped) off-gas products over AM50 at 670°C

**AM50; average category values of off-products for carrier gases**


**Figure 3.10.** Relative amounts of selected (and grouped) off-gas products over AM50. Values are averages for the different active components and their concentrations, flow-rates and temperatures for the different carrier gases.

**AM50; average category values of off-products for cover gases**


**Figure 3.11.** Relative amounts of selected (and grouped) off-gas products over AM50. Values are averages for the different flowrates, temperatures and carrier gases for the different active compounds.

**Summary, gas analysis**

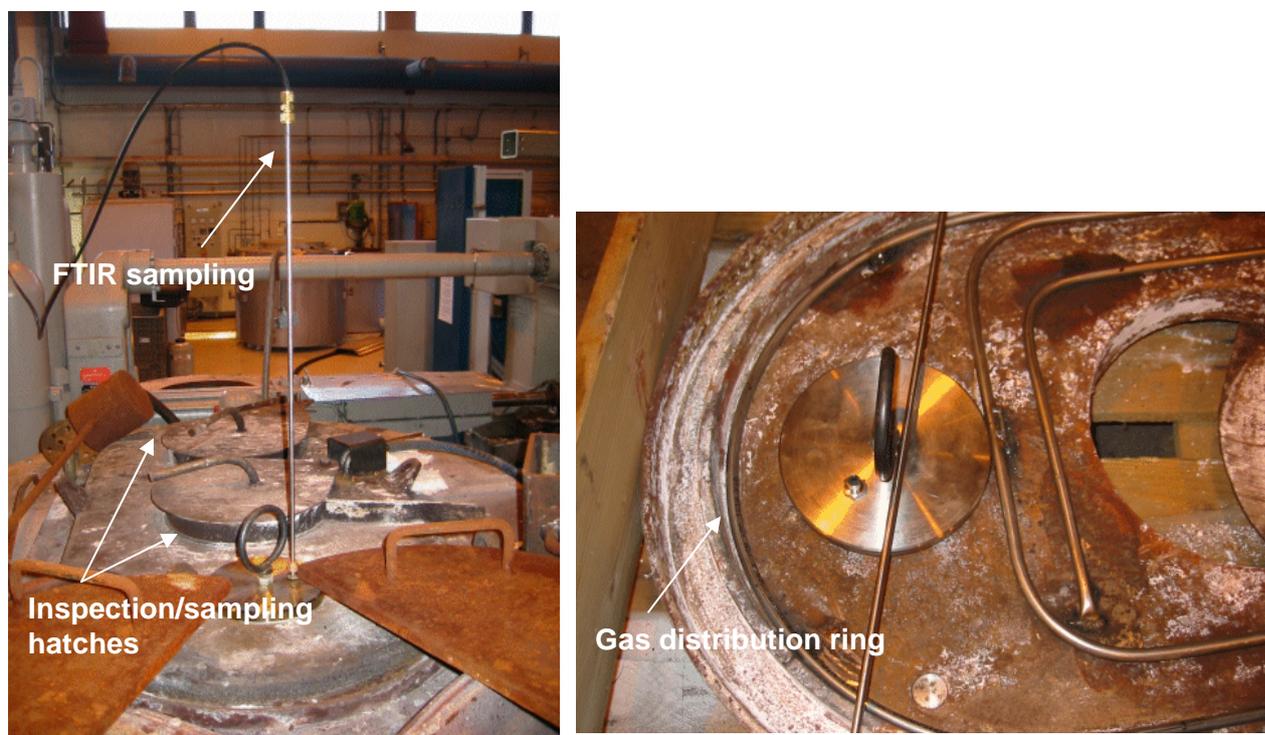
- CO was mainly produced in the furnace gas with CO<sub>2</sub> as carrier gas for each of the tested active compounds HFC 134-a, HFE 7100 and Novec™612.
- HF was generated in the furnace off gas mainly when synthetic or even more so, Argon/synthetic air mixtures, were used as carrier gases. This may be due to elevated moisture levels carried in these gases and/or different gas-magnesium reactions occurring compared to the CO<sub>2</sub>-rich carriers. HF levels were highest when using Novec™612 as active compound in the cover gas.
- While 100% air carrier gas appeared to generate the highest level of off-gas products for Novec™612, CO<sub>2</sub>-rich carriers gave reasonably similar amounts of toxic off-gas species for all of the three active compounds. HFC 134-a gave the highest levels of “high GWP” off-gas species in CO<sub>2</sub>-rich carrier gas.

### 3.4 Pilot Scale Testing of Alternative Cover Gases

To compare the technical and environmental performances of HFC 134-a, HFE 7100 and Novec™612, to each other and to SF<sub>6</sub>, under more realistic pilot scale conditions, a two-week, experimental campaign was carried out at Norsk Hydro's research station in Porsgrunn, Norway. The planned experimental parameters and procedure document for the trials was circulated to and accepted by the IMA SF<sub>6</sub> committee members prior to the commencement of the campaign. This document is attached as Appendix 2.

#### 3.4.1 Experimental Procedures

Experiments were carried out in a "bath tub" furnace which could hold ~500 kg liquid Mg, with a surface area of approximately 0.5m<sup>2</sup>, as illustrated in Figure 3.12. Cover gas mixtures were introduced over the melt surface by means of a gas distribution ring, designed to provide optimal initial (when gases first enter the furnace) distribution of the thermally unstable gases over the magnesium surface. The design and calculations behind the distribution system is further described in Section 3.5. The HFE 7100 and Novec™612 (liquids at room temperature) were evaporated into the selected carrier gas stream using a precision pumping system, as described previously by Milbrath and Owens [11]. The furnace headspace gas for each experimental parameter set was continuously sampled and analyzed through the extractive FTIR method (EPA Method 320) used for EPA studies of various gaseous emissions. During the tests in this furnace, no ingot loading occurred, no metal was withdrawn for casting, and consequently, cover gases were applied to a static surface.



**Fig. 3.12.** Experimental furnace set-up with furnace (**left**) and its lid with gas distribution ring (**right**)

The technical performances of the three replacement compounds and SF<sub>6</sub> were compared under the following conditions:

- In two different carrier gas mixtures; industrial dry air (not synthetic air as in the small scale experiments) and CO<sub>2</sub>+5%dry air;
- Different total gas flow rates; 20, 10, 5 and 2.5 l/min, each gas mixture containing 500±30ppm active compound, i.e different amounts of "fluorine" delivered per unit time;
- Two different alloys; the die casting alloy AM50 (5-5.8% Al) and the sand casting alloy RZ5 (3.5-5% Zn, 0.8-1.7%RE and 0.4-1% Zr); and
- Two different temperatures 680°C (only AM50) and 710°C (AM50 and RZ5).

The testing procedure for each test was:

1. Set total gas flow to chosen flow rate;
2. Wait for furnace atmosphere to stabilize (10, 10, 15 or 30 minutes for the flow rates 20, 10, 5 and 2.5 l/min respectively);
3. Remove dross carefully;
4. Close hatch and wait for 10 minutes;
5. Observe/record surface appearance, collect surface film sample (and in some cases metal sample), dross; and
6. Change gas flow rate and repeat from 1. When changing active compound, flush with 0.7% SO<sub>2</sub> in air for approximately 30 minutes before starting from 1.

The key technical performance criterion was the visual appearance of the melt surface. For an acceptable performance, the surface finish should appear shiny (or dull) metallic without spot fires/smoke or pronounced oxide presence and agglomeration at point 5 in the above procedure list.

### 3.4.2 Results

#### Technical Performance

In Table 3.2, the lowest cover gas flow rates of the ones tested (20, 10, 5 or 2.5 l/min) giving acceptable protection according to the above mentioned criterion for each set of conditions, are summarized. A full set of observations is attached in Appendix 3.

**Table 3.2.** Summary of distributed total gas flows needed (for gases containing 500ppm active compound) to protect a 0.5m<sup>2</sup> Mg-alloy melt surface. Shaded numbers denote conditions tested in long term exposure experiments (2.5 hours). For numbers marked <, the flow was assessed as more than adequate for protection and it was therefore assumed that the minimum flow needed for protection was below the lowest tested flow.

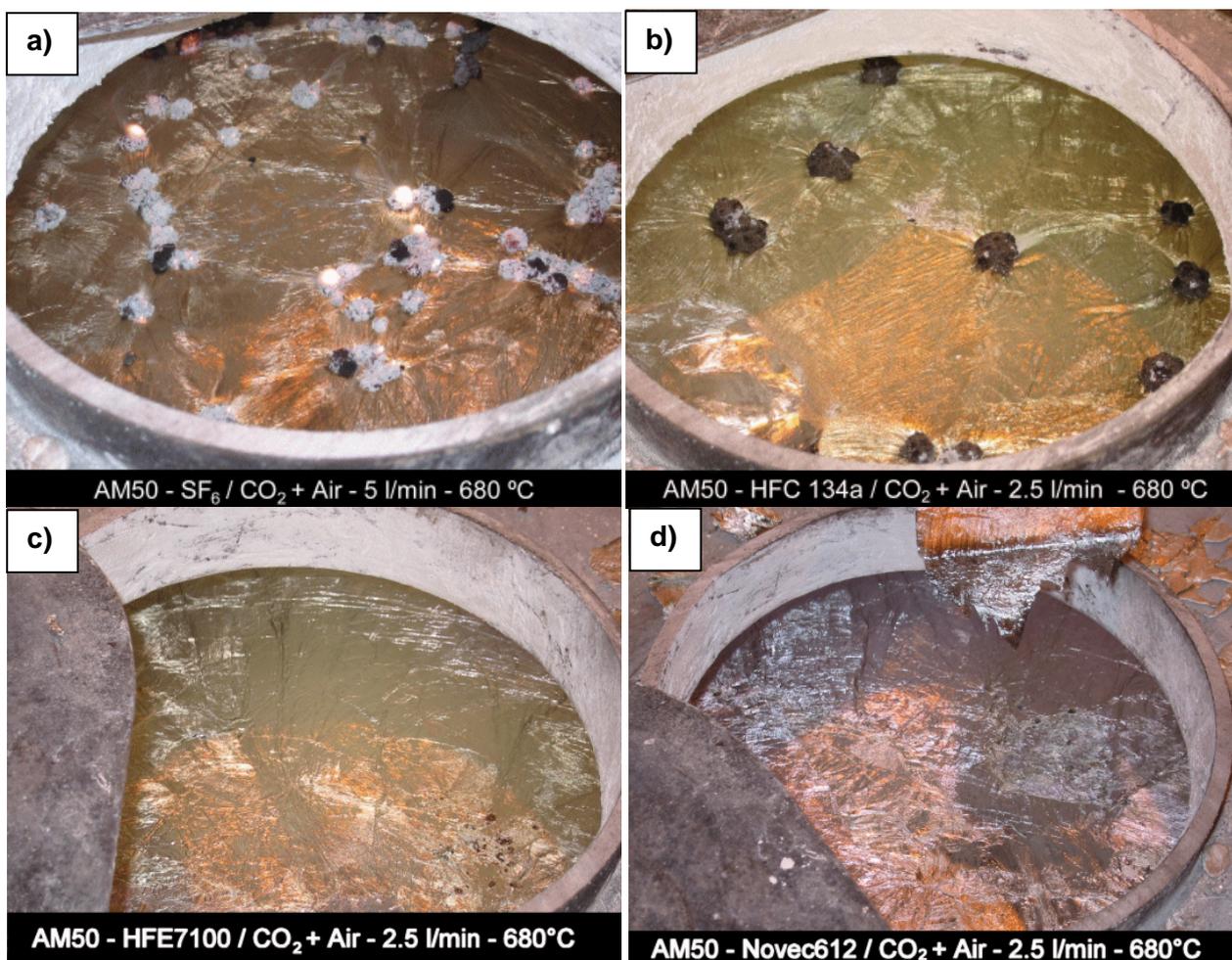
Bath Conditions		Active Compound and Carrier Gas Flow (l/min)							
		SF <sub>6</sub>		HFC 134-a		HFE 7100		Novec™612	
Alloy	Temp. (°C)	Air	CO <sub>2</sub> /Air	Air	CO <sub>2</sub> /Air	Air	CO <sub>2</sub> /Air	Air	CO <sub>2</sub> /Air
AM50	680	20	10	20	5	10	<2.5	10	<2.5
	710	>20	10	>20	5	20	2.5	10	2.5
RZ5	710	>20	>20	>20	5	20	20	10	5

As seen from Table 3.2, all of the potential SF<sub>6</sub> replacements performed better than SF<sub>6</sub> itself under most identical conditions, i.e., the total flow rates needed to protect the surface were generally lower for the three compounds tested against SF<sub>6</sub>. This may be predicted if the thermodynamic stabilities of SF<sub>6</sub> and the three organic molecules are considered. As discussed by Tranell et. al [8], SF<sub>6</sub> is a very stable molecule which is virtually un-destroyed in air at temperatures around 700°C. The fluoro- carbons and the hydro-fluoro carbons will partly react/decompose in air at 700°C to form mainly CO<sub>2</sub> as well as HF and other reactive, COF and CF based species. In CO<sub>2</sub> rich carrier gases, CO will be one of the main reaction products due to the reaction between CO<sub>2</sub> and Mg vapour to form MgO and CO. The efficiency of protection of a given fluorinated gas will be a function of the concentration of reactive fluorinated species at the liquid gas interface.

