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Analysis of Different Inhibitors for Magnesium Investment Casting

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Abstract. Investment casting of magnesium is a well suited process for the production of aeronautic and automotive components. But still, this process has not been properly developed. One reason for that are the reactions between the Mg melt and the ceramics of the mould that produce a non-desired oxide layer on the part surface. These reactions can be inhibited by the use of silica-free slurries with a higher stability than conventional ones. Another way is using inhibitors, chemical compounds based in fluorides that react with the melt, creating a protective surface layer in the casting. With the aim of developing a reaction-free process, alumina moulds with a stepped geometry have been constructed. These provide different interface conditions. Conventional SF_6, non-conventional KBF_4 and $NaBF_4$, and environmentally friendly FK inhibitors have been tested on. As a result, KBF_4 has been identified as the most suitable inhibitor for magnesium investment casting. Furthermore, the analysis of the cooling curve of different interfaces has provided essential information about the reaction mechanism of the inhibitors.

1. Introduction

Investment casting of magnesium is a process well suited for the production of aeronautic and automotive components, as light density components in medium and small series are obtained. But still, this process has not been properly developed and one reason for that are mold-metal reactions. Due to its large negative Gibbs free energy value, MgO is one of the most stable compounds. This means that, in investment casting, the refractory oxides of the mould tend to decompose thermally and form the more stable MgO compound. As a result, molten magnesium reacts with commercial shell materials (aluminosilicates) producing a non-desired oxide layer on the part surface. Severe surface reactions may even cause the destruction of the mould [1].

Reactions occur in the interface between the mold and the metal. It is known that the severity of the reaction rises with the increase of temperature and holding time. Thus, it can be considered that mold-metal reactions are dependent on the mold material, the melt and the temperature-time curve of the interface (cooling rate of the interface).

Mold-metal reactions in investment casting can be inhibited by non-conventional slurries, with a higher negative ΔG value than conventional ones. Just considering oxide stability, regardless of kinetics, it can be supposed that Mg melt needs more time to decompose a more stable mould. In that case, during decomposition time, the interface will be cooled enough to avoid the appearance of reactions. Another way of avoiding reactions is the usage of inhibitors. Inhibitors are chemical compounds, typically based in fluorides, which prevent chemical reactions: When molten magnesium enters in the cavity of the mould, fluorides react with Mg creating the new compound MgF_2 that will contribute to form a protective layer between molten Mg and the mould [2]. Inhibitors effectiveness is dependent on its formation rate: it has to be higher than magnesia's, for a certain interface conditions.

Another problem concerning to Mg casting is magnesium melt protection, as the melt needs to be protected from the atmosphere. For this purpose, through the last decades several gaseous inhibitors have been developed and some of them have also been tried out in Mg investment casting. SF_6 has proved to be the most efficient one in Mg melt protection and close chamber castings. The carrier gas and the required SF_6 amount have also been well studied during the last years [2, 3, 4]. However, due to its negative global warming effect, SF_6 is no longer environmentally acceptable. In fact, 1 pound of SF_6 is equivalent to over 22,000 pounds of CO_2 in its impact on global warming. Owing to that, in the last years, several environmentally friendly gases have been developed to protect the Mg melt [5]:

Table 1. Atmospheric Lifetimes and Global Warming Potentials of SF_6 Replacements [5].

Compound	Life Time (years)	GWP	
CO_2	100-150	1	
$C_3F_7C(O)C_2F_5$	0,014	1	KFs
CF_3CH_2F	13,6	1600	HFCs
CF_3CHF_2	32,6	3800	
C_3F_8	2600	8600	PFCs
C_4F_{10}	2600	8600	
C_6F_{14}	3200	9000	

HFC and KF-s are the most interesting ones from the environmental point of view. Moreover, HFC-134a has already been tested as an investment casting inhibitor with good results [6]. Fluoroketones, unlike SF_6, are low boiling liquids that can be evaporated into a carrier gas stream like the 3M^{TM} Novec^{TM} 612 Magnesium Protection Fluid. The experiments carried on Mg melt protection have already achieved good results [5].

