THERMOPHYSICAL PROPERTIES AND MICROSTRUCTURE
OF SELECTED MAGNESIUM ALLOYS

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Abstract

This contribution is aimed at characterisation of thermo-physical properties and microstructure of chosen non-ferrous alloys based on magnesium. The influence of inoculant addition and thermal expose on dilatometric behaviour of castings prepared from Mg-Al alloys is also determined. Simultaneously, the influence of metallurgical treatment of a casting sample prepared by gravity casting method on microstructure is also evaluated.

Key words: Magnesium alloy, casting, microstructure, thermal expansion

1. INTRODUCTION

Magnesium is the fourth most frequently occurred metal on the Earth and at the same time after sodium it is the most widespread metal in sea water what represents its almost inexhaustible amount. Its mass density (1.74 g·cm⁻³) compared with that one of iron is a quarter and in comparison with aluminium it is by a third lower. Magnesium in a pure form, due to its rather low strengths and a poor cold weldability, isn’t used in practice. The highest amount of primary magnesium is used for alloying the aluminium alloys and on the second place there is the preparation of magnesium alloys for casting manufacture. Magnesium based alloys are ranged among the lightest structural materials. Thanks to it they are ranged, together with titanium alloys, among materials distinguishing with high specific strength that is expressed by the strength to mass density ratio. For that reason the questions are very prospective materials that are subject of interest of a number of industrial branches. In this regard the composite materials or plastics can compete with them. An import of these alloys consists in applications demanding sufficient strength and low mass density. Thanks to those properties their utilization is reasonable especially in automobile design. Recently it is important to use the castings particularly for seats, instrument panels, gearboxes, engine parts, wheels (especially of racing cars) etc. Continuously growing consumption of magnesium and its alloys in automobile industry is evident in global range. The interannual growth goes to 15 %. A question of recycling the used alloys is also connected with this extensive use. [1] From the point of view of castings manufacture following advantages, besides high specific strength, are counted among the most important properties:

- good running ability that can be improved in combination with pressure casting,
- good shielded weldability,
- possibility of using the high machining speeds.

A disadvantage of magnesium alloys is considerable magnesium activity in particular to oxygen. This fact complicates melting and pouring itself of these alloys when it is necessary to use special inhibitors, covering fluxes or protective atmosphere. From the point of using the castings from those alloys a steep decrease of strength under increased temperatures (above 120 °C) is especially important. This behaviour limits their use for thermally stressed parts (e.g. cylinder heads, engine blocks). For those applications the alloys of the Mg-Al-Sr or Mg-RE types were developed.

From this point of view the so called thermal stability of the alloy is also important. The work pays attention particularly to the thermal stability of Mg-alloys that was evaluated with the aid of dilatometric analysis and under the influence of metallurgical interventions (inoculation) on these studied parameters.
2. PROPERTIES AND THE USE OF MAGNESIUM ALLOYS

2.1 Magnesium alloys for foundry use

Foundry alloys are binary systems completed with other alloying additions for the purpose of improving the technological and mechanical properties, corrosion and heat resistance etc. Basic systems are Mg-Al, Mg-Zn, Mg-Mn and Mg-Li that can be further on completed with other accompanying elements as Zr, Th, Si, Ti, rare earth metals (RE) etc. From the point of view of evolution the alloys of the Mg-Al type alloyed with other metals as e.g. Zn, Mn, Si, Sr, etc. are the oldest and most frequently used ones. With aluminium content above 7% the castings from these materials can be thermally treated when they are precipitatively hardened with the formation of a precipitate of the Mg$_{17}$Al$_{12}$ phase. The Mg-Mn type alloys have particularly higher shrinkage and a worse running ability but they have a better corrosion resistance and they are weldable. Structure of castings from those alloys is rather coarse-grained what negatively influences the achieved mechanical properties that are rather low ones. This effect can be partly eliminated with a small addition of silicon. A similar effect has zircon that is used in amount of 0.25 – 0.7% and it considerably improves the strength characteristics of alloys of the Mg-Zn type. In those materials a similar effect has also the use of RE. These additives considerably extend the application field of these alloys for heat stressed parts (about 300 °C). The Mg-Zn-Zr-RE alloys have for instance the creep resistance better than refractory aluminium alloys with achieving lower mass density [2]. From the point of view of evolution the Mg-Li alloys are the youngest type characteristic with very low mass density of 1.3 – 1.5 g·cm$^{-3}$. It decreases with growing Li content and at the same time the mechanical properties are decreasing too. A problem of these materials is their high reactivity in molten state, low creep resistance, and unstability of mechanical properties under room temperatures. [3]

