

C. RAPIEJKO*, B. PISAREK*, T. PACYNIAK*

EFFECT OF Cr AND V ALLOY ADDITIONS ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AM60 MAGNESIUM ALLOY

WPLYW DODATKÓW STOPOWYCH Cr i V NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MECHANICZNE STOPU AM60

The paper presents the results of the investigation of the effect of Cr and/or V alloy additions on the microstructure and mechanical properties of the magnesium AM60 alloy. The examinations are performed within the frames of a project aiming at the elaboration of an experimental and industrial technology of producing constructively complex elements of machines and devices made of magnesium alloys with the method of investment casting. It has been proven that small numbers of Cr and V alloy additions improve the strength properties: Rm, A%, and the hardness HB of the obtained casts. The experimental casts were made in ceramic molds.

Keywords: investment casting technology, AM60, Cr and/or V addition, microstructure, mechanical properties

W pracy przedstawiono wyniki badań wpływu dodatków stopowych Cr i/lub V na mikrostrukturę oraz właściwości mechaniczne stopu magnezu AM60. Badania prowadzone są w ramach projektu, którego celem jest opracowanie technologii doświadczalnej i przemysłowej wytwarzania złożonych konstrukcyjnie elementów maszyn i urządzeń ze stopów magnezu metodą wytapianych modeli. Wykazano, że niewielkie ilości dodatków stopowych Cr i V poprawiają właściwości wytrzymałościowe: Rm, A%, oraz twardość HB otrzymanych odlewów. Odlewy doświadczalne wykonano w formach ceramicznych.

1. Introduction

In the recent years, magnesium alloys, due to their relatively low mass, have been of an increasingly big interest mostly to the automotive industry [1]. These alloys characterize in a significantly lower mass than that of light aluminium alloys, yet they also possess much worse mechanical properties. In order to improve their mechanical properties, magnesium alloys are enriched with various alloy additions, such as: antimony, yttrium [2], calcium [3], tin [4], titanium [5] and other [6-8]. There are no global literature reports on any examination of the effect of chromium or vanadium additions on the mechanical properties of magnesium alloys. On the basis of the analysis of the literature, it can be stated that the add additions of Cr and V improves the mechanical properties of various metal alloys such as: spheroidal cast iron [9], aluminum alloys [10,11] and bronzes [12]. The aim of this work was the examination of the effect of a Cr and V addition on the mechanical properties of experimental casts made of AM60 magnesium alloy in ceramic molds.

2. Test methodology

The experimental casts were prepared in ceramic molds according to the investment casting method. The molds were

made of refractory materials Refracoarse (flour and sands). They were composed of 7 coatings applied in mixers and a fluidizer at the foundry „Armatura” Łódź, Poland. Each coating was created as a result of applying a binder on a wax mold and next pouring sand of a particular granularity onto it. After the ceramic mold had been dried, it was used to cast a mold mass in an autoclave at 150°C. Next, the mold was fired at 960°C in a tunnel furnace. After the firing, the ceramic molds were cooled down to 180°C, and then they were flooded with liquid metal of 800°C±5°C. The chemical composition of AM60 alloy is presented in Table 1.

TABLE 1
Chemical composition of AM60 alloy

| Chemical composition, wt. % | | | | | | | |
|-----------------------------|----|----|------|------|-------|-------|-------|
| Mg | Al | Zn | Mn | Si | Fe | Cu | Ni |
| 93.697 | 6 | 0 | 0.23 | 0.05 | 0.004 | 0.008 | 0.001 |

The plan of the experiments, which made it possible to determine the effect of the changes in the amount of the added additions of Cr and V on the mechanical properties of the examined alloy, was implemented with the use of the Box-Wilson method in the surrounding of the central point, at two levels: „+” and „-”,Δ. The AM60 magnesium alloy constituted the, so called, object in the planned experiment, as has been pre-

* ŁÓDŹ UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF MATERIALS ENGINEERING AND PRODUCTION SYSTEMS, 1 STEFANOWSKIEGO STR., 90-924 ŁÓDŹ, POLAND

sented in Figure 1(a). The discussed object is described by the characteristics of $Y=f(X_1, X_2, D)$, where Y (Output Y) is constituted by the selected mechanical properties of the alloys R_m , $R_{p0.2}$, A , HB , and $X_1 = Cr\%$, $X_2 = V\%$ mark the object inputs (Control X), D designates the immeasurable disturbance (Disturbance D) and C (Constant C) describes the constant process parameters (e.g.: temperature of the metal, temperature of the mold etc.). The scheme of the experiment settings is presented in Table 2 and Figure 1 (b).

