

CORROSION OF THE WE43 AND MSR-B MAGNESIUM ALLOYS IN CO₂

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Preliminary Note – Prethodno priopćenje

The kinetics of WE43 and MSR-B magnesium alloys oxidation was tested in CO₂ atmosphere. The measurement of the oxidation speed was conducted with continuous thermo gravimetric method in the eutectic melting temperature (530 °C). This temperature has been defined with the differential scanning calorimetric (DSC) method. The corrosion products were analyzed with Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) methods. On the WE43 alloy the double layer scale is being created, with good protective properties. Under the scale layer the internal oxidation of the alloy takes place. The oxide layer on MSR-B alloy is thin and irregular.

Key words: corrosion, cast magnesium alloys, oxidation, structure, CO₂ atmosphere

INTRODUCTION

The magnesium alloys are usually being used in ambient temperature. However during the melting and casting the alloys are exposed to high temperature. This change the chemical properties and the condition of surface layer of the product [1 - 4]. It was found [5], that initial stadium of the magnesium reaction with oxygen proceed in three stages: chemisorptions of oxygen on the magnesium surface, creation and coalescence of oxide secretions, creation of compact oxide layer. Usually the Mg alloys are melted in protective gas layer (CO₂, SO₂, SF₆), in order to avoid the oxidation [6, 7]. Beryllium and calcium came out an effective elements, that increase the oxidation durability. It was found, that 3 - 8 ppm of beryllium may substantially increase the Mg alloys resilience to oxidation [8].

Fan and others [9] proven, that the addition of 0,3 wt. % of Ca causes the increase of combustion temperature of pure magnesium of 120 °C. However, despite high combustion temperature, actual Mg alloys with the beryllium and calcium additions hasn't found any use in the industry, because poor mechanical properties and toxicity of beryllium. Latest research shows, that yttrium may increase the oxidation resilience of Mg alloys and high mechanical properties. In order to create outside oxide layer Y₂O₃, the yttrium concentration in the alloy should be higher than 8 %, which increases the cost of the product [10].

The aim of the work, was to compare the corrosion resilience of WE43 and MSR-B magnesium alloys in the atmosphere that contains the carbon dioxide, in the temperature close to the eutectic melting temperature.

TEST MATERIALS AND METHODS

The corrosion tests were conducted on the WE43 and MSR-B magnesium alloys. The analyzed alloys differed with yttrium and silver content (Table 1).

Table 1 **Chemical analysis of the examined alloys /wt.%**

| Alloy | Y | Ag | Zr | RE | Mg |
|-------|-----|-----|-----|-----|------|
| WE43 | 4,3 | - | 0,3 | 3,4 | rest |
| MSR-B | - | 2,4 | 0,4 | 2,5 | rest |

RE - rare earth elements

The samples with the dimensions 10 x 2 x 15 mm were grinded on abrasive papers of 1 200 factor. The oxidation measurement were conducted with the use of thermo-weighing scale of Setaram. The reaction atmosphere was CO₂ (CO₂ consisted of 0,1 % CO). The gas flow speed was 1,2 l/h. The tests were conducted in the temperature of 530 °C, which is slightly below eutectic melting temperature. The eutectic temperature for the WE43 and MSR-B alloys is respectively 537 and 534

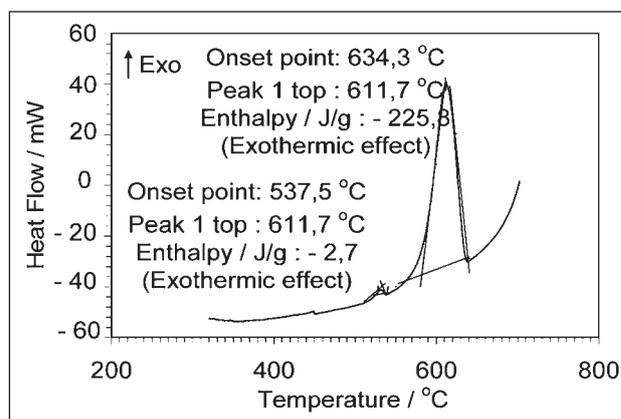


Figure 1 The DSC curve obtained during the cooling of WE43 magnesium alloy

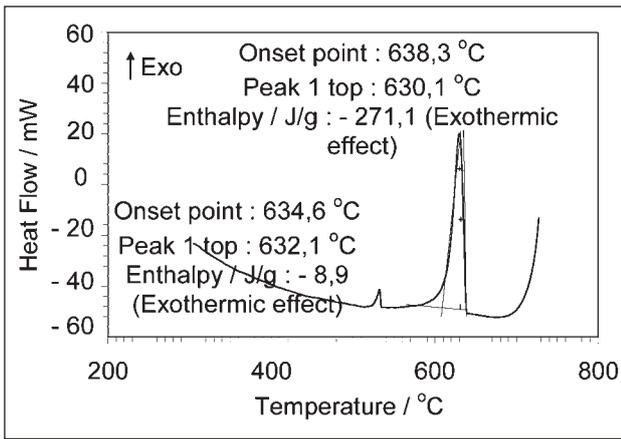


Figure 2 The DSC curve obtained during the cooling of MSR-B magnesium alloy

°C, and liquidus temperature 634 and 638 °C. The transformation temperatures were defined with the DSC method (Figures 1 and 2). The tests on the products of the corrosion were conducted with scanning electron microscope Hitachi S - 4200 and x-ray spectrometer with energy dispersion of Thermo Noran.

