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Iron presence in the technology of Mg-Al casting

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Abstract

The article provides the results of investigations regarding an effect of AZ91 magnesium alloy on iron present in the walls of a crucible operating in the furnace of a die casting machine. It is commonly assumed that liquid magnesium remains neutral in respect of iron, and therefore steel crucibles are believed to be the best solution in the technology of magnesium casting. However, careless handling of magnesium alloy, badly adjusted temperature of holding, and the use of protective gas may result in a dangerously quick thinning of the crucible walls, and hence in their shorter life and greater risk of magnesium penetrations.

Keywords: Mechanization and automation of casting processes; Mg based alloys; Crucible for magnesium alloys; Die casting; Segregation of chemical elements.

1. Introduction

Die casting is the process used most often in manufacture of various elements from magnesium alloys. There are two types of die casting machines, viz. cold-chamber machines and hot-chamber machines. An element common to both types is the locking system, i.e. the system of opening and closing of half dies. The differences in the technology mainly regard the technique by which molten metal is fed to the injection system and the design of the injection system itself. In hot-chamber machines, the furnace is a part integral to the machine; a „gooseneck" is submerged in molten metal with injection plunger operating in it and forcing the metal into a die. Metal is fed to the chamber automatically through ports in the gooseneck. In cold-chamber machines, the furnace is operating as a separate and autonomous unit; metal is fed to the shot chamber by special sleeve or by robot equipped with a pot. In both cases, the injection plunger is operating at an enormous speed of several metres per second which produces in the injection port a velocity of over 100 m/s [1]. This enables manufacture of castings with a typical fine-grained structure which, nevertheless, is not free from the defects of porosity. Automation of the process and short pouring times are the main reason why die casting technology is an excellent solution for large-lot production, specially for automotive, electronic, or electrical applications.

Somehow, the whole process of magnesium alloys casting is associated with the presence of iron. Magnesium is melted and held in steel crucibles. The tools used for cleaning of the crucible, and thus entering directly in contact with molten metal, are made of steel. The whole injection system, i.e. the „ gooseneck" and the shot sleeve are made of steel. During final stage of the casting process, metal enters the die which is made of steel, too. At this point it should be emphasized that even the least content of iron in magnesium alloy will have a very adverse effect on the corrosion resistance of magnesium, and vice versa, magnesium alloy may have a very adverse effect on the behaviour of steel elements.

Table 1.
Chemical composition of AZ91 alloy according to the current standard [2].

Chemical composition [%]	Al	Zn	Mn	Si	Fe	Cu	Ni	Other elements each
Acc. to PN-EN 1753 [2]	8,5-9,5	0,45-0,9	>0,17	<0,05	<0,004	<0,025	<0,001	<0,01

Therefore, the present article has been devoted to a research regarding mutual relations between magnesium alloy and steel of which the crucible is made. The results of the research are discussed below.

2. Experimental conditions

Samples for investigations were provided by the P.Z. ALPHA Die Casting Foundry in Krakow. Laboratory examinations were conducted at the Department of Non-Ferrous Alloys, Faculty of Foundry Engineering, AGH University of Science and Technology in Krakow. The Foundry operates one hot-chamber die casting machine of the 400t locking force; metal is melted in a resistance furnace of 80 kW power.

Fig. 1. Die casting machine for Mg alloys. See from the right: furnace, injection system, locking system with die, control desk.

The charge were ingots of AZ91D alloy (the alloy is made by MEL Company), no process scrap was used.

Magnesium was melted and cast under the atmosphere of protective gas of the following composition: 0,4% SO_2 + dry air. No covering and refining salt was used. The temperature of magnesium alloys casting was 620 – 635°C. In furnace interior it ranged to about 750°C. The crucible, which during investigations remained in the furnace of the machine, has been in operation for 2.5 years and has been used only for melting of AZ91D alloy. During routine cleaning of the crucible, a few plate-like objects were found on its bottom. They were taken out, examined for chemical composition and subjected to metallographic analysis. Standard metallographic sections were prepared by wet grinding and final polishing with diamond paste. The chemical composition was determined by several methods: 1) averaged determination of the composition: C – by LECO technique; Mn, Cr, Ni, Mg, Zn – by AAS technique, Fe – by titration, Al – by gravimetry; 2) detailed examination of the composition: scanning IEOL-ISM 5500LV microscope with EDX IXRF-SYSTEMS attachment for X-ray microanalysis.

