APPLICATION OF MagOxide METHOD FOR CLEANLINESS EVALUATION OF MAGNESIUM ALLOYS

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Abstract

A new method named “MagOxide” aiming at evaluating the MgO and Al-Mn-Fe intermetallics in magnesium alloys was developed by DSM’s Research Division.

The newly developed method is based on wet chemistry procedure and is compatible with the Fast Neutron Activation analysis (FNAA) technique. The method was successfully implemented on a variety of primary and recycled Mg alloys.

The present paper aims at presenting the systematic correlation results obtained by FNAA and “MagOxide” methods when primary and recycled Mg alloys of AZ and AM series were analyzed.

Introduction

The growing use of magnesium alloys in various applications including safety related parts require alloys with high ductility and energy absorption properties. Those properties are significantly affected by the metal cleanliness along with metal chemistry that was traditionally considered as the main quality criterion for magnesium alloys [1-3].

At present it is well known and documented that properties of magnesium alloys are deteriorated by an increased amount of non-metallic inclusions, particularly by MgO [4]. For example the castability performance and mechanical properties of magnesium and its alloys are adversely affected by the presence of inclusions, particularly MgO particles. In addition, the size of the largest inclusions may restrict the minimum thickness of certain metal products. Non-metallic inclusions may also reduce machinability, tool wear and cause deterioration of the surface quality. Hence, the metal cleanliness of ingots includes the complete removal of all non-metallic inclusions. These inclusions may enter the process stream as surface oxides or residuals from lubrication or release agents used in the die casting process. The high oxidation potential of magnesium usually results in inclusion contents considerably higher than that of aluminum [5, 6].

In general the growing application of magnesium die castings in the automotive industry leads to an increasing amount of clean scrap, which should be recycled due to economic and environmental needs.

It is evident that for the production of high quality recycled magnesium alloys which can compete with alloys produced from primary magnesium, it is necessary to provide a high level of internal cleanliness. This is in addition to the required chemical composition, which is defined in ASTM Standard B93/93M-94b.

Thus, in order to produce high-quality virgin and recycled magnesium alloys the characteristics of inclusions should be identified, and efficient and reliable method for quantifying MgO particles is required. Such method will enable to correlate mechanical properties to quantity, type and morphology of non-metallic inclusions and will assist to develop new reliable methods for refining and recycling processes and quality control of magnesium alloys.

There are three major methods, which are in use today for MgO determination [7]. The first group of those methods that include Fast Neutron Activation Analysis (FNAA), Glow Discharge Mass Spectroscopy and Glow Discharge Atomic Emission Spectroscopy is related to physical measurements methods. All of those methods have low detection limits and high accuracy but they are very expensive. In addition the FNAA method requires a neutron source such as a nuclear reactor, which usually is not accessible.

The second group of methods is based on fracture surface examination. Two of them should be pointed out in this group, namely K-mold method and a method developed by DOW Magnesium based on light reflectance technique [4, 5]. The K-mold method is considered only as a relative method used for comparison of several alloys. DOW Magnesium used brightness measurements in order to quantify MgO particles in recycled alloys. However, this technique exhibits very high detection limit ~0.2% and can not comply with the requirements for well refined high-purity alloys.

The third group of methods is based on filtration of liquid metal with subsequent analysis of inclusions captured by filter using the methods of quantitative metallography [7, 8]. This method allows analyzing along with MgO also other types of second phases, for example Al-Mn intermetallics. However, the accuracy of this method seems to be limited. In addition the quantity and morphology of oxides in ingots or die cast components may be different from those observed on the filter due to different solidification conditions.

The newly developed wet chemistry method in question (MagOxide) allows quantifying MgO and Al-Mn intermetallics in pure magnesium and magnesium alloys. This method is currently being used as routine technique at DSM’s casting house as part of the quality control process.

This paper aims at demonstrating the capability of the new method and its correlation with the results obtained by FNAA. Several examples of using the new method for quality control of virgin and recycled material are presented.