RESULTS AND DISCUSSION

The course of corrosion of the testes alloys has been shown in the Figure 3. The mass increment of WE43 alloy can be described with the parabolic function:

$$\left(\frac{\Delta m}{s}\right)^2 = k_p \cdot t$$

where:

$\left(\frac{\Delta m}{s}\right)$ – unitary mass increment after a time *t*,

k_p – constant of reaction speed, g² · cm⁻⁴ · s⁻¹.

The process of the MSR-B alloy corrosion is complicated. At the initial stage, the mass increase is insubstantial – around 0,5 mg. The morphology of created scale on the alloys is variable and depends on their chemical composition. On the outside surface of WE43 alloy there are the convexed areas and flat spaces with even corrosion process (Figure 4).

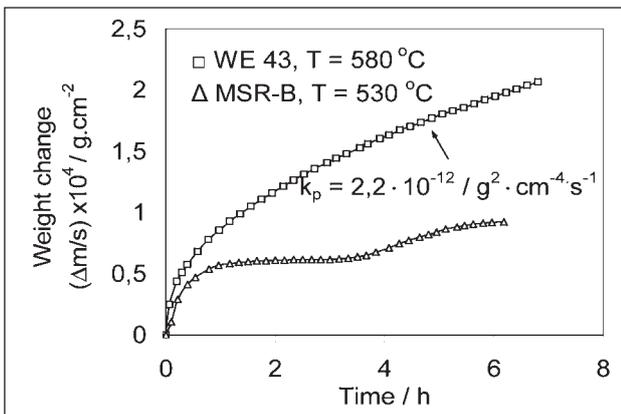


Figure 3 The kinetics of WE43 and MSR-B alloys oxidation in CO₂ (T = 530 °C)

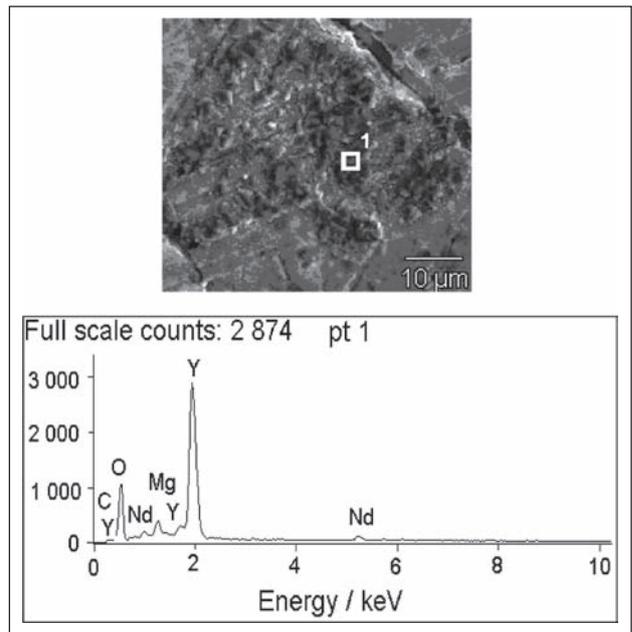


Figure 4 The morphology and chemical composition of the outer surface of the scale in the WE43 alloy after oxidation in CO₂ (T = 530 °C)

The thickness of the oxide layer is around 6 μm and is built on globular and elongated grains (Figure 5).

The yttrium and magnesium concentration in the outer layer is respectively 95,5 and 4,5 wt. %, and in the internal layer 99,1 and 0,9 %.

