



ENGINEERING
NOVEL-RESULT
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XPS and Electron Microscopy Study of Oxide-Scale Evolution on Ignition Resistant Mg-3Ca Alloy at Low and High Heating Rates

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Abstract

Earlier work by the authors suggested that the formation of molten eutectic regions in Mg-Ca binary alloys caused a discrepancy in ignition temperature when different heating rates are used. This effect was observed for alloys where Ca content is greater than 1 wt%. In this work, the effect of two heating rates (25 °C/min and 45 °C/min) on the ignition resistance of Mg-3Ca is evaluated in terms of oxide growth using X-ray Photoelectron Spectroscopy. It is found that the molten eutectic regions develop a thin oxide scale of ~100 nm rich in Ca at either heating rate. The results prove that under the high heating rate, solid intermetallics are oxidized forming CaO nodules at the metal/oxide interface that eventually contribute to the formation of a thick and non-protective oxide scale in the liquid state.

1. Introduction

The development of ignition-resistant magnesium (Mg) alloys for cabin components of commercial planes has gained a renewed interest since their ban was lifted in an update of the SAE aerospace standard AS8049C (Gwynne, 2015) in 2014. The use of Ca to increase ignition resistance has been particularly preferred for both commercial and experimental alloys (Sakamoto et al., 1997; Shih et al., 2004; Tekumalla & Gupta, 2017; Villegas-Armenta & Pegguleryuz, 2020). However, some underlying mechanisms such as the sensitivity of ignition temperature (T_i) to heating rate and the effect of microstructure evolution have been missing. The main factor driving ignition resistance, is the slowing down of Mg oxidation, which increases the surface temperature drastically and leads to Mg vaporization and ignition. An earlier study by the authors (Villegas-Armenta et al., 2020) has found that the T_i of Mg-2wt%Ca and Mg-3wt%Ca alloys were affected by heating rate, with little to no effect on pure Mg and Mg-1wt%Ca. The results showed that, unlike observations on biomass materials (Cai et al., 2018; Huang et al., 2018; Mishra & Mohanty, 2018), where a low heating rate leads to longer oxidation times and low ignition temperature, the low heating rate in binary Mg-2wt%Ca and Mg-3wt%Ca alloys leads to a high ignition temperature. The longer time elapsed allowed the formation of molten eutectic pools covering the alloy surface, which are resistant to oxidation. A high heating rate quickly oxidizes Ca, which forms a protective scale at first,

but becomes crack-prone upon thickening and leads to extensive Mg oxidation, vaporization and early ignition. In this paper, we present a complementary analysis of the oxide scale growth on a Mg-3Ca alloy during continuous heating. Two heating rates, which exhibited very drastic differences in ignition behavior, were studied.

2. Methods

A Mg-3Ca binary alloy was synthesized by permanent mold cast as per the method presented in (Villegas-Armenta *et al.*, 2020). Likewise, details of sample preparation and the interrupted continuous heating tests were presented in the same work (Villegas-Armenta *et al.*, 2020). Two different continuous heating rates were used for the interrupted tests: 25 °C/min (Low Heating Rate – LHR) and 45 °C/min (High Heating Rate – HHR). The tests were interrupted at 350 (solid), 560 (semi-solid) and 700 (liquid) °C. The chemical composition of the Mg-3Ca alloy was determined by the NADCAP certified laboratory Genitest Inc *via* Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The resulting composition was (in wt%): 2.98 Ca, 0.005 Mn, 0.006 Al, 0.003 (Cu, Ni, Si) and balance Mg. Characterization was carried out using a SU3500 Hitachi Scanning Electron Microscope (SEM), a Thermo Scientific K-Alpha X-ray Photoelectron Spectroscopy (XPS) and a FEI Tecnai G² F20 200 kV Cryo-Scanning Transmission Electron Microscope (TEM). TEM samples were extracted using a FIB-SEM Helios Nanolab 660 DualBeam. Additionally, the software CrysTBox (Klinger, 2017) was used as an auxiliary tool to define the diffraction patterns.