The Magshield system is another method proposed for the SF_6 replacement [7]. It is based on the heat-decomposition of boron bearing powder KBF_4, which releases the protective gas BF_3. KFB_4 has already been used as an additive in sand castings to prevent magnesium metal-mold reactions, with good results. However, the addition of KBF_4 to the layers of investment moulds has lead to bad results [1, 3]. As the mould is usually first sintered at 850-1000ºC, those fluorine-containing compounds that are unstable below this temperature are mostly lost, whereas those that are stable above this temperature will not break down at Mg casting temperature.

$NaBF_4$ is also used as an inhibitor in sand castings. This chemical is not as effective as KBF_4, and therefore, larger amounts are added to the sand mixture. KBF_4 and $NaBF_4$ are similar chemicals in their properties, but one noticeable difference is the solubility of these salts in water. KBF_4 is only slightly soluble in water (4.4 g/l at 20ºC) whereas $NaBF_4$ is highly soluble in water: 973 g/l at 20ºC. Cingi [1] has solved the problems arisen from adding powders to investment casting mould: instead of adding, he prepared aqueous solutions of powders. Thanks to the high solubility of this chemical he prepared aqueous $NaBF_4$ solutions by dissolving 36.5 g powder per liter of H_2O. Afterwards the sintered molds were dipped in the inhibitor liquid. During the preheating of the mould, the BF_3 protective gas was released, observing large reductions of the reactions [1].

2. Experimental Procedure

Figure 1 shows the casting mould and the part in red color. The component has a stepped geometry with general dimensions of 80x60 mm, being the steps 2, 4 and 8 mm wide. The three different steps will provide different interface conditions, thus different reactions can be expected for them. The part has been fed by five casting gates, which are 16 mm wide. A Foseco commercial filter has been employed, the Stelex 10 ppi filter and the casting alloy is the AZ91E alloy. The first layer of the mould has been constructed with Al_2O_3 as the mould face coat material and stucco, and SiO_2 binder. The backup layers have been made of conventional aluminosilicates, since they do not take part in the mould-metal reactions.

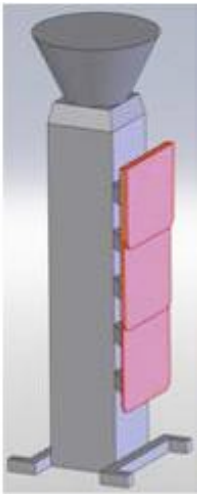


Figure 1. Mould to be casted. The component is shown in red colour

Figure 2. Wax model of the mould. 2 thermocouples have been placed in each step

The thermal history of each step has been recorded with 2 thermocouples. One has been placed in top of the casting gate, where the area is 16 mm wider than that of the other thermocouple of the same step. In summary, 6 thermocouples have been placed in each mould, recording the temperature-time curves for widths of 2, 18, 4, 20, 8 and 24 mm respectively. Figure 2 shows one of the wax models, were the thermocouple sheaths have already been placed in the surface of the part. The essays have been performed at two different temperatures to cover a wider range of interface conditions. Magnesium casting temperatures have been set to 745ºC and 725ºC, due to the necessity to use high temperatures to fill thin walled complex geometries in magnesium casting. The mould preheating temperatures are respectively 545ºC and 520ºC, for the same reason [8].

SF_6, $NaBF_4$, KBF_4 and FK inhibitors have been analysed in this work. Aqueous solutions of $NaBF_4$ and KBF_4 inhibiting powders have been prepared. Solutions have been made adding 38 gr of powder per liter of warm water at 65ºC, which is the solubility limit of KBF_4 at that temperature. FK has also been employed in liquid state. As it is not soluble in water, moulds have been dipped directly in this inhibiting liquid prior to the preheating of the mould. In order to analyze SF_6 effectiveness, moulds have been flushed with 4% SF_6 in CO_2 at 5l/min for 60 sec during the mould preheating and for 90 sec outside the furnace, before the open chamber casting. To compensate the cooling of the mould during the flushing, higher preheating temperatures, of 630ºC and 605ºC have been used with this inhibitor. Table 2 summarizes the chosen parameters for the inhibitor essays:

3. Results

Moulds without any inhibitor have given severely reacted castings, as expected, and both, high and low temperature essays (1 and 2 in table 2), have provided very similar results. The reactions have even penetrated the mould so high-pressure water blast had to be used to remove the stuck ceramic from the casting surface.

