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**Mechanical properties and corrosion behaviours of the as-cast ZK40 alloys
modified with individual additions of CaO, Gd, Nd and Y**

São Carlos

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Orientador: Prof. Dr. Haroldo Cavalcanti Pinto

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RESUMO

BUZOLIN R. H. Propriedades mecânicas e comportamento à corrosão de ligas fundidas ZK40 modificadas com adições individuais de CaO, Gd, Nd e Y. 100p. Dissertação (Mestrado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2016.

O efeito da adição individual de óxido de cálcio (CaO), Gd, Nd e Y foi investigado na microestrutura, propriedades mecânicas e resistência à corrosão de ligas ZK40 fundidas. As características microestruturais foram analisadas via microscopia óptica, microscopia eletrônica de varredura, microscopia eletrônica de transmissão, difração de Raios-X e “Scanning Kelvin Atomic Probe Force Microscopy”. O comportamento à compressão e à tração das ligas à temperatura ambiente foi investigado. Espectroscopia eletroquímica de impedância, evolução de hidrogênio e ensaios de imersão em solução de 0.5% em peso de NaCl foram utilizados para avaliar a resistência à corrosão. Os resultados dos ensaios mecânicos e corrosão foram relacionados com a microestrutura. A adição de 2% em peso de Gd melhorou a ductilidade, ao passo que a adição de Nd resultou na piora das propriedades mecânicas. A adição de 2% em peso de Gd e 1% em peso de Y resultou na melhora da ductilidade. A adição de 1% em peso de Y causou uma melhora na ductilidade e a adição de CaO não teve impacto benéfico nas propriedades mecânicas. A resistência à corrosão foi melhorada com a adição de CaO e Gd. A modificação da liga ZK40 com a adição de Gd abre novas perspectivas no desenvolvimento de ligas Mg-Zn.

Palavras-chave: Ligas de Magnésio, Mg-Zn-Zr, Gd, Nd, Y, CaO, terras raras, corrosão, propriedades mecânicas.

ABSTRACT

BUZOLIN R. H. Mechanical properties and corrosion behaviours of the as-cast ZK40 alloys modified with individual additions of CaO, Gd, Nd and Y. 100p. Dissertação (Mestrado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2016.

The effect of individual additions of calcium oxide (CaO), Gd, Nd and Y was investigated on the microstructure, mechanical properties and corrosion resistance of the as-cast ZK40 alloy. The microstructural features were analysed using optical, scanning and transmission electron microscopy, X-ray diffraction and Scanning Kelvin Atomic Probe Force Microscopy. The compressive and tensile behaviours of the as-cast alloys at room temperature were investigated. Electrochemical Impedance Spectroscopy, hydrogen evolution and weight loss under immersion in 0.5 wt.% NaCl solution were used to evaluate the corrosion behaviour. The results of the mechanical and corrosion tests were correlated with the microstructures. The 2 wt.% Gd addition enhanced the ductility, while the Nd addition resulted in deterioration in mechanical properties. The addition of 2 wt.% Gd and 1 wt.% Y resulted in the improvement of the ductility. The addition of CaO did not affect the mechanical properties while the 2 wt.% Nd deteriorate it. The 1 wt.% Y addition enhanced the ductility. The CaO addition did not caused enhancement in mechanical properties. The corrosion behaviour was enhanced with the addition of CaO and Gd. The modification of ZK40 with Gd opens up new perspectives in the development of Mg-Zn based alloys.

Keywords: Magnesium alloys, Mg-Zn-Zr, Gd, Nd, Y, CaO, rare earth, corrosion, mechanical properties, effect of minor additions

Publications List

As result of this work and other investigations that I have performed during my masters concerning the ZK40 alloys modified with CaO, Gd, Nd and Y, four papers were produced and are find attached in the following pages.

Investigation of compression behavior of Mg-4Zn-2(Nd,Gd)-0.5Zr at 350°C by *in situ* synchrotron radiation diffraction

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Keywords: ZK40, RE additions, deformation behaviour, *in situ*, synchrotron radiation

Abstract

As-cast Mg-4Zn-0.5Zr, Mg-4Zn-2Gd-0.5Zr and Mg-4Zn-2Nd-0.5Zr alloys were investigated by *in situ* synchrotron radiation diffraction during hot compression at 350 °C using the facilities of P07 beamline of Petra III at Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany. The specimens were heated at a rate of 100 K/min and compressed with an initial strain rate of $1.1 \times 10^{-3} \text{ s}^{-1}$ up to 30 % strain. The addition of rare earth elements improved the yield strength from 23 MPa in the Mg-4Zn-0.5Zr alloy up to 40 MPa in the alloy with Nd and Gd. Continuous dynamic recrystallization played an important role in the Mg-4Zn-0.5Zr alloy during deformation and twinning was not dominant. Discontinuous dynamic recrystallization occurred in the Mg-4Zn-0.5Zr alloy as well as the Mg-4Zn-2Gd-0.5Zr. In the Mg-4Zn-2Gd-0.5Zr and Mg-4Zn-2Nd-0.5Zr alloys the contribution of twinning to deformation was observed at 350 °C. Reasons for these differences will be discussed with respect to microstructures of the alloys.

Introduction

The increased demand from the automotive industry for weight reduction and more environmentally-friendly materials, with a view to reduce exhaust gases, has initiated research in the field of lightweight materials, especially in Mg alloys [1]. Significant research is still needed on processing, alloy development, joining, surface treatment, corrosion resistance and mechanical properties improvement of Mg alloys.

Conventional magnesium alloys exhibit poor formability at ambient temperatures [2], due limited number of independent active slip systems available at room temperatures to allow an arbitrary shape change. Even though Mg alloys display some plasticity at room temperature, especially with a finer grain size and through solute additions, [2], wrought processing, such as extrusion, rolling or forming are problematic at room temperatures. Therefore, higher temperatures (>225 °C) have been used to deform Mg alloys, at which non-basal slip and deformation twinning can be activated [3].

Wu et al. [4] investigated the compression behaviour of ZK60 Mg alloy at different temperatures and found out that 250-350 °C was the most suitable range of temperature for the ZK60 alloy. The microstructure was more homogeneous at this range of temperature and exhibited almost no twins with hot compression

temperature greater than 350 °C. 350 °C is a typical extrusion temperature for ZK alloys [2], thus understanding the deformation behavior of the ZK based alloys at 350°C is of importance for future alloy development.

ZK alloys are one of the high strength wrought magnesium alloys that are commercially available and are also used in the cast form. The addition of Rare Earth (RE) elements to these alloys [5] results in improved castability and elevated temperature strength [6]. RE additions refine grain size mainly due to constitutional supercooling [7]. Furthermore they weaken the anisotropy thus improve the ductility of Mg alloys [8]. Therefore, Mg-Zn-RE-Zr system is of great interest for research.

In situ high energy X-ray diffraction (HEXRD) is a unique method to investigate the dynamic microstructural processes during mechanical loading in the bulk of the materials [9]. Azimuthal-angle vs. Time plots (AT-plots) hold information about grain size evolution, grain imperfection, grain rotation, and grain orientation relationships, texture evolution, that can be correlated with crystallographic and dislocation slip, sub-grain formation, twinning, recrystallization, recovery and grain growth, which are the responsible physical processes for the microstructural changes [9].

The present work investigates the influence of Gd and Nd addition on the compression behaviour of the ZK40 alloy combining *in-situ* radiation synchrotron study, which provides new insights into the real-time evolution of the microstructure, and electron backscattered diffraction (EBSD) in order to study the deformed structure.

Experimental Procedures

The alloys were prepared by permanent mould direct chill casting [10] and the actual chemical composition is listed in Table 1. The Gd was added as an Mg-4 wt.%Gd alloy. The Nd was added as pure element. The melt was held at 750 °C for 10 min and then poured into a mould preheated to 660 °C and held for another 15 min in another furnace at 660 °C for final cooling with water. The permanent mould direct chill casting procedure was used for a homogeneous distribution of alloying additions. The specimens for the *in situ* compression were machined with 5 mm diameter and 10 mm length.

Figure 1: Optical micrographs typical of as-cast (a) ZK40; (b) ZK40-2Gd; (c) ZK40-2Nd.

For metallographic characterization of the as-cast and the deformed samples, they were mounted in epoxy and ground using SiC paper down to 2500 grit and then polished using 3 µm diamond solution. OPS solution with 1 µm diamond suspension was used as the last step of polishing. The specimens for optical microscopy (OM) were etched with acetic-picral solution and the specimens for EBSD were washed with 0.5 vol% nitric acid in ethanol solution for 5 seconds.

The optical analyses were performed using the light optical microscopy Leica DMI 5000. The SEM used was a Zeiss FEG-SEM Ultra 55 attached with a Hikari detector and a TSL-OIM software package for EBSD analysis. The measurements were performed at a voltage of 15 kV using a working distance of 13 mm and an area of 80 µm x 80 µm using a step size of 0.1 µm. The maps were measured in the centre of the deformed specimen to ensure a similar area to that measured during diffraction analysis.

In-situ synchrotron high energy X-ray diffraction has been performed using the facilities of DESY (Deutsches Elektronen-Synchrotron) at P07 – Petra III with a beam having an energy of 100 keV ($\lambda=0.124$ nm) and a cross section of 1.0 mm x 1.0 mm. Diffraction patterns were recorded at a frame rate of 1/s by a PerkinElmer 1621 flat panel detector (200 µm x 200 µm) which was placed at a distance of 1535 mm from the specimen position. The acquisition time was 1.0 s. the detector to sample distance was calibrated with a LaB₆ standard powder sample and the software Fit2D[®] was used for evaluating the data.

The compression specimens were mounted into a chamber of a dilatometer DIL 805A/D (TA Instruments, Hüllhorst, Germany), combined with an induction coil modified so the beam can pass through the sample [11]. The specimens were heated to the intended temperature (350 °C) at a rate of 30 °C s⁻¹ and held at this temperature for 3 min before the compression started. The specimens were compressed with a constant deformation speed of 0.01 mm s⁻¹ and the tests were carried out up to 0.3 of strain. The Debye-Scherrer rings were then analysed using Fit2D software and treatment into azimuthal-angle vs. time plots (AT-plots) plots was undertaken using ImageJ[®] software.

Results

The optical micrographs of the as-cast ZK40, ZK40-2Gd and ZK40-2Nd alloys are presented in Figure 1. The ZK40 and the ZK40-2Gd alloys exhibited cellular structures whereas the ZK40-2Nd showed a more pronounced dendritic structure. The ZK40-2Gd alloy exhibited a heterogeneous microstructure with coarse grains surrounded by fine grains. For the ZK40-2Gd and ZK40-

2Nd alloys the intermetallic phases were semi-continuously distributed along the grain boundaries, whereas the ZK40 had small eutectic compounds along the grain boundaries.

Table 1: The chemical compositions of the alloys investigated.

Chemical Composition				
Alloys	Gd %wt	Nd %wt	Zn %wt	Zr %wt
ZK40	-	-	5.00	0.53
ZK40-Gd	1.70	-	4.50	0.55
ZK40-Nd	-	2.35	4.60	0.50

The true stress-strain curves for the *in situ* compression tests are shown in Figure 2. ZK40 exhibited a 0.2% proof stress of 23 MPa and a maximum stress of 28 MPa. For the ZK40-2Gd alloy and ZK40-2Nd alloy, an increase in both the 0.2% proof stress and the maximum stress was observed. For the ZK40-2Gd alloy maximum stress and 0.2% proof stress were 56 and 40 MPa respectively and for ZK40-2Nd alloy they were 47 MPa and 39 MPa, respectively. In addition, the alloys modified with Gd or Nd show softening after reaching the maximum stress.

Figure 2: Compressive true stress strain curves alloys investigated at 350°C

The Debye-Scherrer rings recorded during the *in situ* synchrotron radiation compression tests were converted into azimuthal/time plots to investigate the phenomena that are ongoing during the deformation and are shown in Figure 3. The planes of interest were the {11 $\bar{2}$ 0} and the {10 $\bar{1}$ 3} as twinning can be observed comparing the timelines evolution for these planes. Figures 3 (a), 3 (b) and 3 (c) display the AT-plots for the ZK40, ZK40-2Gd and

ZK40-2Nd, respectively. Blurring of the timelines after the initial stages of compression is observed for the ZK40 alloy. The ZK40-2Nd alloy differs at the initial stages, where thicker timelines can be observed and the blurring of the timelines occurred at a higher strain than for the ZK40. The ZK40-2Gd does not show pronounced blurring of the timelines. The appearance of new timelines and dots in the AT-plots and the thickening of these spots after the initial stages can be observed for the ZK40-2Gd. The change in the intensity of the coupled pairs of diffraction lines $\{11\bar{2}0\}$ - $\{10\bar{1}3\}$ indicate tensile twinning in Mg. The maximum normalised values of these peaks are plotted against the deformation in Figure 4. It is noted that all alloys show increase in intensity of one reflection with a corresponding decrease in the other, which is representative of tensile twinning.

Figure 3: AT-plots derived from the *in situ* synchrotron radiation diffraction during compressive deformation of (a) ZK40, (b) ZK40-2Gd and (c) ZK40-2Nd alloys. CD represents the compression direction.

The SEM micrographs of the deformed microstructures are shown in Figure 5. The red circles highlight the areas where the cleavage of the intermetallic particles was observed for the ZK40-2Gd alloy (Figure 5 (b)) and ZK40-2Nd alloy (Figure 5 (c)). This was not observed for the ZK40 alloy (Figure 5 (a)).

Figure 5: SEM micrographs of the deformed microstructures showing cracks in intermetallic particles (a) ZK40, (b) ZK40-2Gd and (c) ZK40-2Nd.

Figure 4: Change in the intensity for the $\{11\bar{2}0\}$ and $\{10\bar{1}3\}$ reflections during compressive deformation.