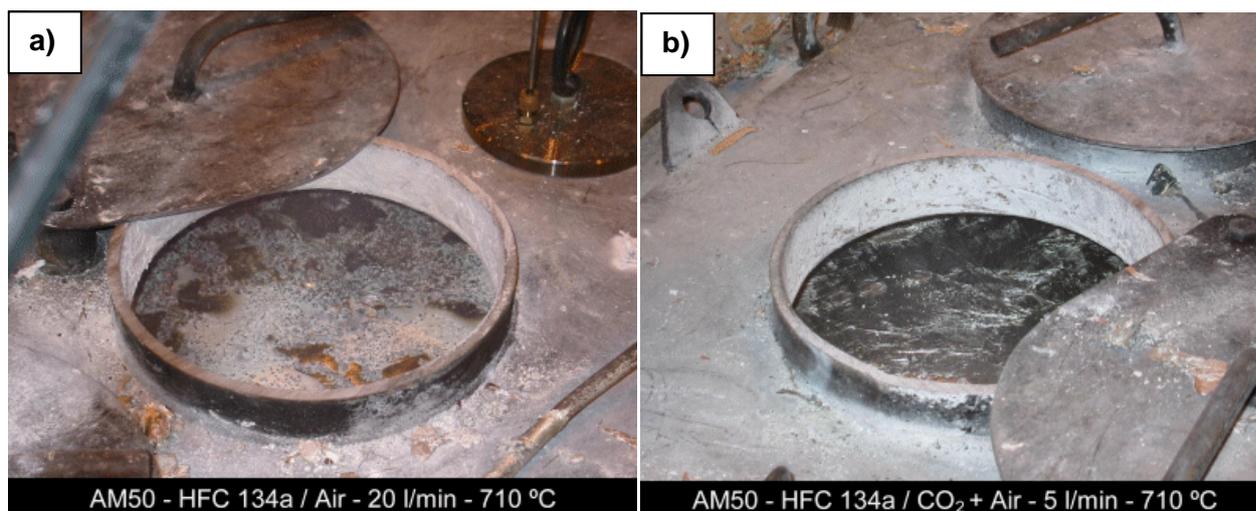
This is illustrated by the different flow rates needed when using different compounds. The amount of HFC 134-a (4 Fluorine atoms per molecule) needed to protect the surface per unit time is consistently higher than the amounts needed for both HFE 7100 (9 fluorine atoms per molecule) and Novec™612 (12 fluorine atoms per molecule). The difference in protection efficiency, exemplified for AM50 alloy at 680°C, using CO<sub>2</sub>/5% air as carrier at a total flow rate of 2.5 l/min (5l/min for SF<sub>6</sub>), is illustrated by Figures 3.13 a-d.

As noted in Table 3.2, much less active compound is needed per unit time to protect the surface in a CO<sub>2</sub>/5% air carrier gas than in a 100% air carrier gas. In 100% air, oxidation of Mg with O<sub>2</sub> to MgO is not limited by the supply of oxygen and the oxidation can hence be expected to proceed faster than in CO<sub>2</sub>/air, where mass transfer of O<sub>2</sub> may limit the rate of oxidation. A higher rate of oxidation will require a higher concentration of fluorine at the Mg liquid-gas interface to form the protective MgO-MgF<sub>2</sub> film. This is more pronounced at higher temperatures where the Mg oxidation kinetics is faster. The difference in protection efficiency between different carrier gases may also partly be due to different decomposition products (giving different "availability" of fluorine) forming in different carrier atmospheres. The difference in protection efficiency between 500 ppm HFC 134-a in 100% air and CO<sub>2</sub>/5% air carrier at 710°C, is illustrated in Figures 3.14a and b.

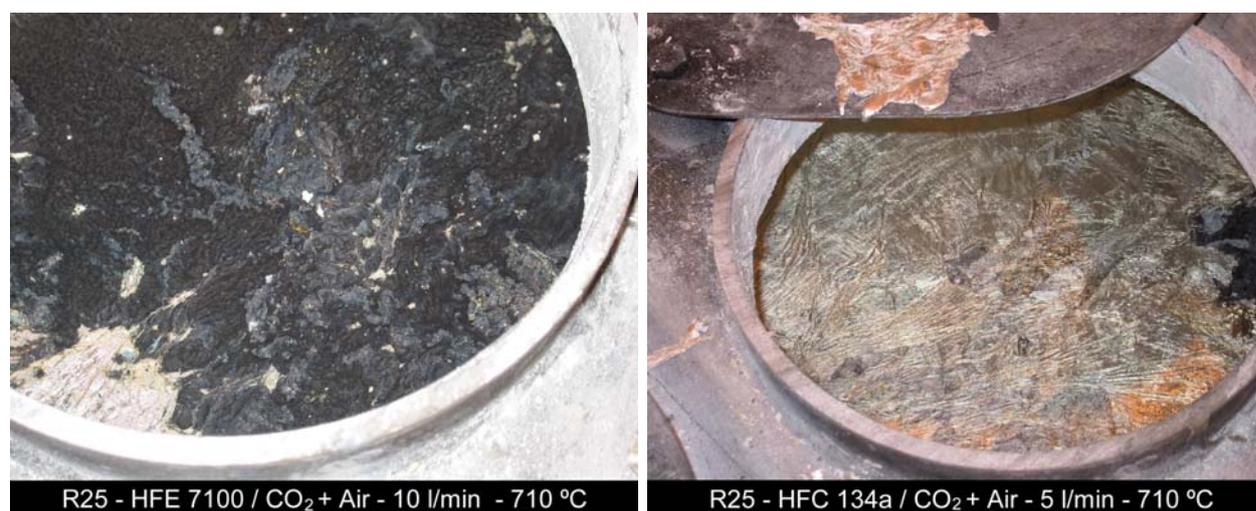
It was also observed that it is generally more difficult to protect the RZ5 alloy than the AM50 alloy, which may be due to the pronounced presence of both Zn and Zr in the RZ5 alloy. Especially HFE 7100 (in addition to SF<sub>6</sub>) appeared to have a problem in protecting RZ5 with a resulting dark crusty surface at gas flows below 20 l/min, as illustrated by Figure 3.15.



**Fig. 3.13.** Protection of AM50 alloy at 680°C, using 500ppm concentration of different F-containing active compounds in 2.5 l/min CO<sub>2</sub>/5% air carrier gas. **a)** SF<sub>6</sub> (note! 5l/min gas) **b)** HFC 134-a **c)** HFE 7100 **d)** Novec™612



**Fig. 3.14** The difference in protection efficiency of 500ppm HFC 134-a in 100% air vs CO<sub>2</sub>/5% air at 710°C a) in 100% air b) in CO<sub>2</sub>/5% air



**Fig. 3.15** Comparison of the performance of HFE 7100 and HFC 134-a in CO<sub>2</sub>/5% air carrier gas at 710°C on RZ5 alloy.

In order to confirm that the "minimum" flow rates identified to protect the AM50 alloy for 10 minutes were also adequate for long term exposure, 2.5 hour exposure experiments were carried out under the conditions highlighted in Table 3.3. After the 2.5 hours had passed, all 4 compounds (including SF<sub>6</sub>) still provided adequate protection without significant oxide build-up. The resulting surface film from tests with SF<sub>6</sub>, HFC 134-a and HFE 7100 were shiny metallic while the surface after 2.5 hours exposure to Novec™612, was dull grey metallic. This type of surface is generally indicative of a relatively thick and fluorine-rich protective film which is caused by an excess of fluorine (in terms of what is actually needed for effective protection).

After 2.5 hours of constant flow, cover gases were removed and the time until magnesium fire developed was measured. For SF<sub>6</sub> and HFC 134-a, it took approximately 2 minutes before spot-fires started to appear while it took 4.5 and 10 minutes respectively for HFE 7100 and Novec™612. This test demonstrated, and confirmed previous observations, that running a cover gas mix with high fluorine concentration results in a pronounced "residual" effect. The residual effect is linked to the formation of thick surface films which have high concentrations of fluorine. When fire had gained momentum in each of the cases, it was effectively quenched with each of the three new active compounds tested. The concentrations of active compound in carrier gas

(CO<sub>2</sub>/5%air) used for quenching were HFC 134-a – 100%, HFE 7100 – 1.7% and Novec™612 – 2.1%. Note that this campaign did not set out to determine the **relative** performances of the compounds as fire quenchers.

The technical performance of the three active compounds HFC 134-a, HFE 7100 and Novec™612, compared to each other and to SF<sub>6</sub>, can be summarized as:

- All three active compounds give better melt surface protection than SF<sub>6</sub> under each of the tested conditions. In this test, adequate protection was defined as a calm metallic (dull or shiny) surface without smoke/spot-fires or white/black oxide build-up over time. The overall compound ranking, in order from highest to lowest total gas flow needed to protect a given magnesium melt surface (i.e, in this case this equals most to least amount of active compound delivered) was found to be; SF<sub>6</sub>, HFC 134-a, HFE 7100, Novec™612. The ranking corresponds to the amount of fluorine available for protection at the temperature tested.
- All three compounds have significantly better protection properties in CO<sub>2</sub>/air than in 100% air. This is especially the case for HFC 134-a.
- It is significantly more difficult to protect AM50 at 710°C than at 680°C. Air is not a suitable carrier gas at 710°C.
- More fluorine per unit time is generally needed to protect the RZ5 alloy than the AM50 alloy. HFE 7100 does not appear to be a good protectant for RZ5.
- While their relative performances were not compared, all of the three active compounds, and SF<sub>6</sub>, are effective magnesium fire quenchers

### **Environmental Performance**

The potential SF<sub>6</sub> replacements were compared and assessed on the basis of three types of associated emissions (assuming the primary active compound is not toxic in itself):

- "Un-destroyed" active compound, contributing to net outgoing GWP gases;
- High GWP off gas products; and
- Corrosive and toxic off gas products.

These emissions – both the presence and concentration of active compounds and off gas species – are determined by numerous factors such as: thermo-chemical properties of the active compound, type of carrier gas, molten alloy temperature and composition, melt surface area and total cover-gas flow rate.

As indicated in the experimental section, the method used to measure the type and concentration of gases in the furnace headspace – and thus supposedly in the furnace off-gas – was an extractive FTIR method. The FTIR measurements were carried out by representatives of 3M™ in Europe and the US. Generally, the analysis procedure consists of drawing a gas sample continuously through an FTIR cell with a pump at a rate of about 1-3 L/min and collecting spectra. Furnace headspace gas was taken about 4-5 cm below the furnace cover with a stainless steel tube fastened to the cover with a swagelok fitting (see Figure 3.12). The detection limits were about 1-2 parts per million by volume (ppmV) for all analytes. The method was reported to have ±5-10% accuracy overall. Data reported refers to average values over a measurement period. A full set of analytical data, as provided by 3M™ is attached in Appendix 4.