Table 2. Parameters employed in the experimental essays.

	Mould Material	Binder	Alloy	Inhibitor	Magnesium Casting T (ºC)	Mould Preheating T (ºC)
1	Al_2O_3	SiO_2	AZ91E	Nothing	745	550
2					720	525
3				$NaBF_4$	745	550
4					720	525
5				KBF_4	745	550
6					720	525
7				FK	745	550
8					720	525
9				SF_6	745	630
10					720	605

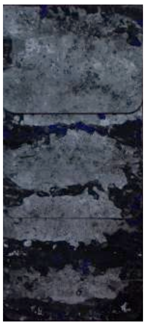
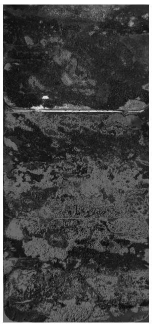
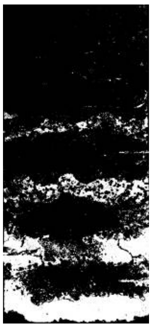
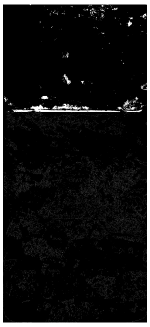
However, some areas have still remained unclean, as it can be seen in picture 1 in table 3, in black color). SF_6 has not provided better results: the surface of castings 9 and 10 has also completely reacted, except a small area in the edge of the 8 mm step. This suggests that, during pouring and casting, SF_6 flew away from the mould and that a small volume of the inhibiting gas was trapped in the 8 mm step cavity, protecting the Mg melt. In contrast, the employment of KBF_4 and $NaBF_4$ has provided non-reacted areas on the casting. Both inhibitors have shown, predictably, a decrease in the number of reactions in the essays at lower temperatures. For these two inhibitors, reactions have not been so severe, so surfaces without stuck ceramic have been found after the shell removal.

Moulds inhibited with fluoroketones were destroyed during the casting. This may be due to a reaction between the liquid inhibitor and the ceramic mould. During mould preheating, products formed due to the thermal decomposition of the inhibitor could also have caused this destruction.

The effectiveness of the different inhibitors has been evaluated by the quantitative method developed by Cingi [1]. In the same way, digital pictures of all the samples have been taken and processed by an image processing software until only the reacted areas (black) and non-reacted areas (white) have been revealed. An image analyzer has been used to measure the amounts of white and black pixels, converting this number to the reacted surface area of each casting. The results of this analysis are given in table 3, where KBF_4 has clearly proved to be the most effective inhibitor: essay no. 6 has been the less reacted: only 68.32% of its surface reacted. However, essay 5, performed at 745-550ºC, has given worse results than those performed with $NaBF_4$. Explanation for that can be found in the analysis of the cooling curves recorded by the thermocouples of each mould, in figure 3.

Temperatures recorded in essay 5 are higher than the ones recorded in both $NaBF_4$ essays. The time until the alloy has reached liquidus temperature is also higher: between 225-550 sec for essay 5 against 150-225 sec in essay 3 and 100-250 in essay 4. Because of that, the severity of the reactions in essay 5 increased and the 90.78% of the surface was covered with mould-metal reactions. In fact, the interface conditions of essay 6, KBF_4 at low temperatures, are even more severe than the ones recorded in essay 3 ($NaBF_4$ at high T). Although temperature values are similar for both, the liquidus time in essay 6 is longer: around 200-325 sec, which reaffirms KBF_4 as the best inhibitor. This liquidus time values correspond to the seconds when the thermocouples reach first and last the liquidus temperature in the T-t curves, as it can be seen in picture 3.