Experimental Procedure

Quantitative determination of MgO inclusions

The wet chemistry method named "Magoxide" is based on chemical dissolving of the magnesium matrix and subsequent analysis of MgO residues by ICP (Inductively Coupled Plasma Emission Spectrometer).

The analytical procedure is as follows:

1. Dissolving 2-3 gr. sample in a mixture of organic solutions, which dissolve both the Mg-matrix and intermetallic compounds such as β-phase – $Mg_{17}Al_{12}$. However the MgO particles and Al-Mn-Fe intermetallics remain insoluble in liquid solution. This action is conducted in Argon inert atmosphere at 30º-40ºC in order to eliminate the reaction between organic solvents and water.
2. The solution is filtered and residues are rinsed with boric acid and distilled water.
3. The Mao and Al-Mn-Fe residues are dissolved in warm choric acid and filtered. The filtrate is then analyzed by ICP spectrometer.

The Mg concentration obtained by ICP can be converted to the concentration of MgO or oxygen assuming that the magnesium remained after dissolving in organic solution is only bound to oxygen. It should be pointed out that in contrast to most of the other methods Dam's technique also allows to quantify a weight fraction of Al-Mn-Fe intermetallics and their phase composition. Due to the fact that in this method the small samples (2-3 go) are used, the correct sampling and good statistics are very important. Hence, Dam's quality control practice includes analysis of 3 ingots per batch. The ingots are selected from the start, middle and end of a batch. The samples for analyses are taken from 6 different regions located near the surface and in the core, at both ends and in the middle of each ingot.

Metallurgical Characterization

Chemical analysis was conducted with a Baird DV-5 spark emission spectrometer. The microstructural analysis was carried out using an optical and a scanning microscope equipped with EDS. A standard salt spray test was used to evaluate the corrosion resistance using samples 60x40x10mm that were cut out from the tested ingots. Fluidity properties were analyzed using the spiral mold test. The fluidity index L_f was determined as the length of solidified metal in spiral.

Results and Discussion

Three series of experiments were conducted in order to establish correlation between the results obtained by FNAA and "MagOxide" wet chemistry method. In the first series the specially selected samples containing an increased amount of MgO were analyzed (Figure 1).

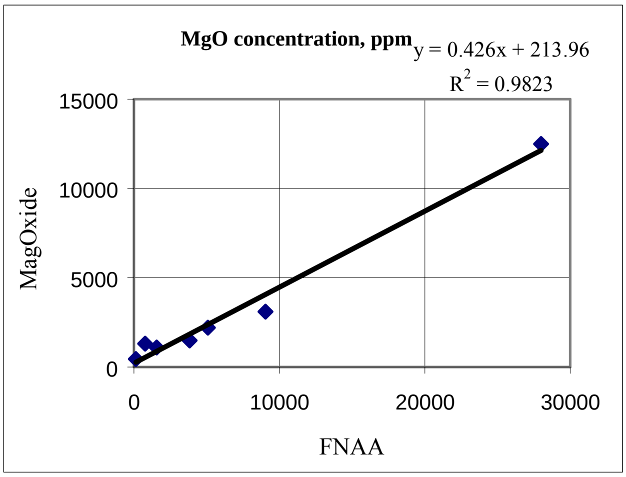

Figure 1: Correlation between FNAA and "MagOxide" analyses

The second series of tests relates to primary and recycled ingots of AZ91 alloy produced by different companies (Figure 2). It should be pointed out that FNAA data for the first and second series of experiments were obtained by two independent companies. The results of the analyses for the third series of tests performed on AZ91D, AM60B and AM50A alloy ingots produced by DSM are given in Table I and demonstrate that there is a good correlation between the results obtained by both methods.

