

ADVANCED RECYCLING AND ENVIRONMENT FRIENDLY PROTECTION OF LIGHT METALS

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Abstract

The protection of liquid light metals from oxidation is a major issue in recycling and melting processes in the light metal industry. The light metals Al and Mg oxidise easily and “protective chemicals” are used in processing both metals. Mixtures of sodium and potassium chlorides have been widely used in the recycling of aluminium scraps. Due to the good protective behaviour of aluminium oxide on top of liquid aluminium a lot of work has been carried out to reduce the amount of salt in the recycling process. In combination with the development of tilt able rotary furnaces, low salt and ultra low salt processes have been developed. Salt free processes have attained commercial status and the process control of the gases and the amount of free oxygen is now becoming more and more of an issue.

Reactive gases are used in the magnesium industry to prevent Mg fires and oxidation of the liquid metal. Reactive gases like SF₆ or SO₂ do not meet environmental standards due their extremely high global warming potential or toxicity. The protection of magnesium melts using solid CO₂ was developed in co-operation between Linde Gas and academic and industrial partners. Within the last year the amount of CO₂ has been dramatically reduced to make the new application competitive. Protection of liquid Mg by solid CO₂ represents the best environment-friendly standard to comply with the Kyoto objectives.

Introduction

Today aluminium and magnesium play an important role in the reducing the weight of modern cars. Today only 1-1.5% of a typical medium sized car are made out of Mg, aluminium is the major light metal in the automotive sector and almost 10% of cars are produced using Al. In general European cars contain more light metals than American or Japanese cars, but the increase in using light metals is visible all over the globe [1-3]. Several car manufacturers plan to increase the ratio of magnesium in particular to gain a further reduction in weight [4]. Aluminium and magnesium have to meet a number of challenges to fulfil the needs of further growth. Both metals are more expensive than high-strength steels and both metals oxidise easily even in environments which contain very low amounts of oxygen. Both metals can be recycled easily and the protection of the hot liquid plays a major role in the prevention of metal losses due to oxidation. Protection by molten salts reduces the oxidation of aluminium, but increases also the energy consumption in the melting process due to the fact that the salt mixture

has to be heated and the heat transfer from the flame into the bath is hindered by the salt layer on top of the liquid. As already mentioned, both metals oxidise easily, but aluminium has now become the key light metal in the industry. The “handling” of Al is much easier than processing magnesium metal due to its different behaviour in the oxidation process. Liquid aluminium forms a dense oxide layer whose volume is larger than the volume of the metal (see Fig. 1).

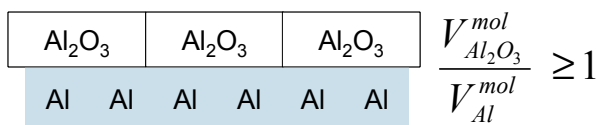


Fig. 1: Pilling-Bedworth ratio of Al/Al₂O₃. The dense protective layer reduces further oxidation.

The ratio of oxide volume to metal volume (so called Pilling-Bedworth ratio) is greater than one, which explains the protective effect of the aluminium oxide. As the Pilling-Bedworth ratio for magnesium is 0.81 [5], no dense oxide layer is formed and the protection of liquid magnesium plays a major role in the protection of magnesium (see Fig. 2).

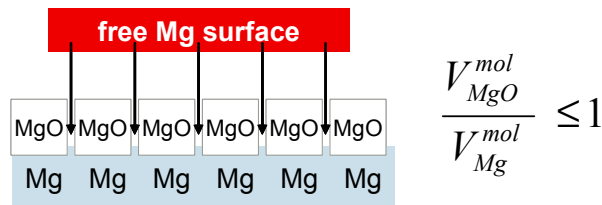


Fig. 2: Pilling-Bedworth ratio of Mg/MgO. The formed oxide has a lower volume and is not able to protect the metal from oxidation.

