2008-01-0376

Recycling Technology guidelines of MRI die casting alloys

G. Gertsberg, O. Bar Yosef, B. Bronfin, N. Fantetti, N. Moscovitch

Dead Sea Magnesium Ltd

ABSTRACT

Creep-resistant HPDC alloys MRI153M and MRI230D are designated to replace HPDC aluminum alloys in the production of different automotive and non-automotive components. Due to the specific chemical compositions of the MRI alloys; they contain alkaline elements (Ca, Sr) with high affinity to Cl ions, fluxless technology must be used for recycling

The present paper describes an technology which was developed for recycling MRI alloys. This technology combines simultaneous bubbling and stirring during batch processing. This operation is performed in order to improve metal cleanliness and reduce the process duration, thereby increasing its efficiency. The mechanical properties of recycled alloys were tested and compared with those of primary alloys.

The influence of clean scrap dilution with primary material was also explored. The results obtained illustrate a moderate influence of scrap addition on mechanical properties. This effect should be considered for a wide range of die cast components production.

The paper also presents guidelines for MRI alloys scrap handling and recycling.

INTRODUCTION

High-pressure die casting is the dominant process for manufacturing magnesium alloy parts with high productivity at a relatively low cost. This is the dominant process for magnesium alloys being used by the transportation industry. MRI 153M and MRI 230D alloys are patented die cast magnesium alloys developed by Dead Sea Magnesium Ltd. and Volkswagen AG and designated for high temperature applications[1-3]

MRI 153M is a beryllium-free, creep-resistant, magnesium alloy, which combines good castability with the capability of long operation at temperatures up to 150ºC under high stresses. This gives the alloy great potential for applications such as oil pans, bedplates, valve covers, intake manifolds, etc.

MRI 230D is a die casting alloy, which was developed to address powertrain applications such as engine blocks and cylinder heads where service temperatures may reach 190ºC. The alloy has excellent creep resistance combined with adequate castability, high strength and superior corrosion behavior [4].

However, using MRI alloys for the production of automotive drive-train components cannot be expanded without development and implementation of reliable recycling technology, which is a key factor in determining the cost competitiveness of magnesium alloys for automotive applications. In accordance with current market demand, recycled alloy ingots are required to meet the same stringent quality criteria as primary alloys in terms of chemical composition and oxide content.

Two main recycling methods based on flux and fluxless refining are known and well documented [5, 6]. However for commercial AZ and AM magnesium alloys flux recycling remains the method of choice for the largest recyclers, die casters and primary producers. This is attributed to the fact that this method is considered a relatively low cost, proven technology which provides high recoveries (typically 95-98%) of metal of sufficient quality that it is considered competitive with primary magnesium alloys. However, flux recycling has significant disadvantages related to risk of flux contamination and the formation of corrosive vapors that are irritating to human labor and result in accelerated corrosion of buildings and equipment.

Fluxless recycling methods have not found intensive industrial implementation due to its increased cost, lower recovery rates compared to flux based process and difficulties in handling lower grades of scrap.

With regard to creep-resistant HPDC Mg alloys, the situation is more complicated as these alloys contain specific alkaline-earth alloying elements (Ca, Sr) that have higher affinity to Cl ions than Mg (The specific element are listed in the US patent No. 6,139,651, Oct. 31, 2000)[1]. Unfortunately all existing recycling fluxes are based on $MgCl_2$, which will react with Ca and Sr resulting in their depletion. Hence, these alloys will require a fluxless recycling process or a flux process based on using special very expensive salts like $SrCl_2$ [7], which could be considered as economically unacceptable. Furthermore, the experience gained in the Mg industry with fluxless recycling of common magnesium alloys of AZ and AM series cannot be automatically transferred and applied to advanced creep-resistant alloys due to significant differences in the type, chemical composition, density and morphology of oxide inclusions formed in those alloys. Therefore the recycling kinetics in terms of melt temperatures, settling time, intensity of argon treatment (gas flow, size of gas bubbles, sparging time, etc.) is of limited help.

The aim of the present work was to identify and develop advanced recycling technology, which will provide a simplified process and higher efficiency. In addition, the paper also discusses the effect of clean scrap additions on the mechanical properties of die castings produced with MRI alloys and the conventional alloys AZ91D and AM60B

EXPERIMENTAL PROCEDURE

The present paper discloses a fluxless refining method which is based on inert gas bubbling in order to float the non-metallic inclusions (NMI) to the melt surface [5,6,8]. This process requires the use of a protective gas atmosphere.