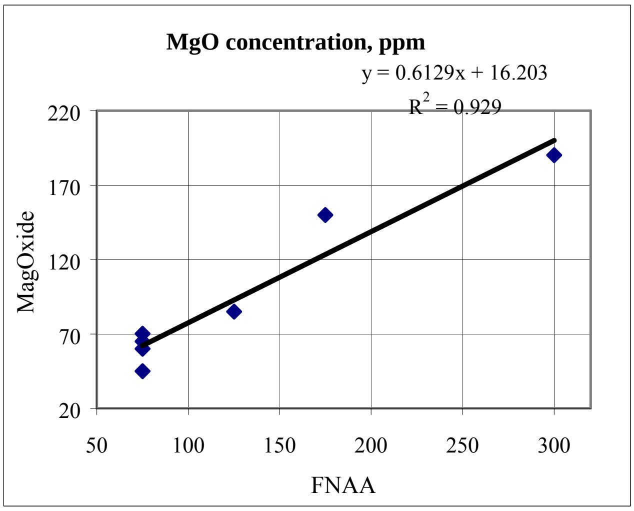

Figure 2: Correlation between FNAA and "MagOxide" analyses

The analysis of data presented in Figure 1 and Figure 2 indicates an adequate correlation between FNAA and "MagOxide" methods. However the absolute values obtained by the "MagOxide" method are as a rule two times less than those obtained by FNAA. In explanation of these results two issues should be taken into consideration. First, it is evident that both bulk and surface oxygen are measured by FNAA but no correction on surface oxygen was done for FNAA results.

The second issue relates to uneven distribution of MgO particles through the samples. This fact along with the difference in sample dimensions should also be taken into consideration for comparison of the results obtained by both methods. Hence, summarizing results presented in Figures 1 and 2 and in Table I one can conclude that there is an acceptable correlation in the MgO determination performed using FNAA and the wet chemistry methods.

Table I Oxygen and MgO Content in Ingots Produced by DSM

No.	Alloy	FNAA		"MagOxide" – Wet Chemistry method
		Oxygen [ppm]	MgO [ppm]	MgO [ppm]
1.	AZ91D	<50	<125	103
2.		<50	<125	133
3.		<50	<125	133
4.		<50	<125	90
5.	AM60B	<50	<125	61
6.		<50	<125	67
7.		<50	<125	59
8.	AM50A	<50	<125	66
9.		<50	<125	64
10.		<50	<125	83

The use of "MagOxide" method in the evaluation of recycled material

Recycled ingots received from six different companies were used for the present evaluation. In addition, primary alloy ingots were used as reference.

The chemical compositions of recycled ingots are given in Table II. This table demonstrates that the chemical compositions of ingots received from companies A-E were in agreement with the requirements of ASTM Standard B93/B93M-94B for primary AZ91D ingots. However, the ingots received from company F revealed an increased concentration of iron (0.0055%) and silicon (0.068%).

Table II Chemical Compositions of Recycled AZ91 Ingots

Company	Al %	Mn %	Zn %	Si ppm	Cu ppm	Ni ppm	Fe ppm	Be ppm
A	8.7	0.21	0.70	50	5	6	21	8
B	8.9	0.18	0.64	210	42	8	26	10
C	8.6	0.19	0.64	330	24	6	16	8
D	8.9	0.24	0.74	520	53	10	22	5
E	8.9	0.25	0.72	680	36	7	25	10
F	8.6	0.17	0.72	680	73	8	55	5
Primary	9.0	0.23	0.74	30	5	7	21	9
ASTM B93/ 93M-94b	8.5 - 9.5	0.17-0.40	0.45-0.90	≤500	≤250	≤10	≤40	NS

The wet chemistry method was used for quantitative measurements of MgO inclusions (Table III). This Table illustrates the fact that MgO concentration in ingots recycled by various companies may differ by order of magnitude. For example, from 42 ppm in ingots produced by Company A to 472 ppm in those produced by Company F. In addition, the results obtained clearly demonstrate that ingots produced by companies C and F were very inhomogeneous regarding MgO refining. On the other hand, it is evident that MgO concentration in the best-recycled ingots is similar to that in the primary ingots.