The crucible was made by W. PILLING, a company which makes crucibles for numerous manufacturers of die casting machines and furnaces for melting of magnesium alloys and scrap remelting. The crucible was made from two plates rolled together. The outer layer of 4 mm thickness was made from a heat-resistant 1.4828 steel material. Owing to an addition of over 9% nickel, the steel is characterised by an austenitic structure free from any products of transformation. This material is insensitive to impact loads and sudden changes of temperature. It reveals no tendency to the grain growth at high temperatures, is characterised by the creep resistance higher than the ferritic grades of steel and by good plastic deformability in all processes, but is sensitive to the effect of sulphur-containing gases. Machining of this steel poses more difficulties than that of a ferritic grade. The critical temperature at which lamination in the air occurs is 1000°C [3].

Table 2.
Percent content of the main elements of 1.4828 steel [3].

Alloying constituents of 1.4828 steel [%]				
Cr	Ni	Si	Mn	C
20,0	12,0	2,0	0,7	0,1

The inner layer should be made from low-carbon steel (below 0,12%.) Highly adverse effect of nickel and carbon on the corrosion resistance of magnesium alloys is the reason why the content of these two elements should be kept at a level of 0,1% each [4]. In the crucible used for the experiments, the inner layer had a thickness of 18 mm and was made from low-alloy 1.0345 steel. The crucible was assembled by electrical welding.

Table 3.
Percent content of the main components of 1.0345 steel [5].

Alloying constituents of 1.0345 steel [%]													
C	Si	Mn	P	S	N	Al.	Cu	Cr	Ni	Mo	Ti	V	Nb
Max. 0,16	Max. 0,35	0,6-1,2	Max. 0,025	Max. 0,015	Max. 0,012	Min. 0,02	Max. 0,3	Max. 0,3	Max. 0,3	Max. 0,08	Max. 0,03	Max. 0,02	Max. 0,02

Fig. 2. Crucible for melting of magnesium alloys - left; furnace interior– right.

3. Studies on reactions occurring between the crucible material and magnesium – based AZ91D alloy

During standard production run, on the bottom of the crucible, a few plates of an unknown origin were found. The plates were very heavy, so right at the beginning the presence of magnesium compounds was excluded.

Fig. 3. Plates removed from the crucible bottom during casting of magnesium-based AZ91 alloy.

Fig. 4. A fractured specimen of the examined plate.

The removed plates were 2-7 mm thick. In their shape they resembled the bottom and the walls of the crucible - some were flat, other were rounded as if coming from the crucible corners or from the wall edges and bottom. The plates were very brittle.

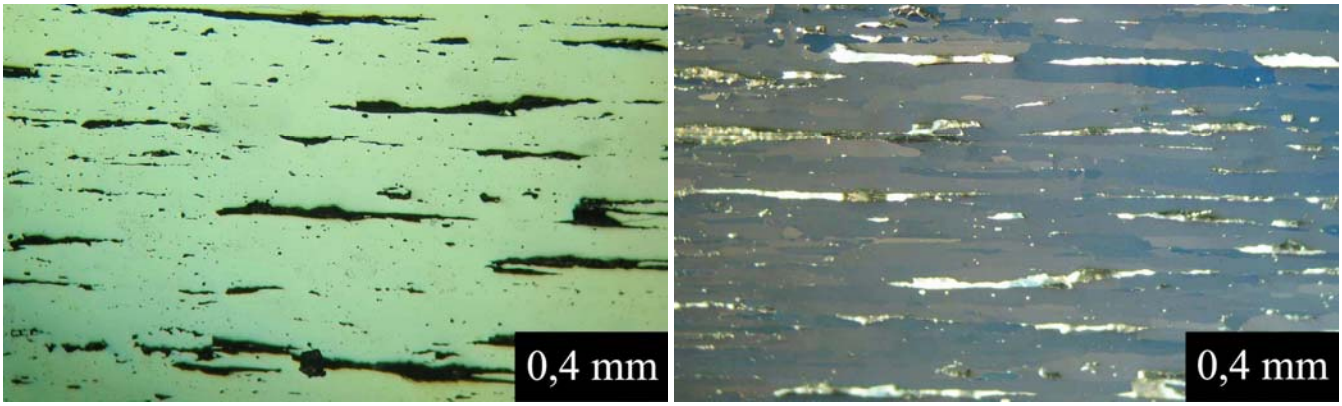

Fig 5. Microstructure on a longitudinal section of the examined specimen; the photograph on the right was taken under polarised light