Before reporting the measured off-gas data, below are some general comments related to the experimental conditions and their effect on the measured results:

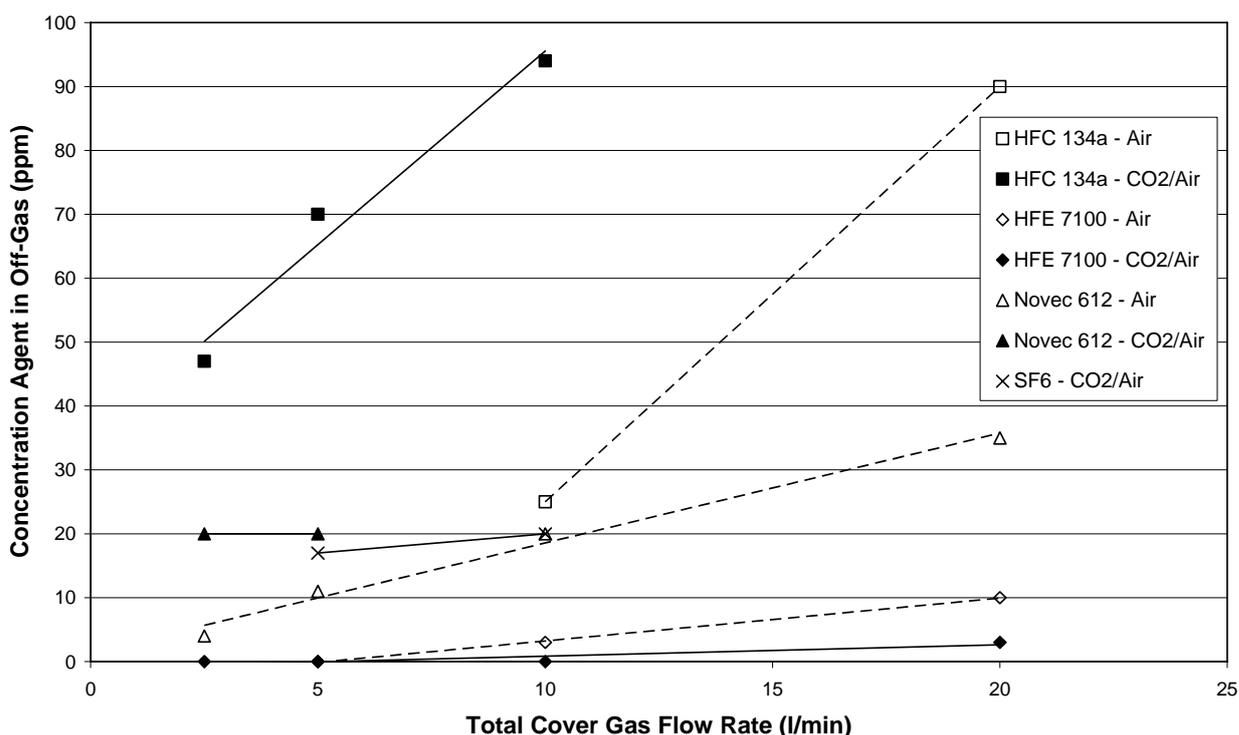
1. As the same metal bath was used (for each alloy) during the trials, melt history needs to be considered in evaluating the values of various concentrations. Although SO<sub>2</sub> was used to flush the melt in between different active compounds, in addition to meticulous drossing, some carry over of analytes may be expected. For example, it appears that the gen-

eral HF levels in off-gas increased with increased melt exposure to fluorine-containing gas during a day of experiments. This may be due to build-up of fluorine in the furnace and/or in the metal. From these experiments, the origin of this observation could not be determined

2. The level of certain analytes, particularly HF, is not constant during the measuring period and hence, its average concentration is reported in the comparison graphs. It is apparent that HF levels spike when the hatch was opened since this allowed ambient (moist) air to flow in and react with fluorine accumulated in the surface film. This was especially evident with Novec™612 which under many experimental conditions "over-provided" the melt surface with fluorine (i.e., the surface became dull and the film very (un-necessarily) thick). Spikes in HF, associated with opened hatches, generally coincided with reverse peaks of other analytes as the furnace gas is partly replaced with ambient air.
3. For the SF<sub>6</sub> tests, SF<sub>6</sub> levels in the off gases were much lower than expected from its high temperature properties. This means that either the experimental conditions used (good gas distribution over the melt surface) provided an opportunity for SF<sub>6</sub> to react extensively or, that large fractions of the SF<sub>6</sub> introduced leaked out of the furnace. Given that a very low concentration of SF<sub>6</sub> (like the more unstable compounds) was used and in many cases provided adequate protection, significant destruction/decomposition of SF<sub>6</sub> must have taken place. In addition, the measured concentrations of high fluorine-containing off gas products (such as C<sub>3</sub>F<sub>8</sub>) were much higher for SF<sub>6</sub> than for the other compounds. **Hence, with some reservation, we have chosen to report the measured concentrations of gases on "face value". Extensive gas testing will naturally be needed to verify this data to make more substantiated claims.**

### Primary species

In Figure 3.16, the concentration of undestroyed SF<sub>6</sub>, HFC 134-a, HFE 7100, and Novec™612 in the off-gases over AM50 alloy at 680°C, are illustrated. It can generally be said that, when using gas flow rates close to the protective limit (i.e., just enough fluorine species "needed for protection" delivered per unit time), the utilisation of available fluorine was very high, and in some cases complete. Interestingly, and as opposed to the efficiency of protection, the measured level of primary compound destruction was higher in air than in CO<sub>2</sub>/air for both HFC 134-a and Novec™612. HFE 7100 measured a higher level of destruction in CO<sub>2</sub>/air than in 100% air. In CO<sub>2</sub>/5% air and at the minimum flow rate which was deemed protective for each active compound, the following average destruction rates were calculated (total cover gas flow rate in brackets): HFC 134-a (5 l/min) ~85% destruction, Novec™612 (2.5 l/min) ~95% destruction (Note! Novec™612 had not reached its protection limit, i.e., less than 2.5 l/min would be required to effectively protect the surface at a Novec™612 concentration of 500ppV and therefore subsequent destruction and by-products may not be representative), SF<sub>6</sub> (10 l/min) ~97% destruction and HFE 7100 (2.5 l/min), ~100% destruction.

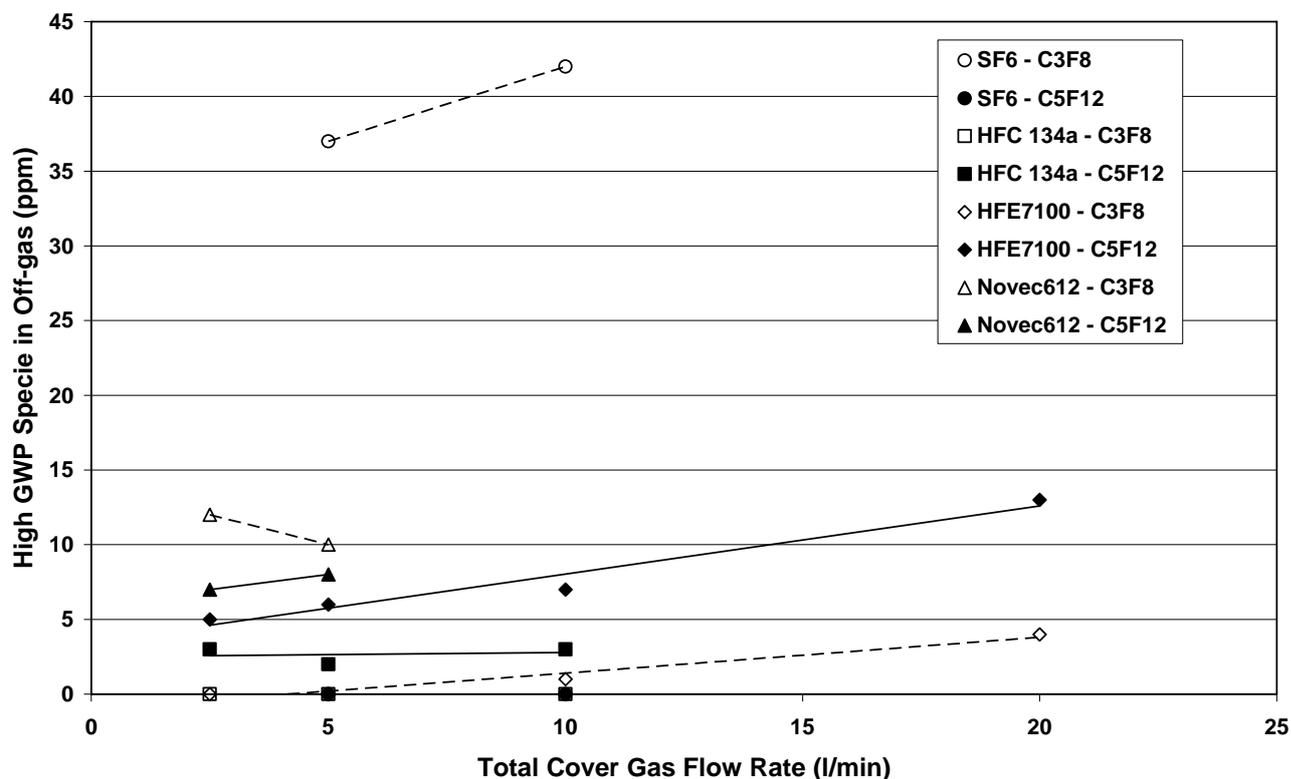


\* The outlet concentration of SF<sub>6</sub> in air was not recorded

**Fig. 3.16.** Primary un-destructed compound in off-gas over AM50 alloy at 680°C, as measured with FTIR

### High GWP secondary off-gas products

The only off-gas high GWP species detected with any consistency were C<sub>3</sub>F<sub>8</sub> and C<sub>5</sub>F<sub>12</sub> which differed from the off-gas analysis of the lab scale experiments. These PFC's have GWP's of 7000 and 7500 respectively, and thereby contribute significantly to the total off-gas high GWP account. The measured concentrations of these species in the outlet gases over AM50 alloy at 680°C, using the active compounds in CO<sub>2</sub>/5% air carrier gas, are illustrated in Figure 3.17. As seen from the figure, the outlet gas contained "significant" concentrations of C<sub>3</sub>F<sub>8</sub> (in terms of contribution to total GWP species in furnace off-gas)- between 35 and 45 ppmV - but no detectable C<sub>5</sub>F<sub>12</sub> when SF<sub>6</sub> was used for protection. Outlet gases from the use of both the HFC 134a and the HFE 7100 contained more C<sub>5</sub>F<sub>12</sub> (0-15 ppmV) than C<sub>3</sub>F<sub>8</sub> (0-5ppmV). Outlet gases from the use of Novec™612 contained similar amounts of the two species at concentrations between 7-12 ppmV. For Novec™612 and HFE 7100, these secondary species - while in low concentrations - will make up most of the total greenhouse gas emission in the off-gas, compared to the primary undestructed species. For HFC 134-a, secondary products have a higher GWP than the primary specie but the impact of the secondary products on the total GWP account will be more dependent on relative concentrations. The total green house gas impact of undestructed SF<sub>6</sub> and its secondary C<sub>3</sub>F<sub>8</sub> gas product is many times higher than that of either of HFC 134-a, HFE 7100 and Novec™612, as illustrated by Table 3.3. In comparing the three new species, HFE 7100 has the lowest total GWP gas emission per unit time followed by Novec™612 and HFC 134-a. It should, however, be noted that Novec™612 had not reached its protective limit and hence may be more comparable with HFE 7100 at lowest effective compound concentration.



**Fig 3.17.** Concentrations of  $C_3F_8$  and  $C_5F_{12}$  in the off-gas over AM50 alloy at 680°C protected with different active compounds in  $CO_2/5\%$  air carrier gas.

**Table 3.3.** Estimate of total emission of high GWP gases based on measured concentrations in off-gas over AM50 alloy at 680°C using  $CO_2/5\%$  air as carrier gas. Note!  $CO_2$  has not been included in this account.

In Outlet Gas (conc.(ppV)× GWP)	Active Compound (total cover gas flow for minimum protection, l/min)			
	SF <sub>6</sub> (10)	HFC 134-a (5)	HFE 7100 (2.5)	Novec™612 (2.5)
Primary Compound	20×23900	70×1300	0×390	20×1
Secondary Product*	42×7000	2×7500	5×7500	19×7184
<b>Total ppV GWP equiv. in off-gas</b>	<b>772000</b>	<b>106000</b>	<b>37500</b>	<b>136516</b>
<b>Normalised amount GWP equiv / min (using 2.5 l/min as baseline)</b>	<b>3088000</b>	<b>212000</b>	<b>37500</b>	<b>136516</b>

\*Weighted on the basis of GWP  $C_3F_8$  = 7000 and GWP  $C_5F_{12}$  = 7500 (IPCC 1996 Guidelines values)