The weight fraction and chemical compositions of Al-Mn-Fe intermetallics determined by ICP and EDS techniques are given in Table III.

Table III Parameters of MgO and Al-Mn Intermetallic Compounds in Recycled AZ91 Ingots

Company	Weight fraction of MgO, ppm	Weight fraction of Al-Mn-Fe intermetallics, %	Typical composition of Al-Mn-Fe intermetallics, at %
A	42±12	0.419±0.018	$Al_{62.1}Mn_{37.7}Fe_{0.2}$
B	75±19	0.396±0.027	$Al_{62.8}Mn_{36..9}Fe_{0.3}$
C	125±64	0.426±0.025	$Al_{62.5}Mn_{37.4}Fe_{0.1}$
D	87±24	0.446±0.025	$Al_{62.1}Mn_{37.7}Fe_{0.2}$
E	93±24	0.494±0.023	$Al_{60.8}Mn_{39.1}Fe_{0.1}$
F	472±345	0.344±0.019	$Al_{60.1}Mn_{38.8}Fe_{1.1}$
Primary	35±6	0.417±0.011	$Al_{60.5}Mn_{39.3}Fe_{0.2}$

The weight fraction of Al-Mn-Fe intermetallics assessed by ICP analysis of residues, which were separated from ingots, is similar for all recycled ingots. The small variations observed are in agreement with the difference in chemical composition regarding Mn and Fe revealed by spark emission spectrometry (Table II).

Table III illustrates that intermetallic compounds, which are present in all recycled ingots and have a similar atomic fraction X_i of Al and Mn (X_{Al}=0.60-0.62 and X_{Mn}=0.37-0.39 respectively). These values comply with the concentration range for Al_8Mn_5 intemetallic compounds: X_{Al}=0.52-0.66 and X_{Mn}=0.34-0.48 [9]. However, these particles contain different atomic fractions of Fe, from 0.2 to 1.1%. A difference in iron content may affect corrosion resistance [10, 11].

Fluidity properties and corrosion resistance

Fluidity is the ability of the molten metal to continue to flow as it continues to cool down and even while it is starting to solidify.

Fluidity strongly depends on the material's chemical composition and internal cleanliness, casting temperature and mold temperature. These parameters affect, in turn, viscosity, surface tension, the character of surface oxide film and the manner in which the particular alloy solidifies. Furthermore, the fluidity is a function of the nature of the interface between the metal and mold walls. In spite of these remarks, such tests are useful for the simulation of actual casting situations and can be used for the comparative assessment of alloys castability.

The experimental results obtained in terms of the fluidity index measurements are shown in Table IV.

Table IV Fluidity Properties of Recycled AZ91 Alloys

Company	Fluidity index L_f, mm			Corrosion rate, MPY
	L_f min	L_f max	L_f average	
A	205	230	220	24±4
B	183	218	203	28±6
C	121	208	185	40±22
E	187	203	192	21±3
F	105	215	172	40±2
Primary	202	235	225	25±2

This table demonstrates that alloys recycled by Companies A and B exhibited the best fluidity properties. On the other hand, the ingots recycled by companies C and F revealed non-homogenous fluidity properties. For example, scattering fluidity index L_f
From 105 mm to 215 mm was observed during the testing of ingots from Company F. Such fluidity behavior can be related to the difference in amount and distribution of MgO oxides and slight variations in Al content. It was shown that MgO particles might reduce the fluidity of liquid metal during filling of the spiral mold. Comparison of the results given in Table III and Table IV demonstrates that fluidity index is affected by cleanliness of magnesium alloys and may be considered as an indication of recycling efficiency.
The corrosion behavior of magnesium alloys is significantly influenced by common alloying elements such as Al, Zn, Mn, Si, type of casting process and heat treatments that considerably affect the microstructure [12]. Currently, it is documented that the presence of heavy metal impurities (Fe, Ni, Cu) represents the most detrimental factor affecting the corrosion properties of commercial magnesium alloys. Chloride inclusions also increase corrosion rates. On the other hand, it is generally accepted that MgO inclusions do not have a direct effect on the corrosion resistance [13].
The results of salt spray testing on recycled ingots are listed in Table 4. All recycled ingots exhibited a corrosion rate comparable to that of primary ingots. However, the ingots from Companies A and E showed the best performance and revealed good chemical and structural integrity. The increased corrosion rate of the ingots recycled by Company F can be a result of higher iron content in Al-Mn-Fe intermetallic compounds. An increase in Fe content within an Al-Mn-Fe intermetallics leads to an increased potential difference that indicates a high cathodic efficiency of such particles [10].