3. Results

Fig. 1 presents the heating curves Mg-3Ca samples obtained at HHR and LHR. The T_i for Mg-3Ca alloy measured previously by the authors (Villegas-Armenta *et al.*, 2020) is also indicated in Fig. 1 for both heating rates. Fig. 2 shows the oxide scale evolution analyzed through XPS at each interrupted test. The vertical red dotted line describes the etch level at which the Mg metallic signal in the Mg KLL region was detected. This is considered to be the metal/oxide interface. Fig. 3 shows the surface of both HHR and LHR samples at 560 °C. At this stage (semi-solid state) samples start displaying significant microstructural differences. The LHR sample show a widespread covering of molten and

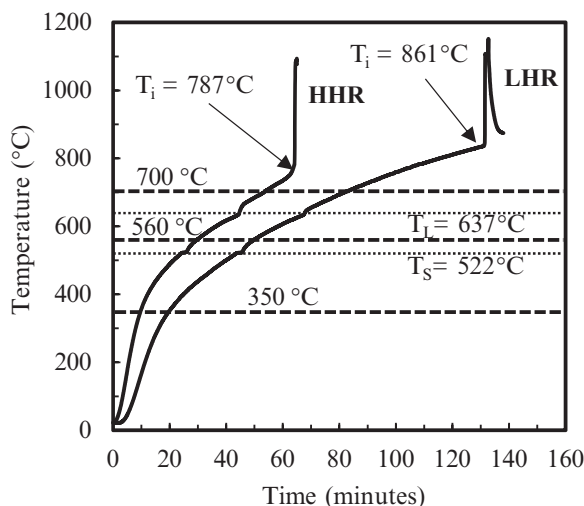


Fig. 1. Ignition curves of the Mg-3Ca alloy heated using a HHR and a LHR. The liquidus and solidus temperatures are indicated as thin dotted lines. The interrupted ignition test lines are indicated as thick dotted lines.

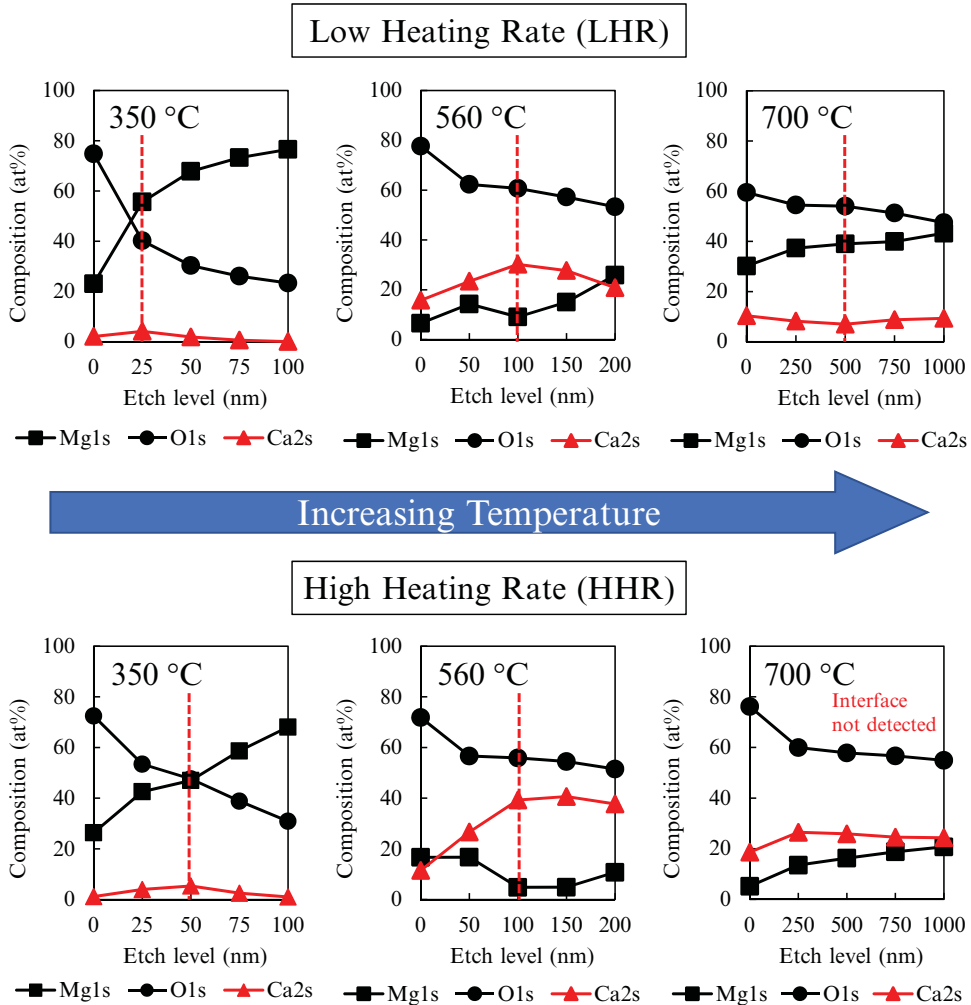


Fig. 2. XPS surface analysis of the HHR and LHR. Samples interrupted at 350, 560 and 700 °C. The red dotted line represents the approximate position of the metal/oxide interface.

re-solidified eutectic phases while the HHR shows a more restricted covering along with internally oxidized CaO-rich nodules coming from remaining solid intermetallics. The small micrographs on the upper right corner of each image show the cross sections extracted through FIB that were analyzed using TEM. In Fig. 4, the SAED patterns confirmed that the re-solidified intermetallics are in fact Mg₂Ca using either heating rate, while the oxide scale over them is thin (80 to 110 nm) and rich in CaO with apparently no MgO being formed.