EBSD inverse pole figure maps are shown in Figure 6. The ZK40 contain recrystallized grains along the grain boundaries, region A in Figure 6 (a). Sub-grain formation is observed in region B while no tensile twins were observed. The ZK40-2Gd contains a significant number of recrystallized grains at the grain boundary as indicated by C, Figure 6 (b). In addition, tensile twins are observed in the final microstructure, region D. Tensile twins were also observed in the ZK40-Nd, Figure 6 (c). However, almost no recrystallized grains at the grain boundaries were observed for ZK40-Nd. In order to investigate in more details the sub-grain formation, grain reorientation average deviation (GROD) maps was used to study the effect of recrystallization on the microstructure of the alloys and are shown in Figure 6 (d-f). GROD maps show the deviation in orientation of a measurement point from the average orientation of the grain to which the point belongs [12]. The highest misorientation values were observed for the ZK40-2Gd alloy, whereas the lowest s for the ZK40 alloy. The highest values are at the grain boundary and the large misorientation is observed for the alloys modified with Gd or Nd addition.

Discussion

In an *in situ* experiment it is possible to investigate the evolution of various deformation, recovery and recrystallization mechanisms and the manner they act during compression. There are essentially four phenomena that are observed on the AT-plots: recrystallization; recovery, which was not clearly observed for the

Figure 6: (a-c) EBSD inverse pole figure maps of samples after a total compressive strain of 30% at 350°C and (d-f) Grain reorientation deviation maps for the same areas as in (a-c) (a, d) ZK40, (b, e) ZK40-2Gd and (c, f) ZK40-2Nd.

alloys in study; grain rotation, which is shown by the bending of the timelines, and grain growth, which is very unlikely to happen during deformation. In addition, the discrete timelines correspond to individual grains. Investigating the AT-plots (Figure 3) an intensive recrystallization is noticeable at the initial stages, which is showed by the appearance of new timelines. Subsequently, the timelines bend due to the rotation of the grains by the reason of the plastic deformation process. Afterwards, these timelines blur as a result of the great amount of sub-grain formation. Eventually, the reflections broaden, merging into the final texture of the material. Such sequence is common for the three alloys investigated.

The impact on the mechanical behaviour during compression at 350°C of the addition of Gd or Nd was significant as indicated by the increase in the 0.2% proof stress and maximum stress measured for ZK40-2Gd ZK40-2Nd alloys, Figure 2. The intermetallic particles were partially broken by cleavage for the ZK40-2Gd and ZK40-2Nd during compression, indicating that and these particles hinder the stress transfer between grains at the grain boundaries. The cleavage of the intermetallic particles also explains the softening observed for the ZK40-2Gd and ZK40-2Nd.

In the ZK40 alloy recrystallization is more pronounced from the early stages of deformation. It is likely that some grains had twinned because their orientation was energetically favourable. However, such event was not pronounced for this alloy and residual twins were not observed in the inverse pole figure map, Figure 6 (a). The highly deformed and elongated grains of the ZK40 alloy, Figure 6 (a), exhibited a large fraction of sub-grains highlighted in region B.

In the case of the ZK40 alloy no intermetallic phases hinder the grain boundary which allows grain sliding, thus lowering the energy stored at the grain boundary during deformation, which was not favourable for twinning. However, the changes of the maximum value of selected diffraction lines of the integrated line profiles during deformation show presence of some twinning. The decrease of the intensity of the $\{11\bar{2}0\}$ and increase of the intensity $\{10\bar{1}3\}$ indicates increase in the twin volume fraction. It is noted in Figure 6 (d) that the smallest GROD values was found for the ZK40, highlighting the impact of the particle pinning the grain boundary of ZK40-2Gd and ZK40-2Nd alloys. This is likely to be one of the reasons, twinning was more favourable for alloys with Gd and Nd; and responsible for the higher strength observed.

AT plots of ZK40-2Gd alloy, Figure 3 (b), shows that the timelines are thicker which suggest that the CDRX was not so pronounced for this alloy. In addition, the number of new timelines that appear during the intermediate stages of deformation is much higher than for the other alloys, which explain the higher volume of recrystallized grains found along the grain boundaries. On the other hand, the ZK40-2Nd alloy shows AT plot similar to that of ZK40, Figure 3. For the ZK40-2Gd alloy the less pronounced activity of the CDRX caused a higher strength compared with the ZK40-2Nd, which exhibit a higher activity as observed in Figure 3 (b).

Conclusion

In situ synchrotron radiation diffraction was performed for as-cast specimens of ZK40, ZK40-2Gd and ZK40-2Nd at 350°C and results reveal that the deformation mechanisms differ between the

ZK40 and the alloys modified with Nd or Gd addition. Among the mechanisms, the CDRX is observed practically for all alloys, evidenced by the sub-grain formation and the blurring of the timelines in the AT-plots. Such phenomenon was more pronounced for the ZK40 alloy and ZK40-2Nd alloy. The broadening of the reflections for the ZK40 alloy suggests the grains had more freedom to slide than for the modified alloys. The intermetallic phases of the modified alloys were partially broken after deformation, illustrating the pinning of the grain boundaries which resulted in the softening subsequent to maximum stress.

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References

- 1 M. O. Pekgulyuz, K. U. Kainer, A. A. Kaya, eds. *Fundamentals of magnesium alloy metallurgy* (Philadelphia, PA, USA: Woodhead Publishing, 2013).
- 2 M. M. Avedesian, H. Baker, *Magnesium and magnesium alloys* Metal Park, OH, USA: *ASM Speciality Handbook*, (ASM International, 1999).
- 3 M. H. Yoo, *et al.*, "Non basal deformation modes of HCP metals and alloys: Role of dislocation source and mobility," *Metall. Mater. Trans A*, 33 (2002), 813-822.
- 4 Y. Wu, *et al.*, "Flow Behavior and microstructure of ZK60 magnesium alloy compressed at high strain rate". *Trans. Nonferrous Metals Soc China*, 24 (2014), 930-939.
- 5 T. E. Leontis, "Magnesium and Magnesium Alloys - The Room and Elevated Temperature Properties of Some Sand Cast Magnesium-base Alloys Containing Zinc," *Transactions of the Metallurgical Society of AIME*, 185 (1949), 327.
- 6 Q. Li, Q. Wang, Y. Wang, X. Zeng, W. Ding, "Effect of Nd and Y addition on microstructure and mechanical properties of as-cast Mg-Zn-Zr alloy," *J Alloys and Compd*, 427.1 (2007), 115-123.
- 7 M. B. Yang, *et al.*, "Microstructure, tensile and creep properties of as-cast Mg-3.8Zn-2.2Ca-xCe ($x=0, 0.5, 1$ and 2 wt.%) magnesium alloys," *J Rare Earths*, 30 (2012), 181-188.
- 8 N. Stanford *et al.*, "Effect of microalloying with rare-earth elements on the texture of extruded magnesium-based alloys," *Scripta Mater.*, 59.7 (2008), 772-775.
- 9 K.-D. Liss, and K. Yan., "Thermo-mechanical processing in a synchrotron beam," *Mater. Sci. Eng.: A*, 528.1 (2010), 11-27.
- 10 F. R. Elsayed, *et al.*, "Magnesium Permanent Mold Castings Optimization" *Mater. Sci. Forum* 690 (2011), 65-68.
- 11 D. Tolnai, *et al.* "Study of the solidification of AS alloys combining in situ synchrotron diffraction and differential scanning calorimetry" *Mater. Sci. Forum*, 765 (2013), 286-290.
- 12 S. I. Wright, M. M. Nowell, and D. P. Field, "A Review of Strain Analysis Using Electron Backscatter Diffraction," *Microscopy and Microanalysis*, 17 (2011), 316-329.

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In situ synchrotron radiation diffraction investigation of the compression behaviour at 350 °C of ZK40 alloys with addition of CaO and Y

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ABSTRACT

The evolution of the microstructure during compression is investigated with *in situ* synchrotron radiation diffraction in as-cast ZK40, ZK40-2CaO and ZK40-1Y Mg alloys. The specimens were compressed at 350 °C with a strain rate of 10^{-3} s^{-1} until 30% deformation. The Y containing alloy showed the highest 0.2% proof strength in compression of 35 MPa at 350 °C which is double that of the ZK40 alloy, while the CaO added alloy shows a moderate increment at 23 MPa. The Y containing alloy shows some work hardening, while the CaO modified and the ZK40 alloys do not show work hardening after yield. Synchrotron radiation diffraction timelines show that continuous and discontinuous dynamic recrystallization occurs during deformation of the ZK40 alloy while a small amount of dynamic recrystallization was observed in the ZK40-1Y alloy. However, dynamic recrystallization was not present in the ZK40-2CaO alloy. SEM-EBSD analysis conducted on the deformed samples shows a significantly high volume fraction of twins in the Y and CaO containing alloys which was absent in the ZK40 alloy. The modified deformation behaviours observed in the CaO and Y containing alloys were attributed to the presence of intermetallic particles found at the grain boundaries and to the role of Ca and Y in stabilising twinning.

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1. Introduction

The high specific strength [1] of Mg alloys, makes these alloys attractive for potential applications where weight reduction is of importance. Thus, research and development of Mg alloys for possible industrial applications have increased recently [2–4]. Conventional Mg alloys exhibit poor formability at room temperature [5], thus the mechanical processing is done at higher temperatures ($> 225 \text{ °C}$) to activate non-basal slip and to reduce twinning [6]. The deformation behaviour and dynamic recrystallization of Mg alloys have been investigated thoroughly [7–9] and several dynamic recrystallization mechanisms at different temperatures have been reported [10–12].

Alloys based on the Mg–Zn system are low in cost and have relatively good mechanical properties [13]. The ZK60 (Mg–6.0Zn–0.6Zr (wt%)) alloy is a commercially available wrought Mg alloy which shows a good combination of strength and ductility.

Recently, there are numerous attempts to enhance the strength and ductility through the modification of alloy chemistry with the addition of quaternary and quinary additions [14–15]. Wu et al. [16] investigated the compression behaviour of the ZK60 alloy at different temperatures and found that the range between 250 °C and 350 °C was the most suitable to deform this alloy.

The role of Ca additions on the microstructure modification [17,18], mechanical properties [19,20] and texture randomisation [17,21,22] has been reported in literature for both commercial and experimental magnesium alloys. It has been shown that the Ca additions alone improved the ignition resistance [23] of Mg alloys. Recently the addition of CaO was found to improve the ignition resistance of Mg alloys [24], and CaO reduces to form MgO and Mg_2Ca [25] providing an easier route to add Ca to Mg alloys. The addition of Ca to ZK series alloys lead to the refinement of the rod like β_1 and plate like β_2 precipitates and enhanced the creep resistance [26]. The Mg–Zn–Ca system was investigated with different Zn contents by Oh-ishi et al. [25]. It was found that a Ca:Zn ratio of $\sim 1:3$ (wt%) shows the best enhancement in age hardening which can be further enhanced by the addition of Nd [27].

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Additionally, the cast and heat treated Mg-Ca-Zn alloys show enhanced creep resistance both in tension [27] and compression [28]. The extruded and hot rolled Mg-Zn-Zr alloys containing Ca show enhancement in mechanical properties and the modification of the strong basal texture gives rise to a weaker texture [21]. The elevated temperature deformation of Ca containing Mg alloys shows that Ca plays an important role in elevated temperature deformation of Mg based alloys [17,18,29]. However, the exact role of Ca additions during hot deformation of Mg alloys, especially in Mg-Zn-Zr based alloys, remains unclear.

The role of Y in Mg based alloys has been studied extensively. The microstructure and mechanical properties of Mg-Zn based alloys are modified by the addition of Y depending on the ratio of Y/Zn. When this ratio is large, i.e. Y rich alloys containing Zn, then fine scaled LPSO (long period stacking ordered) structures are observed [30]. With intermediate ratios of Y/Zn, [31,32] Y modified the grain boundary phases for icosahedral phases containing Y and Zn. In the extruded alloys containing icosahedral phase a reduction in the yield anisotropy between compressive and tensile yield strengths was observed [31], and the increased strength was attributed to increased load transfer between the matrix and the second phase [33]. The addition of Y to Mg-Zn alloys shows enhanced tensile yield strength and ultimate tensile strength without significant loss in ductility [34]. Farzadfar et al. [35] found that in Mg-Zn-Y-Zr alloys did not show texture randomisation following hot compression and annealing unlike the binary Mg-Y alloys. However this is not consistent with other observations by Xu et al. [32]. Additionally, the retardation of recrystallization was observed in Mg-Y alloys which were not observed in Mg-Zn-Y alloys following hot deformation and annealing [35]. In binary Mg-Y alloys, Y accommodates the c-axis deformation through accelerating the c+a axis glide [36], which weakens the deformation anisotropy and thus improves ductility. Transmission Electron Microscopy (TEM) experiments and Density Functional Theory (DFT) calculations suggested that the addition of Y to Mg alloys results in the decrease of the intrinsic stacking fault energy (SFE) leading to the subsequent promotion of the (c+a) slip [37]. Recent investigations with *in situ* neutron diffraction show that the solute strengthening effect of Y which increased the critically resolved shear stresses (CRSS) for basal slip, (a+c) slip and twinning compared with pure Mg, with basal slip showing the smallest increment in hardening [38]. The increased ductility observed was due to the accommodation of strain by grains in softer orientations during deformation [38]. Even though there is a significant collection of work on the effect of Y additions to Mg and Mg-Zn-Zr alloys there are some discrepancies the observations associated with hot deformation and microstructure evolution.

X-ray and neutron diffraction are well established characterization methods to investigate the structure of various crystalline materials. Recently, it became possible to perform these measurements *in situ* which allow detection of the dynamic microstructural processes that occur during mechanical loading in real time [39–47]. The azimuthal angle-time plots (AT-plots) give information on grain size evolution, grain rotation, texture evolution, strain and strain anisotropy, that can be correlated with dislocation slip, sub-grain formation, twinning, recovery, recrystallization and grain growth, which are the physical processes responsible for the microstructural changes [39]. Using *in situ* synchrotron radiation diffraction during compression testing the formation and the propagation of twins, grain rotation and the formation of recrystallized grains may be observed. These provide a real time insight into the processes that contribute to the evolution of microstructure during deformation, especially at elevated temperatures where many dynamic processes, such as recovery and recrystallization, contribute to the deformation. As these observations are made in parallel to deformation step, the global

strains required for each of these events to occur may be elucidated at a given temperature and strain rate. It is well known that during elevated temperature deformation a number of competing processes such as twinning, dislocation motion and recovery and recrystallization take place. With the aid of *in situ* experiments an understanding of which of these modes control the deformation at different parts of a deformation curve may be understood. It is envisaged that understanding of the contributions from various deformation modes available at the elevated temperature though *in situ* investigation of microstructure evolution during deformation will a rudimentary insight into more complex deformation processes that occur during thermos-mechanical treatments.