### Toxic/corrosive secondary gas products

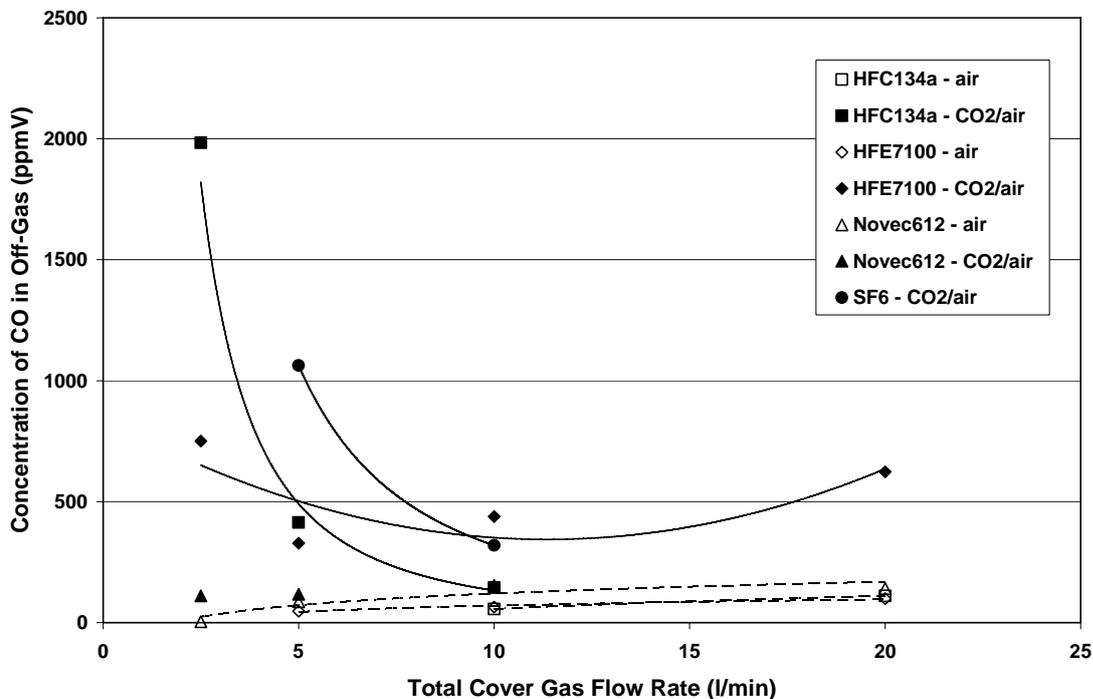
Three toxic/corrosive species were detected in the outlet gases:

- CO
- HF
- $COF_2$

The by far overall highest concentration of a toxic gas by-product is that of CO. The concentration of CO is generally higher - from around 100ppmV and up to above 1000 ppmV - when CO<sub>2</sub> is used as a carrier. With air as the carrier gas, the presence of CO in the off-gas is a consequence of the carbon content in the active compound (i.e. SF<sub>6</sub> in 100% air carrier does not generate a CO by-product (not counting the CO formation originating from reaction with the small CO<sub>2</sub> content in natural air) and the concentration in outlet gas is naturally lower. From the experimental work, it was observed that, when using CO<sub>2</sub> as the carrier, the concentration of CO goes up significantly when the concentration of fluorine in the system is lower. This may be due to reaction between Mg and CO<sub>2</sub> to form MgO and CO when there is not enough fluorine-compound in the cover gas to form MgF<sub>2</sub>. For air as the carrier gas, the concentration of CO goes down with decreasing concentration of active compound. This is illustrated in Figure 3.18. Close to 2000 ppmV of CO was measured when protection had failed, using HFC 134-a in CO<sub>2</sub>/5% air carrier at total flow of 2.5 l/min over AM50 alloy at 680°C. Similarly, close to 1100 ppmV CO was measured when SF<sub>6</sub> in CO<sub>2</sub>/5% air carrier at total flow rate of 5 l/min over AM50 alloy at 680°C, failed to protect the molten metal.

The second most common toxic specie in the off-gases was HF. As mentioned at the start of this section, HF appears to form in excess when the surface film (and the top layer of liquid magnesium) is saturated with fluorine. The high fluorine species (Novec™612 and HFE 7100) generally generate more HF under the same conditions than the ones containing less fluorine per molecule. Thus, for the purpose of minimizing HF generation, it is important not to "over-protect" with the high fluorine gases. It was also found that the concentration of HF in the off-gases was generally higher with 100% air as carrier than with CO<sub>2</sub>/air.

The least prevalent of the toxic species in off-gas was COF<sub>2</sub>. COF<sub>2</sub> was only detected when Novec™612 or high (>10 l/min) flow rates of HFE 7100 were used. The concentrations of COF<sub>2</sub> measured were mostly in the sub 5ppm range with large standard deviations. COF<sub>2</sub> under these conditions can thus be considered present but its absolute concentration unreliable. .



**Fig. 3.18** Concentration of CO in off-gas measured over AM50 alloy at 680°C for various active compounds and carrier gases.

The environmental performance of the three active compounds, as compared to each other and SF<sub>6</sub>, may be summarized as:

- All three replacement compounds provide a lower total greenhouse gas impact than SF<sub>6</sub>.
- The relative CO<sub>2</sub>-equivalent emission for the three compounds, under **technically** optimal conditions (i.e., at each compounds individual protection limit), was from best to worst; HFE 7100, Novec™612, HFC 134-a and SF<sub>6</sub>. It should however be noted that Novec™612 had not reached its protective limit (i.e., less gas would be adequate for protection than the minimum flow used in this campaign) and therefore, its relative rating may be questionable as less GWP products are expected with less fluorine compound delivered.
- In terms of toxic/corrosive emissions, more CO is emitted when CO<sub>2</sub> is used as carrier gas and when protection is failing. Fluorine rich gases generally generate more HF.

### 3.5 Computational Fluid Dynamics (CFD) Modelling of Gas Flow in Pilot Scale Testing Furnace

Computational Fluid Dynamics (CFD) through software package FLUENT™, was applied to predict the distribution and estimate the amount of the cover gas in the “bath-tub” furnace used in pilot scale campaign at Norsk Hydro’s facilities. This tool was also applied to design the gas supply system and calculate the “carry-over” times for replacing the gas atmosphere at different gas flow rates.

#### 3.5.1 Problem Description – Injection of Cover Gas into a Holding Furnace

The active compound gas is injected into the holding furnace with a carrier gas. The protective compound is in a small concentration and properly mixed with the carrier gas. The protection and carrier gases are distributed inside the furnace by a gas injection system.

The cold (compared to the metal) gas is injected into the free space of the furnace, which is heated from below (the metal surface) and cooled from above (the furnace lid). This is an unstable situation, where the gas is heated at the bottom, flows upwards, and is replaced by cold gas. If the furnace is open to the atmosphere, the hot gas will escape, while cooler gas enters from the atmosphere into the furnace. Therefore, the furnace must be properly sealed to maintain a slightly higher pressure inside the furnace than outside. The gas should escape the furnace along the perimeter, either by a controlled leakage through the lid seal or by a perforated pipe that is connected to a valve and an off-gas system. If the gas is dangerous to operators or the environment, the last option is appropriate.

When operations are performed on the furnace (e.g., ingot loading, drossing), one or more hatches have to be opened, and the furnace will be exposed to the atmosphere. The hot gas will escape rapidly through the open hatches. The metal will lose some of its protection, and the operators and the environment will be exposed to the furnace headspace gas. When the hatches are closed, the protection must rapidly be restored to avoid oxidation/burning. Assuming that the metal surface was properly protected before opening of the hatches, it is useful to know how long the protection will last, i.e. how long the protective oxide film can exist without additional cover gas. The protective film might be disturbed by convection in the melt. Heat is supplied through the side walls of the holding furnace, and there might be an upward motion in the metal along the perimeter of the furnace.

The mechanisms of gas protection are not known in detail. Some gases are **relatively** stable (like SF<sub>6</sub>) and some of the new gases like HFC 134-a, HFE 7100 and Novec™612 decompose when exposed to heat. For more stable gases it might be beneficial to pre-heat before injection. This ensures a higher volumetric flow rate due to volume expansion, and less violent mixing. For less stable gases, the temperature should be kept low until injection to preserve the chemical composition.

In the following section, the following subjects are addressed:

- What is the time needed to fill the furnace with cover gas?
- What happens to the protection when a hatch is opened?
- What is the influence of various furnace/gas parameters?
- What is the best way to distribute the cover gas into the furnace headspace?

It is important to point out that this is a fluid flow study which does **not** consider chemical aspects of the gases such as decomposition and reaction. The denotations used in the following text are identified as:

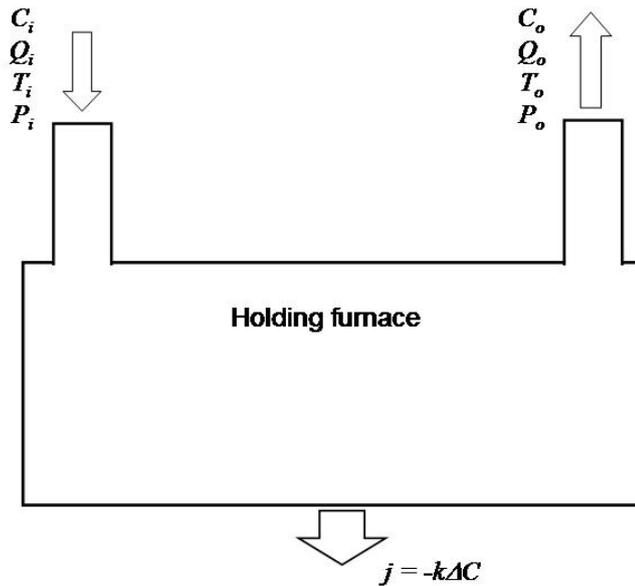
A	Area (of metal surface)	$m^2$
C	Volume fraction of protection gas in carrier gas	
$C_p$	Specific heat	$Jkg^{-1}K^{-1}$
d	Diameter of hole	$m^2$
D	Diameter of gas pipe	$m^2$
f	Friction factor	
g	Acceleration of gravity	$ms^{-2}$
h	Heat transfer rate	$Wm^{-2}K^{-1}$
K	Pressure loss factor	
L	Length of gas pipe	m
$\dot{m}$	Mass flow rate	$kgs^{-1}$
N	Number of holes in gas pipe	
Q	Volumetric gas flow rate	$m^3s^{-1}$
t	Time	s
T	Temperature	K
u, U	Gas velocity	$ms^{-1}$
V	Furnace volume	$m^3$
x	Distance from gas pipe to metal surface	m
$\Delta p$	Pressure drop	$Pam^{-1}$
$\rho$	Density of gas	$kgm^{-3}$
$\tau$	Time scale	s

### Subscripts

e	Exit value
h	Heat exchanger
g	With reference to gas before inlet
i	Pipe hole / inlet
p	Protection gas
pipe	Gas pipe
o	outlet
m	metal

### 3.5.2 Modeling of Bath Tub Furnace System Used in Pilot Scale Campaign

Figure 3.19 is a conceptual schematic diagram of the bath tub furnace used during the pilot scale campaign described in Section 3.4, which is used for the modeling study.



**Fig. 3.19** Diagram of furnace to illustrate the computation of relaxation time.

The model assumes ideal mixing in the furnace, which is plausible due to natural convection, so that the output composition of gas is the same as the bulk gas composition inside the furnace (not to be confused with the input composition of gas). Further assume that the pressure is approximately constant, i.e. the over-pressure in the furnace is small compared to the atmospheric pressure. The model assumes ideal gas. The rate of change of the mass  $\dot{m}_p$  of protection gas (active compound) is:

$$\dot{m}_p = \frac{d}{dt}(\rho_o V C_o) = \rho_i Q_i C_i - \rho_o Q_o C_o - \rho_o A k (C_o - C_m) \quad (1)$$

Solving for the outlet concentration of protection gas  $C_o$ , we get

$$C_o = C_i \left( \frac{1}{1 + \frac{kAT_i}{Q_i T_o}} \right) \left( 1 - \exp\left[-\frac{t}{\tau}\right] \right) \quad (2)$$

The most important parameter is the time scale for filling the furnace headspace with cover gas:

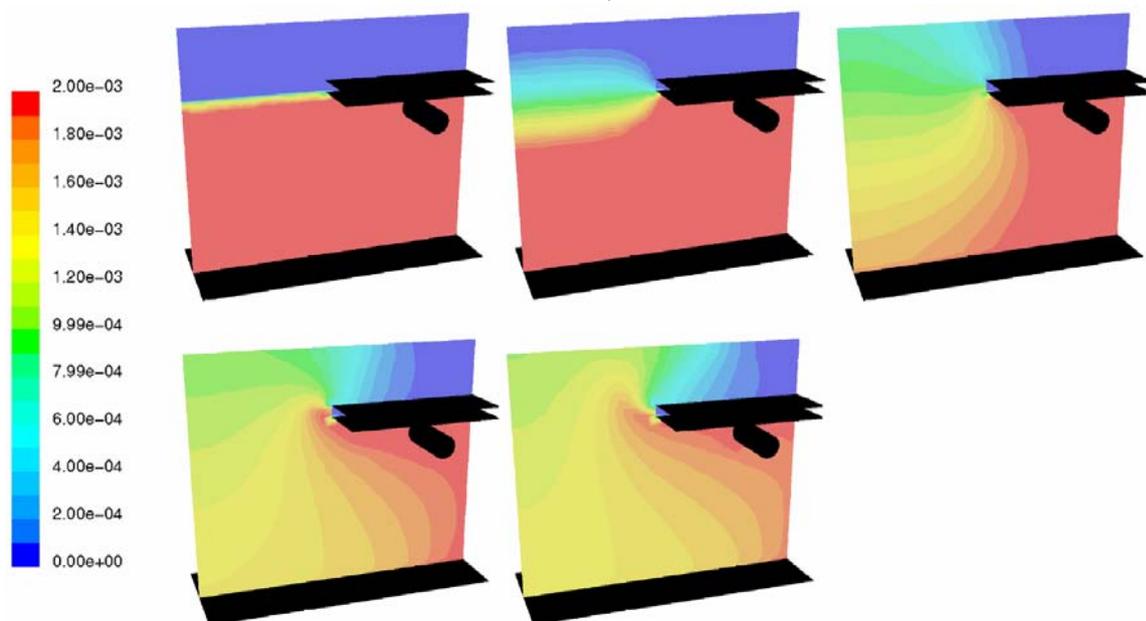
$$\tau = \frac{V}{Q_i \frac{T_o}{T_i} + kA} \quad (3)$$

When the rate of consumption of protection gas is slow (only due to reaction at the metal surface, mass transfer coefficient  $k \cong 4 \cdot 10^{-5} \text{ m/s}$ ), the time scale is approximately  $\tau = V/Q_o$  as expected. For the bath-tub furnace used in the pilot scale experiments, using the input parameters from Table 3.4, the estimated time to fill the furnace headspace with cover gas at a total cover gas flow rate of 20 N(normal)/min is 71 s.