To minimize the risk of fire in magnesium melting processes and to reduce contamination of the melt by oxidation products, it is indispensable to shield the melt against the ambient atmosphere during treatment. Today SF₆ or mixtures of N₂-SO₂ are used in magnesium melting furnaces to protect magnesium melts from oxidation. Over the last 30 years the overwhelming majority of magnesium casters have used gas mixtures containing SF₆ to prevent the oxidation of molten magnesium. However, SF₆ has a high GWP-factor (Global Warming Potential: contribution to the heating of the earth’s atmosphere) of 23900, referring to damage to the earth’s atmosphere caused by CO₂. At the Kyoto summit [6], the gas was listed as one of six gases whose use was to be restricted. According to the new EU regulation [7], the use of sulphur hexafluoride in magnesium die-casting will be pro-

hibited from 1st January 2007, except where the quantity of SF₆ used is below 500 kilograms per year.

Protection by molten salts in aluminium recycling processes: from salt through low salt to no salt processing

Aluminium recycling is a now familiar technology with an established industry today. More than 9 million tons of secondary aluminium were produced in 2004. Recycled “secondary” aluminium represents more than 30% of the global aluminium supply and a further increase in secondary aluminium is expected. In 2002 secondary aluminium (670 kt) exceeded primary aluminium production (650 kt) in Germany. Other countries showed similar growth in aluminium recycling shares. A great deal of research had been conducted to increase the efficiency of aluminium recycling processes by reducing energy consumption, increasing productivity or by reducing the salt needed for the recycling process in rotary furnaces.

Aluminium recycling with salt

Most secondary aluminium in Europe is produced in fixed-axis rotary furnaces (see Fig. 3). Oxy-fuel burners in combination with WASTOX[®] oxygen lances are used to reduce emissions and reduce the energy consumption in the melting process. Salt mixtures containing NaCl and KCl are used to protect the hot aluminium surface from oxidation by hindering the oxygen flow towards the metal.



Fig. 3: Typical fix-axis rotary salt furnace (double pass) with oxy-fuel burner and oxygen lance (WASTOX[®]) for recycling of scraps in a rotary salt process.

In recent years the amount of salt in the recycling process has been reduced as a result of increasing recycling prices for the salt and increasing landfill costs. The salt factor is defined according to the following equation [8]:

$$SF = \frac{m_{\text{salt}} \cdot 100}{[m_{\text{input}} \cdot (100 - \eta_{\text{metal}})]}$$

in which m_{salt} is the amount of salt, m_{input} is the amount of material charged and η_{metal} is the yield in the Al recycling process. In the development of Al recycling processes in fixed axis rotary furnaces, large salt factors of 1.5 to almost 2 are used and a value of 1.8 is a often published value [9].

In the past 10 years tilt able rotary salt furnaces have entered the aluminium industry. The main advantage of tilt able furnaces is reduced charging and taping times, which results in higher productivity values. In a joint project, Linde Gas, Corus Aluminium Voerde and Hertwich Engineering developed in the URTF (universal rotary tilt able furnace, see Fig. 4) which has become the state-of-the-art in the recycling of dross and aluminium scraps.



Fig. 4: Two tilt able rotary furnaces for low and ultra low salt recycling (URTF at STENA Aluminium) with oxy-fuel burners and oxygen lances (WASTOX[®]) for recycling of aluminium scraps.

After several furnaces had been introduced it became clear that lower salt requirements were necessary and thus the low salt process with salt factors of less than 1.0 was developed. The development of tilt able furnaces in combination with the lower salt requirement reduced the specific salt input per ton from 200-300 kg/t_{Al} (“low salt”) to values much lower than 70 kg/t_{Al} (“ultra low salt”).

Salt free recycling of Aluminium: The AluMonte melting concept

Since 2003 Linde Gas has developed a new concept for salt free recycling of aluminium scraps together with AluMonte (a technology company in Austria). This patented technology [10] reduces the costs of processing aluminium scraps and allows the full volume of the rotary furnace to be used (see Table 1).