Table 3. Quantitative analysis of the effectiveness of the inhibitors tested.

Essay nº	1	3	4	5	6	9
Picture						
Processed Image						
% Area	% 99,3	% 84,41	% 81,87	%90,78	%68,32	%97,76

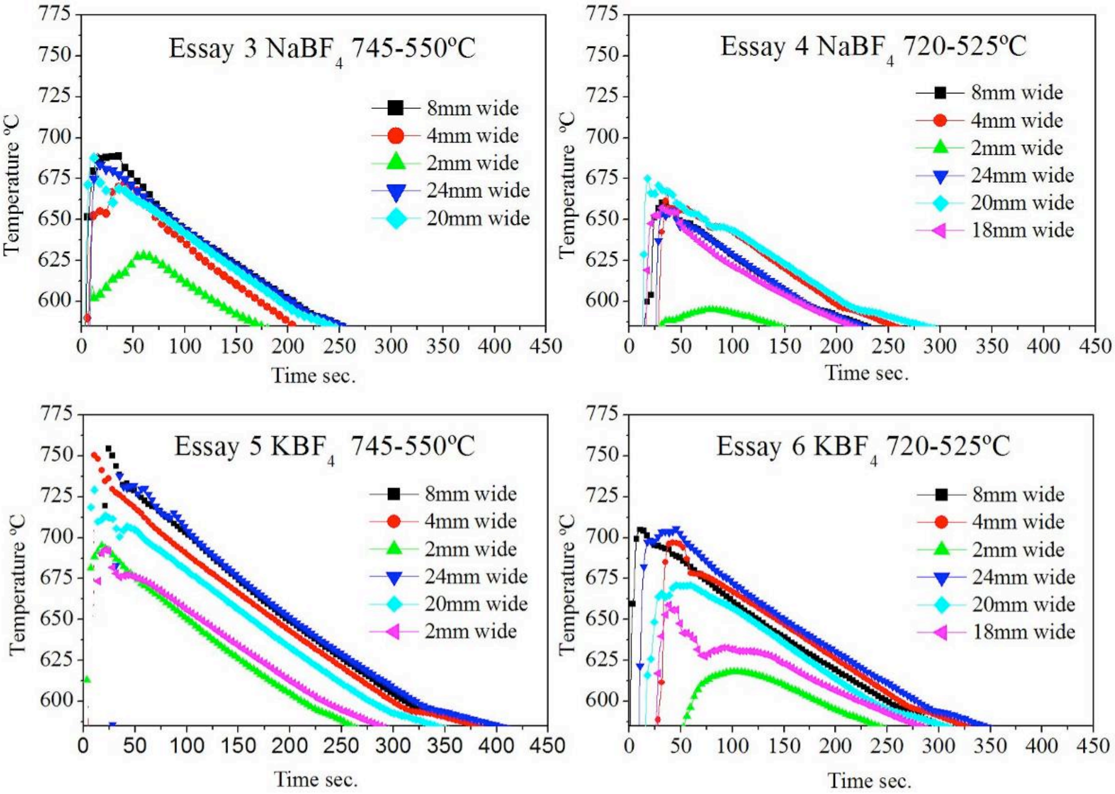


Figure 3. Time-temperature curves for essays 3, 4, 5 and 6. Only temperature values above the AZ91E melting point are shown.

More information can be extracted from the cooling curves. Both $NaBF_4$ essays have shown clean surfaces only in the location of the 2 and 4 mm width thermocouples. Therefore, $NaBF_4$ inhibitor could be considered an effective inhibitor for those castings with surface cooling conditions equal or less severe than the corresponding to those thermocouples. Figure 4 shows all the curves recorded in the $NaBF_4$ essays, were the 4 thermocouples that registered clean surfaces are painted in red.

