

# Modification of Surface Behaviour of Magnesium Alloys – Mg-Y System

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## Abstract

Magnesium has potentially wide industrial applications, its low density being the driving force behind the recent surge of interest. Magnesium alloying is required for engineering applications, and the nature of the alloys' surface is of importance. The aim of this project is to develop a detailed understanding of the influence of specific alloying elements on the oxidation and electroplating behaviour of magnesium alloys.

Yttrium is a rare earth metal suitable for alloying due to its ability to inhibit reactivity of molten magnesium and to enhance its corrosion resistance. The surface properties of magnesium-rich Mg-Y alloys, cast under ambient conditions, are influenced by yttrium content. At low yttrium contents (0.05 and 0.2 wt. %), magnesium and yttrium oxides coexist in the surface region. The surface of Mg-1.0Y alloy predominantly consists of a robust layer of  $Y_2O_3$ , and preferential oxidation of yttrium in this alloy results in the formation of Mg-depleted surface region. Yttrium alloying affects depth distribution of carbon in the surface region.

This work is part of an ongoing study into the effect of alloying elements on surface properties of magnesium, and its results will be explored further with regard to corrosion resistance.

## Introduction

The nature of the alloys' surface is important in many practical applications. Alloying magnesium (Mg) with yttrium (Y) appears beneficial due to its ability to inhibit reactivity of molten magnesium and to enhance its corrosion resistance.

Another notable aspect is the effect of carbon dioxide on surface phenomena. Recent studies observed the inhibitive effect of carbon dioxide on long-term corrosion of pure magnesium [1]. Microscopic studies revealed that ambient concentrations of carbon dioxide contribute to the corrosion resistance of magnesium in air due to the formation of magnesium hydroxy-carbonate films. A similar inhibitive effect was reported for the case of NaCl-induced corrosion of magnesium alloys as well as for corrosion of AZ91 alloy [2].

Despite these insightful investigations, there is a limited amount of data on the composition of surface region and the control thereof. This study provides a concise description of surface properties of cast Mg-Y alloys. The analysis is focused on the sub-surface region of up to 8 nm, and particular emphasis is placed upon carbon content. X-ray photoelectron spectroscopy is used as a main investigative tool.

## Experimental Procedure

XPS spectra were obtained using a Kratos AXIS Ultra spectrometer equipped with a monochromatized X-ray source (Al K $\alpha$ ). The XPS depth profiling was carried out using 4.75 keV Ar<sup>+</sup> ions. Background subtraction and quantification of wide spectra was performed using CasaXPS software. The sputter time-distance conversion is given in Ref. [3]. Table 1. gives nominal composition of the alloys tested and results from the chemical analysis.

Table 1. Nominal composition of alloys tested.

Nominal Composition	Y content (chem. analysis)
Mg	0
Mg-0.05Y	0.06
Mg-0.2Y	0.13
Mg-1.0	0.83

The alloys were cast in the ambient atmosphere at room temperature. Preparation of Mg-1.0Sr alloy was carried out in a vacuum-casting furnace (Leybold-Heraeus) controlled by Induction generator. Casting was carried out in Ar (99.999%) under atmospheric pressure.

## Results and Discussion

Yttrium content in the surface region of selected Mg-Y alloys is presented in Fig. 1, which shows that it is significantly affected by its concentration. The yttrium content is higher than the nominal composition of the bulk for all three alloys investigated. In particular, the surface of Mg-1.0Y alloy appears to be dominated by yttrium. These data show that visual changes in the alloys' surface (Fig. 2) are due to surface enrichment of yttrium.

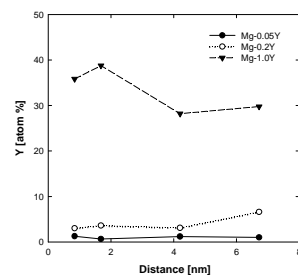


Fig. 1. Atomic concentration of yttrium vs. distance.

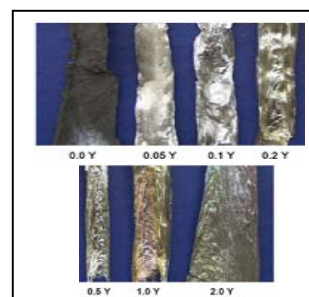


Fig. 2. Surface of cast Mg-Y alloy series (wt.% Y).