Table 1: Influence of the salt factor on the use of a 15 t rotary furnace with amount of salt per ton of charged scraps at an assumed yield of 85%.

salt factor	technology	scrap [t]	salt [kg]	salt/metal [kg _{salt} /t _{Al}]
1.8	fixed-axis	11,800	3200	271
1.0	fixed-axis	13,000	2000	153
0.5	URTF	13,875	1125	81
0.1	URTF	14,775	225	15
0.0	AluMonte	15,000	0	0

The AluMonte melting technology is a tilt able rotary furnace which can be tilted in both directions (see Fig. 5). The furnace is heated using an oxygen-air-natural gas burner, and a bouncing shield opposite the burner is used to control the overpressure of the furnace and to recover the heat of the flue gas. The oxygen and the CO values of the furnace gas atmosphere are controlled continuously so that the oxygen concentration inside the furnace is almost zero.



Fig. 5: AluMonte melting furnace with bouncing shield to control overpressure inside the rotary furnace.

AluMonte and Linde Gas completed the development of this new melting concept in 2004 and renewed the co-operation contract. In 2004 the first furnace was sold to a customer in Slovakia. A second furnace was sold in February 2005 to a customer in Hungary - this furnace will commence operations in autumn 2005.

The results of the first reference furnace in an industrial environment verified the data obtained in lab tests and with the pilot furnace. Since summer last year more than 6500 tons of aluminium scraps have been recycled using this new technology. 40 different kinds of scraps have been recycled which had been divided into 12 different "classes" of scrap. The first reference furnace was a small furnace with a volume of 6.2 tons attaining a maximum productivity of 2.8 t/h was reached. Four to six charges are necessary to fill the furnace. Depending on the amount of contamination and the weight-volume ratio productivities of 2,0 to 2,8 t/h were reached after installation of a charging machine. The yield in recycling was 86-95% (with an average of almost 90%) due to the use of unsorted scraps including iron scraps (4-12 wt% of iron inside the scrap).

Compared to the old reverb technology available at the customer the yield increased by more than 10%. The measured energy consumption in the process was between 350 and 400 kWh/t_{Al}, which is a very low value for recycling processes and much lower than the energy consumption observed by recycling in the old reverb furnace. The overall recycling costs have been reduces significantly. Another significant benefit in the test was that the iron "pick-up" was negligible and very low iron concentrations were obtained.

Other benefits resulting from the absence of aggressive chlorides included

- Longer life time of refractory material
- Less adhesion of dross on the refractory
- No "wet salt washing" of the rotary required
- Lower chlorine-related emissions

Protection by gases in magnesium melting processes: How to fulfil Kyoto standards

Magnesium and its alloys are increasingly used to substitute not just other metals but also plastics. The decisive factors are excellent properties such as low density, good casting properties, electromagnetic shielding, high specific strength and elasticity. Magnesium and aluminium are neighbours in the periodic system of elements and have several properties in common, such as low melting point or melting energy (see Tab. 2). But magnesium and aluminium show a lot of differences, such as different vaporisation points and the energy needed to heat the metal up from room temperature to melting point.

Table 2: Properties of Mg and Al.

Property	Mg	Al	Unit
Atomic weight	24.31	26.99	g/mol
Melting point	650.0	660.4	°C
Vaporisation point	1103	2467	°C
Density	1.738	2.699	g/cm ³
Energy from RT to mp	308	108	kWh/t
Melting energy	102	110	kWh/t
Vaporisation energy	1515	3344	kWh/t
Surface tension at mp	520	865	mN/m

The protection of liquid magnesium surfaces was carried out by using salts, alloying elements, inert gases or reactive gas mixtures. The salt-based fluxes used to be used to protect molten magnesium from oxidation during the melting and casting operations. Salt based protection is still the most used technology in the recycling of magnesium, but gases are more frequently used in the magnesium casting industry. Protecting the molten metal under a blanket of inert gas such as argon or helium is dangerous, because no protective layer is formed on the melt surface and the metal is free to evaporate, resulting in safety hazards when the furnace ambience is exposed to air due to a violence reaction [11].