**Table 3.4** Parameters from large scale experiment. Mass transfer rate was estimated using experimental correlation from Cengel [12].

Parameter	Symbol	Value	Unit
Metal surface area	$A$	0.456	$m^2$
Hatch area		0.049	$m^2$
Furnace gas volume	$V$	0.0684	$m^3$
Gas flow rate	$Q_N$	20	Nl/s
Mass transfer rate	$K$	$4 \cdot 10^{-5}$	m/s
Temperature inlet	$T_i$	100	$^{\circ}C$
Temperature outlet	$T_o$	500	$^{\circ}C$

CFD was also applied to study the decay of protection gas concentration as a hatch in the furnace lid is opened. Corresponding to the volume served by a single gas nozzle, 1/18 of the furnace volume (The gas distribution ring on the furnace lid in the pilot furnace had 18 nozzles) is calculated. Figure 3.20 show that the concentration rapidly decays by approximately 30% in the first second. The subsequent decay was much slower. By keeping the concentration 30% above minimum (for sufficient protection), the hatch can be kept open for sufficient time to do the necessary operations. In this example, the hatch area was approximately 10% of the metal area and thus the ratio between volume and area is  $V^{2/3}/A = 0.37$ .



Mass fraction of protection gas at times 0, 0.01, 0.38, 0.88, 1.13 seconds

**Fig. 3.20** Mass fraction of protection gas in a plane perpendicular to the metal surface, and cutting through the gas pipe and the lid

CFD modelling was also applied to look at the design of the pipes delivering the gas into the furnace. As in the case with a gas distribution ring, when the gas pipe has several holes along its length, the pressure drop in the pipe should be at least one order of magnitude lower than the pressure drop in the holes to ensure even gas distribution over the holes:

$$\frac{1}{2} \rho u_i^2 K \geq 10(2 f \rho U_{pipe}^2 \frac{L}{ND}) \quad (4)$$

This can be reformulated to:

$$\frac{A_i}{A_{pipe}} \leq 0.75 \sqrt{\frac{D}{NL}} \quad (5)$$

The pressure drop in the system is approximately:

$$\Delta p \cong \rho \left( \frac{Q_i}{NA_i} \right)^2 \quad (6)$$

The gas injection system must therefore be able to handle this pressure drop.

The gas exits from the hole with a velocity that should be large enough to overcome the buoyancy forces due to the temperature gradients in the flow. The ratio between the buoyancy and the inertial forces should therefore satisfy:

$$\frac{\Delta \rho g x}{\frac{1}{2} \rho u^2} < 1 \quad (7)$$

This can be reformulated to:

$$u > \sqrt{\frac{\Delta T g x}{T}} \quad (8)$$

The velocity should be maintained above  $u_c$  down towards the metal surface. A free jet decays according to the inverse square-root of the distance, see Townsend [13]:

$$\frac{u}{u_0} \cong \sqrt{\frac{d}{x - x_0}} \quad (9)$$

The constants have been estimated in an earlier report Bech [14]:

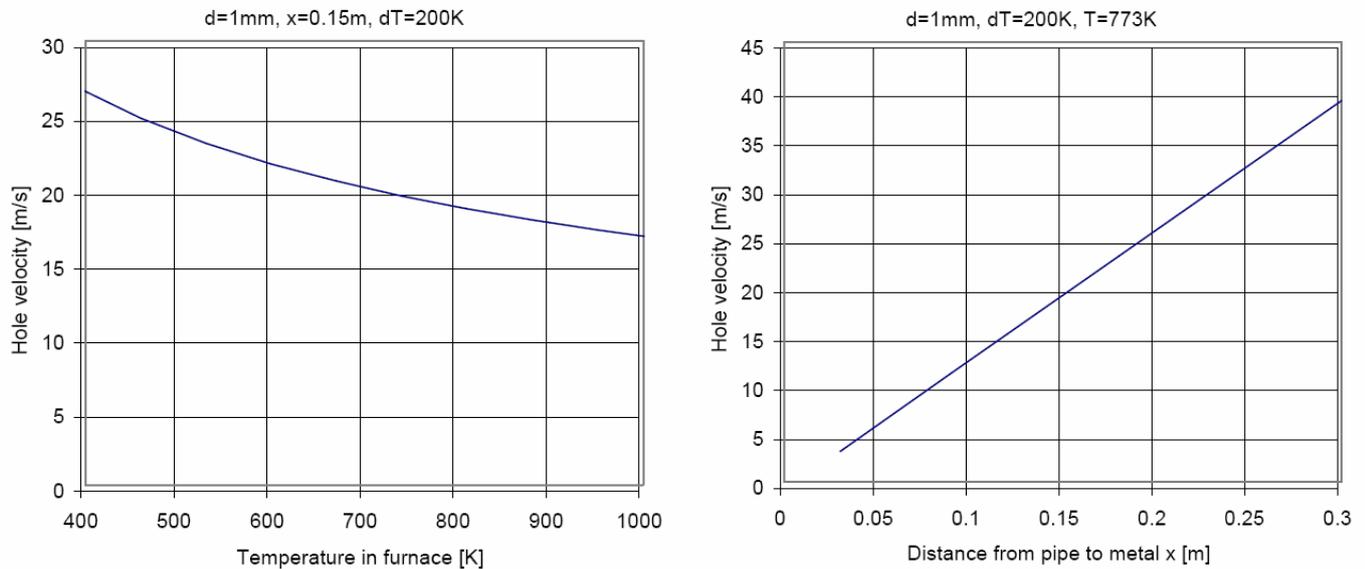
$$u = 0.384 u_i \left( \frac{x}{d} - 11.5 \right)^{-\frac{1}{2}} \quad (10)$$

Let  $u = u_c$  and substitute Eq. (9) in Eq. (7) to get a limiting hole velocity:

$$u_{i,c} = \frac{Q_c}{NA_i} = 2.63 \sqrt{\frac{\Delta T}{T} g x \left( \frac{x}{d} - 11.5 \right)} \quad (11)$$

For gases (such as HFC 134-a, HFE 7100 and Novec™612) that decompose rapidly at high temperature, it is believed that it is an advantage if the cover gas is brought in contact with the metal surface as fast as possible to avoid decomposition before reaction with magnesium vapour/liquid to form the protective film. Previous studies by Bech [15] indicate that the gas flow jet thus should be directed towards the surface, and not in a spreading angle. For our experimental set-up, the jet velocity in the holes should be at least 25 m/s to allow the gas stream to reach the metal surface, as calculated with equation (10). With 18 holes at  $d = 1$  mm, a total gas flow rate of 7.5 NI/min gives a sufficient velocity for the primary gas jet to reach the surface. The flow velocity needed at an outlet hole for the gas jet to reach the metal as a function of distance between hole and metal surface or furnace temperature is illustrated in Figures 3.21 a and b. The experimental results given in Section 3.3 showed that sufficient protection is obtained through a combination of cover gas flow rate and active compound concentration. Hence, it may not be necessary for the

gas jet to physically contact the metal surface provided the compound concentration is high enough.



**Fig. 3.21** Gas velocity at outlet hole needed for the gas jet to reach the metal surface as a function of **a)** distance between gas pipe and metal for a given hole diameter ( $d$ ), temperature difference between furnace temperature and metal surface ( $dT$ ) and metal surface temperature ( $T$ ). **b)** Temperature in furnace for a given hole diameter ( $d$ ), temperature difference between furnace temperature and metal surface ( $dT$ ) and distance between gas pipe and metal surface ( $x$ ).

As it is easier for the gas jet to reach the metal surface if the difference in temperature between metal surface and inlet gas is small, it may be useful for gases (such as  $\text{SF}_6$ ) which do not decompose easily to pre-heat the gas. A simple design equation for a heat-exchanger is given by Cengel [12]:

$$T_e = T - (T - T_g) \exp\left(-\frac{hA_h}{\dot{m}C_p}\right) \quad (14)$$

Assuming  $h = 5 \text{ Wm}^{-2}\text{K}^{-1}$  (Cu piping), the length of pipe  $L = A_h/(\pi D)$  needed to heat the gas to temperature  $T_e$  may be calculated. In a practical application, the first gas outlet hole in a gas distribution ring should hence be positioned after length  $L$ . The heat exchanger wall (the pipe wall) is at temperature  $T$ , which is approximately equal to the temperature inside the furnace.

### 3.5.3 Short Summary, CFD modelling study

It has been shown that CFD modelling may be applied to evaluate design parameters of a closed Mg furnace in order to obtain a desired gas flow in the furnace. Parameters such as distance between gas inlet pipe and metal surface, gas inlet hole diameter, temperature difference between furnace temperature and metal surface as well as gas velocity are important parameters to the overall furnace gas flow.

## 4. ALTERNATIVE MEANS OF MAGNESIUM MELT PROTECTION

### 4.1 Summary – Alternative Means of Magnesium Melt Protection

The possibility of preventing liquid magnesium from excessive oxidation by saturating the metal with fluorine - which may help form the protective MgO/MgF<sub>2</sub> film on the metal surface - was investigated. As a first step, the solubility of fluorine in pure liquid magnesium was determined. Fluorine-saturated metal was subsequently exposed to air and the surface reactions observed to determine if dissolved fluorine would prevent or delay surface oxidation. A theoretical consideration of the viability of this concept was also carried out. The results of the study are summarized as:

- The solubility of fluorine in liquid pure magnesium and the alloys AM50 and RZ5 has successfully been investigated through liquid metal-MgF<sub>2</sub> equilibration experiments in the temperature interval 650 to 950°C.
- Samples of equilibrated (as above) metal have been analysed for fluorine through two different and repeatable methods, GDMS and SIMS. Due to the lack of standards for the GDMS analysis, the results of the SIMS analysis appears the most reliable.
- At common magnesium processing temperatures around 700°C, the fluorine solubility in pure magnesium is measured to approximately 10 ppm, using the SIMS method.
- The solubility of fluorine in both AM50 alloy and RZ5 alloy is not significantly different to that of pure magnesium.
- It was experimentally found that pure magnesium could not be effectively protected in 100% air atmosphere purely by dissolved fluorine at the saturation level.
- Fluorine flux from a fluorine-saturated Mg melt should **theoretically** not be limiting to providing fluorine to a surface film in order to maintain its fluorine concentration. It is therefore likely that the failure of a fluorine saturated melt to provide protection to the magnesium surface indicates that the mechanisms through which a fluorine containing cover gas forms a protective film (fast, chemical vapour deposition – like formation of MgO and MgF<sub>2</sub>) are instrumental to melt protection.
- It is, however, believed that more experiments, using 100% CO<sub>2</sub> as cover gas over fluorine saturated magnesium alloys, should be carried out to further investigate the protective properties of dissolved fluorine.

### 4.2 Introduction

Tranell et.al. [8] concluded that the initial, fast, reactions between magnesium, oxygen and fluorinated species – which facilitate the formation of the protective film on liquid magnesium - mainly take place in the gas phase when using cover gas magnesium protection. It was, however, also predicted and observed that reactions between liquid magnesium and fluorine do take place to form MgF<sub>2</sub> at the film/liquid Mg interface. Subsequently, it was speculated that it may be possible to protect liquid magnesium from excessive oxidation by saturating the metal with fluorine, which may help form the MgO/MgF<sub>2</sub> film on the metal surface. In order to investigate the viability of this, the solubility of fluorine in liquid magnesium was determined. Fluorine-saturated metal, by means of magnesium/or aluminium fluorides, was subsequently exposed to ambient air and the surface reactions observed to determine if dissolved fluorine would prevent or delay surface oxidation. These investigations are reported in Section 4.3. Section 4.3 also contains a theoretical consideration of the viability of alternative magnesium protection through use of dissolved fluorine instead of cover gas.