The aim of this study is to investigate the influence of CaO and Y addition on the elevated temperature deformation at 350 °C of ZK40 alloy with *in situ* synchrotron radiation diffraction, which provides new insights into the real-time evolution of the microstructure. The results are correlated with post mortem electron backscattered diffraction (EBSD), which provides information on the deformed microstructures.

2. Experimental procedure

The alloys were produced by permanent mould indirect chill casting [48]. Mg was molten under protective gas (98 vol% Ar, 2 vol% SF₆) in an electric resistance furnace. Zn and CaO were added to the melt in the pure form, while Y was added as Mg10 wt% Y and the Zr as Zirmax[®] alloy (Mg-33 wt% Zr). After mixing, the melt was poured into a preheated (660 °C) thin walled steel mould at a temperature of 750 °C. The mould was then held at 660 °C for 15 min before immersing into water at 10 mm s^{−1} until the top of the melt was in line with the cooling water. Actual composition of the alloys investigated are provided in Table 1.

The samples were mounted in epoxy and ground using SiC paper, then polished using 3 µm diamond suspension followed by OPS solution with 1 µm diamond suspension as the last step of polishing. The microstructures for optical microscopy (OM) were etched with an acetic-picric solution [5]. The optical microscopic analysis was performed using a Leica DMI 5000 light optical microscope. The grain sizes were measured using methods described in ASTM standard E112-13 [49] using a minimum of 5 images. The specimens for EBSD were unetched but washed with 0.5 vol% nitric acid in ethanol solution for 5 s and then washed with ethanol to remove any trace of the nitric acid. The scanning electron microscopy (SEM) investigation was performed using a Zeiss FEG-SEM Ultra 55 microscope equipped with a Hikari detector and a TSL-OIM software package for EBSD analysis. The EBSD measurements on the compressed samples were performed on an area 80 µm × 80 µm, with a step size of 0.1 µm close to the centre of the deformed specimen to ensure a similar area to that of those samples measured during the diffraction experiment. The minimum grain size was chosen to be 10 µm with a confidence index of 0.09. All microstructures of deformed samples are presented so that the compression direction is parallel to the horizontal direction of the page.

Table 1
Actual chemical compositions of the alloys investigated.

Chemical composition (wt%)				
Alloys	Ca	Y	Zn	Zr
ZK40	–	–	5.00	0.53
ZK40-2CaO	1.00	–	4.30	0.55
ZK40-1Y	–	1.15	4.00	0.40

The *in situ* synchrotron radiation diffraction experiments were performed at the P07 beamline of PETRA III, DESY (Deutsches Elektronen-Synchrotron). A monochromatic beam with the energy of 100 keV ($\lambda=0.0124$ nm) with a cross section of 1.0×1.0 mm² was used for the current investigation. For the *in situ* compression experiments cylindrical specimens were machined from the cast ingots with a diameter of 5 mm and a length of 10 mm. The diffraction patterns were recorded with a PerkinElmer 1622 flat panel detector with a pixel size of 200×200 μm^2 , which was placed at a sample-to-detector distance of 1535 mm from the specimen (distance was calibrated with a LaB₆ standard powder sample). The acquisition time for each image was 1 s. The specimens were placed in the chamber of a DIL 805 A/D dilatometer (TA Instruments, Hüllhorst, Germany), combined with a modified heating induction coil so the beam passes only through the sample [50]. The specimens were heated to 350 °C at a rate of 30 K s⁻¹ and held at this temperature for 3 min before the deformation to ensure temperature homogeneity. The specimens were compressed with an initial strain rate of 1.1×10^{-3} s⁻¹. The tests were terminated at a total strain of 0.3.

The morphology of the Debye-Scherrer rings was then analysed using the Fit2D[®] software and converted into azimuthal-angle time (AT) plots using the ImageJ[®] software package. The two dimensional diffraction patterns were radially transformed into azimuthal angle – 2Θ plots, by stacking sections of the plots acquired through the measurement at a given 2Θ angle which is attributed to reflections originating from the chosen crystallographic plane which is used to construct the azimuthal-angle time (deformation) plots. The time measured may be correlated with the applied true strain as each diffraction pattern was recorded at a specific strain through the measurement.

3. Results

The optical micrographs and SEM images of the as-cast ZK40, ZK40-2CaO and ZK40-1Y alloys are shown in Fig. 1. The grain size of ZK40 was evaluated to be 72.43 ± 2.55 μm , for ZK40-2CaO 75.94 ± 5 μm , while for ZK40-1Y a grain size of 86.06 ± 4.53 μm was measured. The intermetallic phases were distributed semi-

Fig. 2. True stress–true strain curves obtained during compression at 350 °C.

continuously along the grain boundaries in the ZK40-2CaO and ZK40-1Y alloys, whereas the unmodified ZK40 alloy contained discrete intermetallic particles along the grain boundaries, Fig. 1 (d–f). All investigated alloys exhibit a cellular microstructure in the as-cast condition.

The true stress–true strain curves from the *in situ* compression experiments are shown in Fig. 2. A 0.2% compressive proof strength ($\sigma_{0.2}$) was measured to be 17 MPa in ZK40 alloy, while the maximum stress (σ_{max}) was 26.5 MPa. In the ZK40-2CaO a $\sigma_{0.2}$ of 23.3 MPa was observed which followed a decrease in the true stress. The ZK40-1Y alloy exhibited the highest 0.2% compressive proof strength, at 35 MPa, and a maximum compressive stress of 65.6 MPa. The ZK40-1Y alloy shows work hardening following yield while ZK40 and ZK40-2CaO alloys do not, in fact ZK40-2CaO shows softening after the yield.

The AT-plots of the $\{10\bar{1}0\}$ planes and the $\{0002\}$ planes from the *in situ* synchrotron radiation diffraction measurements illustrating the deformation are plotted in Fig. 3. During the initial stages of deformation, i.e. in the elastic regime, the diffraction patterns did not change significantly. The blurring of the timelines,

Fig. 1. (a–c) Optical and (d–f) SEM micrographs of as-cast ZK40 (a, d), ZK40-2CaO (b, e), and ZK40-1Y (c, f).

Fig. 3. Azimuth angle vs timeplots obtained during *in situ* synchrotron radiation diffraction during compressive deformation of (a) ZK40, (b) ZK40-2CaO and (c) ZK40-1Y alloys. CD represents the compression direction.

i.e. the trace of a given reflection over deformation can be observed in region I of Fig. 3(a) for ZK40 alloy. In the plastic deformation regime a tendency of broadening of the reflections and merging of timelines to develop the final texture of the material can be observed (II), as shown in Fig. 3(a). Region III shows inclination of the timelines, which is attributed to grain rotation. During plastic deformation new timelines appear from blurred regions, in region IV in Fig. 3(a), which is attributed to the formation of recrystallized grains.

Regions V and VI in Fig. 3(b) show blurred regions due to the sub-grain formation for the ZK40-2CaO alloy. In region VII of Fig. 3 (c) the appearance of timelines was observed at the start of the plastic deformation and these timelines continue to remain through the deformation. Regions showing the appearance of new timelines associated with recrystallization could be observed in the ZK40-1Y alloy in the later stages of deformation.

The optical micrographs of the deformed samples are shown in Fig. 4. Twins were seldom observed in the ZK40 alloy while the ZK40-2CaO and ZK40-1Y alloys both contain a significant fraction of twins distributed through the microstructure. The number density of twins is higher in the CaO modified alloy compared with the Y modified alloy. The EBSD inverse pole figure (IPF) maps of the compressed samples are shown in Fig. 5(a-c). The corresponding KAM (Kernel average misorientation) maps for each alloy corresponding to the IPF are illustrated in Fig. 5(d-f). The ZK40 alloy, Fig. 5(a and d), contain recrystallized grains along grain boundaries, which correspond to regions with low misorientations on the KAM maps, and an example of recrystallized grains is shown in Region A in Fig. 5(a). Additionally, there are regions within grains which have slightly different misorientations, as shown in Region B. In KAM maps these regions correspond to regions with low misorientations bound by lines with an angle of misorientation between 1° and 2° , and such regions can be described as sub grains. Generally, ZK40 alloy did not contain regions where the misorientation within the grains was more than 2° .

The ZK40-2CaO alloy contained many regions where the misorientation within the grain was relatively large, Fig. 5(b) and (e). There is no evidence of recrystallization in the regions examined in ZK40-2CaO alloy. The ZK40-2CaO alloy contained a large density of twins and sub grains as indicated by regions B, C and D,

Fig. 4. Optical microstructure of samples after a total compressive strain of 30% at 350 °C (a) ZK40, (b) ZK40-2CaO, and (c) ZK40-1Y.

respectively, Fig. 5(b). The corresponding KAM map, in Fig. 5(e), shows that in the area corresponding to region D in Fig. 5(b) there are sub grain boundaries containing a higher misorientation angle with the nearest neighbour than that observed within the grains. The twin observed in region D contains regions of high misorientation within indicative of sub grain formation. The ZK40-1Y alloy behaved in a manner similar to the ZK40-2CaO alloy with significant number density of twins (e.g. region E) and sub grains (region F), Fig. 5(c). However, unlike ZK40-2CaO, ZK40-1Y also contained recrystallized grains (region G), Fig. 5(c). The areas, in Fig. 5(f), corresponding to the regions containing sub-grains, on

Fig. 5. EBSD inverse pole figure maps (a–c) and Kernel average misorientation angle maps (d–f) for the samples subjected to a total compressive strain of 30% at 350 °C (a,d) ZK40, (b,e) ZK40-2CaO, and (c,f) ZK40-1Y.

Fig. 5(c), contain walls of high misorientation within grains inside, with only negligible amount of misorientation. The recrystallized grains are identified as grains where there is a misorientation of $\sim 10^\circ$ or more between the grains, but there is no large scale misorientation within the grains. The SEM micrographs of the deformed ZK40, ZK40-2CaO, and ZK40-1Y alloys are shown in Fig. 6. The red circles highlight the areas where intermetallic particles seem to fracture. The micrographs of the samples prior to deformation did not contain fractured particles along the grain boundaries.

4. Discussion

The modified alloys contain semi-continuously distributed intermetallic particles along the grain boundaries, and content of Y and Ca in solution is not significant. CaO was not observed in the final microstructure, only intermetallic compounds containing Ca, as reported previously by Wiese et al. [24] CaO disassociates during melting and solidification. Apart from slight differences of Zn content, the matrix is similar between the alloys. Therefore, the different compression behaviours exhibited among the alloys in the present study is likely to be due to the intermetallic compounds along the grain boundaries and possible differences in solute content in Mg matrix. The maximum compressive strength of the ZK40-2CaO alloy was lower than the ZK40 alloy even though the yield strength of the alloy was slightly higher, suggesting that the intermetallic particles containing Ca were not effective in preventing deformation along grain boundaries, i.e. the Ca containing intermetallic particles did not contribute to work

hardening of the alloy. The strengthening caused by the presence of the Y containing compounds along the grain boundary, on the other hand, was pronounced. The flow curves show that yield strength and maximum compressive strength of ZK40-1Y were the highest among the studied alloys. As illustrated in Fig. 6, the deformed specimens exhibit cleavage of the intermetallic compounds in ZK40-2CaO and ZK40-1Y, evidencing the reinforcement effect that led to an increment of the yield strength observed during deformation at 350 °C in the ZK40-1Y alloy, i.e. the stress required to deform and consequently break the Y containing compounds is much higher than those in the ZK40 alloy. The softening behaviour subsequent to yielding observed in the CaO and Y containing alloys attributed to the cleavage of these intermetallic particles, as a significant softening behaviour is not observed in ZK40 alloy.

There are three mechanisms of dynamic recrystallization (DRX) operative: continuous dynamic recrystallization in Mg alloy, discontinuous dynamic recrystallization, and dynamic recrystallization associated with twinning [51]. The evolution of these mechanisms can be obtained from the AT-plots and the investigation of the deformed microstructure. These processes played important roles on the evolution of the microstructure during the compression at 350 °C for each alloy. In this way, during the initial stages of deformation no changes in the timelines are observed at the AT-plots for the three investigated alloys. Entering the plastic behaviour, the diffraction timelines tend to rotate toward the compression directions in case of $\{10\bar{1}0\}$ planes, while a rotation away from the compression direction was observed for the (0002) reflections. Such events were more pronounced for the ZK40 alloy, as can be noticed in the AT-plots in region III. Such process has

Fig. 6. SEM micrographs of the samples deformed to a total strain of 30% in compression showing cracks in intermetallic particles (a) ZK40, (b) ZK40-2CaO, and (c) ZK40-1Y.

been observed previously during and prior to high temperature deformation by Schmoelzer et al. [42], and it is attributed to grain rotation, which occurs to accommodate strain build up within the microstructure.

The highly deformed and elongated grains of the ZK40-2CaO alloy, shown in region C in Fig. 5(b), show a grain that was possibly a sub-grain formed during the deformation, and the low-angle grain boundaries were transformed into high-angle grain boundaries through absorption of the dislocations. Therefore, these sub-grains became dynamically recrystallized grains by continuous dynamic recrystallization [4]. Investigating the KAM values distribution for the same region shows that high values are exhibited in region K in Fig. 5(e), suggesting that this region is highly

deformed. By blurring of the timelines in AT-plots in Fig. 3(b), region IV and region VI, it is suggested that the active recrystallization process during compression was continuous dynamic recrystallization.

In the ZK40-1Y alloy, a highly deformed microstructure is observed, Fig. 5(c) and (f), which is similar to that in ZK40-2CaO alloy. In region G in Fig. 5(c) sub grain formation is highlighted. Similarly in the KAM maps, region O in Fig. 5(f), where the misorientation value was high, indicates the presence of a large amount of sub grains. Correspondingly, in the AT-plots, Fig. 3(c), a pronounced blurring of the timelines was observed. This process was also observed in the ZK40 alloy. However, comparing the three alloys it is clear that the blurring of the timelines was less pronounced for the ZK40 alloy. Likewise, the Kernel maps in Fig. 5 (d) shows that ZK40 alloys exhibit the lowest misorientation values within the grains.