Regarding to KBF_4, clean surfaces were only achieved in essay 6, corresponding to the 2 and 8 mm width. However, as it can be seen in figure 4, curves corresponding to 18 and 20 mm widths should also have given clean surfaces. This can be due to a bad positioning of the thermocouples, or to a not uniform dipping of the mould in the inhibitor solution. Anyway, further analysis of the cooling curves and its shape in relation with the mould-metal reactions should be performed.

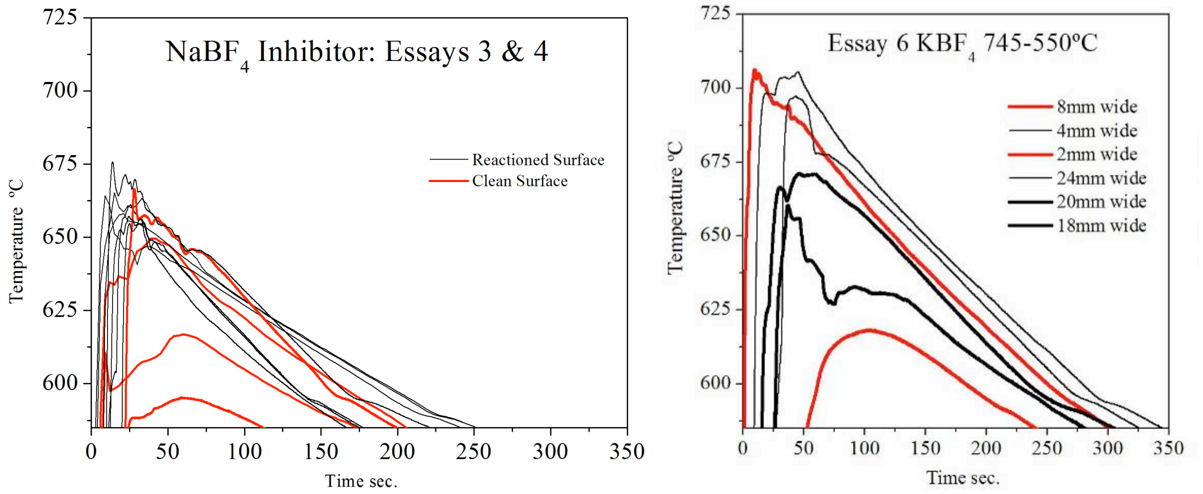


Figure 4. Analysis of the time-temperature curves of $NaBF_4$ essays and Essay 6.

4. Conclusions and Further Work

Five different inhibitors were tested on an alumina mould with silica binder, with the aim of selecting the most suitable inhibitor for magnesium investment casting. Severe interface conditions have been selected and recorded with thermocouples to obtain essential information about the reaction mechanisms. As a result, several conclusions have been extracted from the work performed:

- Severe reactions have taken place when no inhibitors have been used. Reactions have even penetrated in the mould and as a result, after the shell removal, stuck ceramic has been found in the casting surface. Cleaning with high-pressure water still has left some stuck ceramic, which suggests a depth penetration. Thus, the severe experimental conditions employed in the experiments, force the use of inhibitors to obtain reaction free surfaces.
- The employment of liquid FK has lead to mould destruction. FK are not effective in liquid state, but since gaseous FK are employed in melt protection new trials with gaseous FK should be performed.
- SF_6 has not been effective as inhibitor in open chamber investment casting. Surfaces of the casting were almost completely reacted, suggesting that the inhibitor has flown away during the filling of the mould. A continuous feed of this gas may be necessary to protect magnesium.
- $NaBF_4$ has been effective under certain conditions. Analysis of the T-t curves recorded from the thermocouples provided the necessary conditions to obtain clean surfaces.
- KBF_4 has proved to be the most effective inhibitor. Best results were obtained with this inhibitor with only the 68,32% of the surface having reacted.

- Further analysis of the cooling curves and its shape in relation with the mould-metal reactions should be performed.

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