The process is performed continuously and may combine several sub processes as follows:

- Inert gas (usually argon) bubbling/sparging – the flow of small gas bubbles results in release of impurities in the suspension by “wetting” them. These clusters of impurities (mostly oxides) will float to the surface of the liquid and the heavier impurities will settle. The main parameters are gas flow, size of gas bubbles, sparging time and melt temperature.

- Filtering – mechanical separation of the non-metallic impurities, especially those containing oxides. The main parameters are filtering perforation size, filter size, location of the filter and the temperature of the melt.

- Settling of impurities – separation based on the difference of densities, in which part of the heavier impurities (metallic and non-metallic impurities) sink to the bottom of the crucible. The main parameters of this process are time and temperature.

Based on incorporating the above, the recycling procedure developed for MRI alloys includes following main stages: scrap melting down, refining, settling, and ingot casting.

If the Fe content at the end of the settling stage is higher than 0.004%, casting of recycled ingots should be carried out at a lower temperature.

Figure1 presents the flow chart for recycling MRI alloys.

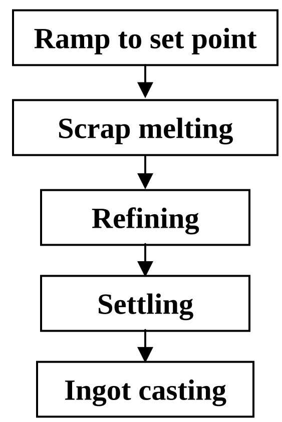

Figure 1. Flow chart of the recycling process

The above procedure applies to both MRI 230D and MRI 153M alloys. However, in order to simplify discussion all further results will be presented only for MRI 230D alloy.

MELTING DOWN OF THE INITIAL SCRAP

Common scrap after few months storage was used for experimentation. The MgO content in this scrap was determined by the wet chemistry method "Magoxide", which was calibrated against FNAA [9]. It was found that the averaged MgO content was around 1500 ppm.

The melting down procedure includes the following steps. Initially, around 10% of the crucible volume is filled by the scrap which is then heated to 690°C. The protective atmosphere containing CO_2+0.5% SF_6 is used Once the temperature reaches this set-point, more scrap is added incrementally (about 5wt. % at a time). This is followed by gentle agitation, in order to avoid aggressive attack on the melt surface. When all the scrap has melted down, stirring is conducted for 10 min followed by settling for additional 15 min. At that point samples for chemical analysis are taken and adjustment of chemical composition should be done if necessary in order to meet the specification requirements.

REFINING PROCEDURE

Different variants including long term settling, bubbling and bubbles dispersion by stirring were examined for this stage. During the development of this process an innovative tool entitled Bubbstir was designed and installed. This device allows simultaneous argon bubbling and moderate stirring. Bubbstir features a calm melt surface and fine bubbles that are homogeneously dispersed throughout the crucible volume. During the Bubbstir process, most of the non-metallic inclusions rise to melt surface and can be easily removed by skimming. The generated thin layer also protects the melt from ignition.

As Bubbstir'ing is completed, skimming is to be done in order to remove the entire contaminated layer. Then settling for 15 min should be done at 690ºC in order to allow non-metallic inclusions to settle/sink down to the bottom of the crucible.

The efficiency and bubbling times for Bubbstir were compared with the results obtained from common bubbling at three temperatures 670, 690 and 710°C. At each temperature an optimal bubbling time was selected according the results of fracture testing (see table 1).

Table 1. Adjustment of parameters for fluxless batch recycling MRI 230D alloy

Process	**Temperature [°C]**	**Time [minutes]**
Settling	670	15,30,60
	690	
	710	
Bubbling	670	30,60
	690	
	710	
Bubbstir	670	10,15,30,60
	690	
	710	
Bubbstir & Settling	670	Bubbstir 5,**10** Settling **15**,30
	690	
	710	

SETTLING & BUBBLING

In order to optimize the settling time, a set of experiments was conducted using different settling times of 15, 30 and 60 minutes at each of the above temperatures. The certain combination of the Bubbstir stage parameters and settling time was chosen in order to optimize the process following criterion of tested fracture clearness (Table 1). During settling, the alloy chemical composition particularly the Fe content should be carefully analyzed. If the Fe concentration is higher than 40 ppm, settling should be conducted at lower temperature but not less than 670°C, according to die casting temperature.