The disadvantages of these methods have been partially overcome by using reactive gas systems, in which a chemical reaction between a gas and the molten metal produces a thin protective film on the surface of the melt. Over the last 30 years the vast majority of magnesium casters have used gas mixtures containing SF₆ to prevent the oxidation of molten magnesium. However, SF₆ has a

high GWP-factor (see above) of 23900. According to new EU regulations [7], the use of sulphur hexafluoride (SF_6) in magnesium die-casting will be prohibited from 1st January 2007, except where the quantity of SF_6 used is below 500 kilograms per year. As a result, the magnesium industry is looking for a suitable, environmentally acceptable replacement. In order to find alternatives, an R&D group was funded by the German Federal Ministry of Education and Research with participants from science and industry (University of Hanover, Linde AG, Audi AG and Laukötter GmbH). The new technique for protecting magnesium melts by covering them with CO_2 snow was developed and tested on a laboratory scale [11,12].

Basics of Linde Gas' CO_2 -snow technique

By feeding liquid CO_2 under pressure, solid CO_2 is generated through gas expansion at a nozzle inside the furnace. This CO_2 -snow is deposited on the molten metal (see schematic drawing in Fig. 6) and decreases the surface temperature of the melt (sublimation temperature CO_2 : -78.5°C at 1.013 bar; cooling capacity: 573 KJ/kg), which leads to a decrease of the exhaust velocity of the magnesium.

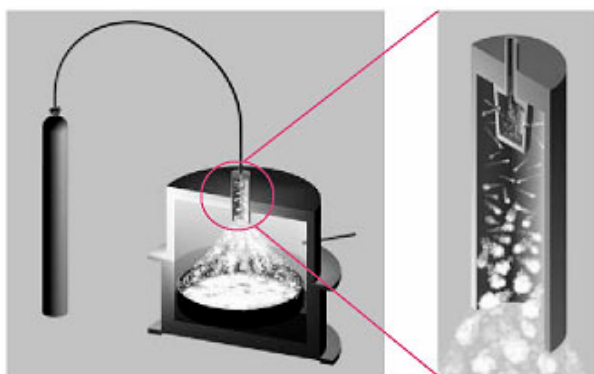


Fig. 6: Schematic drawing of the CO_2 -snow technique. Liquid CO_2 is carried into the snow machine and expands through the blast pipe.

When a specific temperature is reached, CO_2 is placed on top of the surface of the metal. Due to the energy input from the melt, sublimation of the CO_2 -snow starts and a CO_2 gas flow prevents oxygen from penetrating the surface. The temperature of the surface of the melt is reduced to levels below 600°C , but only in the top layer (5-10 mm). As already shown by Karger et al. [11-12], CO is not formed by adding CO_2 -snow to the hot metal.

Experimental CO_2 -snow technique

The evaluation of this patented technique [13] was carried out by several long-term tests over 8 hours a day in the foundry of Laukoetter Gusstechnik GmbH in Wadersloh. As a medium-size company focusing on the die casting of light metals, Laukötter is a typical example of a supplier for the automobile industry. A warm chamber furnace with electrical resistance heating was retrofitted

for the implementation of the tests. Since the simulations of the snow distribution were very complex, a model of the crucible was built in order to adjust the snow distribution on the furnace geometry. The different levels of metal bath (depending on the casting operations) were taken into consideration the tests on the model (Fig. 7). The results were taken into account by implementing the CO_2 -snow installation on the furnace.



Fig. 7: Model of the furnace with functioning CO_2 -snow technique to analyse different fillings of the furnace.

The changes in the bath surface temperature during the covering of molten magnesium with CO_2 -snow were investigated using an infrared camera. Image evaluation provided information on the required snowing duration and intervals. The bath protection concept also provided for immediate snowing in an emergency. CO_2 was supplied from a Linde LIQUITRANS 600 tank in which the CO_2 is cooled to a temperature between approx. -25°C and -16°C and pressurised at approx. 16-22 bar. The CO_2 consumption was measured by a balance and volumetric measurements. AZ91 was used as an input material. The crucible can hold approx. 250 kg of magnesium. The casting temperature was 640°C . During the tests bodies of grinding machines were produced, weighing approx. 200 g. Charging was conducted manually and internal recycling was carried out during the tests. After several hours of protection by solid CO_2 , liquid magnesium with dross was taken out of the furnaces. Cross-sections of several specimens were taken and analysed using electron probe micro analysis (EPMA) to measure the influence of CO_2 dry ice protection on the metal quality.