XPS results indicate that Ca tends to be higher at the metal/oxide interface for both heating rates with a similar approximate thickness. For the HHR however, the Ca content increases significantly in the semi-solid and liquid stages, confirming the previously exposed theory of profuse Ca oxidation being the driving force for early ignition (Villegas-Armenta et al., 2020). The re-solidified regions in the semi-solid state have the same characteristics regardless of the heating rate used. CaO nodules are formed from the solid intermetallics that oxidize in the HHR sample. In the LHR sample, the slower heating allows the partial melting of the interdendritic regions instead of their localized oxidation.

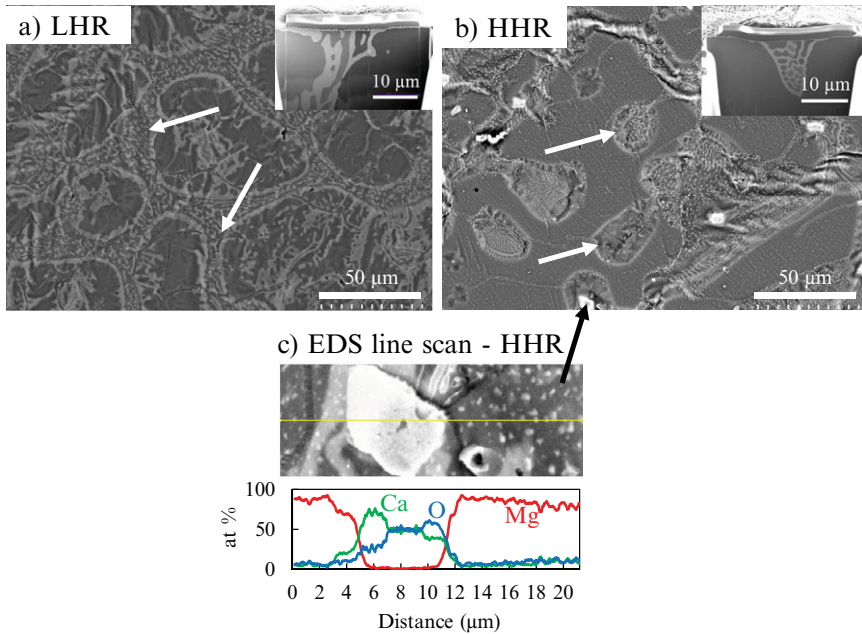


Fig. 3. SEM micrographs of the sample surface in the semi-solid state (560 °C) (a) LHR; (b) HHR. (c) EDS line scan of one of the oxide nodules observed in the HHR sample.