2.2 Influencing the structure of magnesium alloys

Mechanical properties to a considerable extent are influenced by structure and possible defects or internal inhomogeneity of the material. This can be influenced by the choice of the alloy or by proposed technological process of castings manufacture. The best strength properties achieve the castings poured in metal moulds that can be additionally improved by e.g. the use of pressure or low-pressure casting process. An intensive heat transfer from the solidifying casting into those moulds results in fine grained structure and a high quality surface. Then in case of pressure casting the resulting product can contain a number of internal cavities for the reason of volume changes or the presence of gases in the mould cavity. A special casting process in a liquid-solid state is also used at present when thixotropic properties of this phase are utilized. Then the result is high quality structure with high strength characteristics and excellent internal quality of castings without porosity. With casting in expendable moulds made from moulding mixtures or in ceramic moulds the structure is coarse grained for the reason of a lower cooling effect. This can be partly eliminated by a suitable choice of materials with a higher heat conductance. But the most effective is a possibility of adding a suitable element or a combination of them when a number of effective crystal nuclei is increased. Then the result is a similar structure as of castings poured in moulds with high cooling effect. This effect called inoculation is commonly used for aluminium alloys when particularly the elements Ti, B, Ag, RE, Sc, Zr, etc. are used. In case of magnesium alloys the use of e.g. Zr, Si, FeCl$_3$ or MgCO$_3$ having a similar effect can be found in works by authors from abroad [4]. As one of the most important elements the carbon can then serve in a form of various organic or inorganic compounds. In industrial conditions the C$_2$Cl$_6$ compound is commonly used what results in obtaining fine grained structure of sufficient quality. It is possible to find also other utilization of carbon compounds in a form of Al$_4$C$_3$ carbides [5]. The effect of individual inoculants will be evident in dependence on the used alloy type. Works by inland authors [2] aimed at metallurgical treatment of the most frequently used foundry alloy AZ91 were published in recent years. An important influence of sodium on fine grained structure of the basic solid solution and eutectics has been proved. Then a question remains – to find its optimum amount.
3. **EXPERIMENTAL PART**

3.1 **Description of used magnesium alloys**

The experiment was aimed at checking the influence of the inoculant addition on achieved microstructure (grain refinement) and material properties. Four grades of magnesium alloys of the Mg-Al type were chosen for this purpose. They were in particular the alloys marked according to the ASTM standard as AZ91, AM60, AMZ40 and AJ62 chemical composition of which is given in Table 1. The AZ91 and AM60 alloys are ranged among quite common foundry alloys destined particularly for manufacture of castings by gravity or pressure casting. The AMZ40 alloy was patented in 2006 by the DaimlerChrysler AG company as a material destined for pressure casting of interior castings in automobile design. Very low mass density given by a low content of basic alloying elements – aluminium, manganese, and zinc – is an advantage. Strontium as an additive element in content of 0.2 – 3.0 % increases the creep resistance and similarly as the RE it improves running ability of magnesium alloys. Castings from the AJ62 alloy used in the experiment show very good strength properties under increased temperatures, low porosity share and at the same time very good running ability [6]. This material finds continuously more frequent applications particularly in manufacture of cast parts used in conditions where they are thermally stressed. As typical examples of using the AJ62 alloy they are e.g. castings of engine cylinder heads and other engine parts in automobile applications thermally stressed to operating temperatures (200 – 250 °C) [7]. For that reason they can serve as a cheaper alternative of magnesium alloys alloyed with RE that show a higher heat resistance but they are considerably more expensive.