### 4.3 Alternative Magnesium Protection - Dissolved Fluorine

#### 4.3.1 Solubility of Fluorine in Magnesium and Its Alloys

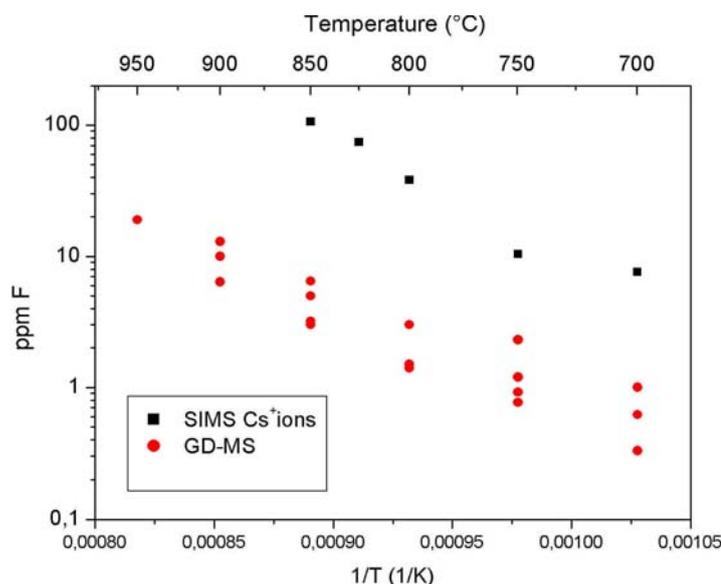
##### Experimental

The solubility of fluorine in pure magnesium and in the alloys AM50 and RZ5 was measured by equilibrating the respective metal in magnesium fluoride crucibles under Argon. The solubility was measured in the temperature range 650°C to 950°C. For further details on the experimental procedure and first rounds of results, see the SINTEF Annual Report to the IMA 2001 [16] or Aarstad, Syversten and Engh [17].

As reported in the SINTEF status report to the IMA of June 2002, there were serious issues in finding a reliable/accurate method of analysing the metal samples for fluorine. Accurate analysis is of course essential to determining the fluorine solubility accurately. Measurements with the SINTALYZER (an electro chemical method) and the Glow Discharge Mass Spectrometry (GDMS) methods have previously been reported. In addition to these analysis methods, a third method was used: Secondary Ion Mass Spectrometry (SIMS). Both the SIMS and the GDMS methods gave reproducible analytical results.

##### Results

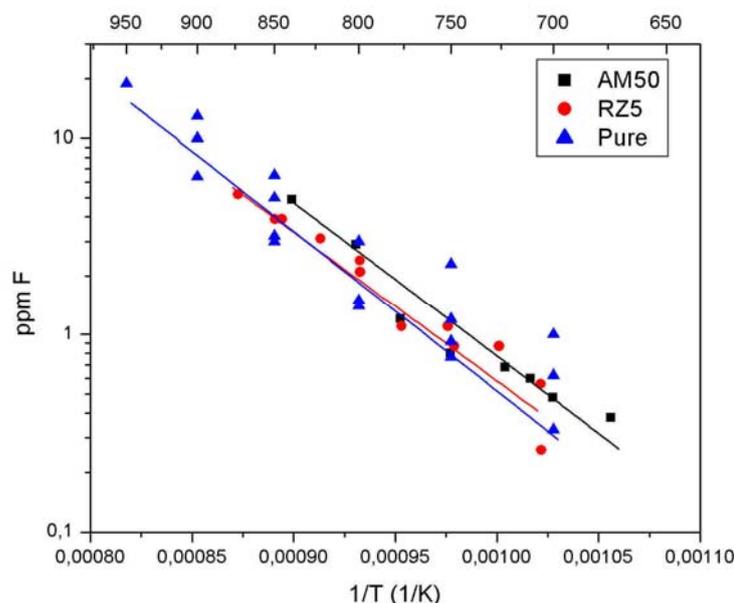
Figure 4.1 shows the solubility of fluorine in pure magnesium in equilibrium with  $MgF_2$ , as measured with SIMS and GDMS respectively.



**Fig. 4.1** Solubility of fluorine in magnesium in equilibrium with magnesium fluoride as a function of temperature, as determined by SIMS and GDMS respectively.

As can be seen in Figure 4.1, the numerical results of the two analytical methods vary considerably. However, both show an increasing trend for the solubility of fluorine with increasing temperature. The results from the GDMS analysis seem to lie approximately a factor ten lower than the SIMS results. At a typical magnesium processing temperature of 700°C, the SIMS analysis determined the fluorine solubility of around 10 ppm while the GDMS showed a solubility of around 1 ppm. Although not repeatable, the original SINTALYZER results were of the same order of magnitude as the SIMS results. The GDMS laboratory used for the analysis (SHIVA Technologies Inc., Syracuse, NY USA) did not have accurate standards to trust the absolute values of the fluorine-concentration [18]. The SIMS laboratory (Chalmers in Gothenburg, Sweden) used an implantation of 19 fluorine ions into one of the samples sent to them as standard. Fluorine-measurements before and

after implantation enabled the determination of fluorine in the original sample. This procedure gave some degree of confidence in the absolute fluorine levels in the equilibrated samples.



**Fig. 4.2** Solubility of fluorine in pure magnesium and magnesium alloys in equilibrium with magnesium fluoride as a function of temperature, as analysed by GDMS.

Figure 4.2 compares the solubility of fluorine in pure magnesium to the solubility in the alloys. The GDMS method was at the time of the analysis considered the best available (SIMS had not yet been tested) and consequently samples were analysed by GDMS. Due to the expense in this type of analysis, samples were not re-analysed by SIMS. The relative difference in fluorine-solubility between pure Mg and its alloys is however well illustrated with the GDMS measurements. As can be seen from Figure 4.2, the difference in fluorine-solubility between pure magnesium and the two alloys RZ5 and AM50 is not significant.

The measured equilibrium concentration of fluorine in liquid magnesium gave some confidence, in that if the diffusion coefficient of fluorine in molten magnesium is high enough (i.e the rate with which fluorine in bulk metal can be transported to the liquid/gas interface), the dissolved fluorine should be sufficient to supply the metal surface and thereby protect the melt from rapid oxidation.

#### 4.3.2 Testing the viability of oxidation protection through introducing fluorine via the Mg melt

One way of providing fluorine continuously to the magnesium melt may be to establish contact between  $\text{MgF}_2$  and magnesium melt, in a manner similar to the equilibration experiments where a  $\text{MgF}_2$  crucible was used. Provided the  $\text{MgF}_2/\text{Mg}$  equilibrium was maintained, the dissolved fluorine should be enough to supply the Mg surface.

The oxidation resistance of fluorine-saturated, pure magnesium was tested by pressing a briquette of  $\text{MgF}_2$ -powder and submerging the briquette in molten metal. When saturation was achieved (which required 4 to 6 hr equilibration time while flushing the crucible with cover gas / synthetic air +  $\text{SF}_6$ ), the cover gas was closed and melt surface raked.

Unfortunately, no increased oxidation resistance of fluorine saturated magnesium was observed as compared with “fluorine free” metal. Reasons for this may be:

- The transport of fluorine to the metal surface is too slow.
- Poor contact (wetting) between the magnesium melt and the  $\text{MgF}_2$ -briquette prevents fast establishment of the  $\text{MgF}_2/\text{F}_{\text{diss}}$  equilibrium.
- The reaction between dissolved fluorine and molten magnesium does not take place to a large degree at the metal surface and thus not helping to build a protective film.

In order to make sure that a potential problem of poor wetting between  $\text{MgF}_2$  and liquid magnesium was avoided, it was decided to try a different route. Since  $\text{AlF}_3$  is not thermodynamically stable in contact with liquid magnesium at processing temperatures around  $700^\circ\text{C}$ , it was predicted that a reaction according to equation (13) would take place.



where the underlining of Al means that the aluminium is dissolved in the liquid magnesium. The change in Gibbs energy for this chemical reaction is negative and according to FactSage 5.2 [19] given by:

$$\Delta G = (-177000 + 1.635 \cdot T(K)) \text{ J/mole} \quad (14)$$

The negative Gibbs free energy of reaction (14) at typical Mg processing temperatures ( $\sim 700^\circ\text{C}$ ) may allow a swifter formation of  $\text{MgF}_2$ .

This experiment was done by pressing a briquette made of  $\text{AlF}_3$ -powder, and immersing this into liquid AM50 alloy which was kept at  $700^\circ\text{C}$  for 6 h. The reason for using AM50 was that this alloy already contains up to 5 % Al and thus, dissolved Al resulting from reaction (5) would not substantially affect the composition of the alloy.

Unfortunately, this way of adding fluorine did not seem to increase the oxidation resistance of fluorine saturated AM50 as compared to “fluorine free” AM50.

With the negative results of the oxidation resistance trials, it was considered important to make a theoretical consideration to assess if the measured fluorine solubility was actually high enough to provide effective melt protection.

#### 4.3.3 Theoretical Consideration - Is the measured fluorine solubility high enough to provide melt protection?

In order to answer this question confidently, a set of physical properties - such as the fluorine diffusion coefficient in molten magnesium – has to be well documented. Seeing that such properties, in the case of the magnesium/fluorine system, can not be found in the reference literature, relevant properties have to be estimated in order to make a **rough** evaluation of the answer to the title question. The first step in the evaluation is to look at the transport of fluorine from the bulk melt to the surface.

##### Thickness of diffusion boundary layer

In molten metal baths, there are almost always some temperature gradients. These gradients result in convection and hence mixing of dissolved elements. However, close to a surface there is a laminar boundary layer where the flow is parallel to the surface. Across this boundary layer, the transport of a given element is governed by Brownian diffusion, driven by concentration differences. The flux ( $n$ ) (number of moles per area and time) of a solute is given by Fick's first law:

$$\dot{n} = -D \frac{dc}{dz} \quad (55)$$

where  $D$  is the diffusion coefficient for the solute in the solvent and  $dc/dz$  is the concentration gradient in the  $z$ -direction (perpendicular to the surface).

In line with the lack of solubility data for fluorine in liquid magnesium, the value of the diffusion is not documented in common reference literature. It is possible to estimate the diffusion coefficient of fluorine in liquid magnesium ( $D_F$ ) from kinetic theory [20].

$$D_F = \frac{k_B T}{2\pi\mu d} \left( \frac{m_{Mg} + m_F}{2m_F} \right)^{0.585} \quad (16)$$

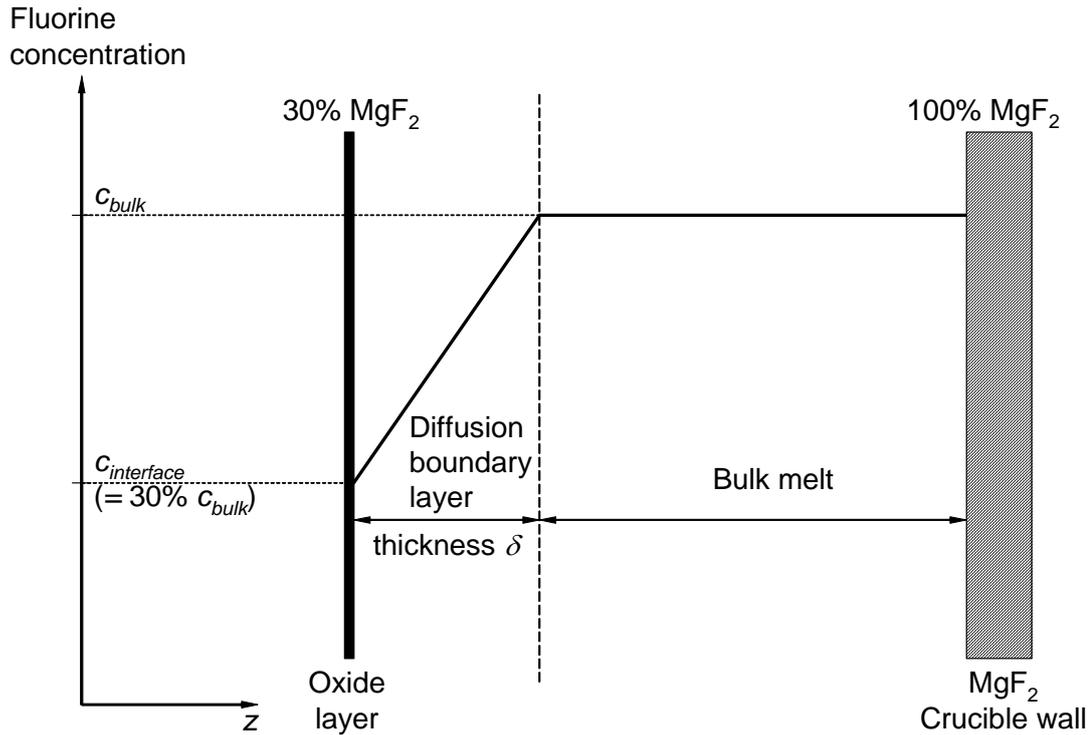
In the equation,  $k_B$  is the Boltzmann constant,  $T$  the melt temperature,  $\mu$  the melt viscosity,  $d$  the diameter of a fluorine atom, and  $m_i$  the molar mass of substance  $i$ . With tabulated physical data for viscosity of liquid magnesium, ionic radius of fluorine, and molar masses [21], and a melt temperature of 983K, the diffusion coefficient becomes

$$D_F = 8.1 \cdot 10^{-9} \text{ m}^2/\text{s} \quad (17)$$

The concentration gradient can be approximated to be equal to the concentration difference over the boundary layer divided by the thickness of the boundary layer,  $\delta$ .

$$\dot{n} \approx D \frac{c_{bulk} - c_{interface}}{\delta} \approx D \frac{0.7 \cdot c_{bulk}}{\delta} \quad (18)$$

where, in the rightmost term, the interface-concentration of fluorine is assumed to be 30% of the bulk concentration. The justification for this assumption arises from calculation of the Pilling-Bedworth Ratio (PBR). As previously described, a dense oxide layer requires  $1 \leq \text{PBR} \leq 2$ . And, in order to get an average PBR, of a mixture of MgO (PBR = 0.81) and MgF<sub>2</sub> (PBR = 1.45), equal to unity, the amount of MgF<sub>2</sub> in the oxide layer must be >30% (by volume). Therefore, the equilibrium fluorine concentration at the interface must be 30% of the bulk concentration (= concentration in the melt near the pure MgF<sub>2</sub>-surface). This is shown schematically in Figure 4.3.