In the ZK40-1Y alloy, in region F of Fig. 5(c), a significant amount of recrystallized grains are observed at the grain boundaries. The recrystallization occurs at the original grain boundaries. The recrystallized grains grow through the migration of grain boundaries during the hot deformation process; the appearance of new timelines is shown in AT-plots (Fig. 3(c), region VII). This was not observed in the ZK40-2CaO alloy, suggesting that discontinuous dynamic recrystallization was not operative in the ZK40-2CaO alloy. This suggests that the sub-grain formation was less active in the initial stages during the ZK40-1Y alloy compared with ZK40-2CaO alloy. The KAM maps exhibit the highest values of misorientation at the sub-grain boundaries, indicating that these sites may initiate recrystallization. In ZK40-1Y alloy the particles along the grain boundaries possessed significantly higher strength than the ZK40-2CaO alloy, as was suggested by the flow curves. Therefore, these particles have hampered grain boundary sliding more efficiently and accommodate a higher stress during the compression, which was beneficial to nucleation and growth of recrystallized grains in the ZK40-1Y alloy.

In terms of the impact of twinning on the structure, once nucleated, the $\{10\bar{1}2\}$ twins grow laterally, followed by a small amount of dislocation plasticity, which relaxes the local stresses at the extremities of the twins, causing further twin growth [52]. Twin propagation and growth are responsible for the hardening and texture evolution characteristic of Mg alloys subjected to plastic deformation [53,54]. The inverse pole figure map, in Fig. 5 (b), shows three twins (regions B, D and E). A large amount of strain is observed in region L in Fig. 5(d), indicated large misorientation angles, suggesting that, although the grain has twinned, its orientation and the pinning caused by the presence of the intermetallic compounds at the grain boundary was favourable for twin nucleation. Even though such effect is not clearly visible in the AT-plots (Fig. 3(b)) due to the intensive blurring of the timelines, it is noted that at the end of the deformation there are no visible $\{10\bar{1}0\}$ planes with their reflections close to 90° or 270° . Thus, it is expected that twins engulf grains with this orientations completely. Since no traces of discontinuous dynamic recrystallization were observed in the microstructure after deformation, the energy created during compression is released by twinning and continuous dynamic recrystallization. In the same way, regions I and H of Fig. 5(f) show twins in the microstructure after compression for the ZK40-1Y alloy. In Fig. 5(f) KAM map show high values of misorientation in the regions with twins, as highlighted in region M. Pinning due to intermetallic compounds and the hindering of the grain sliding is not favourable for discontinuous recrystallization of the ZK40-1Y alloys. On the other hand, since there is no semi-continuous distribution of intermetallic compounds hampering the grain slide, and only small intermetallic particles at the grain boundaries, the grains had more freedom to deform in ZK40 alloy. Therefore, dynamic

recrystallization was more pronounced for this alloy and the twinning not present in the deformed microstructure.

In ZK40-2CaO and ZK40-1Y alloys twins that form in the microstructure are stable during deformation and did not show signs of recrystallization at the twin boundaries. This suggests that the twins are stable and resistant to growth or recrystallization. Ostapovets and Gröger [55] simulated the strain along the tensile twin boundaries and found that there is an alternating compressive and tensile strain on the atoms along the twin boundary plane. Segregation of Gd and Zn to the twin boundaries was reported by Nie et al. [56], where Gd and Zn solute atoms segregate along twin boundaries, when a compressed Mg1Gd0.5Zn (at%) alloy was heat treated at 150 °C for 3 h. This was observed with advanced transmission electron microscopy techniques. They further reported that twins were stable following heat treatment of Mg0.2Gd (at%) alloy after annealing at 300 °C for 20 min, while such twins were not stable in Mg0.4Zn (at%) alloy after similar thermal treatments. A recent observation by Zeng et al. [57] found in Mg-0.3Zn-0.1Ca (at%) alloys, following deformation at room temperature and annealing at 350 °C for 15 min, Ca and Zn segregated to the grain boundaries. They observed that both Mg-0.1Ca (at%) and Mg-0.3Zn-0.1Ca (at%) alloys retained the twinned microstructure and retarded recrystallization during annealing for up to 15 min at 350 °C, but the reasons behind the retention of twinning during annealing and retardation of recrystallizations is not clear. It has been reported that Y and Ca have similar effects in Mg terms of texture modification as observed for Gd in Mg [58,59]. As Ca and Y are both larger atoms similar to Gd or Nd, it is likely that Ca or Y and Zn atoms segregate to the twin boundaries during deformation and stabilize the twin boundaries preventing recrystallization. Even though Nie et al. [56] and Zeng et al. [57] illustrate what happens during annealing of deformed microstructures, the question, whether the same process occurs during hot compression at 350 °C, remains unclear and needs to be clarified further.

5. Conclusions

The evolution of the microstructure changes during compression was investigated with *in situ* synchrotron radiation diffraction for as-cast specimens of ZK40, ZK40-2CaO and ZK40-1Y at 350 °C, and results reveal that the deformation mechanisms differ between the ZK40 and the ZK40 alloys with CaO or Y additions. From the results the following conclusions can be drawn:

- Continuous dynamic recrystallization is observed during compression for ZK40, exhibited in the AT-plot by the blurring of the timelines.
- Continuous and discontinuous dynamic recrystallization occurs during the deformation in the ZK40-2Y alloy, evidenced by the presence of sub-grains and new grains at the grain boundary. On the other hand, dynamic recrystallization was not pronounced for the ZK40-2CaO alloy.
- The influence of the intermetallic compounds in pinning the grain boundary, hampering grain sliding, caused more significant changes in terms of the mechanical behaviour for ZK40-1Y alloy than for the ZK40-2CaO alloy, which can be attributed to the strength of each intermetallic compound.
- The increased yield and maximum strength for the ZK40-1Y alloy can be explained by the presence of intermetallic particles. The surprisingly similar behaviour between the ZK40 alloy and ZK40-2CaO alloy can be attributed to the low strength of the intermetallic particles that were distributed along the grain boundaries of the ZK40-2CaO alloy.

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References

- [1] M. Perkguleryuz, K. Kainer, A. Kaya, *Fundamentals of Magnesium Alloy Metallurgy*, 1st ed., Woodhead, Philadelphia, 2013.
- [2] Z. Yang, J.P. Li, J.X. Zhang, G.W. Lorimer, J. Robson, Review on research and development of magnesium alloys, *Acta Metall. Sin. (English Letters)* 21 (2008) 313–328.
- [3] M.K. Kulekci, *Int. J. Adv. Manuf. Technol.* 39 (2008) 851–865.
- [4] C.H. Cáceres, *Mater. Des.* 30 (2009) 2813–2822.
- [5] M.M. Avedesian, H. Baker, *Magnesium and magnesium alloys*, in: *ASM Speciality Handbook*, ASM International, Metal Park, OH, 1999.
- [6] M.H. Yoo, J.R. Morris, K.M. Ho, S.R. Agnew, *Metall. Mater. Trans. A* 33 (2002) 813–822.
- [7] H.J. McQueen, E. Evangelista, J. Bowles, G. Crawford, *Met. Sci.* 18 (8) (1984) 395–402.
- [8] S.E. Ion, F.J. Humphreys, S.H. White, *Acta Metall.* 30 (1982) 1909–1919.
- [9] Z. Ya, Z. Xiaoqin, L. Chen, D. Wenjiang, *Mater. Sci. Eng. A* 428 (2006) 91–97.
- [10] A. Galiyev, R. Kaibyshev, G. Gottstein, *Acta Mater.* 49 (2001) 1199–1207.
- [11] E.I. Poliak, J.J. Jonas, *Acta Mater.* 44 (1996) 127–136.
- [12] L. Shubo, W. Yanqiu, Z. Mingyi, W. Kun, *Trans. Nonferrous Met. Soc.* 14 (2004) 306–310.
- [13] S.M. He, L.M. Peng, X.Q. Zeng, W.J. Ding, Y.P. Zhu, *Mater. Sci. Eng. A* 433 (2006) 175–181.
- [14] T. Homma, C.L. Mendis, K. Hono, S. Kamado, *Mater. Sci. Eng. A* 527 (2010) 2356–2362.
- [15] S.-Y. Chang, H. Tezuka, A. Kamio, *Mater. Trans.* 38 (1997) 526–535.
- [16] Y. Wu, H. Yan, S. Zhu, J. Chen, A. Liu, X. Liu, T. Nonferr, *Metal. Soc.* 24 (2014) 930–939.
- [17] J. Hofstetter, S. Rüedi, I. Baumgartner, H. Kilian, B. Mingler, E. Oovoden-Karadeniz, S. Pogatscher, P.J. Uggowitzer, J.F. Löffler, *Acta Mater.* 98 (2015) 423–432.
- [18] T.Y. Kwak, H.K. Lim, W.J. Kim, *Mater. Sci. Eng. A* 648 (2015) 145–156.
- [19] A.A. Luo, *Int. Mater. Rev.* 49 (2004) 13–30.
- [20] A. Suzuki, N.D. Saddock, J.R. Terbush, B.R. Powell, J.W. Jones, T.M. Pollock, *Metall. Mater. Trans. A* 39 (2008) 696–702.
- [21] Y. Chino, T. Ueda, Y. Otomatsu, K. Sassa, X. Huang, K. Suzuki, M. Mabuchi, *Mater. Trans.* 52 (2011) 1477–1482.
- [22] B. Zhang, Y. Wang, L. Geng, C. Lu, *Mater. Sci. Eng. A* 539 (2012) 56–60.
- [23] S.-H. Ha, J.-K. Lee, H.-H. Jo, S.-B. Jung, S.K. Kim, *Rare Met.* 25 (2006) 150–154.
- [24] B. Wiese, C.L. Mendis, D. Tolnai, A. Stark, N. Schell, H.-P. Reichel, R. Brückner, K. U. Kainer, N. Hort, *J. Alloy. Compd.* 618 (2015) 64–66.
- [25] K. Oh-ishi, R. Watanabe, C.L. Mendis, K. Hono, *Mater. Sci. Eng. A* 526 (2009) 177–184.
- [26] C.J. Bettles, M.A. Gibson, K. Venkatesan, *Scr. Mater.* 51 (2004) 193–197.
- [27] X. Gao, S.M. Zhu, B.C. Muddle, J.F. Nie, *Scr. Mater.* 53 (2005) 1321–1326.
- [28] L. Katsarou, K. Suresh, K.P. Rao, N. Hort, C. Blawert, C.L. Mendis, H. Dieringa, *Magn. Technol.* 2015 (2015) 419–423.
- [29] T.Y. Kwak, W.J. Kim, *Mater. Sci. Eng. A* 615 (2014) 222–230.
- [30] S. Yoshimoto, M. Yamasaki, Y. Kawamura, *Mater. Trans.* 47 (2006) 959–965.
- [31] A. Singh, M. Watanabe, A. Kato, A.P. Tsai, *Mater. Sci. Eng. A* 385 (2004) 382–396.
- [32] D.K. Xu, L. Liu, Y.B. Xu, E.H. Han, *Mater. Sci. Eng. A* 443 (2007) 248–256.
- [33] Y. Chino, S. Kensuke, M. Mabuchi, *Mater. Sci. Eng. A* 513 (2009) 394–400.
- [34] D.K. Xu, L. Liu, Y.B. Xu, E.H. Han, *J. Alloy. Compd.* 426 (2006) 155–161.
- [35] S.A. Farzadfar, M. Sanjari, I.-H. Jung, E. Essadiqi, S. Yue, *Mater. Sci. Eng. A* 528 (2011) 6742–6753.
- [36] S.R. Agnew, M.H. Yoo, C.N. Tomé, *Acta Mater.* 49 (2001) 4277–4289.
- [37] S. Sandlöbes, M. Friák, S. Zaeferrer, A. Dick, S. Yi, D. Letzig, et al., *Acta Mater.* 60 (2012) 3011–3021.
- [38] N. Stanford, R. Cottam, B. Davis, J. Robson, *Acta Mater.* 78 (2014) 1–13.
- [39] K.-D. Liss, U. Garbe, H. Li, T. Schambron, J.D. Almer, K. Yan, *Adv. Eng. Mater.* 11 (2009) 37–40.
- [40] K.-D. Liss, K. Yan, *Mater. Sci. Eng. A* 528 (2010) 11–27.
- [41] K.-D. Liss, T. Schmoelzer, K. Yan, M. Reid, R. Dippenaar, H.J. Clemens, *Appl. Phys.* 106 (2009) 044914–044916.
- [42] T. Schmoelzer, K.-D. Liss, P. Staron, S. Mayer, H. Clemens, *Adv. Eng. Mater.* 13 (2011) 685–699.
- [43] I. Lonardelli, N. Gey, H.-R. Wenk, M. Humbert, S.C. Vogel, L. Lutterotti, *Acta Mater.* 55 (2007) 5718–5727.
- [44] P. Suwanpinij, A. Stark, X. Li, F. Römer, K. Herrmann, T. Lippmann, W. Bleck, *Adv. Eng. Mater.* 15 (2014).
- [45] K.-D. Liss, K. Yan, M. Reid, *Mat. Sci. Eng. A* 601 (2014) 78–85.
- [46] K. Yan, K.-D. Liss, U. Garbe, J. Daniels, O. Kirstein, H. Li, R. Dippenaar, *Adv. Eng. Mater.* 11 (2009) 771–773.