**Table 1 Chemical composition of used magnesium alloys**

<table>
<thead>
<tr>
<th>alloy</th>
<th>Zn</th>
<th>Al</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Ca</th>
<th>Be</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D</td>
<td>0.56</td>
<td>8.80</td>
<td>0.06</td>
<td>0.004</td>
<td>0.20</td>
<td>0.004</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
<td>0.00</td>
</tr>
<tr>
<td>AM60</td>
<td>0.07</td>
<td>5.78</td>
<td>0.03</td>
<td>0.001</td>
<td>0.33</td>
<td>0.003</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
<td>0.00</td>
</tr>
<tr>
<td>AMZ40</td>
<td>0.14</td>
<td>3.76</td>
<td>0.02</td>
<td>0.001</td>
<td>0.34</td>
<td>0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
<td>0.00</td>
</tr>
<tr>
<td>AJ62</td>
<td>0.01</td>
<td>5.78</td>
<td>0.04</td>
<td>0.001</td>
<td>0.35</td>
<td>0.003</td>
<td>0.001</td>
<td>0.008</td>
<td>0.001</td>
<td>2.92</td>
</tr>
</tbody>
</table>

3.2 **Casting of test samples**

Magnesium alloys were melted in an electric resistance furnace in a metal crucible from low alloy steel. Magnesium alloys are highly reactive thanks to high magnesium affinity to oxygen. For that reason the material was treated during melting with an agent of a trade mark EMGESAL. This material in a form of covering and refining flux serves for limiting the alloy oxidation and for cleaning the melt from possible inclusions. Test samples for evaluation of structure and thermophysical properties were cast in a metal mould from cast iron. At the same time these castings served for evaluation of thermomechanical properties of the mentioned alloys. Results were published by the authors [8] and they are not a subject of this contribution. During casting of individual samples both temperature of the metal mould and casting temperature too were observed. For the reason of achieving a sufficient running ability of the material and increasing its life time the mould was preheated to operating temperature (450 °C ± 30 °C). Casting temperatures and operating temperatures were kept in a narrow range for as high as possible limitation of influence of different cooling effect. A part of castings from individual alloys was metallurgically treated with the addition of an agent of a trade mark EMGESAL MG T200 that has a function of an inoculant and obtaining the fine grained structure and the growth of mechanical properties are expecting results.
4. ACHIEVED RESULTS

4.1 Microstructure of test castings

Microstructure of magnesium alloys was studied on casting samples for checking of inoculation influence. In spite of the fact that the mould was kept on operating temperature its high cooling effect was evident in some cases. Fine grained structure occurs on the edges of test castings that were in contact with the mould material. Microstructure of the AZ91 alloy without the inoculant addition is evident on Fig. 1. Structure is formed by the α+β eutectics with the occurrence of the Mg₁₇Al₁₂ tabular precipitate. In case of this alloy inoculation (Fig. 2) an increased amount of the precipitation phase can be observed. In the AM60 alloy (Fig. 3) there is evident a considerable effect of inoculation. In comparison with the AZ91 alloy there is a lower content of the Mg₁₇Al₁₂ precipitate and eutectics in structure. Microstructure achieved with the addition of the inoculant (Fig. 4) is considerably finer grained with clearly evident grain boundaries. In case of the AMZ40 alloy (Figs. 5 and 6) and the AJ62 alloy (Figs. 7 and 8) the effect of inoculation wasn’t perceivable on the obtained structure. From the chemical point of view the AMZ40 alloy contains very low amount of alloying elements what is perceivable on structure that is formed in particular by the α primary phase and the eutectics without the presence of precipitates. On the contrary very different structure is represented by the AJ62 alloy where besides the basic α solid solution altogether 3 types of intermetallic phases – (Al,Mg)₄Sr, Al₃Mg₁₃Sr – and a very low amount of Mn₅Al₆ can be found.
4.2 Dilatometric analysis of test samples

Heat expansion of the material (linear changes) is usually characterized by a mean temperature coefficient (coefficient of linear expansion):

\[ \alpha_T = \frac{l_T - l_{T_o}}{l_{T_o} (T - T_o)} = \frac{1}{l_{T_o}} \left( \frac{dl}{dT} \right) \]  

(1)

where:
- \( \alpha_T \) – coefficient of linear heat expansion
- \( l_0 \) – sample length under reference (e.g. laboratory) temperature
- \( dl \) – change of the sample length
- \( dT \) – difference in temperatures