Conclusions

1. An adequate correlation between MgO concentration measurements performed by FNAA and by the newly developed Wet Chemistry method ("MagOxide") was obtained. Hence, MagOxide method can be considered as an inexpensive and reliable technique for cleanliness evaluation of primary and recycled material.
2. Metallurgical examination of the AZ91D ingots produced by various recycles have shown that the quality of recycled ingots in terms of chemical composition and internal cleanliness are comparative with the quality of the primary AZ91D ingots.
3. The result of the present research demonstrated that adequate recycling technology could provide the quality of the recycled material that complies with the requirements of the automotive industry.

References

1. "Standard Specification for Magnesium Alloys in Ingot Form for Sand Castings, Permanent Mold Castings and Die Castings", ASTM B93/B93M-94b, Annual Book of ASTM Standards, vol. 02.02, (American Society for Testing and Materials, Philadelphia, PA, 1995).

2. J.C. Grebetz, Day and A.G. Haerle, Qualification of Recycled Magnesium Type 1 Die Castings, (IMA Proceedings, May 1998), 8-15.

3. J.C. Grebetz and D.L. Albright, Recycled Magnesium Alloys for High Ductility Automotive Applications, (SAE Technical Paper 960413, Detroit, MI, 1996).

4. A.G. Haerle, et al., The Effect of Non-Metallic Inclusions on the Properties of Die Cast Magnesium, (SAE Technical Paper 970331, Detroit, MI, 1997).

5. H. Hu and A. Luo, "Inclusions in Molten Magnesium and Potential Assessment Techniques", JOM, 10, (1996), 47-51.

6. G.A. Rozak, Investigation of the Quality and Corrosion Resistance of Recycled AZ91D Magnesium Ingot, (SAE Technical Paper 940412, Detroit, MI, 1994).

7. P. Bakke and D.O. Karlsen, Inclusion Assessment in Magnesium and Magnesium Base Alloys, (SAE Technical Paper 970330, Detroit, MI, 1997).

8. D. Oymo, et al., Particle Removal in Recycled AZ91D Mg Alloy, (The Recycling of Metals, Amsterdam, Netherlands, 1994), 251-258.

9. A. Jangsson, A Thermodynamic Evaluation of the Al-Mn System, (Met. Trans., A., vol.23A, 1992), 2953-2962.

10. O. Lunder, K. Nisancioglu and R.S. Hansen, Corrosion Behavior of Die Cast Magnesium-Aluminum Alloys, (SAE Technical Paper 930755, Detroit, MI, 1993).

11. P. Uzan, D. Eliezer and E. Aghion Corrosion Behavior of Recycled Magnesium

AZ91,(3rd International Magnesium Conference, Manchester, UK, 1996),40-43.

12. B.E. Carlson and J.W. Jones, The Metallurgical Aspects of the Corrosion Behavior of Cast Mg-Al Alloys, (Light Metal Processing and Applications, CIM Conference, Quebec, 1993), 833-847.

13. P. Bakke, Measurement and Removal of Inclusions and Hydrogen in Magnesium, (Ph.d. Thesis, University of Trondheim, 1992).