TABLE 2
Experimental plan for AM60 magnesium alloys with Cr and V additions

| | Mass concentration, wt. % | |
|--|---------------------------|-------------|
| Control X_S ($S=\{1,2\}$) | $X_1 = Cr$ | $X_2 = V$ |
| Central point $E_c(Cr_0, V_0)$ | 0.05 | 0.05 |
| Test step ΔX_S | 0.05 | 0.05 |
| Upper level $X_S + \Delta X_S$ | 0.1 | 0.1 |
| Lower level $X_S - \Delta X_S$ | 0 | 0 |
| Experiment number, n | $E_n(Cr, V)$ | |
| 1 | 0.1 | 0.1 |
| 2 | 0.1 | 0 |
| 3 | 0 | 0 |
| 4 | 0 | 0.1 |

The metal was cast in a laboratory crucible resistance furnace with the capacity of 5 kg, in a S235JRG2 steel crucible (PN-EN 10025-2:2005).

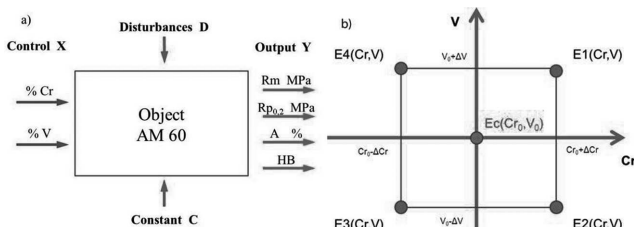


Fig. 1. Discussed non-linear object in the planned experiment for AM60 magnesium alloys (a), experiment plan for AM60 magnesium alloys with Cr and V additions (b)

Inside the furnace, a protective atmosphere was applied, composed of a mixture of Ar+SF₆, pressure 0.15-0.20 MPa. The gas flow equaled 10 cm³/min for SF₆ and 500 cm³/min for Ar. Due to the high tendency of chromium and vanadium additions for gravitational segregation, the magnesium alloy together with the additions was intensely mixed in the crucible. In order to visualize the particular phases, the microsections were etched with a reagent of the following composition: 1 ml acetic acid, 50 ml distilled water and 150 ml ethyl alcohol. The microstructure of the examined alloys was observed by means of an optic microscope Nikon Eclipse MA200. In order to identify the chemical composition in the particular points of the cast microstructure, the samples were observed with a scanning microscope S-4200 with an EDX analyzer, accelerating voltage of 15 kV. With the aim of determining the basic mechanical properties, that is: R_m , $A\%$, a testing machine

Instron 4485 was used, according to the standard EN-ISO 6892/1. The hardness tests were performed by the Brinell method according to standard PN-EN ISO 6506-1:2006.

3. Results of AM60 magnesium alloy with Cr and V additions

In Figures 2÷4 (a,b) present the microstructures of AM60 alloy with addition Cr and/or V, solidifying in a ceramic mold, which were observed by means of an optic microscope (a) and the microstructures were observed with a scanning microscope (b) respectively:

- 0.1% V (Fig. 2 (a,b)),
- 0.1% Cr (Fig. 3 (a,b)),
- 0.1% V and 0.1% Cr (Fig.4 (a,b)).

Tables 3,4,6 show the results of the chemical composition EDX analysis in the examined points of the researched alloys, respectively:

- 0.1% V (Tab. 3),
- 0.1% Cr (Tab. 4),
- 0.1% V and 0.1% Cr (Tab. 6).

The microstructure of AM60 alloy with additions V and/or Cr, similarly to that of AM60 alloy, is composed of phase α_{Mg} + eutectic ($\alpha_{Mg} + \gamma(Mg_{17}Al_{12})$) with the clearly refined eutectic $\alpha_{Mg} + \gamma(Mg_{17}Al_{12})$, as compared to the initial AM60 alloy. The surfaces of the examined alloys samples underwent a relatively fast oxidation and thus oxygen was identified of the analysis.

In the microstructures of the examined alloys, the mass concentration of Al in the phase varied α_{Mg} a relatively great range of from about 4 to 8% (Fig. 2÷4, Tab. 3,4,6). The eutectic magnesium-aluminium phase has its magnesium atomic fraction close to that of phase $Mg_{17}Al_{12}$ (Fig. 2 (a,b), Table 3: points 1,2). In the microstructure of the AM60 alloy with additions of V precipitations of a non-equilibrium complex intermetallic phase were identified, which originated from the added addition of vanadium ($VMnMgSi$)₁₇Al₁₂ (Fig. 2a) and ($V_{6.78}Mn_{6.15}Mg_{4.35}Si_{0.72}Al_{12.00}$) (Fig.2 (b), Tab. 3, point: 3 and 4).