Thermodynamical consideration supports these observations. The Gibbs free energy, given as a function of atomic concentration of yttrium (Fig. 3), confirms the favourable formation of  $Y_2O_3$ . At melting temperature of Mg in the ambient atmosphere, concentration of Y as low as  $3.5 \times 10^{-7}$  at. % is needed to obtain positive Gibbs energy. As a control experiment, we prepared a Mg-0.05Y alloy by casting in argon. XPS spectra of such alloys showed a conspicuous absence of Y.

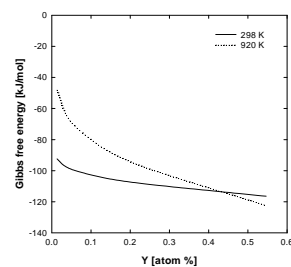


Fig. 3. Gibbs free energy vs. yttrium concentration in Mg-Y alloy.

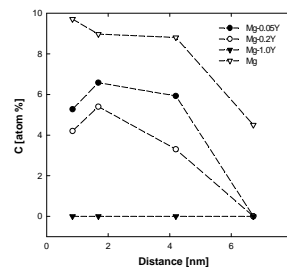


Fig. 4. Atomic concentration of carbon vs. distance in surface region of Mg-Y alloys.

The amount of carbon in the surface region of Mg-Y alloys is given in Fig. 4. It shows that carbon content gradually decreases with distance, and the addition of Y decreases the amount of carbon species. Thermodynamic treatment supports carbon uptake from carbon dioxide in air. Fig. 5 shows the variation of  $CO_2$  pressure with temperature. All points on the lines represent the unique  $CO_2$  pressure required for maintenance of relevant equilibria.

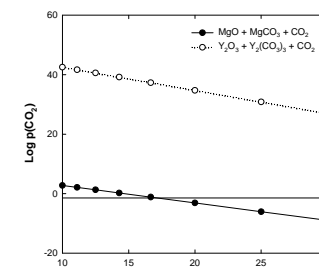


Fig. 5. The variation of the  $CO_2$  pressure needed for maintenance of the equilibria  $MgO(s) + CO_2(g) \rightarrow MgCO_3(s)$ , and  $Y_2O_3(s) + CO_2(g) \rightarrow Y_2(CO_3)_3(s)$ . The horizontal line indicates atmospheric levels of  $CO_2$ .

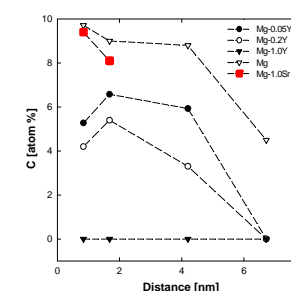


Fig. 6. Atomic concentration of carbon vs. distance for pure magnesium, Mg-Y series, and Mg-1Sr alloy.

If the actual  $CO_2$  partial pressure is greater than the equilibrium pressure, the carbonate is stable, while below the equilibrium line  $CO_2$  and oxides are more stable. Clearly, as cooling occurs, formation of  $MgCO_3$  (thence, carbon uptake) is favoured. The reaction of formation of  $Y_2(CO_3)_3$  is very unfavourable under ambient conditions, which accounts for the absence of carbon species in Y-dominated surfaces.

To provide further support for the effect of yttrium on carbon distribution, we examined carbon distribution in Mg-1Sr alloy prepared in exactly the same manner (Fig. 6). The carbon content in Mg-1Sr alloy is similar to that found for pure magnesium. This is attributed to the position of the equilibrium line of strontium carbonate, which lies close to  $MgCO_3$ , thus favouring carbon uptake.

## Conclusions

- The surface chemistry of Mg-Y alloys is affected by nominal concentration of Y.
- Whereas MgO and  $Y_2O_3$  coexist in the surface of alloys with a low yttrium content, higher nominal concentrations (approx. > 1 wt.%) result in the formation of Y-dominated surfaces and magnesium-depleted sub-surface region.
- Yttrium alloying affects depth distribution of carbon in the surface region of magnesium. Pure magnesium and low-yttrium-content Mg-Y alloys contain carbonate species confined to the outermost surface region of approx. 7 nm.
- These results clearly demonstrate that alloying enables to control the surface composition and to 'fine-tune' the amount of carbon in the surface region of magnesium alloys.

## References

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