Results

The long-term test conducted at Laukoetter Gusstechnik showed a reliable operation of the snow machine and good protecting behaviour of the CO_2 -snow for the molten magnesium. The tests revealed several areas in need of improvement, which have now been implemented in the development of the next generation of CO_2 -snow machine. Some of these improvements are:

Better isolation for the CO_2 snow machine: The snow machine was not well isolated and therefore ice formation occurred on the snow machine. This led to a loss of liquid CO_2 in the system and a lower CO_2 snow formation was observed. After isolating the CO_2 snow machine

a much lower loss of liquid CO₂ was observed and a much higher formation of snow was observed.

Better isolation of pipes and wires: The snow machine was not the only critical factor; the pipes for the liquid CO₂ also had to be isolated to avoid CO₂ gas formation in the pipe. By improving the isolation of the pipes a further decrease in CO₂ consumption was observed. Fig. 8 shows an inside view of the charging door of the furnace with CO₂-snow falling on top of the liquid magnesium.

Dimensions of the CO₂ snow machine: A further result of the tests at Laukötter was a resizing of the machine. After several days of operation no adhesion of Mg, MgO, or dust inside the CO₂ machine was observed, so that the length of the CO₂ snow machine was reduced. This reduction of the geometry of the machine also improved CO₂ distribution during operation, which will also affect the protection behaviour of the system.



Fig. 8: CO₂-snow falls on top of the surface of the liquid magnesium and protects the metal from oxidation.

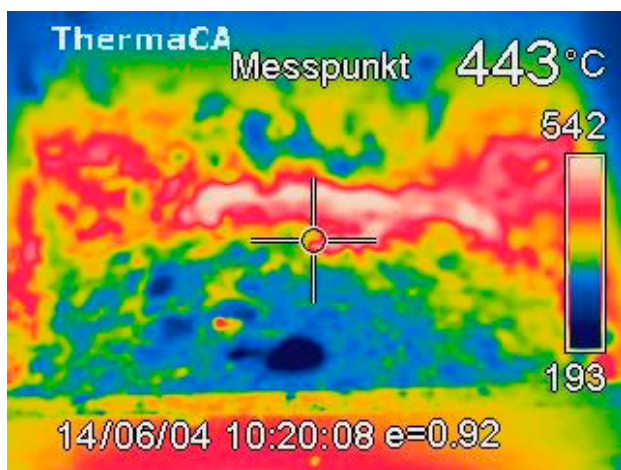
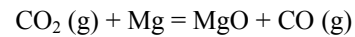


Fig. 11: Infrared picture of the furnace (charging side) with cold temperatures in the centre and higher temperatures in the corners.

Extinguishing fire with CO₂-snow: During the tests and especially after dross removal some small fires had been

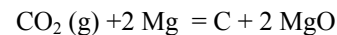
observed on the surface of the metal. By using a “bridging button” the furnace operator can add solid CO₂ to the system until the fire is extinguished. After using this button the system went back to “normal”, fully controlled operations. The extinguishing of the fire can be explained by the large cooling effect of the solid CO₂, because gaseous CO₂ should react at a higher temperature with liquid Mg to form CO and MgO as follows:



By adding cold CO₂ snow to the fire, the cooling capacity of solid CO₂ prevents the reaction from continuing and the sublimation of CO₂ to gaseous CO₂ prevents further contact between the melt and oxygen. In the case of nitrogen burning, generated CO₂ replaces the nitrogen in the burning areas, because the speed of the sublimation is higher in hotter areas of the surface.