In the microstructure of the AM60 alloy with addition of Cr, precipitations of a non-equilibrium complex intermetallic phase rich in chromium were identified, presented in Figure 3 (a). The phase was observed and analyzed by means of scanning microscopy with the EDX analysis: it is probably a complex phase of the AlCr₂ type with a non-equilibrium concentration of additives, e.g. Al_{1.00}Cr_{2.12}Mg_{0.74}Mn_{0.17}Fe_{0.04} or Al_{1.00}Cr_{2.14}Mg_{0.36}Mn_{0.17} (Fig.3 (a,b), Tab. 4 point: 2 and 3).

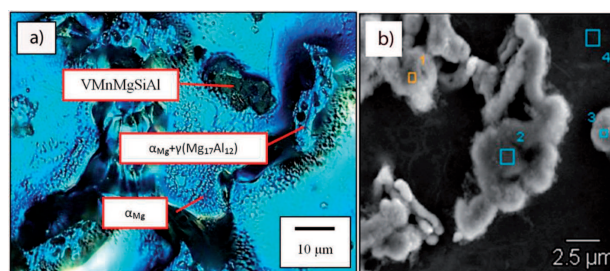


Fig. 2. Microstructure of AM60 +0.1% V alloy solidifying in a ceramic mold observed by means of optic microscope (a) and scanning microscope (b)

TABLE 3

Results of the chemical composition analysis of AM60+0.1% V alloy

| Point of analysis | Element | Element concentration in alloy, % | | Phase or system of phases |
|-------------------|---------|-----------------------------------|--------|---|
| | | Weight | Atomic | |
| 1 | Mg | 10.2 | 16.2 | type $\alpha_{Mg} + \gamma(\text{Mg}_{17}\text{Al}_{12})$ (mass precipitations $(\text{VMnSiMg})_{17}\text{Al}_{12}$) |
| | Al | 24.5 | 35.0 | |
| | Si | 2.0 | 2.6 | |
| | V | 31.3 | 23.7 | |
| | Mn | 32.0 | 22.5 | |
| 2 | Mg | 18.0 | 27.0 | type $\alpha_{Mg} + \gamma(\text{Mg}_{17}\text{Al}_{12})$ (mass precipitations $(\text{VMnSiMg})_{17}\text{Al}_{12}$) |
| | Al | 23.2 | 31.3 | |
| | Si | 1.6 | 2.2 | |
| | V | 28.7 | 20.5 | |
| | Mn | 28.5 | 18.9 | |
| 3 | Mg | 9.3 | 14.5 | type $\gamma(\text{Mg}_{17}\text{Al}_{12})$ $\text{V}_{6.78}\text{Mn}_{6.15}\text{Mg}_{4.35}\text{Si}_{0.72}\text{Al}_{12.00}$ |
| | Al | 28.6 | 40.0 | |
| | Si | 1.8 | 2.4 | |
| | V | 30.5 | 22.6 | |
| | Mn | 29.8 | 20.5 | |
| 4 | Mg | 91.2 | 92.0 | α_{Mg} |
| | Al | 8.8 | 8.0 | |

TABLE 4

Results of the chemical composition analysis of AM60+0.1% Cr alloy

| Point of analysis | Element | Element concentration in alloy, % | | Phase or system of phases |
|-------------------|---------|-----------------------------------|--------|--|
| | | Weight | Atomic | |
| 1 | Mg | 96.2 | 96.6 | α_{Mg} |
| | Al | 3.8 | 3.4 | |
| 2 | Mg | 10.7 | 18.1 | type AlCr_2 $\text{Al}_{1.00}\text{Cr}_{2.12}\text{Mg}_{0.74}\text{Mn}_{0.17}\text{Fe}_{0.04}$ |
| | Al | 16.2 | 24.6 | |
| | Cr | 66.3 | 52.2 | |
| | Mn | 6.1 | 4.2 | |
| | Fe | 1.2 | 0.9 | |
| 3 | Mg | 5.7 | 9.9 | type AlCr_2 $\text{Al}_{1.00}\text{Cr}_{2.14}\text{Mg}_{0.36}\text{Mn}_{0.17}$ |
| | Al | 17.2 | 27.2 | |
| | Cr | 71.0 | 58.2 | |
| | Mn | 6.1 | 4.7 | |
| | Al | 3.8 | 3.4 | |

In the alloy microstructure with additions of V and Cr, precipitations of a non-equilibrium complex intermetallic phase were identified, which originated from the introduced addition of vanadium and chromium $(\text{MgMnVCSi})_{17}\text{Al}_{12}$ (Figure 4 (a)). The phase was observed and analyzed with the use of scanning microscopy with the EDX analysis as one of probably the $\text{Mg}_{17}\text{Al}_{12}$ type $(\text{Mg}_{9.51}\text{Mn}_{5.78}\text{V}_{1.10}\text{Cr}_{0.80}\text{Si}_{0.80}\text{Al}_{12.00})$ (Fig. 4 (a,b), Table 6, point: 4).