Linear heat expansion was measured on above described samples with the Netzsch DIL 402C/7 dilatometer. Experiments ran in the temperature interval of 20 ± 5 °C up to 350 °C with heating and cooling rate of 15.0 K/min with holding time of 30 min at maximum temperature (isotherm) in protective argon atmosphere (99.9999 % Ar) with constant gas flow of 20 ml/min. The size of used samples was as follows: mean length of 20 mm and mean diameter of 6 mm. Samples of non-inoculated (marked as name of sample – non) and inoculated materials (marked as in) were divided into 2 groups. The first group was used in the as cast state without previous heat stressing and the second one after heat stressing them (250 °C/30 min) in the argon atmosphere for checking the influence of increased temperature during stressing the castings in real conditions. This parameter is very important from the point of view of using those materials for heat stressed cast parts e.g. of driving gears of cars. Table 2 contains results of measurements of the coefficient of linear heat expansion (\( \alpha_T \)) for the chosen temperature interval (20 ± 5 °C up to 350 °C) including the greatest change of length under temperature of 350 °C (max \( l_{350} \ °C \)). The table gives resulting values for samples without heat stressing (\( T_{lab} \)) and after heat stressing (250 °C/30 min) - \( T_{250} \).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( T_{lab} ) max ( l_{350} °C ) (%)</th>
<th>( \alpha_T \times 10^{-6} ) (K(^{-1}))</th>
<th>( T_{250} ) max ( l_{350} °C ) (%)</th>
<th>( \alpha_T \times 10^{-6} ) (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91 non</td>
<td>0.97</td>
<td>29.6319</td>
<td>0.96</td>
<td>27.7702</td>
</tr>
<tr>
<td>AZ91 in</td>
<td>0.97</td>
<td>28.8887</td>
<td>0.92</td>
<td>27.3736</td>
</tr>
<tr>
<td>AM60 non</td>
<td>0.97</td>
<td>28.7385</td>
<td>0.86</td>
<td>26.2843</td>
</tr>
<tr>
<td>AM60 in</td>
<td>0.91</td>
<td>26.2465</td>
<td>0.87</td>
<td>26.0252</td>
</tr>
<tr>
<td>AMZ40 non</td>
<td>0.93</td>
<td>28.2639</td>
<td>0.63</td>
<td>18.1402</td>
</tr>
<tr>
<td>AMZ40 in</td>
<td>0.58</td>
<td>17.3364</td>
<td>0.58</td>
<td>17.1782</td>
</tr>
<tr>
<td>AJ62 non</td>
<td>0.98</td>
<td>28.8727</td>
<td>0.86</td>
<td>26.1917</td>
</tr>
<tr>
<td>AJ62 in</td>
<td>0.62</td>
<td>18.1686</td>
<td>0.58</td>
<td>17.5744</td>
</tr>
</tbody>
</table>
It is evident from the measured values that the studied quantities were close connected with metallurgical treatment of the melt – the addition of inoculating agent. The highest value of the coefficient of linear heat expansion \((29.6319 \times 10^{-6})\) was obtained for the AZ91 alloy without inoculant addition, for the sample in the as cast state without following heat stressing. On the contrary the lowest value \((17.1782 \times 10^{-6})\) was achieved for the sample of the AMZ40 alloy after heat stressing. Very low values of studied parameters were also achieved for samples of the AJ62 alloy. This fact confirms the suitability of this alloy for manufacture of heat stressed castings, e.g. engine parts. It can be stated that after the chosen heat stressing that served as a partial imitation of heat stress in practical applications the \(\alpha_T\) has decreased. At the same time the inoculation effect was reflected in considerable decrease of values of studied quantities.

5. CONCLUSION

In the work the magnesium alloys were studied that are destined for foundry applications. An influence of the inoculant addition on microstructure and thermophysical properties was studied in particular. This metallurgical intervention had a positive influence on decreasing the value of the coefficient of linear heat expansion. This parameter is important from the point of view of using the parts in heat stressed applications. The inoculant addition also positively influenced the structure of cast samples. Structure was finer grained and thus the higher utility properties of products from alloys treated in such a way can be expected. Next works will be aimed at the influence of an inoculant kind and cooling effect of the mould on the studied quantities.

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