The sample for visual fracture surface examination should be taken from the crucible prior to casting in order to verify the melt initial cleanliness (Fig.2)

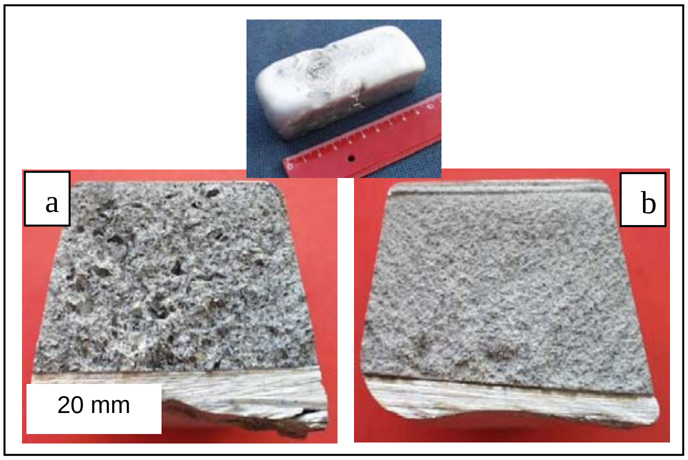

Figure 2. Visual appearance of MRI 230D coupon fracture surface.
(a)- Before recycling (b)- Recycled

RESULTS

INTERNAL CLEANLINESS AND MELT LOSS

The objective of this newly developed process was to achieve in minimal time internal cleanliness similar to that of primary alloy combined with minimal melt losses as well. Of course, mechanical properties of die castings produced in recycled ingots must be similar to those for primary alloys.

The results on NMI removing are presented in Figs 3 and 4. It is evident that using the Bubbstir process leads to deeper refining and lower melt losses compared with common bubbling process. Even after 10 minutes of Bubbstir'ing the MRI230D melt was cleaned. Therefore one can conclude that the Bubbstir technology enables to achieve optimum efficiency, due to homogeneous distribution of very fine bubbles. Compare to the bubbling, such procedure is fine but aggressive in his action.

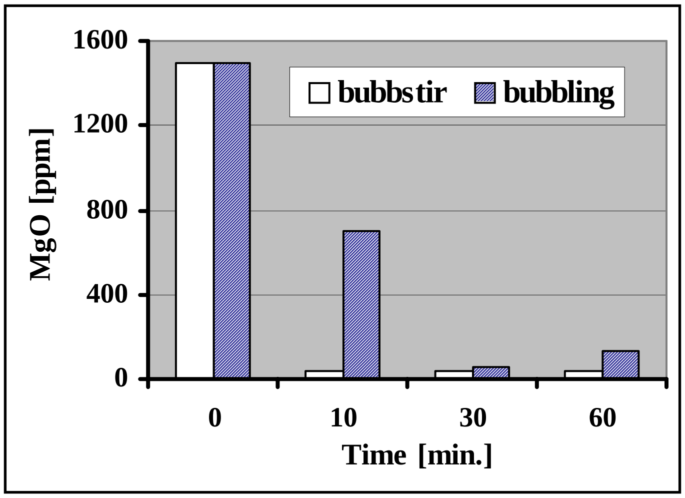

Figure 3. Reduction of the MgO content in MRI 230D melt depending upon settling time at 690 °C and type of recycling procedure.

On the other hand, Fig.4 illustrates that for material with such level of initial cleanliness (~1500ppm of MgO) conducting only settling without any bubbling does not provide acceptable cleanliness in terms of quantity and morphology of NMI. It is clear that even after 30min of settling the material with initial high quantities of inclusions still need to be recycled.

It also should be noted that over the Bubbstir stage and subsequent settling at different temperatures no deviation from chemical composition outside the specified requirements for MRI 230D alloy with regard to the Ca, Sr and Fe contents, as well as, rest elements.

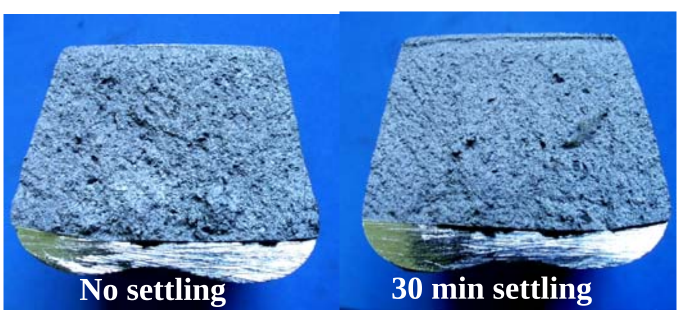

Figure 4: Visual appearance of MRI 230D coupon fracture surface after settling at 690°C of 30minuts. (No bubbling was performed)

MECHANICAL PROPERTIES

The recycled ingots under optimal bubstir conditions, as was described, were re-melted and tensile, impact, and creep samples were cast using a IDRA OL-320 cold chamber die casting machine with a 345 ton clamping force. During casting no adjustments of the process parameters were required compared to casting parameters set for primary MRI 230D alloy [10,11].