**Fig. 4.3** Fluorine concentration profile and diffusion boundary layer thickness in the melt. The oxide layer is made up of 30% MgF<sub>2</sub> and 70% MgO by volume (26% MgF<sub>2</sub> by mass).

If the calculated thickness of the diffusion boundary layer is extremely thin (~sub-microns), the measured solubility, and thus the fluorine flux, would not be sufficient to maintain a protective oxide layer. It has previously been reported [16] that the average oxide/fluoride film growth rate during the first minute of exposure to fluorine-containing gas is approximately:

$$R = 2.5 \text{ nm/s} \tag{19}$$

The flux of fluorine needed to give the measured film growth rate is thereby:

$$\dot{n} = 7.2 \cdot 10^{-5} \text{ mol/m}^2\text{s} \tag{20}$$

Then with the use of a measured fluorine solubility (SIMS-data) at 973 K of

$$c = 10 \text{ ppm} = 0.84 \text{ mol/m}^3 \tag{21}$$

The thickness of boundary layer where diffusion must occur should not exceed

$$\delta_{\text{max}} \approx 66 \mu\text{m} \tag{22}$$

According to Guthrie [22], the diffusion boundary layer in molten metals are often on the order of  $10^{-6} - 10^{-5}$  m. Therefore, the measured fluorine concentration **should** be able to give a high enough flux of fluorine to the surface for effective melt protection.

**Convection velocity and contact time**

Another approach to this problem is to look at the melt convection and the mass transport of fluorine through the boundary layer. The situation is again that there is convection in the bulk material and a laminar boundary layer near the surface.

If we define a mass transfer coefficient as:

$$\dot{n} = k(c_{bulk} - c_{interface}) \approx 0.7 \cdot k c_{bulk} \quad (23)$$

where again it has been assumed that the interface concentration is 30% of the bulk concentration of fluorine. The mass transfer coefficient can be estimated by the use of Higbie's formula [20]:

$$k = \sqrt{\frac{4D}{\pi t}} \quad (24)$$

The time  $t$  in the equation is the contact time a fluid element in the bulk material, adjacent to the diffusion boundary layer, is in contact with the boundary layer.

By using the estimated diffusion coefficient (equation ( 17 )), the measured growth rate and flux (equation ( 19 ) and ( 20 )), and measured fluorine solubility (equation ( 21 )), the contact time must not exceed:

$$t \leq \frac{4D_F}{\pi} \left( \frac{0.7 \cdot c_{bulk}}{\dot{n}} \right)^2 = 0.7 s \quad (25)$$

Again convection in a heated crucible gives a contact time of at least the same order of magnitude as calculated. This means that the estimated maximum contact time also indicates that it **should** be possible to provide sufficient fluorine flux to the oxide to maintain a protective oxide layer.

The fluorine flux should, therefore, **theoretically** not be limiting to providing fluorine to a surface film in order to maintain its fluorine concentration. It is therefore likely that the failure of a fluorine-saturated melt to provide protection to the magnesium surface indicates that the mechanisms through which fluorine-containing cover gas forms a protective film (fast, chemical vapour deposition – like formation of MgO and MgF<sub>2</sub>) are instrumental to melt protection. It is however recommended that before abandoning this concept, more experiments, using 100% CO<sub>2</sub> as cover gas over fluorine saturated magnesium alloys, should be carried out to further investigate the protective properties of dissolved fluorine.

## 5. REGULATORY AND ECONOMIC ISSUES

During the IMA-SINTEF collaboration, experimental research on both “conventional” magnesium protection through cover gases, as well as “alternative” magnesium protection through dissolved elements (fluorine and others) was carried out. This report has aimed at **technically** summarizing the research results. Hence, this last section has been dedicated to some non-technical comments which are not suited in the above text. These comments mainly concern legislative and economic issues regarding the use of various cover gases.

### Legislation

Following its Kyoto Protocol commitments, the EU has taken a step towards regulating the use and emission of certain fluorinated gases. With the proposal of August 2003 to the European Parliament [10], the use of both SF<sub>6</sub> and HFCs, are targeted. If the proposal is accepted, the use of HFC 134-a in vehicle air conditioners – its primary area of use - will be phased out between the years 2009 and 2018, potentially carrying some emission charges in the phase-out period. This will likely have large implications to the use of HFC 134-a as a magnesium protectant – both as far as legislation and subsequent pricing goes. To the knowledge of the authors, no proposals for regulation of HFC's yet exist in other parts of the world. Neither HFEs nor ketones are yet targeted for regulation. This illustrates that while the technical and environmental performance of HFC-134a is in many ways comparable with that of lower GWP primary compounds such as HFE7100 and Novec™612, its use may well be restricted in certain parts of the world due to legislation.

### Economy/Pricing

Although it would not be wise to choose an SF<sub>6</sub> replacement purely based on economic considerations, cover gas cost is certainly an important parameter for the individual magnesium processor in a product price suppressed market. Hence, for a site implementation of a new cover gas blend, a gas "optimization" study – based on technical and environmental performance but with an element of economic consideration – is necessary. As discussed in Section 3, the efficiency of protection is coupled to the amount of available fluorine delivered to the magnesium surface per unit time. Hence it follows that if the cost difference between active compound and carrier gas is relatively small, it would be economically feasible to lower the carrier gas flow rate (of which the quantity used is relatively large) and increase the concentration of active compound in the carrier gas if protection is still adequate. If the active compound is much more expensive than the carrier gas, this will not make economic sense. The price picture is of course complicated by environmental considerations. In cases where the carrier gas itself is a greenhouse gas (such as CO<sub>2</sub>), the total greenhouse gas emission account may not be improved by an increase in carrier gas flow. This will have an effect on the total price of use in areas where CO<sub>2</sub> equivalents have a price of emission (i.e., a carbon tax).

It is the authors' understanding that the current price per mol gas equivalent of HFC 134-a < HFE 7100 < Novec™612. This order – which is the reverse order of the amount of compound needed to protect a given magnesium melt surface – may or may not change with changes in legislation and associated availability/pricing. This further illustrates the strong coupling between technical, environmental and economic factors involved when choosing an alternative cover gas system.

As indicated above, the choice of carrier gas will have an impact on the total economics of protection. The three most used carrier gases are dry air, N<sub>2</sub> and CO<sub>2</sub> – alone or in various mixtures. Of these carrier gases, dry air is normally the cheapest with N<sub>2</sub> and CO<sub>2</sub> similar in price. The choice of carrier gas will again be an evaluation of technical performance (the tested active compounds all performed better with less O<sub>2</sub> present), environmental performance (different off-gas products and degree of decomposition) and price, both of the carrier gas itself and potential associated emission.

**Recommendation**

In Section 3 of this report, an attempt to make an objective comparison of the technical and environmental performances of HFC 134-a, HFE 7100 and Novec™612, based on the results of the IMA/SINTEF collaboration project, has been made. It is, however, important to note that results obtained in the study were gathered in small scale and/or over a rather short period of time (laboratory or a two-week campaign) with a number of experimental constraints. It is therefore recommended that the technical and environmental impact of chosen cover gas parameters (gas mix, flow rate, gas distribution etc) is studied over a longer period of time, in order to make a more statistically reliable evaluation of their overall and comparative performances.

With the changing market place and legislation – carrier gas and active compound prices vary. CO<sub>2</sub> equivalents are already a trading commodity; therefore, it would be useful to establish a flexible parameter matrix from which the net "impact" (technical, environmental, cost) of use of any given cover gas mixture can be evaluated.

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## **APPENDIX I: EXPERIMENTAL MATRIX, LABORATORY TESTING**

See spreadsheet entitled "Appendix 1.xls"

## **APPENDIX II: EXPERIMENTAL PLAN FOR PILOT INDUSTRIAL SCALE TRIALS**

Industrial scale trials at Norsk Hydro in Porsgrunn are included as a part of the 2<sup>nd</sup> year activities in the IMA-SINTEF-project "SF<sub>6</sub>/SO<sub>2</sub> Alternatives for Protection of Molten Magnesium". Here we want to test the most promising solutions found from our previous laboratory experiments in Trondheim in a larger scale.

In all magnesium metal casting processes the molten metal is first kept in one or two melting/holding furnaces. This will usually be a well-controlled situation where the metal surface is still and the atmosphere can be controlled thanks to a closed furnace cover with only small leakages from the surrounding air. Under such conditions the metal is well protected by a steady supply of a cover gas such as SF<sub>6</sub> or SO<sub>2</sub> in low concentration in 100% air or air/CO<sub>2</sub>. This well-controlled situation is occasionally disturbed by the need to add new metal (liquid or ingots) or removing dross from the melt surface. In these cases the protective surface film is disturbed, and the furnace cover is opened for a short while so that "fresh" ambient air is admitted to the metal surface. The molten metal will often be kept in the holding furnace for long times (hours or days).

From the holding furnace the metal can be cast in different ways, including casting of ingots, sand casting, and high-pressure die-casting. During ingot casting the molten magnesium is poured into semi-open moulds and cooled relatively slowly. During the pouring and cooling the mould needs to be protected by a relatively high concentration of a cover-gas. In sand casting and high-pressure die-casting the mould filling and melt cooling is much faster. In addition these moulds are more closed, preventing air from reaching most of the cast parts during cooling. Thus the need for cover gas protection during sand casting and high-pressure die casting is smaller.

The detailed technical solutions for all casting operations vary from caster to caster. We hence propose to first perform tests with a well-controlled holding furnace to establish the protection efficiency of alternative cover gases (HFC 134a, HFE 7100 and Novec™612) compared to SF<sub>6</sub>. This is a situation comparable to our laboratory experiments except for the larger scale. The three new protective compounds will be tested in the holding furnace on pure Mg and the two alloys AM50 (die-casting) and RZ5 (sand-casting). The "castability" of the AM50 alloy after exposure to the new compounds, compared to SF<sub>6</sub>, will also be tested in a die casting trial. The casting properties of RZ5 and Pure Mg will not be tested. Detailed descriptions of the systems to be used and the experimental parameters are suggested below.

For all experiments, the Beryllium level of the melt will be checked and systematically kept constant with partial tapping and metal replacement (and/or potential Al-Be alloying). This is important since Beryllium very effectively helps to protect molten magnesium and it will hence effect the results if its concentration varies substantially.

## System description

### Holding furnace

A 500 kg, 140 kW melting/holding furnace will be used. It has a surface area to be protected of approximately 0.5 m<sup>2</sup>, and three hatches in the furnace lid for melt transfer and drossing/metal additions.

### Cover gas distribution geometries

The furnace is covered by a 10 mm steel plate with hatches for adding metal and removing dross. The cover gas is distributed from a 10mm diameter stainless steel pipe welded to the underside of the lid. 20 holes with diameter 1.0 mm are drilled through the pipe wall to distribute the gas. The first 100 cm of the pipe act as an temperature conditioner, with no holes. The positioning of the pipe and the holes are optimised using fluid dynamics, and shown in the Figure II-1. The gas must cover the metal surface. Furthermore, the cover gas concentration should be increased sufficiently rapidly after a hatch has been opened to ensure adequate protection. A single gas nozzle will be used in some experiments to test the importance of a more sophisticated gas distribution system. The CFD (Computational Fluid Dynamics) calculations done for the furnace will be provided in the Annual Report.