Temperature distribution: The temperature distribution on top of the material was observed using an infrared camera (see Fig. 9). Generally a homogeneous distribution was observed with higher temperatures in the corners of the furnace (charging side). This kind of test cannot be used for quantitative results because the IR-system is calibrated for liquid magnesium. In the corners of the furnace a mixture of MgO and Mg exists and therefore a higher error bar must be considered.

Influence on material quality: Gaseous CO₂ is not inert and forms C, CO and MgO when it reacts at higher temperatures with liquid magnesium:



With *solid CO₂* the interface between the liquid magnesium and the gaseous atmosphere is cooled down to extremely low values and no increase in CO concentration was observed in gas analysis measurements.

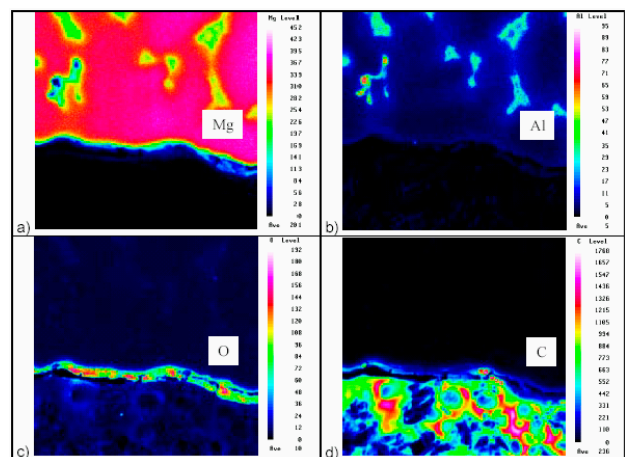


Fig. 12: EPMA analysis and element mapping of Mg, Al, O and C on a cross-section of AZ91 after several hours of CO₂ snow protection operations. No C was found in the alloy.

The EPMA measurements (see Fig. 12) showed no detectable carbon inside the alloy AZ91, which demonstrates that the cooling effect of the solid CO₂ prevents C

formation. In all experiments no influence on metal quality was found.

Competitiveness of CO₂ snow technology: Fig. 13 shows the current status of protection costs with CO₂ snow in comparison to the air-SF₆-solution.

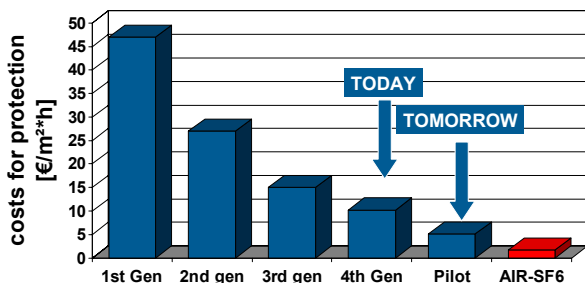


Fig 13: Protection costs in Mg die casting processes with CO₂-snow technology and air-SF₆ benchmark.

During development the costs for protecting liquid Mg were reduced dramatically. With a further improvement in liquid CO₂ management the “time-to-snow” period will be reduced and we expect a further reduction of more than 50%, so that the protection costs with our pilot product will be very close to the air-SF₆ benchmark.

Conclusion

Protecting liquid light metals is a complex issue and the different properties of aluminium and magnesium complicate the development of new applications. The Pilling-Bedworth ratios of aluminium and magnesium explain why it was possible to develop a salt free process for the recycling of aluminium scraps. Protection of aluminium surfaces is not necessary if extremely good control of the oxygen content can be guaranteed. After several years of development from “wet” salt-rich recycling through low salt to an ultra-low salt process, the no salt process is now ready for market. Previous problems which hindered the no salt process have been solved and similar yields and productivities can be achieved using the AluMonte melting process.

A process was developed for protecting liquid magnesium melts for die casting processes with CO₂ snow and the consumption was reduced dramatically to make the technology competitive. Until now no influence on CO₂ protection was observed in terms of material quality or influence on the casting process. CO₂ consumption was reduced from the beginning to the end of the tests by a factor of 4. Further improvements in the CO₂ machine will enable this new technique to become the best alternative to replace SF₆ and SO₂ to ensure an environmentally friendly protection of magnesium.

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