The tensile, impact and creep properties of recycled MRI 230D alloy are shown in table 2 and Fig.5 in comparison with typical properties for primary alloy. It is evident that the mechanical properties of the recycled material were almost identical to typical primary MRI230D alloy.

Table 2. Mechanical properties of recycled and primary MRI 230D alloy

Alloy	TYS [MPa]	UTS [MPa]	E [%]	Impact strength [J]
MRI230D primary (typical)	180	245	5	6
MRI230D recycled	176±2	234±10	5±1	5±1

The results of creep testing primary and recycled MRI 230D alloys at 180°C for 200 hours under stress of 70 MPa are presented in Fig. 5. As in the case of tensile properties, no visible difference was found. Thus, based on the results obtained one can conclude that new technology enables to produce recycled MRI 230D alloy with the performance similar to that of primary alloy.

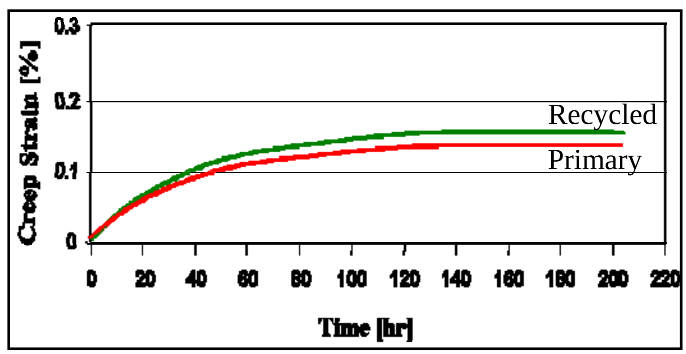

Figure.5. Creep strain achieved in MRI 230D alloy for 200 h testing at 180°C under stress of 70 MPa

THE EFFECT OF CLEAN SCRAP ADDITIONS

Another option for scrap treatment is addition of the scrap to primary ingots of the relevant alloy directly HPDC'ing. However, this method is recommended only for clean scrap that was just generated during preceding HPDC process. Scrap that has been stored under unstable environment conditions must be subjected to the recycling process as described above.

Experiments on the scrap additions were performed in order to find the maximum allowable scrap percentage which does not degrade alloy performance.

In addition to MRI 230D, also two common alloys AZ91D and AM60B were tested. All the scrap used was generated directly during the casting process in order to save time and exclude the preheating process of the scrap. During the different stages of the HPDC process the melt was contaminated by the scrap progressively. Samples were taken for visual and quantitative MgO determination. Standard ASTM tensile and impact strength bars were cast along with cylindrical samples (diameter of 10 mm and 100 mm length) that were used for salt spray corrosion testing for 240 hours (ASTM B-117). All samples produced were X-rayed prior to testing.

Different variants of the scrap additions are shown in Table 3 and Fig.6. As can be seen, even in the most contaminated variants the MgO content did not exceed 600 ppm

The mechanical and corrosion properties of all the alloys depending on the added scrap percentage are shown in Tables 3-5 and Fig.6.

The results obtained distinctly show that for all three alloys additions of clean die casting scrap in the range of 11 to 41% have very low effect on mechanical properties and corrosion performance.

Table 3. The effect of the scrap percentage on the mechanical properties of MRI 230D alloy

Alloy	Scrap [%]	MgO [ppm]	TYS [MPa]	UTS [MPa]	E [%]	Impact strength [J]	Corrosion [mcd]
MRI230D	0	128	176±8	242±10	5±1	5±2	0.10±0.01
	11	280	164±14	234±9	5±1	5±1	0.07±0.03
	21	339	175±6	238±14	5±1	5±1	0.08±0.03
	33	419	171±10	237±10	5±1	5±1	0.09±0.04
	41	522	177±7	239±10	5±1	5±2	0.13±0.03

Table 4. The effect of the scrap percentage on the mechanical properties of AZ91D alloy

Alloy	Scrap [%]	MgO [ppm]	TYS [MPa]	UTS [MPa]	E [%]	Impact strength [J]	Corrosion rate [mcd]
AZ91D	0	28	165±3	275±6	7±1	10±2	0.12±0.02
	11	109	161±4	267±13	7±2	11±4	0.15±0.02
	21	108	158±8	274±6	9±1	10±3	0.18±0.02
	33	129	165±1	268±13	7±2	11±2	0.15±0.03
	41	153	164±2	278±8	9±2	12±4	0.17±0.09