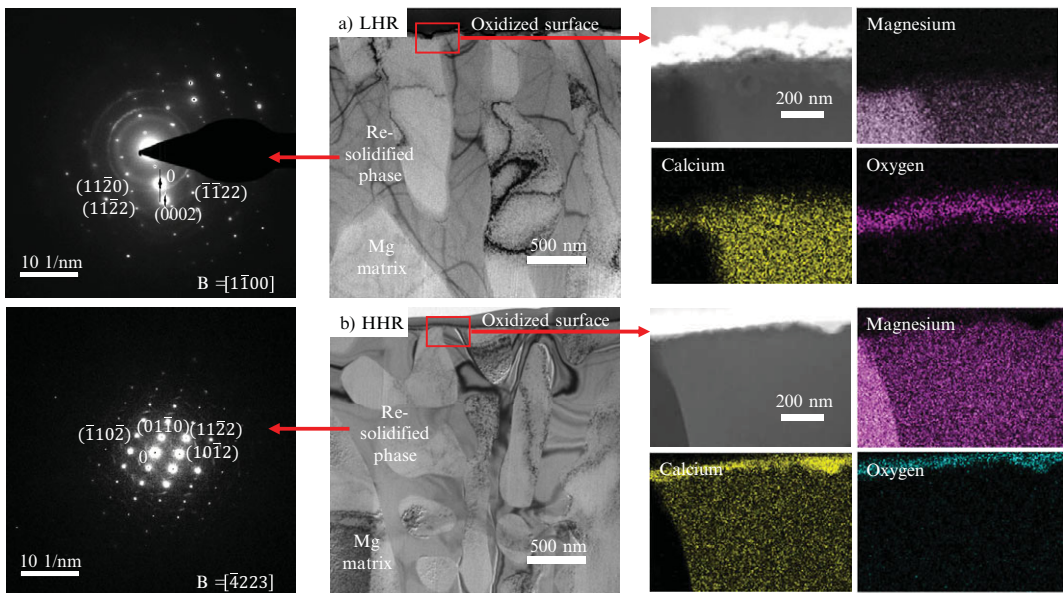


Fig. 4. TEM bright field images of FIB-extracted cross-sections for (a) LHR and (b) HHR. SAED pattern (left) of the re-solidified phase and EDS map (right) of the oxidized surface.

4. Conclusions

The present work confirmed the observations made previously by the authors; using XPS surface analysis to study the oxide scale growth of Mg-3Ca alloy during ignition testing indicate that Ca concentrates at the metal/oxide interface. Despite both samples having similar characteristics regarding oxide

characteristics and re-solidified phases in the semi-solid state, the internally oxidized CaO nodules in the HHR sample promote the formation of a thick oxide scale prone to cracking once the liquid state is reached.

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Author contributions. L.A. Villegas-Armenta, M.O. Pekguleryuz and R.A.L Drew conceived and designed the study. L.A. performed the experimental work. L.A. Villegas-Armenta wrote the article while M.O. Pekguleryuz and R.A.L Drew reviewed and improved the contents.

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Conflicts of Interest. L.A. Villegas-Armenta, R. A. L. Drew and M. O. Pekguleryuz declare none.

Data availability statement. The data that support the findings of this study are available by contacting the corresponding author of this publication, upon reasonable request.

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Peer Reviews

Reviewing editor: Dr. Eva Unger

Lund University, Lund, Sweden, 221 00

This article has been accepted because it is deemed to be scientifically sound, has the correct controls, has appropriate methodology and is statistically valid, and has been sent for additional statistical evaluation and met required revisions.

doi:10.1017/exp.2020.41.pr1

Review 1: XPS and Electron Microscopy Study of Oxide-Scale Evolution on Ignition Resistant Mg-3Ca Alloy at Low and High Heating Rates

Reviewer: Ali Arslan Kaya 

Date of review: 10 July 2020

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Conflict of interest statement. Reviewer declares none.

Comments to the Author: This is a useful work clarifying some important details of the generally known effect of Ca on the ignition resistance of Ca-containing magnesium alloys. Presenting further details, such as the microstructures prior to ignition tests and a comparison with those after the ignition tests were undertaken, would have added further value to the work. There exist a good spectrum of literature work on the effect of Ca addition to Magnesium. The reference list of this work may be considered somewhat short in benefiting from those reported works of others.

Score Card

Presentation



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Is the conclusion consistent with the results and discussion? (40%)

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Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)

3/5

Review 2: XPS and Electron Microscopy Study of Oxide-Scale Evolution on Ignition Resistant Mg-3Ca Alloy at Low and High Heating Rates

Reviewer: Dr. Yuan Chunmiao 

Date of review: 12 July 2020

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Conflict of interest statement. Reviewer declares none

Comments to the Author: This paper gives experimental results on the oxide-scale evolution of Mg-3Ca Alloys. Different heating rates were discussed based on the XPS and SEM/TEM results. All conclusions made in the paper are well supported by the data presented. A minor revision is suggested before its publication.

1) The heating rate is the unique variable in this study, but only two heating rates were considered in this manuscript. Is this enough to draw a convincing conclusion?

2) Some studies (see references) indicated the lower heating rate may result in a lower ignition temperature for biomass materials due to much longer heating time and a much slower process of oxidation. This is contrary to the result in Fig. 1. It would be better to give more explanation on the ignition mechanism of Mg alloy.

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Huang, J., Liu, J., Chen, J., Xie, W., Kuo, J., Lu, X., Chang, K., Wen, S., Sun, G., Cai, H., Buyukada, M., Evrendilek, F., 2018. Combustion behaviors of spent mushroom substrate using TG-MS and TG-FTIR_ Thermal conversion, kinetic, thermodynamic and emission analyses. *BIORESOURCE TECHNOLOGY* 266, 389–397.

Score Card

Presentation



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Context



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Is the objective of the experiment clearly defined? (25%)

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Analysis



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Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)

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