- [47] K. Yan, D.G. Carr, M.D. Callaghan, K.-D. Liss, H. Li, *Scr. Mater.* 62 (2010) 246–249.
- [48] F.R. Elsayed, N. Hort, M.A. Salgado-Ordorica, K. Kainer, *Mater. Sci. Forum* 690 (2011) 65–68.
- [49] Test Methods for Determining Average Grain Size, (n.d.), doi: <http://dx.doi.org/10.1520/e0112-96r04e02>.
- [50] D. Tolnai, G. Szakacs, G. Requena, A. Stark, N. Schell, K. Kainer, N. Hort, *Mater. Sci. Forum* 765 (2013) 286–290.
- [51] J. Bettles, M. Barnett, *Advances in Wrought Magnesium Alloys: Fundamentals of Processing Properties and Applications*, Woodhead Publishing, Oxford, 2012.
- [52] R.E. Reed-Hill, E.P. Dahlberg, W.A. Slippy, *Trans. AIME* 233 (1965) 1766–1771.
- [53] S.R. Agnew, M.H. Yoo, C.N. Tome, *Acta Mater.* 49 (2001) 4277–4289.
- [54] L. Capolungo, I.J. Beyerlein, C.N. Tome, *Scr. Mater.* 60 (2009) 32–35.
- [55] A. Ostapovets, R. Gröger, *Model. Simul. Mater. Sci. Eng.* 22 (2014) 025015.
- [56] J.F. Nie, Y.M. Zhu, J.Z. Liu, X.Y. Fang, *Science* 340 (2013) 957–960.
- [57] Z.R. Zeng, Y.M. Zhu, M.Z. Bian, C.H.J. Davies, N. Birbilis, J.F. Nie, *Acta Mater.* 105 (2016) 479–494.
- [58] T. Laser, C. Hartig, M.R. Nürnberg, D. Letzig, R. Bormann, *Acta Mater.* 56 (2008) 2791–2798.
- [59] Y. Chino, T. Ueda, Y. Otomatsu, K. Sassa, X. Huang, K. Suzuki, M. Mabuchi, *Mater. Trans.* 52 (2011) 1477–1482.

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In situ synchrotron radiation diffraction study of the role of Gd, Nd on the elevated temperature compression behavior of ZK40

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ABSTRACT

As-cast ZK40, ZK40-2Gd and ZK40-2Nd Mg alloys were investigated by *in situ* synchrotron radiation diffraction during compression at elevated temperature. The addition of rare earth elements increased the compressive yield strength from 23 MPa in the ZK40 alloy up to 40 MPa in the alloy with Nd or Gd. The azimuthal angle–time plots and electron back scattered diffraction maps from the compressed samples reveal that all the three alloys deform by grain rotation and crystallographic slip to obtain the final texture after compression. Continuous dynamic recrystallization played an important role in the ZK40 alloy during deformation, while twinning was not dominant. Discontinuous dynamic recrystallization was observed in the ZK40-2Gd. In the ZK40-2Gd and ZK40-2Nd alloys twinning also plays an important role during deformation at 350 °C. It is proposed that the pinning of the grain boundaries by the intermetallic phases was a main factor responsible for the observed differences in the deformation behavior.

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1. Introduction

There is an increased demand for better fuel efficiency through light weight constructions in the transport sector. Mg, being the lightest of the structural metals, is an ideal material to replace heavier counterparts such as steel and aluminum alloys in structural components [1]. It is well known that conventional Mg alloys exhibit poor formability at ambient temperatures [2], mainly due to the limited slip systems available. Wrought processing is therefore not feasible at room temperature and has to be conducted above 225 °C where the activation of non-basal slip becomes possible [3].

Mg–Zn system possesses potential for the development of low cost Mg alloys [4]. The ZK60 (Mg–6.0Zn–0.6Zr (wt%)) alloy has been reported to show a good combination of strength and ductility and is one of the highest strength wrought Mg alloys commercially available. Recently, there is a large body of work investigating the effect of various elemental additions on the enhancement of strength and ductility through modification of grain boundary particles [4–7], especially the effect of rare earth (RE) additions [8,9]. These investigations report enhancement of strength and ductility of the as-cast and the extruded ZK60. The RE

addition to the Mg–Zn–Zr system [10], typically ZE41 [11] resulted in improved castability and elevated temperature strength. From this element group especially Gd, has been reported to reduce the yield anisotropy (ratio between tensile and compressive yield strength) in extruded alloys [12] and also to reduce the strong basal textures in Mg–Zn–Zr based alloys for Zn contents between 1 and 6 wt% [13,14].

The RE additions on the deformation behavior of the as-cast Mg–Zn–Zr alloys, especially in compression can be informative in understanding the role of these elements during wrought processing, such as hot extrusion and rolling. A number of authors [15,16] have investigated the compressive behavior of ZK60 Mg alloy at high temperatures and attempted to establish different ranges of temperatures where the different deformation phenomenon occur. Wang et al. [16] found that 375 °C was the best temperature for the deformation of the ZK60 alloy. Wu et al. [17] investigated the compression behavior of ZK60 Mg alloy at different temperatures and found that 250–350 °C was the most effective range of temperatures for the ZK60 alloy. Post deformation investigation of microstructure using optical microscopy showed that at 350 °C at two different strain rates the microstructure did contain almost no twinning. The microstructure contained a high density of recrystallized grains at 350 °C and above. It remains unclear if recrystallization occurs dynamically or due to static recrystallization.

High energy X-ray and neutron diffraction has been utilized to

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investigate various metallic alloys [18–26], showing the capabilities of *in situ* characterization of metallic materials undergoing mechanical loading. *In situ* high energy X-ray diffraction (HEXRD) is a unique method that can investigate the dynamic microstructural processes that occur during mechanical loading in the bulk of the materials [19]. Azimuthal angle–time plots (AT-plots) give information on grain size evolution, grain imperfection, grain rotation, and grain orientation, texture evolution, strain and strain anisotropy, that can be correlated with dislocation slip, sub-grain formation, twinning, recovery, recrystallization and grain growth, which are the physical processes responsible for the microstructural changes [19].

The aim of the present work is to investigate the influence of Gd and Nd additions on the ZK40 Mg alloy during *in situ* compression at 350 °C using synchrotron radiation to provide new insights into the real-time microstructure evolution during deformation.

2. Experimental procedures

The alloys were prepared by permanent mold indirect chill casting as described in [27]. The alloys were melted in an electric resistance furnace under protective atmosphere of Ar with 2% SF₆. The Gd was added as Mg–4 wt% Gd and Zr added as Zirmax[®] alloy (Mg–33 wt% Zr). The Zn and Nd were added as pure elements. After mixing, the melt was held at 750 °C for 10 min. Then the melt was poured into a steel mold preheated to 660 °C which was then held at 660 °C for 15 min and lowered into water at a rate of 10 mm s^{−1} until the top of the melt was in line with the cooling water level. The chemical composition of the alloys was measured with a Bruker S5 X-ray fluorescence spectrometer. For the *in situ* compression experiments cylindrical specimens were machined from the cast ingots with a diameter of 5 mm and a length of 10 mm.

For the metallographic characterization of the as-cast and the deformed samples, they were mounted in epoxy and ground using SiC paper and then polished using 3 μm diamond suspension and then OPS solution with 1 μm diamond suspension as the last step of polishing. The microstructures for optical microscopy (OM) were etched with an acetic-picral solution [2]. The specimens for electron backscattered diffraction studies (EBSD) were not etched but washed with 0.5 vol% nitric acid in ethanol solution for 5 s and then washed with ethanol to remove any trace of nitric acid.

The optical microscopic analysis was performed using a Leica DMI 5000 light optical microscope. The scanning electron microscopy (SEM) investigation was performed using a Zeiss FEG-SEM Ultra 55 attached with a Hikari detector and a TSL-OIM software package for EBSD analysis. The EBSD measurements on compressed samples were conducted on an area of 300 μm × 150 μm with step size of 1 μm close to the center of the deformed specimen to ensure a similar area to that of measured during diffraction analysis. The grain boundaries are defined to have a minimum misorientation of 10° between neighboring points with minimum of 10 points having the same orientation (in this case 10 μm) with a confidence index of 0.09. A sub grain is defined as a region within the grain where at least 10 points share a similar orientation with a boundary misorientation less than 10° but greater than 5°. The kernel average misorientation was determined by calculating the average misorientation between a point in a kernel and surrounding points. All microstructures of deformed samples are presented so that the compression direction is parallel to the horizontal direction of the page.

The *in situ* synchrotron radiation diffraction was performed at the P07 beamline of Petra III, DESY (Deutsches Elektronen-Synchrotron). A monochromatic beam with energy of 100 keV

($\lambda = 0.0124$ nm) and with a cross section of 1.0 mm × 1.0 mm was used. Diffraction patterns were recorded with a PerkinElmer 1622 flat panel detector with a pixel size of 200 μm² which was placed at a sample-to-detector distance of 1535 mm from the specimen (calibrated with a LaB₆ standard powder sample). The acquisition time for each image was 1 s. The specimens were placed in the chamber of a dilatometer DIL 805 A/D (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany), combined with a modified heating induction coil so the beam passes only the sample [28]. The specimens were heated to 350 °C at a rate of 30 K s^{−1} and held at this temperature for 3 min before starting the deformation to ensure temperature homogeneity. The specimens were compressed with an initial strain rate of 1.1×10^{-3} s^{−1}. The tests were terminated at a total strain of 0.3. The morphology of the Debye–Scherrer rings was then analysed using the Fit2D[®] software [29] and converted into azimuthal angle–time (AT) plots [19] using the ImageJ[®] software package [30].

3. Results

The actual chemical compositions of the three alloys are listed in Table 1. The Zn and Nd concentrations were slightly higher than the nominal compositions while the composition of Gd was slightly lower. The optical and SEM micrographs of the as-cast ZK40, ZK40-2Gd and ZK40-2Nd alloys prior to deformation are shown in Fig. 1. The ZK40 (Fig. 1(a) and (d)) and the ZK40-2Gd (Fig. 1(b) and (e)) alloys exhibited cellular structures whereas the ZK40-2Nd (Fig. 1(c) and (f)) showed a more pronounced dendritic structure. In ZK40-2Gd and ZK40-2Nd alloys the intermetallic phases were semi-continuously distributed along the grain boundaries, whereas in ZK40 alloy small intermetallic particles were discretely distributed along the grain boundaries.

The true stress–strain curves from the *in situ* compression tests are shown in Fig. 2. The compressive proof stress ($\sigma_{0.2}$) measured was 22.7, 40.1 and 39.4 MPa for ZK40, ZK40-2Gd and ZK40-2Nd alloys, respectively. An increase in both the proof stress and the maximum compressive stress was observed with the addition of Gd and Nd. The increment to the proof stress was comparable between the ZK40-2Gd and ZK40-2Nd alloys but the maximum compressive stress measured for the Gd containing alloy was higher than that for Nd containing alloy.

The azimuthal angle–time plots (AT plots) [19] from the *in situ* synchrotron radiation diffraction measurements for the three alloys investigated are shown in Fig. 3. AT-plots for the {10 $\bar{1}$ 0} planes and for the (0002) plane are shown as combination of these two reflections, and illustrate both formation of twins and recrystallization. The true stress–strain curves are plotted under each AT-plot so that pertinent points during deformation could be correlated with the AT-plots. During the elastic regime of the deformation the diffraction patterns did not change significantly. As the plastic deformation began a number of phenomena were observed. The AT-plot of Fig. 3(a), region I, exhibits the blurring of the timelines (trace of a given reflection over deformation) for ZK40, as well as the broadening of the reflection and merging of timelines to develop the final texture of the material (II) [24,25]. Grain

Table 1
Chemical compositions of the alloys investigated.

Alloys	Composition of alloying additions (wt%)			
	Zn	Zr	Gd	Nd
ZK40	5.00	0.53	–	–
ZK40-Gd	4.50	0.55	1.70	–
ZK40-Nd	4.60	0.50	–	2.35

rotation was observed for example in region III in Fig. 3(a). Fig. 3 (a) region IV shows the appearance of new timelines especially in the early stages. The AT-plots for the ZK40-2Gd show thick lines that form during compression as indicated in Fig. 3(b) region V and not blurred profiles. In addition, the number of new lines in the intermediate stages, especially after a total strain of 0.1, becomes pronounced as shown in region VI. In ZK40-2Nd, Fig. 3 (c) blurred regions (VII) and the presence of new reflections in the profiles was observed.

To investigate twinning the maximum normalized values of the coupled pairs of integrated diffraction peaks $\{10\bar{1}0\}$ – (0002) were plotted against the total strain as shown in Fig. 4. The change in intensity of these peaks, i.e. increase in the intensity of one peak and decrease in the other, indicates extension twinning in Mg.

Fig. 5 shows the optical microstructures of samples compressed to a total strain of 0.3. The ZK40 alloy, Fig. 5(a), did not contain a significant distribution of twins through the microstructure. However, the Gd and Nd containing alloys show a high volume fraction of twinning following deformation at 350 °C. The area fraction of twins observed in ZK40, ZK40-2Gd and ZK40-2Nd was approximately 0.7%, 7.5% and 6.8%, respectively from the optical micrographs.

EBSD inverse pole figure maps of the samples compressed at 350 °C are shown in Fig. 6. ZK40 alloy contains many recrystallized grains at grain boundaries; marked by region A in Fig. 6(a), while region B highlights a grain that is yet to recrystallize but contains a large number of sub-grains. The region C, Fig. 6(a) shows an area within a grain that looks to be an initially twinned region. The

Fig. 1. (a–c) Optical micrographs and (d–f) SEM micrographs typical of as-cast (a and d) ZK40, (b and e), ZK40-2Gd and (c and f) ZK40-2Nd.

Fig. 2. Compressive true stress–strain curves.

Fig. 4. Change in the integrated intensity for the $\{10\bar{1}0\}$ and $\{0002\}$ reflections during compressive deformation.

Fig. 3. AT-plots obtained during the *in situ* synchrotron radiation diffraction during compressive deformation of (a) ZK40, (b) ZK40-2Gd and (c) ZK40-2Nd alloys. CD represents the compression direction.

misorientation between the partial grains on either side of what is proposed as a twin in region C was found to be less than 5° . This supports the hypothesis that the recrystallized grains formed at a prior twin. The ZK40-2Gd contained a large amount of recrystallized grains at the grain boundaries, region D in Fig. 6(b). The microstructure also contained a significant amount of twins whose boundaries are marked in red, which were analysed to be extension twins. Extension twins were also observed in ZK40-2Nd alloy (Fig. 6(c)) but there were no recrystallized grains at the grain boundaries. The local misorientations within grains were investigated with Kernel Average Misorientation (KAM) analysis, Fig. 7. The blue regions show a low degree of misorientation, e.g. in the recrystallized regions in ZK40 alloy. Both RE containing alloys had a relatively high degree of misorientation along the grain boundaries, Fig. 7(b) and (c). Some grains contained a large degree of misorientation within the grains in all three alloys which corresponds to grains containing sub-grains or dislocation cells from EBSD analysis.

The SEM micrographs of the ZK40, ZK40-2Gd and ZK40-2Nd alloys after deformation are shown in Fig. 8. The circles in Fig. 8

(b) and (c) highlight the areas where intermetallic phases seem to be broken in the ZK40-2Gd and ZK40-2Nd, respectively.