Table 5. The effect of the scrap percentage on the mechanical properties of AM60B alloy

Alloy	Scrap [%]	MgO [ppm]	TYS [MPa]	UTS [MPa]	E [%]	Impact strength [J]	Corrosion rate [mcd]
AM60	0	66	134±2	280±2	19±2	28±3	0.38±0.05
	11	91	131±2	280±6	21±4	26±2	0.40±0.09
	21	187	134±4	279±4	17±3	28±3	0.38±0.04
	33	333	136±1	278±2	16±2	21±6	0.28±0.13
	41	248	132±3	272±6	16±2	24±4	0.34±0.01

Probably this fact should be attributed to relatively low MgO content (less than 600 ppm) that was found in all three alloys. Thus, based on the results obtained one can conclude that at least 20-25% of clean die casting scrap can be added to primary ingots without deterioration of castings performance.

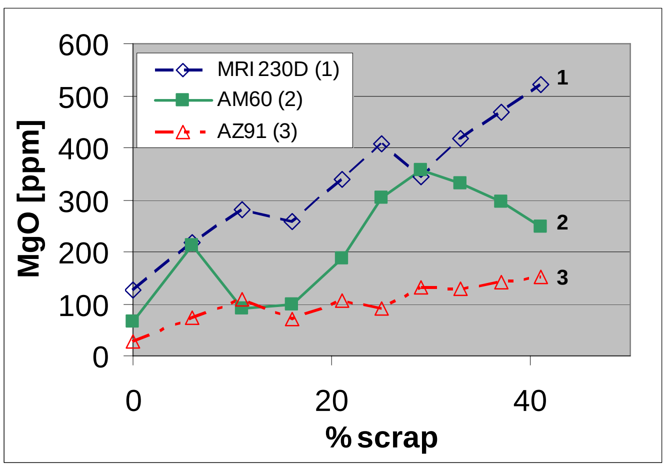

Figure.6. Variation of the MgO content depending on the scrap percentage.

CONCLUSIONS

1. An effective fluxless recycling procedure was developed for DSM creep resistant die casting magnesium alloys MRI230D and MRI153M.
2. The internal cleanliness of recycled alloys in terms of the MgO and Fe contents was in accordance with the requirements set by the DSM internal specification for primary ingots. The mechanical properties of die cast recycled MRI 230D alloy were similar to those of primary alloy.
3. Clean die casting scrap can be added to primary MRI 230D ingots over HPDC process without deterioration of castings performance in terms of mechanical properties and corrosion behavior..

REFERENCES

1. B.Bronfin et al, US Patent 6,139,651, Oct 31, 2000.
2. B.Bronfin et al, US Patent 7,041,179, May 9, 2006.
3. B.Bronfin et al, US Patent 7,169,240, Jan 30, 2007.
4. B.Bronfin et al., "Development of new magnesium alloys for advanced applications", Magnesium alloys and their applications, (ed. K-U.Kainer), Wolfsburg, 2003, 55-61
5. H.Westengen"Recycling", in Magnesium Technology (eds.H.Friedrich and BL.Mordike), 2005, p.633-658.
6. J.E.Hillis, " Magnesium recycling: Flux versus flux-free process. Principles, Advantages and Disadvantages", IMA proceedings, Vancouver, 2007, p.55-66.
7. P. Bakke, "Salt composition to be used with molten magnesium", International patent application WO 2005/118891.
8. J.E.Hillis and W.Mercer "Separation of non-metallic contaminants in fluxless melting and refining of magnesium alloys". SAE 2000-01-1125.
9. Bronfin et al, "Application of MagOxide method for cleanliness evaluation of Magnesium alloys", Magnesium technology 2002, Ed. H.I.Kaplan (Warrendale, PA, TMS, 2002), 55-60.
10. N.Moscovitch. et al.,"Die Casting Technology and Design Principles for Magnesium Alloys", Magnesium automotive and end user seminar, Aalen 2003.
11. G.Gertsberg et al., "Effect of HPDC Parameters on the Performance of Creep Resistant Alloys MRI153M and MRI230D", SAE paper 2005-01-0334, Detroit, MI, 2005.

CONTACT

German Gertsberg
Head of Products Development Department
Dead Sea Magnesium
Tel: +972 (0)86282422
Fax: +972 (0)86282431
Email: germang@dsmag.co.il
Web : www.magnesium.co.il