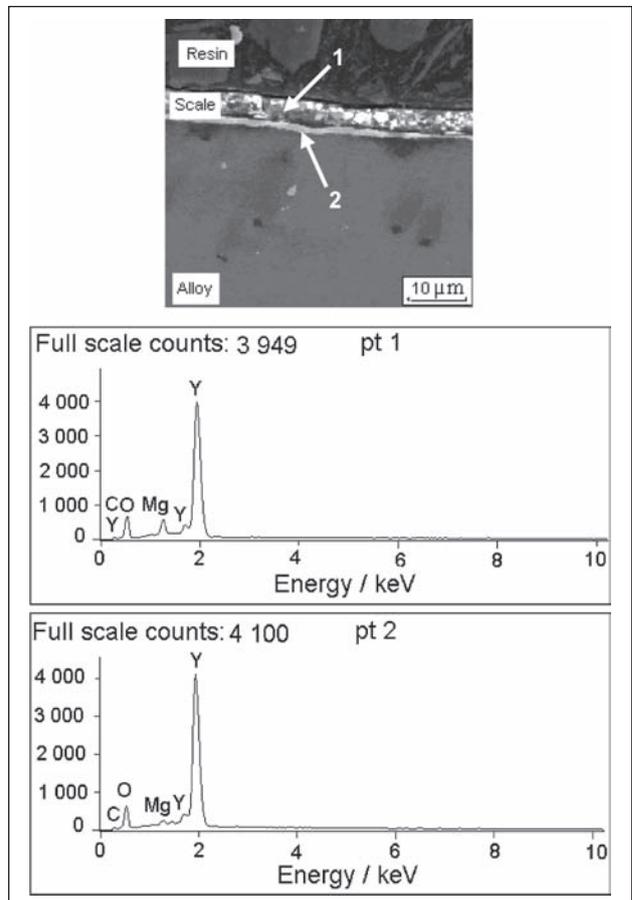


Figure 5 The cross section and chemical content of the scale on WE43 alloy after oxidation in CO₂ (T = 530 °C)

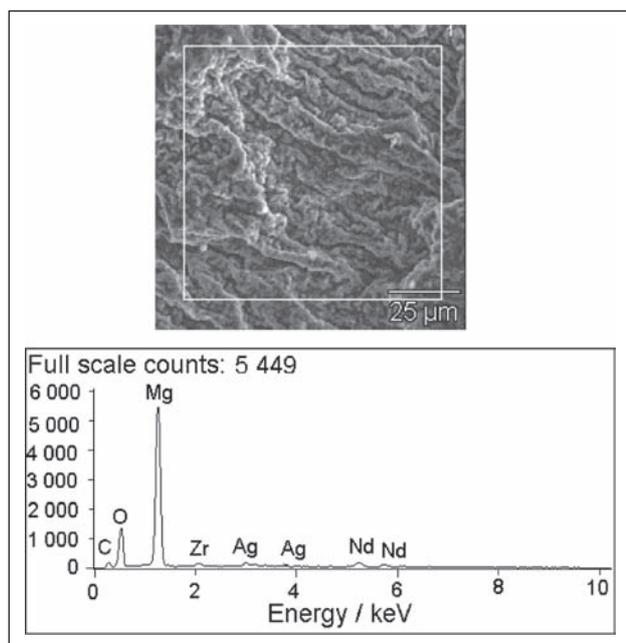
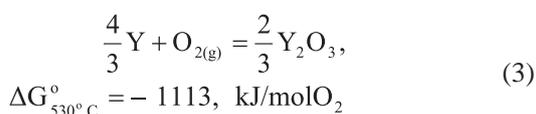
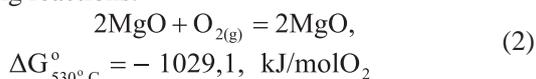


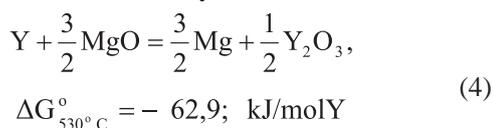
Figure 6 Morphology and chemical content of the outer surface of MSR-B alloy after oxidation in CO₂ (T = 530 °C)

Outside surface of the MSR-B alloy is strongly undulated (Figure 6). Under the discontinuous scale layer, the internal oxidation area is being created. The oxidized area has a form of vesicular cracks (Figure 7).

On the surface of WE43 alloy there are possible the following reactions:



There is also possible, the reaction of transformation of the magnesium oxide into yttrium oxide:



In the atmosphere of CO₂+0,1 % CO the equilibrium partial pressure of oxygen $p_{\text{O}_2} = 10^{-17}$ and is higher, than the decomposition pressure of the MgO and Y₂O₃ oxides. The value of the equilibrium pressure, calculated with the use of HSC software is respectively 10⁻⁶² and 10⁻⁷⁰ Pa. Therefore the reactions (2) and (3) can proceed. Similar mechanism of oxide layers creation on the magnesium alloys with yttrium has been shown in the [11]. From the change value of the Gibbs free energy, it comes, that initially magnesium and yttrium may oxidize at the same time. However, gradually the MgO oxide should dominate, as a result of faster diffusion of Mg²⁺ ions in comparison to Y³⁺ ions diffusion. The Mg²⁺ ions diffusion factor in MgO net is equal to:

$$1 \times 10^{-6} \exp(-150\,000 / RT), \text{ m}^2/\text{s} \text{ [12]},$$

and of Y³⁺ ions in Y₂O₃ oxide:

$$1 \times 10^{-9} \exp(-300\,000 / RT), \text{ m}^2/\text{s} \text{ [13]}.$$

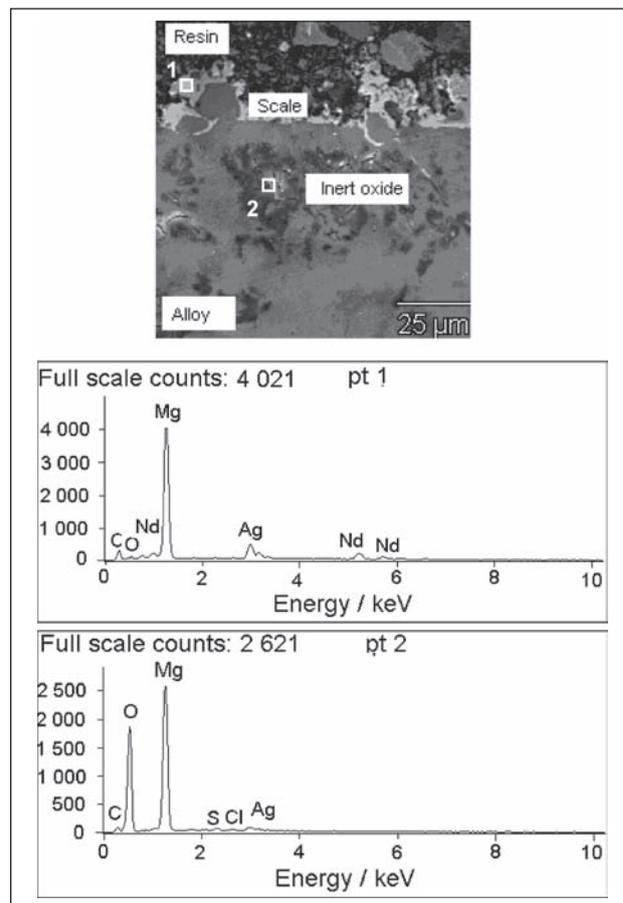
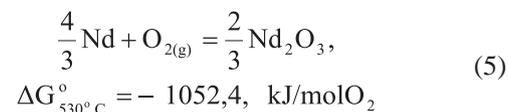


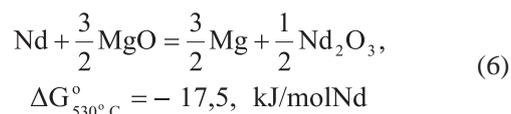
Figure 7 Cross section and chemical content of MSR-B alloy, after oxidation in CO₂ (T = 530 °C)

Hence, in the temperature of 530 °C $D_{\text{Mg}} = 1,7 \cdot 10^{-16}$, and $D_{\text{Y}} = 3 \cdot 10^{-26}$ m²/s. Selective oxidation of magnesium may aid the reduction of MgO oxide by Y (reaction 4). As per Wang [14] the yttrium oxide has better protective properties than magnesium oxide. The mixture of MgO and Nd₂O₃ oxide creates inconsistent, porous layer (Figure 7).

Therefore it is possible, that the oxidizer will dissolve in the alloy, creating areas of internal oxidation. The presence in the neodymium layer shows the possibility of creation of the Nd₂O₃ oxide, as a result of the reaction:



and



In the [15] it was ascertained, that the addition of neodymium changes the oxidation kinetics from linear function to parabolic, increasing the oxidation resilience. The equilibrium concentration of neodymium can be calculated from the formula (7):

$$\Delta G_{530^\circ\text{C}}^\circ = -RT \ln \frac{a_{\text{Mg}}^{3/2}}{a_{\text{Nd}}} \quad (7)$$

(in order to simplify, the activity of Mg was substituted with molar fraction).

In the temperature of 530 °C the concentration is around 6 %wt. Since in the alloy the Nd concentration hasn't exceeded 2%wt, initially the magnesium oxidize before the neodymium. If the concentration would be higher than equilibrium, then the Nd₂O₃ oxide will be created. It was also proven [16], that despite the presence of diffusion barrier, being the Nd₂O₃/MgO oxides, it's role in decreasing the core diffusion of Mg²⁺ cations is limited, especially in high temperature.

CONCLUSIONS

- Corrosion of WE43 alloy in carbon dioxide, in temperature of 530 °C proceeds with parabolic increasing speed. In the same conditions of reaction the corrosion process of MSR-B alloy is more complex and noncompliant to parabolic law.
- Scale created on WE43 alloy, that consist mainly of yttrium and magnesium oxide is a barrier for corrosion processes. The oxide layer on MSR-B alloy is created of magnesium and neodymium oxides. The internal oxidation process occurs.

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Note: The responsible translator for English language is Aleksandra Nowak-Szlabun, Zabrze, Poland