4. Discussion

The as-cast microstructure of the ZK40 alloy was modified with the addition of Gd and Nd. The RE containing alloys contain a semi-continuous distribution of intermetallic particles that reinforced the grain boundaries in ZK40-2Gd and ZK40-2Nd alloys. This observation is consistent with the microstructures of Mg–Zn–Zr alloys with Nd [5] and Gd [4] additions from previous investigations. The increment in the yield strengths observed during deformation at 350°C in the ZK40-2Nd and ZK40-2Gd alloys are attributed to the presence of a semi-continuous network of intermetallic particles. As illustrated in Fig. 8, the deformed samples show fracture of the intermetallic particles in the grain boundary regions in ZK40-2Gd and ZK40-2Nd alloys which was not observed in the ZK40 alloy. The increased compressive yield strength observed in these alloys, double that of ZK40 alloy, is mainly attributed to the increased stress required to deform the intermetallic particles.

The A-T plots in Fig. 3 combined with the EBSD maps in Fig. 6, and KAM analysis in Fig. 7, are used to analyse the deformation behavior of these alloys at 350°C . During the initial stages of deformation, i.e. elastic regime, no changes in the timelines were observed in the investigated alloys. Near the yield point the diffraction timelines tend to rotate toward the compression directions in case of $\{10\bar{1}0\}$ planes, while a rotation away from the compression directions was observed for the $\{0002\}$. This rotation was more significant for the ZK40 alloy (e.g. Region III in Fig. 3(a)) compared with ZK40-2Gd and ZK40-2Nd alloys. The rotation of timelines can be attributed to the grain rotation to accommodate strain build up within the microstructure. At the end of the deformation for all the alloys a tilted timeline structure can be seen on the $\{0002\}$ plots around the transversal direction to the deformation (Fig. 3). This indicates that crystallographic slip with a basal component is activated during deformation as found by Liss et al. [24] in the case of plastic deformation of Mg alloys. Grain rotation has been observed previously in pure Mg during and prior to high temperature deformation by Liss et al. [19]. This has been attributed to grain growth and rotation of grains through formation of sub-grains and recrystallization to an orientation that allow easy deformation [24].

Fig. 5. Optical microstructure of samples after a total compressive strain of 30% at 350 °C: (a) ZK40; (b) ZK40-2Gd and (c) ZK40-2Nd.

In ZK40 alloy the reorientation of grains with their basal plane perpendicular to compression direction was observed from the relatively random microstructure at the beginning of the plastic deformation. From the start of the plastic deformation reflections at an azimuthal angles close to 90° and 270° on {10 $\bar{1}$ 0} planes disappear while the intensities of the (0002) reflections become more prevalent, Fig. 3(a). There is a significant amount of blurring in reflection and appearance of new reflections corresponding to the formation of new grains due to recrystallization and to existing grains, which may become oriented to Bragg position during

deformation. It is noted that at the end of the deformation there are no visible {10 $\bar{1}$ 0} planes with their reflections close to 90° or 270°. Thus, it is expected that during plastic deformation all grains rotate to a favorable orientation as can be seen from the timelines (Fig. 3(a)) or that twins have engulfed grains with these orientations completely. There is some evidence where twins may have undergone recrystallization in Fig. 6(a) region marked C in the EBSD investigations. It is noted in Fig. 4, that there is no change in intensity in {10 $\bar{1}$ 0} planes with the increase in the intensity of (0002) plane, during the majority of the deformation. There was a small increase in intensity in {10 $\bar{1}$ 0} planes at the start which corresponds to a decrease in the intensity of (0002). Post mortem EBSD analysis in Fig. 6(a) did not show many grains with a (0002) orientation on the compression plane but there is evidence of a large number of grains with {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} planes or intermediate planes. It is noted that grains with {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} orientations in the compression plane contained a minimum amount of misorientation within the grains as measured by KAM analysis in Fig. 7(a).

In contrast to the ZK40 alloy, both ZK40-2Gd and ZK40-2Nd alloys retained {10 $\bar{1}$ 0} planes with azimuthal angles close to 90° and 270° to larger strains. The (0002) reflections parallel to azimuthal angles close to 0° and 180° remained until the end of the experiment for ZK40-2Gd alloy, Fig. 3(b). Some of these reflections were there from the start of the deformation while others appear during plastic deformation. It is difficult to see such reflections in ZK40-2Nd alloy due to blurring of reflections along the timelines, Fig. 3(c). The post mortem analysis using EBSD show that there are grains with orientations close to (0002) reflections in the compression plane and all these grains contain a high number density of twins. Additionally, extension twins also form in grains with orientations close to {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0}.

ZK40-2Gd has a highly deformed microstructure with a large fraction of sub-grains, Fig. 6(b), the region E. The sub-grains were highly misorientated with respect to each other. The deformation behavior of ZK40-2Gd is modified by the intermetallic particles pinning the grain boundaries, which hinder grain boundary rotation. The same effect was observed by Zhou et al. [9] for extruded ZK60-RE alloys, where the particle pinning had a significant impact on the dynamic recrystallization. The effect of Gd was more significant during compression at 350 °C than Nd in ZK40 alloy. Investigating the AT-plots, the less blurring of the profile and the thickening of the timelines during compression indicated in Fig. 3 (b) in region V suggest that the continuous dynamic recrystallization was not so pronounced in ZK40-2Gd alloy. The number of new lines that appear during the intermediate stages of deformation, especially after a strain of 0.1, is pronounced, region VI. This explains the large fraction of recrystallized grains found near the grain boundaries for ZK40-2Gd. In ZK40-2Nd the regions F and G in Fig. 6(c) show areas with high sub-grain formation. Fig. 3(c) exhibits a large blurred region (VII) which suggests that a large fraction of sub-grains form in this alloy during compression. The fraction of twins, shown in Fig. 5(c), is significant high for the ZK40-2Nd alloy. Fig. 4 shows a significant change on the intensities of the peaks, which could explain the presence of twins in the microstructure after deformation and the twins that are shown as recrystallized grains.

There is some evidence from post mortem EBSD in Fig. 6(a), that suggest that during early stages of deformation twins form in ZK40 alloy but recrystallization occurs at these twin boundaries leaving no trace of the twins. However, in ZK40-2Gd and ZK40-2Nd alloys twins that form in the microstructure are stable during deformation and did not show signs of recrystallization at the twin boundaries. This suggests that the twins once formed are stable and resistant to growth or recrystallization. Ostapovets and Gröger [31] simulated the strain along the extension twin boundaries and

Fig. 6. EBSD inverse pole figure maps of samples subjected to a total compressive strain of 30% at 350 °C: (a) ZK40; (b) ZK40-2Gd and (c) ZK40-2Nd. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 7. Kernel average misorientation angle maps for the same areas as in Fig. 4 after a total compressive strain of 30% at 350 °C: (a) ZK40; (b) ZK40-2Gd and (c) ZK40-2Nd. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 8. SEM micrographs of the samples deformed to a total strain of 30% in compression showing cracks in intermetallic particles: (a) ZK40; (b) ZK40-2Gd and (c) ZK40-2Nd.

found that there is an alternating compressive and tensile strain on the atoms along the twin boundary plane. Segregation of Gd and Zn to the twin boundaries was reported by Nie et al. [32], where Gd and Zn solute atoms segregate along twin boundaries when a compressed Mg1Gd0.5Zn (at%) alloy was heat treated at 150 °C for 3 h was observed with advanced transmission electron microscopy techniques. They further reported [24] that twins were stable following heat treatment of Mg–0.2Gd (at%) alloy after annealing at 300 °C for 20 min while such twins were not stable in Mg–0.4Zn (at%) alloy after similar thermal treatments. It is likely that Gd and Zn atoms segregate to the twin boundaries during deformation and stabilize the twin boundaries preventing recrystallization.

5. Conclusions

In situ synchrotron radiation diffraction was performed for as-cast specimens of ZK40, ZK40-2Gd and ZK40-2Nd at 350 °C and results reveal that the deformation mechanisms differ between the ZK40 and the ZK40 alloys with Gd or Nd additions. From the results the following conclusions can be drawn:

- (1) Continuous dynamic recrystallization is observed during compression for ZK40, exhibited in the azimuthal angle–time plot by the blurring of the timelines. Moreover, the broadening of the reflections by many degrees suggests the grains had more freedom to rotate compared with the modified alloys.
- (2) ZK40-2Gd and ZK40-2Nd alloys exhibited a highly deformed microstructure. Continuous and discontinuous dynamic recrystallization plays a role during deformation for the ZK40-2Gd alloy, evidenced by the presence of sub-grains and new grains at the grain boundary. On the other hand, discontinuous dynamic recrystallization was not pronounced in the ZK40-2Nd.
- (3) The influence of the intermetallic compounds in pinning the grain boundary, hampering grain rotation, caused more significant change in terms of the mechanical behavior for ZK40-2Gd compared with the ZK40-2Nd.
- (4) The increase in yield and maximum strength for the modified alloys can be explained by the presence of intermetallic particles that hinder stress transfer across the grains.

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References

- [1] M. Pekguleryuz, K. Kainer, A. Kaya, *Fundamentals of Magnesium Alloy Metallurgy*, first ed, Woodhead, Philadelphia, 2013.
- [2] M.M. Avedesian, H. Baker, *Magnesium and Magnesium Alloys*, ASM Speciality Handbook, ASM International, United States of America, 1999.
- [3] M.H. Yoo, J.R. Morris, K.M. Ho, S.R. Agnew, *Metall. Mater. Trans. A* 41 (2002) 813–822.
- [4] S.M. He, L.M. Peng, X.Q. Zeng, W.J. Ding, Y.P. Zhu, *Mater. Sci. Eng. A* 433 (2006) 175–181.
- [5] Q. Li, Q. Wang, Y. Wang, X. Zeng, W. Ding, *J. Alloy. Compd.* 427 (2007) 115–123.
- [6] T. Homma, C.L. Mendis, K. Hono, S. Kamado, *Mater. Sci. Eng. A* 527 (2010) 2356–2362.
- [7] S.-Y. Chang, H. Tezuka, A. Kamio, *Mater. Trans.* 38 (1997) 526–535.
- [8] C. Ma, M. Liu, G. Wu, W. Ding, Y. Zhu, *Mater. Sci. Eng. A* 349 (2003) 207–212.
- [9] H.T. Zhou, Z.D. Zhang, C.M. Liu, Q.W. Wang, *Mater. Sci. Eng. A* 445–446 (2007) 1–6.
- [10] T.E. Leontis, *Trans. AIME* 185 (1949) 968–983.
- [11] B. Lagowski, *AFS Trans.* 85 (1977) 237–240.
- [12] A. Singh, H. Somekawa, T. Mukai, *Scr. Mater.* 56 (2007) 935–938.
- [13] N. Stanford, *Mater. Sci. Eng. A* 527 (2010) 2669–2677.
- [14] J. Bohlen, M.R. Nürnberg, J.W. Senn, D. Letzig, S.R. Agnew, *Acta Mater.* 55 (2007) 2101–2112.
- [15] A. Galiyev, R. Kaibyshev, G. Gottstein, *Acta Mater.* 49 (2001) 1199–1207.
- [16] C.Y. Wang, H.Q. Qi, K. Wu, M.Y. Zhang, *Mater. Sci. Forum* 788 (2014) 93–97.
- [17] Y. Wu, H. Yan, S. Zhu, J. Chen, A. Liu, X. Liu, *Trans. Nonferr. Met. Soc. China* 24 (2014) 930–939.
- [18] K.-D. Liss, U. Garbe, H. Li, T. Schambron, J.D. Almer, K. Yan, *Adv. Eng. Mater.* 11 (2009) 37–40.
- [19] K.-D. Liss, K. Yan, *Mater. Sci. Eng. A* 528 (2010) 11–27.
- [20] K.-D. Liss, T. Schmoelzer, K. Yan, M. Reid, R. Dippenaar, H.J. Clemens, *Appl. Phys.* 106 (2009) 044914-1–044914-6.
- [21] T. Schmoelzer, K.-D. Liss, P. Staron, S. Mayer, H. Clemens, *Adv. Eng. Mater.* 13 (2011) 85–99.
- [22] I. Lonardelli, N. Gey, H.-R. Wenk, M. Humbert, S.C. Vogel, L. Lutterotti, *Acta*

- Mater. 55 (2007) 5718–5727.
- [23] P. Suwanpinij, A. Stark, X. Li, F. Römer, K. Herrmann, T. Lippmann, W. Bleck, Adv. Eng. Mater. 15 (2014).
- [24] K.-D. Liss, K. Yan, M. Reid, Mater. Sci. Eng. A 601 (2014) 78–85.
- [25] K. Yan, K.-D. Liss, U. Garbe, J. Daniels, O. Kirstein, H. Li, R. Dippenaar, Adv. Eng. Mater. 11 (2009) 771–773.
- [26] K. Yan, D.G. Carr, M.D. Callaghan, K.-D. Liss, H. Li, Scr. Mater. 62 (2010) 246–249.
- [27] F.R. Elsayed, N. Hort, M.A. Salgado-Ordorica, K. Kainer, Mater. Sci. Forum 690 (2011) 65–68.
- [28] D. Tolnai, G. Szakacs, G. Requena, A. Stark, N. Schell, K. Kainer, N. Hort, Mater. Sci. Forum 765 (2013) 286–290.
- [29] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Häusermann, High Press. Res. 14 (1996) 235–248.
- [30] M.D. Abramoff, P.J. Magalhaes, S.J. Ram, Biophoton. Int. 11 (2004) 36–42.
- [31] A. Ostapovets, R. Gröger, Model. Simul. Mater. Sci. Eng. 22 (2014) 025015.
- [32] J.F. Nie, Y.M. Zhu, J.Z. Liu, Z.Y. Fang, Science 340 (2013) 957–960.

As cast microstructures on the mechanical and corrosion behaviour of ZK40 modified with Gd and Nd additions

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ABSTRACT

The microstructure of ZK40, ZK40 with 2 wt% of Nd and Gd (ZK40-2Nd and ZK40-2Gd, respectively) were investigated with optical, scanning and transmission electron microscopy, X-ray diffraction and Scanning Kelvin Probe Force Microscopy. The mechanical properties and the corrosion behaviour were correlated with the microstructure. The 2 wt% Gd addition enhanced the ductility, while the Nd addition resulted in deterioration in mechanical properties. The corrosion behaviour was also enhanced with the addition of Gd.