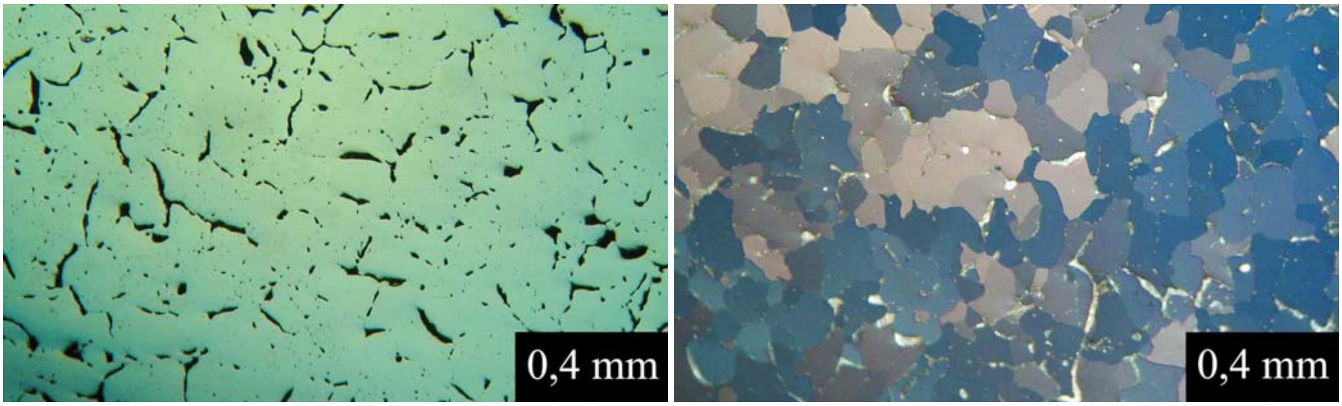

Fig. 6. Microstructure on a transverse section of the examined specimen; the photograph on the right was taken under polarised light

The plates were subjected to metallographic analysis; the results of the analysis are given below. The examinations were carried out on both longitudinal and transverse sections. Due to the application of polarised light, the grains present in the structure were well exposed; they are oriented towards the visible structure discontinuities. The photographs also show the growth of the cells.

In the course of further investigations, averaged composition of plates was examined and the obtained results indicated the presence of over 50% Al, about 40% Fe, over 4% Mn and Mg.

Table 4.
The results of analysis of an averaged chemical composition of plates removed from the crucible bottom.

Chemical composition [%]							
Al	Fe	Mg	Mn	C	Cr	Zn	Ni
51,0	39,5	4,5	4,2	0,08	0,08	0,02	0,01

For the sake of comparison, also more detailed examinations of the chemical composition were carried out by the EDS technique. The places on the specimen where the analysis has been carried out are shown in Figure 7.

The results of the EDS examinations differ slightly from the examinations of an averaged chemical composition of plates removed from the crucible bottom.

Table 5.
The results of analysis of the chemical composition made by EDS in the examined specimen

Examined specimen	Chemical composition [%]		
	Al	Fe	Mn
Measurement 1	55,394	41,787	2,819
Measurement 2	55,791	41,486	2,723
Measurement 3	56,636	41,023	2,341

From the examinations it follows that the plate material is in prevailing part composed of Fe-Al-Mn phase. Manganese occurs in small amounts of 2-4% in all phases. Table 6 shows Fe-Al phases with the respective content of Al. As regards the content of Fe and Al, the composition of the phase present in the examined plates resembles that of a Fe_2Al_5 phase. Since the process of plates formation took a long time, it can be assumed that this is a stable phase. Up to 3% Mn were reported to be present in it.