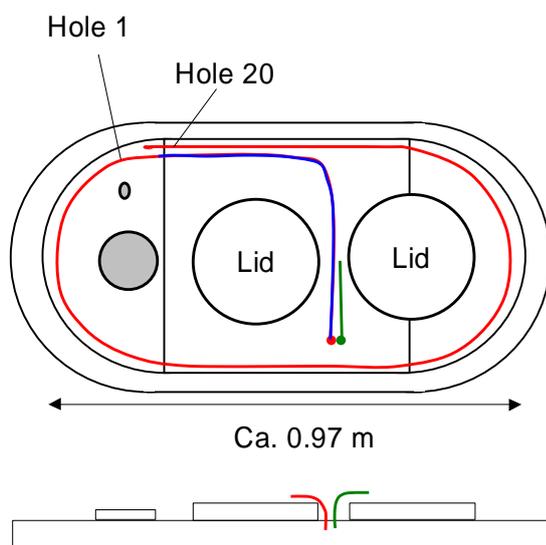


Figure II-1. Schematic of cover gas distribution system.

### Cover gas supply system

The laboratory trials in Trondheim show that both air and particularly CO<sub>2</sub>/5%air with active compound concentration as low as to 0.05% (at cover gas flow rates of 0.5 l/min over a 0.035 m<sup>2</sup> melt surface, equivalent to 7,2 l/min for a 0.5 m<sup>2</sup> melt) protects the melt well. There are also indications that CO<sub>2</sub> /air perform better than pure CO<sub>2</sub>. The results virtually exclude argon/5%air.

The trials in Porsgrunn will involve the two carrier gas systems **100% air** and **CO<sub>2</sub>/5% air**, as well as the four active compound gases: **Novec612**, **HFE7100**, **HFC134a** and **SF<sub>6</sub>**.

The pilot plant facilitates support control of two separate gas flows. The cover gases come in two states, liquid (HFE7100 and Novec612) and in pressurised gas flasks (SF<sub>6</sub> and HFC134a). For SF<sub>6</sub> and HFC 134a, SINTEF will provide flow meters that can deliver 0.27 and 0.20 l/min, respectively. With Q<sub>tot</sub> = 10 l/min, this gives a maximum active compound concentration of 2.7% for SF<sub>6</sub> and 2.0% for HFC134a.

The liquid active compounds, HFE 7100 and Novec™612 will be administered into the gas stream by a precision pump. This pump is provided for the trials by 3M™/Dean Milbrath. 3M™/Dean Milbrath will perform FTIR-analysis of the off-gas products, both inside the holding furnace and in the operator zone of the foundry. Of special interest are the levels of toxic and high-GWP components in the off-gas

### **High-pressure die-casting**

High-pressure die-casting will be performed with AM50 at one temperature, 710°C, when optimal gas mixture conditions are obtained for each carrier gas/active compound system. After a set time period of exposure to each of the three active compounds (+ SF<sub>6</sub>), 20-50 mechanical testing pieces will be cast, which will later be tested.

In the high-pressure die-casting machine in Porsgrunn there is no need for cover-gas protection of the melt. The only point that is protected is the outlet of the dosing pump supplying the metal to the shot-chamber. This has earlier been found to be adequately protected by 100% argon. Thus, if we are able to protect the holding furnace properly with the new cover gases, argon protection in the shot-chamber ought to be safe also for the new cover gases in the high-pressure die-casting trials following the holding furnace trials.

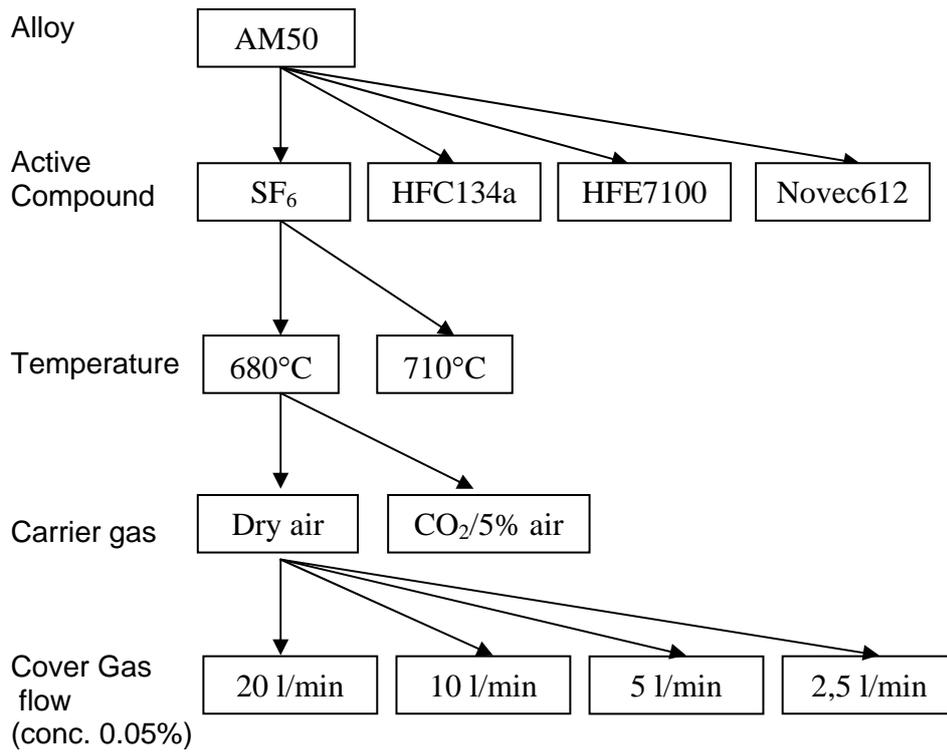
### **Experiments to be conducted**

As seen in Figures II-2 to 4, we will initially (the first week) run a matrix style optimisation testing of the gases on all three alloys. For AM50, two temperatures will be tested, 680 and 710°C, while both pure Mg and RZ5 will be tested only at 710°. During the second week, the optimised conditions will be tested on clean metal for each of the three alloys. For the AM50 alloy, die-casting trials will follow subsequent to the optimised melt experiments.

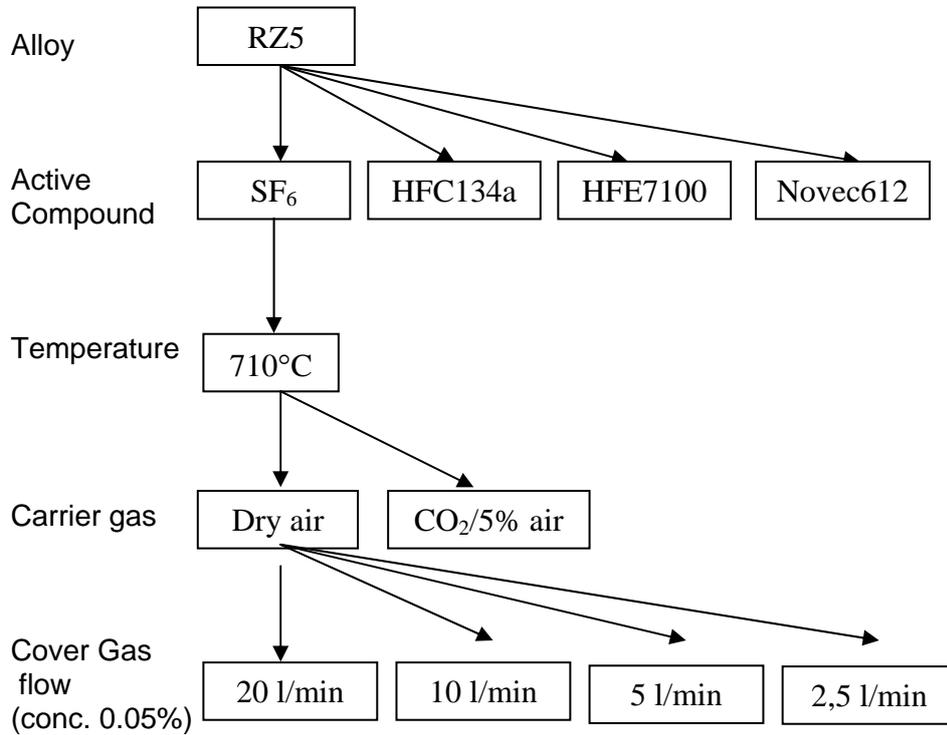
Starting with the CO<sub>2</sub>/5%air carrier gas we will then reduce the cover gas flow-rate from an initial high value (20 l/min) to half of that in steps (10, 5, 2,5 etc.) until protection fails. During this the off-gases will be monitored by FTIR. Following this we will test the fire extinguisher properties of the cover gas by flushing it onto the no longer well-protected surface at a higher flow rate. We will then increase the cover gas flow back to a safe level and test the response to typical operations of a holding furnace such as skimming/cleaning/drossing of the surface and charging of extra metal. Observations of the surface film behaviour/characteristics will be recorded during these operations. In all trials we will use a constant concentration of active compound (may vary but for Novec™612, 0.05%). To minimise the residual effect, SF<sub>6</sub> will be flushed over the melt for a set amount of time between each of the new gases.

After finishing the trials with the CO<sub>2</sub> based carrier gas, repeat the same kind of experiments with a carrier gas of dry air as a reference. After finishing the experiments with both carrier gases we will (for AM50) then increase the temperature of the melt from 680 to 710°C.

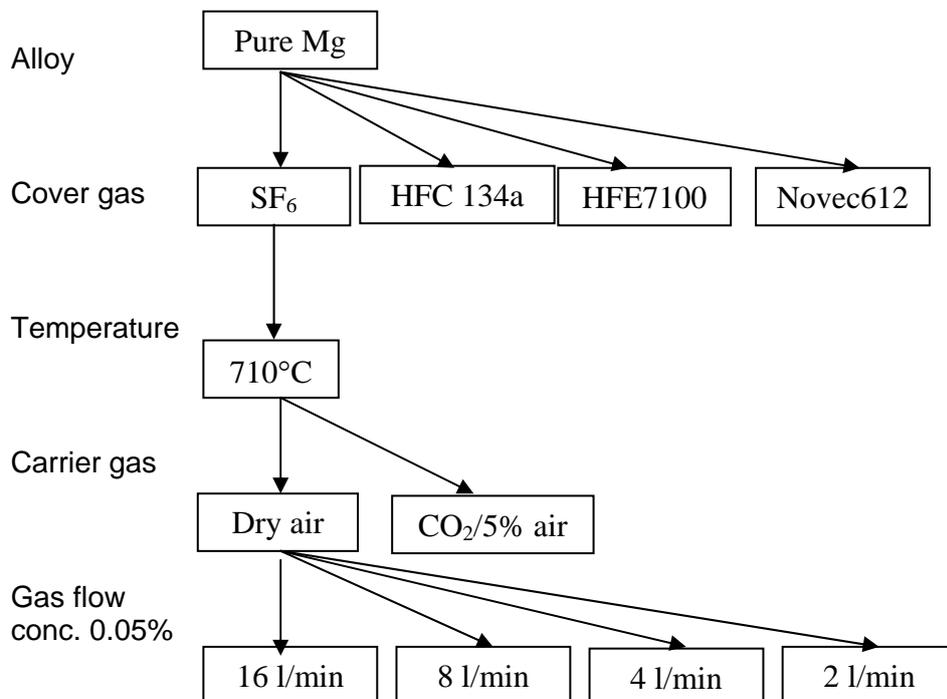
Dross burning (burning/not burning) will be observed during the trials.



**Figure II-2** Flow-chart for the holding furnace experiments with AM50.



**Figure II-3** Flow-chart for the holding furnace experiments with RZ5.



**Figure II-4** Flow-chart for the holding furnace experiments with pure Mg.

**“Algorithm”**

For each (2) Alloy do

    For each (4) active compounds do

        For each (2) Temperature do

            For each (2) Carriergas do

- Start at safe (high) flow of covergas (20 l/min, 0.05%)
- Skim the surface carefully
- Reduce gas flow (concentration fixed at 0.05%) in steps until protection fails (10 minutes at each concentration to equilibrate system, then hold 10 minutes)
- Test fire-extinguishing properties of the gas using a lance with variable gas flow rate. Return to lowest safe flow of cover gas
- Test response to normal operating operations like skimming the surface, observe surface skin properties
- Cast trials: AM50: Die-casting. RZ5 and Pure Mg: No casting

                Change Carriergas

                Change Temperature

- Test long-term performance (over night)

        Change Covergas

- Check Melt cleanliness
- Change Alloy