1. Introduction

Mg alloys offer a high potential for use as lightweight structural materials in the automotive and aerospace industry. However, satisfactory mechanical properties are not enough to promote a magnesium alloy for commercial applications where corrosion resistance also plays an important role. In fact, Mg alloys usually have relatively low corrosion resistance, which is one of the main obstacles that impede the use of magnesium alloys [1].

Several approaches have been developed with the aim of enhancing the corrosion resistance of the Mg alloy involving the addition of alloying elements. The AZ Mg alloys have been extensively studied, such as AZ31 due to mainly its promising applications in forming, or AZ91 for high pressure die casting [2]. The influence of the RE elements on the mechanical properties [3] and corrosion behaviour [4,5] of Mg–Al alloy system has also been investigated. In the AZ system the second phases can act as a galvanic cathode and accelerate the corrosion rate of the matrix if the volume fraction of the second phases is small [6,7]. On the other hand, if there is a larger amount of second phase that it forms as a continuous network it may act as an anodic barrier to inhibit the overall corrosion of the alloy.

In the case of Mg–Zn alloys, the effect of addition of rare earth on the corrosion behaviour has yet not been fully understood [8]. Among these investigations, the as cast ZE41 (Mg–Zn–RE alloy) is in the focus of most of the studies. Compared with the AZ alloys, the eutectic phases in ZE41 are reported to not play the role of corrosion barrier retarding the progress of the corrosion [9]. For ZE41 immersed in 1 N NaCl,

Zhao et al. [9] showed that the corrosion initiated as localised corrosion. It started at some sites on the surface and expanded over the surface forming a thick layer of corrosion products. Neil et al. [10] reported that segregation of Zr in the α -Mg matrix played a distinct role on the early stages of corrosion in the ZE41. However, among the investigated Mg alloy systems, Mg–Zn–Zr (ZK) alloys are one of the higher strength cast alloys available commercially [11]. The small addition of rare earth (RE) elements to the ZK alloys can alter the microstructure and therefore can modify the mechanical properties and give satisfactory corrosion resistance. It is reported that the addition of rare earth (RE) elements and alkaline metals to Mg alloys improves the corrosion resistance [4,5]. The addition of RE [12] enhanced the castability and elevated temperature strength [13]. The RE additions are grain refiners, attributed mainly to the constitutional supercooling [14], which can lead to improved ductility at room temperature [15,16].

However, the role of individual rare earth elements on the mechanical behaviour and corrosion resistance of ZK series alloys has not been fully investigated. The aim of the present work is to study the influence of Gd and Nd additions on the microstructure, mechanical properties and corrosion behaviour.

2. Experimental procedure

2.1. Materials

Pure Mg, Zn, Nd and master alloys Mg 4 wt% Gd and Mg–33 wt% Zr

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Table 1
Analysed chemical compositions.

Alloys	Zn (wt %)	Zr (wt%)	Gd (wt %)	Nd (wt %)	Fe (ppm)	Cu (ppm)	Ni (ppm)
ZK40	5.00	0.53	–	–	11.3	14.1	12.8
ZK40-2Gd	4.50	0.55	1.70	–	6.9	29.2	28.2
ZK40-2Nd	4.70	0.55	–	2.46	11	14.8	28.2

(Zirmax[®]) were used to prepare the alloys. Mg was molten in an electric resistance furnace under protective atmosphere of Ar with 2 vol% SF₆ and held at 750 °C where alloying additions were added to the melt and stirred for 10 min. The melt was poured into a preheated thin walled steel mould, held at 660 °C for 15 min before immersing into water at a rate of 10 mm s^{−1} until the top of the melt was in line with the cooling water. This indirect chill casting procedure was performed in order to provide a homogeneous microstructure. Zr and Gd were measured with Bruker S5 X-ray fluorescence spectrometer. Zn, Nd, Fe, Cu and Ni were measured with a Spectrolab spark analyser.

2.2. Differential thermal analysis (DTA)

Specimens for Differential Thermal Analysis (DTA) were prepared by placing approximately 30–45 mg of the alloys in Mettler Toledo crucible in an Ar atmosphere. The analysis were performed using a Parkin Elmer DTA machine at a heating and cooling rate of 10 K/min in the temperature range from 300 to 700 °C. Three heating and cooling cycles were used for each alloy to ensure repeatability of the measurement.

2.3. Specimen preparation and characterisation

For metallographic characterisation, specimens were ground through successive grades of silicon carbide abrasive papers from P500 to P2500, followed by polishing with a 3 µm diamond suspension and finally in OPS with 1 µm diamond suspension. The specimens analysed by optical microscopy (OM) were etched with an acetic picric acid solution [17] to reveal the constituents of the alloys. The analyses were performed using a reflected light microscope Leica DMI 5000. Grain size was determined according to the ASTM E112-12 standard using the linear intercepts method. Polished samples were examined

with scanning electron microscopy (SEM) using a Zeiss FEG-SEM Ultra 55, aInspect F50 and a Tescan Vega3 SEM using BSE and SE modes. The SEMs were equipped with Energy dispersive X-ray (EDX) spectrometer. EDX spectra profiles were obtained across the grains to determine the distribution of elements. Savitzky-Golay [18] smooth filter was applied using Origin with 20 points of window to fit a 4-degree polynomial.

Phase characterisation of the as-cast specimens was conducted with synchrotron radiation diffraction (SRD) using the facilities of P07 beamline of Petra III, DESY (*Deutsches Elektronen-Synchrotron*). A monochromatic beam with energy of 100 keV ($\lambda=0.0124$ nm) and with a cross-section of 1.0 mm×1.0 mm was used. Diffraction patterns were recorded with a PerkinElmer 1622 flat panel detector with a pixel size of (200 µm)², which was placed at a sample-to-detector distance of 1535 mm from the specimen (calibrated with a LaB₆ standard powder sample). The Pearson crystallographic database was used to obtain the information of possible phases and CaRine crystallographic software was used to simulate the theoretical diffraction patterns for various phases.

The samples for transmission electron microscopy (TEM) were prepared by cutting 0.5 mm slices with Struers Isomat precision saw followed by thinning to 150 µm in thickness using 500 grit SiC paper. Then 3 mm diameter discs were punched using a disc punch and electropolished using a Fischione twin jet electropolisher at −45 °C with a voltage of 50 V in solution of 1.5 vol% perchloric acid in ethanol to perforation. TEM analysis was conducted with a FEI CM 200 transmission electron microscope operating at 200 kV equipped with an Oxford EDAX Energy dispersive X-ray spectrometer (EDX) and quantitative composition measured using standardless thin film technique.

Scanning Kelvin Probe Force Microscopy (SKPFM) working in tapping mode was performed using a Nanoscope IIIa MultiMode microscope. Surface potential maps were obtained using a silicon tip with a platinum coating of 20 nm thickness. The topographic and surface potential images were obtained simultaneously and the tip to sample distance was kept constant at 100 nm. The tested samples were metallographically prepared and polished to a 0.25 µm diamond suspension finish. All measurements were performed at room temperature and the relative humidity was in the range of 40–65%. SEM/EDS analyses were performed in the SKPFM-examined regions to identify the second phases.

Fig. 1. (a)–(c) Optical micrographs and (d)–(f) SEM micrographs typical of as-cast (a), (d) ZK40; (b), (e) ZK40-2Gd; (c), (f) ZK40-2Nd alloys.

Fig. 2. EDX spectra line profiles for the: (a) ZK40; (b) ZK40-2Gd; (c) ZK40-2Nd across a typical grain.

2.4. Mechanical testing

Cylindrical compression specimens with 10 mm diameter and 15 mm length and tensile specimen with diameter of 6 mm were manufactured according to DIN 50125 (ISO 6892-1) from the as cast ingots. Both tests were performed in a Zwick Z050 mechanical testing machine with a strain rate of 0.001 mm/min at room temperature and five samples were tested per alloy.

2.5. Electrochemical measurements

Electrochemical tests were conducted in a stirred aqueous 0.5 wt% NaCl solution at 22 ± 0.5 °C using a Gill AC computer-controlled potentiostat. A typical three-electrode cell with the specimen as the

working electrode (0.5 cm^2 exposed area), a saturated Ag/AgCl electrode as the reference electrode, and a platinum mesh as a counter electrode was used.

Electrochemical impedance spectroscopy (EIS) measurements were performed for immersion times ranging from 1 h to 1 day at room temperature. The frequency range was from 0.01 Hz to 30 kHz and the amplitude of the sinusoidal potential signal was 10 mV with respect to the OCP. The impedance spectra were analysed using ZView® software. The errors for the individual parameters of the equivalent electrical circuits (such as CPE and R) were $\pm 5\%$ and with values of the goodness of fit of the simulated spectra corresponded to χ^2 ± 0.01 .

2.6. Hydrogen evolution measurements

Details of the procedure, design and the relationship between the volume of hydrogen evolution and the mass loss of the specimen can be found elsewhere [19,20]. Hydrogen evolution measurements were performed in 0.5 wt% NaCl naturally-aerated solution for up to 14 days for ZK40 and ZK40-2Gd alloys and up to 7 days for ZK40-2Nd. After the corrosion tests, specimens were characterised with SEM in order to investigate the morphology and composition of the corrosion products.

2.7. Initial steps of corrosion

Immersion tests were performed for 4 h, 8 h and 24 h in 0.5 wt% NaCl naturally-aerated solution in order to investigate the initiation of corrosion process. The final sample surface was prepared with OPS polishing to ensure that the sample preparation did not contribute to the corrosion process. Finally, the corroded surface was investigated with SEM after the removal of the corrosion products by pickling in a solution containing 200 g/L CrO_3 at room temperature for 5–10 min following the ASTM standard G1-90, Designation C5.2.

3. Results and discussion

3.1. Microstructure

The actual compositions of the alloys are given in Table 1. The optical (a–c) and scanning electron microscopy (d–f) for ZK40 (a,d), ZK40-2Gd (b,e) and ZK40-2Nd (c,f) are shown in Fig. 1. Relatively uniform microstructures were observed for each alloy. ZK40-2Nd exhibits the most pronounced dendritic microstructure, and has a more uniform microstructure compared with other two alloys. The ZK40 had an average grain size of 37.4 ± 2.1 μm, the ZK40-2Gd of 46.1 ± 9.1 μm and the ZK40-2Nd had an average grain size of 67.1 ± 5.4 μm.

The SEM micrographs illustrate the area fraction of intermetallic particles, with ZK40, ZK40-2Gd and ZK40-2Nd alloys contained $1.6 \pm 0.5\%$, $5.7 \pm 1.0\%$ and $7.3 \pm 0.6\%$ intermetallic particles, respectively. Additionally, in the ZK40 alloy segregation of Zn towards the grain boundary is observed as illustrated by brighter regions along the grain boundary in Fig. 1(d). ZK40-2Gd (Fig. 2(b)) has higher concentration of Zr within the grain. No significant chemical segregation was observed in the ZK40-2Nd alloy (Fig. 2(c)). The Gd and Nd distribute along the grain boundaries in the modified alloys. In the ZK40 alloy, discrete particles of intermetallic phase are observed randomly at triple points and grain boundaries, illustrated by the insert in Fig. 1(d). The ZK40-2Gd and ZK40-2Nd alloys contains a semi-continuous distribution of intermetallic particles along the grain boundaries. Therefore, the as-cast microstructure of the ZK40 alloy was modified with Gd and Nd. The RE containing alloys contained a semi-continuous network of intermetallic particles reinforcing the grain boundary, Fig. 1. Similar microstructure was reported for the ZE41 alloy [9,10].

The EDX spectra shows the segregation of elements in the alloys investigated, Fig. 2. Zn segregates and a concentration was observed near the grain boundary for the ZK40 and ZK40-2Gd alloys. The

Fig. 3. (a) XRD linescan profiles for the ZK40-2Gd and ZK40-2Nd alloys in the as-cast condition; (b) DTA cooling curves for the ZK40, ZK40-2Gd and ZK40-2Nd alloys.

inverse segregation of Zr is observed for the ZK40-2Gd, while only minor Zr segregation was observed in Nd containing alloy. The RE (Gd and Nd) elements do not seem to segregate within the grain.

The SRD line profiles from all investigated alloys show that they consisted of α -Mg and intermetallic phases, Fig. 3(a), (c), and (e). The intermetallic phase was alloy dependent and the ZK40 alloy contained $MgZn_2$ phase. The ZK40-2Gd contained $(Mg, Zn)_3Gd_2$ intermetallic phase, in addition to α -Mg. Liu et al. [27] reported the presence of the $(Mg, Zn)_3Gd_2$ for a Mg-4.58Zn-2Gd-0.18Zr alloy. Due to the large number of peaks observed in the SRD line profile of the ZK40-2Nd alloy, the intermetallic particles were analysed with TEM to confirm the intermetallic phases, Fig. 4. The composition of the phase was 71.8 ± 7.2 at% Mg 20.3 ± 5.2 at% Zn and 7.9 ± 2.0 at% Nd, Fig. 4(b); and the crystal structure could be indexed according the C centred orthorhombic phase, Fig. 4(c)–(e) (lattice parameters $a=0.97$ nm, $b=1.12$ nm and $c=0.95$ nm) reported by Huang et al. [21]. Only this phase was detected in the ZK40-2Nd alloy and it is addressed as $Mg_{75}Zn_{20}Nd_5$.

All three DTA curves show an exothermic peak, during cooling from 700 °C, at 636–638 °C attributed to the formation of α -Mg, Fig. 3(b),

(d), and (f). In addition, a single peak was observed at 337.7 °C for ZK40 during cooling and the intermetallic phase formation was observed at 496.4 °C for the ZK40-2Gd. This indicated that ZK40-2Gd contained an intermetallic phase different from ZK40. In case of ZK40-2Nd two exothermic peaks were measured, at 487.8 and 466.3 °C. Based on the TEM and the SRD results only one intermetallic phase was observed in the microstructure, denoted as $Mg_{75}Zn_{20}Nd_5$ [21]. This suggests a possible transformation of the intermetallic phase during cooling. A conclusive evaluation of this is beyond the scope of this publication and this will be investigated in a later publication.