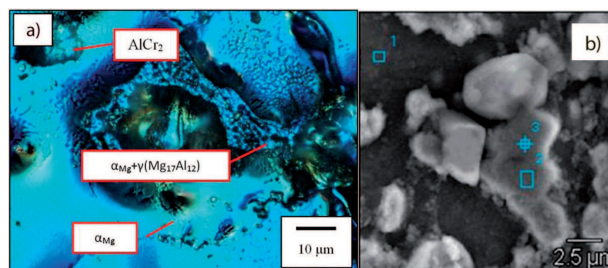


Fig. 3. Microstructure of AM60 +0.1% Cr alloy solidifying in a ceramic mold observed by means of optic microscope (a) and scanning microscope (b)

The mechanical properties of examined AM60 alloy with the Cr and V additions were conducted according to experimental plan (Fig. 1) and are presented in Table 5.

TABLE 5
The mechanical properties of examined AM60 alloy with the Cr and V additions

| Experiment number, n | Mass concentration, wt. % | | Mechanical properties | | | |
|----------------------|---------------------------|-------------------|-----------------------|------|----------------------|----|
| | X ₁ =Cr | X ₂ =V | R _m , MPa | A, % | R _p , MPa | HB |
| 1 | 0.1 | 0.1 | 137 | 1.6 | 121 | 50 |
| 2 | 0.1 | 0 | 131 | 1.58 | 122 | 50 |
| 3 | 0 | 0 | 97 | 0.9 | - | 48 |
| 4 | 0 | 0.1 | 119 | 1.36 | - | 49 |

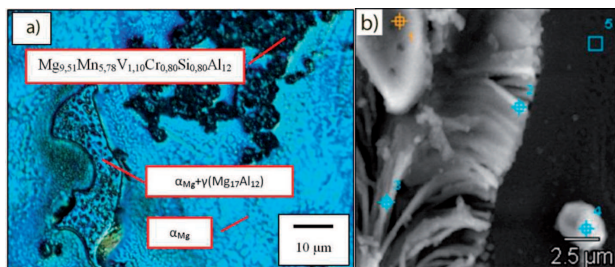


Fig. 4. Microstructure of AM60+0.1% V+0.1% Cr alloy solidifying in a ceramic mold observed by means of optic microscope (a) and scanning microscope (b)

From the point of view of the mechanical properties, the best chemical composition seems to be possessed by the AM60 alloy with a simultaneous addition of 0.1% Cr and V. The Cr and V addition conditions higher mechanical properties and, probably, a higher abrasive wear resistance, due to a higher hardness of the alloy, compared to that of the AM60 alloy without additions.

4. Conclusions

- The add addition of a 0.1% V and/or Cr into AM60 alloy caused the formation of complex intermetallic phases rich with those additions, in the alloy microstructure:
 - Cr is mainly located in the complex intermetallic phases of the AlCr₂ type,
 - V, introduced both individually or simultaneously with Cr, locates itself mostly in the complex intermetallic phases of the $\gamma(\text{Mg}_{17}\text{Al}_{12})$ type.
- The add addition of the V and Cr into AM60 alloy causes a refinement of eutectic $\alpha_{\text{Mg}} + \gamma(\text{Mg}_{17}\text{Al}_{12})$.
- From the performed examinations it can be concluded that the add additions of a small amount of V and/or Cr additions into AM60 alloy significantly increases the mechanical properties of the casts obtained by the investment casting method in ceramic molds.
- A simultaneous add additions of the 0.1% V and Cr into AM60 alloy causes an increase in the tensile strength R_m by 27%, an increase in the elongation $A\%$ by 77% and of the hardness HB by 4%.