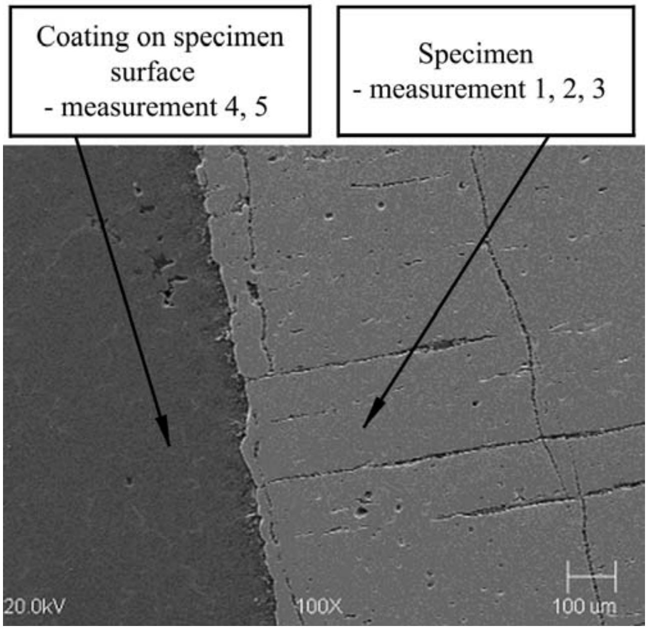

Fig. 7. Places where chemical analysis was made by EDS technique.

Table 6.
Fe-Al phases with Al content [6]

Phase	Al content [%]
Fe_3Al	13,87
FeAl	32,57
$FeAl_2$	49,13
Fe_2Al_5	54,71
$FeAl_3$	59,18
Fe_2Al_7	62,93

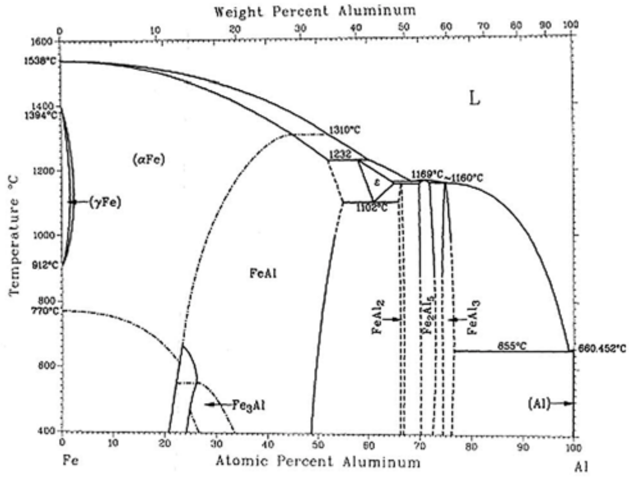

Fig. 8. Phase equilibrium diagram for Fe-Al system [7]

The results of analysis of the chemical composition of the coating (a layer of AZ91 alloy formed when plates were taken out from the crucible) explain in what way the AZ91 alloy may affect iron. The structure of AZ91 alloy is composed of large crystals of the solid solution α and of the, formed at the final stage of solidification, fields of degenerated α+γ phase, having various sizes depending on the solidification rate. A strong segregation of the alloying elements, observed during solidification, is the reason why the α phase formed as a first one is impoverished in aluminium, which is being pushed into the interdendritic spaces, where at a temperature of 437°C the α+γ eutectic is formed. This is further confirmed by the results of the measurements of the chemical composition. Measurement 4 is corresponding to α phase, while measurement 5 to α+γ eutectic. And these, still liquid at 400-600°C, precipitates with high content of aluminium, located in the interdendritic spaces of the solidifying solution α, react wirh iron present in the material of the crucible. As a result of interchanging of Al and Fe atoms in the solid-liquid zone below the point of liquidus, separate precipitates of the columnar Fe_2Al_5 phase are crystallising.

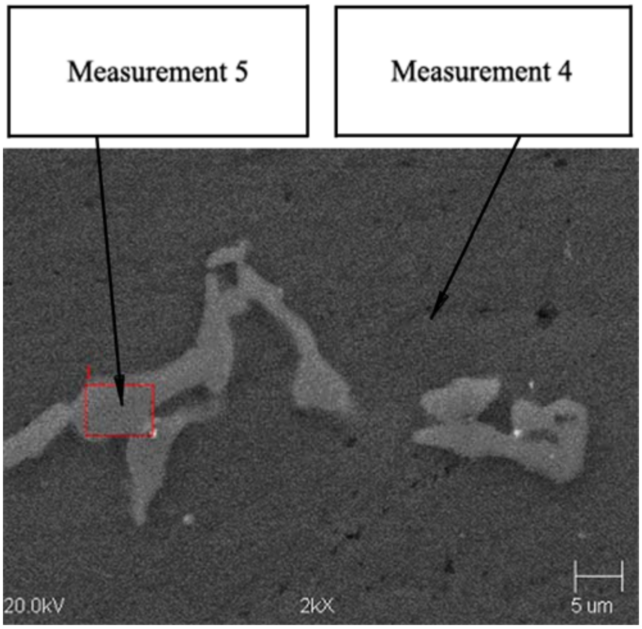

Fig. 9. Detailed designation of places in the coating where the chemical composition was analysed by EDS.