TABLE 6

Results of the chemical composition analysis of AM60+0.1% V+0.1% Cr alloy

| Point of analysis | Element | Element concentration in alloy, % | | Phase or system of phases |
|-------------------|---------|-----------------------------------|--------|---|
| | | Weight | Atomic | |
| 1 | Mg | 64.7 | 67.1 | type $\alpha_{\text{Mg}} + \gamma(\text{Mg}_{17}\text{Al}_{12})$ (mass precipitations $(\text{MgSi})_{17}\text{Al}_{12}$) |
| | Al | 34.9 | 32.6 | |
| | Si | 0.4 | 0.4 | |
| 2 | Mg | 66.0 | 68.3 | type $\alpha_{\text{Mg}} + \gamma(\text{Mg}_{17}\text{Al}_{12})$ (lamellar precipitations $(\text{MgSi})_{17}\text{Al}_{12}$) |
| | Al | 31.8 | 29.7 | |
| | Si | 2.2 | 2.0 | |
| 3 | Mg | 63.8 | 66.2 | type $\alpha_{\text{Mg}} + \gamma(\text{Mg}_{17}\text{Al}_{12})$ (lamellar precipitations $(\text{MgSi})_{17}\text{Al}_{12}$) |
| | Al | 34.7 | 32.5 | |
| | Si | 1.5 | 1.3 | |
| 4 | Mg | 25.6 | 34.0 | type $\gamma(\text{Mg}_{17}\text{Al}_{12})$ $\text{Mg}_{9.51}\text{Mn}_{5.78}\text{V}_{1.10}\text{Cr}_{0.80}\text{Si}_{0.80}\text{Al}_{12.00}$ |
| | Al | 35.8 | 42.9 | |
| | Si | 0.7 | 0.8 | |
| | V | 1.7 | 1.1 | |
| | Cr | 1.2 | 0.8 | |
| | Mn | 35.1 | 20.7 | |
| 5 | Mg | 91.1 | 91.9 | α_{Mg} |
| | Al | 8.9 | 8.1 | |

Acknowledgements

This work was realized within the frames of Project PBS I, financed by the National Centre for Research and Development, Poland. Project ID: 178739 (2013-2015).

REFERENCES

- [1] K.U. Kainer, Magnesium: Proceedings of the 7th International Conference on Magnesium Alloys and Their Applications. Wiley-VCH Verlag GmbH&Co. KGaA. Weinheim (2007).
- [2] Arun Bobby, K.K. Ravikumar, U.T.S. Pillai, B.C. Pai, Effect of Antimony and Yttrium Addition on the High Temperature Properties of AZ91 Magnesium Alloy. *Procedia Engineering* **55**, 98-102 (2013).
- [3] Yu'an Chen, Hao Liu, Ruiyu Ye, Guangqiong Liu, Effects of the addition of Ca and Sb on the microstructure and mechanical properties of AZ91 magnesium. *Materials Science and Engineering A* **587**, 262-267 (2013).
- [4] Hüseyin Sevik, Sezhat Açıkgöz, S. Can Kurnaz, The effect of tin addition on the microstructure and mechanical properties of squeeze cast AM60 alloy. *Journal of Alloys and Compounds* **508**(1), 110-114 (2010).
- [5] S. Candan, M. Unal, E. Koc, Y. Turen, E. Candan, Effects of titanium addition on mechanical and corrosion behaviours of AZ91 magnesium alloy. *Journal of Alloys and Compounds* **509**(5), 1958-1963 (2011).
- [6] N. Balasubramani, A. Srinivasan, U.T.S. Pillai, Effect of antimony addition on the microstructure and mechanical properties of AZ84 magnesium alloy. *Journal of Alloys and Compounds* **455**(1/2), 168-172 (2007).
- [7] A. Srinivasan, U.T.S. Pillai, B.C. Pai, Microstructure and mechanical properties of Si and Sb added AZ91 magnesium alloy. *Metallurgical and Materials Transactions A* **36**(8), 2235-2243 (2005).
- [8] K.Y. Nam, Dae Hyun Song, C.W. Lee, S.W. Lee, Yong Ho Park, Kyung Mox Cho, Ik Min Park, Modification of Mg₂Si Morphology in As-Cast Mg-Al-Si Alloys with Strontium and Antimony. *Materials Science Forum* **510-511**, 238-241 (2006).
- [9] G. Gumienny, Carbide Bainitic and Ausferritic Ductile Cast Iron. *Archives of Metallurgy and Materials* **58**(4), 1053-1058 (2013).
- [10] S. Pietrowski, T. Szymczak, Crystallization. microstructure and mechanical properties of silumins with micro-additions of Cr. Mo. W and V, *Archives of Foundry Engineering* **10**(1), 123-136 (2010).
- [11] R. Władysławski, Effect of water mist on cooling process of casting die and microstructure of AlSi11 alloy, *Archives of Metallurgy and Materials* **55**(3), 939-946 (2010).
- [12] B. Pisarek, Influence Cr on crystallization and the phase transformations of the bronze BA1044. *Archives of Foundry Engineering* **7**(3), 129-136 (2007).