Table 7.
The results of analysis of the chemical composition made by EDS technique in coating on the examined specimen.

Coating on specimen surface	Chemical composition [%]		
	Mg	Al	Zn
Measurement 4	96,266	3,734	-
Measurement 5	64,337	31,131	4,532

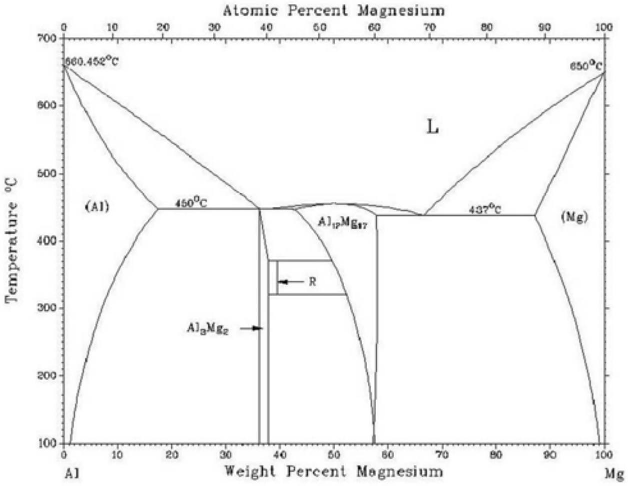

Fig. 10. Phase equilibrium diagram for Mg-Al system [7]

4. Conclusions

In the process of casting magnesium alloys, attention is usually not paid to the reactions which take place with iron. This is, indeed, no problem as long as all the required procedures are duly observed. However, under some conditions, these highly undesired reactions may take place. In this article, a result of this reaction has been described on the example of a crucible - AZ91 alloy system.

The plates found on the crucible bottom were taken out. Their formation may be due to the following events:

1. Gravity segregation of elements in the bath (Mg matrix – 1,7g/cm^3), heavier elements are falling to the crucible bottom: Fe –7,8g/cm^3, Mn – 7,4g/cm^3, Al – 2,7g/cm^3.
2. Holding of alloy at a temperature of 400-600°C which results in the formation of small volumes of molten metal rich in aluminium attacking the walls of the crucible [8].
3. Throwing cold „ingots" into metal bath during alloy manufature which, while melting at the crucible bottom, will cause the precipitation of phases rich in aluminium, which attack the crucible walls.
4. The combined effect of SO_2 acting as a protective gas, of moisture and of high temperature of the crucible (a zone several centimeters high above the metal surface is overheated – the heaters are operating but the heat is not transferred to liquid metal) causes corrosion of the crucible material above the metal surface; the products of this corrosion are spalling from the crucible wall and fall into the metal bath.
5. Manganese present in alloy forms with iron a compound hardly soluble in magnesium which is easily falling to the crucible bottom; an addition of manganese also causes decreased solubility of aluminium in magnesium; a portion of manganese is falling down immediately in the form of $MnAl_3$, carrying with itself the metallic impurities (iron) [9].

The number of the plates was observed to increase when for the weekend the metal temperature was unconsciouly decreased, which would point out to item 2 – a high content of Al and Fe. The same process may be responsible for the plate formation when cold „ingots" are thrown into the bath during production cycle. In both cases, on the crucible bottom and walls will be present the precipitates of solid-liquid phase rich in aluminium. Due to an interchange of Al and Fe atoms at a temperature below the point of liquidus, columnar phases are growing in direction normal to the crucible wall, here they have been recognised as Fe_2Al_5 phases. A stable layer of different thicknesses is formed on the crucible wall, and during e.g. cleaning of the crucible it falls off and down to rest on the crucible bottom.

Irregular stirring of the metal bath (it should be done once per shift) additionally causes alloy segregations– item 1. Compared with its initial content in alloy, manganese without any doubt has penetrated into the examined plates by way of segregation– item 1 and reacted with Fe – item 5.

Summing up it can be concluded that regular stirring and cleaning of the metal bath, maintaining high level of metal in the crucible with minimum volume of protective gas, avoiding holding of Mg-Al alloy at a temperature of 400-600°C, throwing into the bath only ingots well preheated – all these steps should prolong the crucible life on performance and ensure better stability of the AZ91D alloy chemical composition in castings.

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