The potential differences between constituents of the different materials were investigated using SKPFM [22]. Surface potential maps and potential profiles are shown in Fig. 5 for the ZK40 (Fig. 5(a)), ZK40-2Gd (Fig. 5(b)) and ZK40-2Nd (Fig. 5(c)). Fig. 6 illustrates the surface potential maps, potential profiles and chemical composition for the impurities particles found in the ZK40-2Gd alloy (Fig. 6(a)) and for the ZK40-2Nd alloy (Fig. 6(b)). Mg-Zn-Zr-Fe impurities are cathodic with respect to the α -Mg matrix (430 ± 50 mV for the ZK40 alloy and 140 ± 30 mV for the ZK40-2Nd alloy), suggesting the formation of

Fig. 4. TEM analyses for the ZK40-2Nd alloy: (a) the bright field image of the intermetallic phase; (b) EDS line profile for the intermetallic phase; (c)–(e) diffraction patterns for the (001), (101) and (110) zones axis, respectively.

micro-galvanic couples. The intermetallic phases present in the studied alloys were also cathodic with respect to the α -Mg matrix. For the ZK40, ZK40-2Gd and ZK40-2Nd alloys the potential difference between the intermetallic phases and the α -Mg matrix was 50 ± 20 mV, 170 ± 20 mV and 35 ± 10 mV, respectively.

3.2. Room temperature tensile and compression properties

The tensile and compression curves of the investigated alloys are shown in Fig. 7 with pertinent points summarised in Table 2. The ZK40-2Gd has the largest elongation to failure. The tensile tests show improved yield strength and the maximum tensile strength for the Gd modified alloy. The strong bonding between the intermetallic phase and the matrix can be a reason for the enhanced strength of ZK40-2Gd alloy. This effect was reported by Yu et al. [16] for a high strain-rate rolled Mg-5.5Zn-0.6Zr-xGd ($x=0.2, 0.5$ and 0.8 wt%). The yield strength and maximum tensile strength were significantly reduced by the Nd addition. There was no significant difference between compressive and tensile yield strengths of all three alloys. The maximum compressive strength and compression to failure did not show significant deviations from each alloy. However, the ultimate tensile stress (UTS) of ZK40-2Nd is significant smaller than other two alloys and did not show similar amount of work hardening. The elongation to failure was also significantly lower for ZK40-2Nd.

3.3. Corrosion behaviour

Based on the corrosion results, findings reveal that the corrosion resistance in NaCl aqueous solution of ZK40 alloy increases with the addition of Gd and decreases with the incorporation of Nd.

Fig. 8 shows the hydrogen evolution volume up to 7 days (for ZK40-2Nd) and 14 days (for ZK40-2Gd and ZK40) of immersion in 0.5 wt% NaCl. The ZK40-2Nd alloy shows a considerably higher hydrogen evolution volume compared with the ZK40 and ZK40-2Gd alloys. After one day, the hydrogen evolution volume of ZK40-2Nd was $1.07 \pm$

0.15 ml/cm², whereas ZK40 alloy had produced only 0.23 ± 0.01 ml/cm² and the ZK40-2Gd alloy had produced 0.10 ± 0.01 ml/cm² of H₂. Therefore, the amount of H₂ produced by ZK40-2Nd was 5 times higher compared to the ZK40 and approximately 10 times higher than ZK40-2Gd. In the case of ZK40-2Nd alloy, the hydrogen release was very fast so that the test was interrupted after 7 days. For all immersion times, the alloy ZK40-2Gd showed the lowest hydrogen evolution values indicating the enhanced corrosion behaviour.

Hydrogen evolution results show a different tendency for short and long immersion times. At the initial stage of corrosion, an incubation period with a low rate of hydrogen evolution is observed followed by a period of acceleration in hydrogen evolution after approximately 10 h for the ZK40-2Nd alloy, 25 h for the ZK40 and 50 h for the ZK40-2Gd alloy. After approximately 150 h for the ZK40-2Gd and 175 h for the ZK40 alloy the hydrogen evolution volume reached an apparent constant increase rate, indicated by the linearity of curves of these alloys. The ZK40-2Nd alloy did not show such behaviour in the range investigated. These differences might be related with the corrosion layer formed on the surface of the different alloys [28]. After immersion in an aqueous solution, the film of MgO that formed in air will transform into a film consisting mainly of Mg(OH)₂. The volume expansion from MgO to Mg(OH)₂ is attributed as the main disruption of the surface film [29] and could explain the porous microstructure of the Mg(OH)₂ layer in the surface film. The initial incubation period observed during hydrogen evolution attributes to the breakdown of the MgO surface film originating cracks on the corrosion film [28]. However, once the film starts breaking down and corrosion is initiated in a specific area (localised corrosion), repairing of the corrosion film is relatively difficult. Although the dissolved Mg²⁺ can react with OH[−] and deposit Mg(OH)₂ on the Mg surface, the loosely deposited Mg(OH)₂ film does not necessarily cover the cracks. Simultaneously, the hydrogen bubbles generated in the corroding areas can cause localised disruptions to the deposited Mg(OH)₂ preventing the corroding areas from being fully covered by the Mg(OH)₂. The accelerated period of hydrogen evolution is attributed to the intensive localised corrosion activity. Finally, due to the increase of the pH (intrinsically related to the redox reactions of Mg, which produce OH[−] as one of the products), and taking into account that the magnesium corrosion products are stable at high pH [30], the corrosion front stabilise, leading to a nearly linear hydrogen volume increase.

EIS is an effective method to characterize metal corrosion behaviour [23,24]. Fig. 9 shows Nyquist and Bode diagrams of the EIS experimental data for the alloys after 24 h of immersion in 0.5 wt% NaCl solution. The Nyquist diagrams show a capacitive loop at high and intermediate frequencies (HF and MF), which can be attributed to the electrochemical activities in the interface metal/electrolyte (charge transfer resistance and double layer capacitance). The inductive response observed at low frequencies, is mainly related to the instability of the system and to simplify was not included in the fitting.

Based on that, a Randles equivalent circuit [25] was used to fit the EIS experimental data (insert Fig. 9(d) in the example of the fitting of the experimental data for ZK40 alloy). The circuit shows the uncompensated solution resistance (R_{el}), the time constant related to the corrosion process that can be described by the double layer capacitance on the electrolyte/metal interface (Constant Phase Element – CPEDl) and the charge transfer resistance (R_{ct}). Constant Phase Element (CPE) was used instead of capacitances in order to account the non-ideal behaviour of the system [26]. The corresponding electrochemical parameters are presented in Table 3.

R_{el} values were comparable for all the alloys and were in the range between 85 and 100 Ω cm². The diameter of the capacitive loop observed in the Nyquist diagram (Fig. 9(a)) of the ZK40-2Gd alloy reaches Z' values around 1100 Ω cm², which is higher than that of the ZK40 alloy (700 Ω cm²), and significantly higher than the ZK40-2Nd alloy (400 Ω cm²), indicating a higher corrosion resistance of the ZK40-2Gd alloy.

Fig. 5. Surface potential maps and potential profiles for (a), (b) KZ40, (c), (d) KZ40-2Gd and (e), (f) KZ40-2Nd alloys.

CPE-T values of the dielectric layer of ZK40-2Nd ($220.0 \mu\text{F cm}^{-2}$) after 24 h immersion are approximately 2.5 times higher than those of the ZK40 alloy ($75.1 \mu\text{F cm}^{-2}$) and the ZK40-2Gd alloy ($65.6 \mu\text{F cm}^{-2}$). This is associated with the greater active area in ZK40-2Nd alloy exposed to the electrolyte. CPE-n value is the highest for the ZK40-2Gd alloy and the smallest for the ZK40-2Nd alloy, suggesting that there is an increase in the heterogeneity of the surface due to the corrosion process in the ZK40-2Nd alloy. The calculated CPE-T values increased with time for all investigated alloys.

Higher values of the charge transfer resistance ($485.5 \Omega \text{ cm}^2$) for the ZK40-2Gd alloy, after 24 h of immersion, compared to ZK40 alloy ($412.3 \Omega \text{ cm}^2$) and ZK40-2Nd alloy ($133.3 \Omega \text{ cm}^2$) reveals its enhanced corrosion resistance. The R_{ct} decreased for all alloys with the immersion time, due to the propagation of the corrosion process as was reported by Arrabal et al. [31].

Fig. 10 shows the plan view of the corroded specimens, after the removal of the corrosion products, for immersion times of 4 h (Fig. 10(a)–(c)), 8 h (Fig. 10(d)–(f)) and 24 h (Fig. 10(g)–(i)) in 0.5 wt% NaCl solution. In all the cases, localised corrosion is observed characterised by micro “craters” in the α -Mg matrix, with about $1 \mu\text{m}$

of diameter. In the particular case of ZK40-2Nd alloy, localised corrosion along the intermetallic particles was also observed (insert of Fig. 10(c), (f)). This alloy shows the most severe corrosion attack after 24 h of immersion (Fig. 10(i)).

Mainly two factors can be discussed in terms of corrosion behaviour:

- (i) Micro-galvanic effect between the α -Mg matrix and second phases and between the α -Mg matrix and the impurities: In general, this topic has been studied extensively and almost all the intermetallic phases in Mg alloys are more noble compared to the α -Mg matrix, as reported for AZ alloys [32–34], ZE41 [35,36], Mg-xGd-3Y-0.4Zr ($x=6, 8, 10, 12\%$) [37], Mg-10Gd-3Y-0.4Zr [38], Mg-Zn-RE [39], Mg-6Zn-1Y-0.6Zr [40], Mg-Zn-Mn-Si-Ca [41,42], Mg-8Li [43] and Mg-RE (0.5–5% La, 0.5–5% Ce, 0.5–4% Nd) [44]. The SKPFM analysis (Figs. 5 and 6) indicates that for the ZK40-2Gd and ZK40-2Nd the impurities has a higher Volta potential surface potential compared with the matrix, and it is significantly higher than the potential difference between the intermetallic compounds and the matrix. However, the initial steps of corrosion (up to 24 h

Fig. 6. Surface potential maps, composition and potential profiles in regions containing impurities for (a)–(c) KZ40-2Gd and (d)–(f) KZ40-2Nd.

Fig. 7. Typical tensile (a) and compressive (b) nominal stress-strain curves for the ZK40, ZK40-2Gd and ZK40-2Nd alloys.

Table 2

Mechanical properties at room temperature: compression and tensile values for the ZK40 alloy, ZK40-2Gd alloy and ZK40-2Nd alloy.

Tensile properties				Compression properties		
	Yield stress (MPa)	Maximum stress (MPa)	Elongation at failure	Yield stress (MPa)	Maximum stress (MPa)	Elongation at failure
ZK40	101.8 ± 6.7	225.1 ± 15.2	12.8 ± 4.6	106.8 ± 3.0	365.2 ± 3.6	20.6 ± 1.3
ZK40-2Gd	99.8 ± 6.1	227.9 ± 6.5	17.9 ± 1.9	107.3 ± 2.7	360.9 ± 3.8	20.2 ± 1.5
ZK40-2Nd	99.3 ± 2.7	147.5 ± 10.3	3.9 ± 1.0	109.3 ± 2.4	351.3 ± 2.3	22.3 ± 2.1

of immersion) (Fig. 10) does not show strong evidence of microgalvanic effect due to these impurities. Thus, the impurities can act as initiation points of corrosion but did not play an important role on the development of corrosion within the α -Mg matrix. Regarding the corrosion mechanism, for the ZK40 and ZK40-

2Gd alloys, the corrosion started within the grain, as illustrated by the “craters”, Fig. 10(b). Additionally, “micro craters” of $\sim 1 \mu\text{m}$ diameter are observed in the middle of the grain for all alloys, but not close to the grain boundaries in the case of the ZK40-2Gd which is in concordance with other work [10]. The different

Fig. 8. Hydrogen evolution in 0.5 wt% NaCl solution for the ZK40 alloy, ZK40-2Gd alloy and ZK40-2Nd alloy.

corrosion morphology of the alloys might be related to the presence of second phases but also to the chemical segregation of the different alloying elements in the α -Mg matrix. In the case of ZK40 and ZK40-2Gd, the higher concentration of Zn near the grain boundary enhanced the corrosion resistance of this area for the ZK40 and ZK40-2Gd. The segregation of Zn is higher for the ZK40 compared with the ZK40-2Gd. The presence of high amount of Zr

Table 3
Simulated parameters of the electrochemical impedance spectroscopy (EIS) data of the investigated ZK40, ZK40-2Gd and ZK40-2Nd alloys after 24 h.

Time (h)	R_{el} (Ω)	R_{ct} ($\Omega\text{ cm}^2$)	CPE-T ($\mu\text{F cm}^{-2}$)	CPE-P
ZK40				
1	84.7 ± 0.5	702.9 ± 6.7	23.1 ± 0.7	0.880 ± 0.005
3	84.9 ± 0.5	581.2 ± 5.7	31.1 ± 1.0	0.892 ± 0.005
6	87.3 ± 0.6	525.0 ± 6.1	39.3 ± 1.6	0.893 ± 0.007
10	86.4 ± 0.5	494.6 ± 5.3	45.1 ± 1.6	0.909 ± 0.006
16	86.4 ± 0.4	452.0 ± 4.6	64.5 ± 2.1	0.877 ± 0.007
24	85.8 ± 0.4	412.3 ± 4.8	75.1 ± 2.7	0.876 ± 0.006
ZK40-2Gd				
1	84.7 ± 0.9	1131.0 ± 16.5	19.9 ± 1.0	0.868 ± 0.008
3	87.1 ± 0.5	677.5 ± 6.8	24.5 ± 0.8	0.904 ± 0.006
6	87.4 ± 0.5	627.2 ± 6.7	35.2 ± 1.2	0.905 ± 0.006
10	89.3 ± 0.5	594.3 ± 6.0	43.8 ± 1.4	0.906 ± 0.006
16	89.4 ± 0.6	458.7 ± 6.7	45.2 ± 2.1	0.927 ± 0.009
24	88.1 ± 0.4	485.5 ± 5.2	65.6 ± 3.4	0.892 ± 0.006
ZK40-2Nd				
1	94.8 ± 1.0	413.2 ± 7.7	41.6 ± 3.3	0.831 ± 0.013
3	97.3 ± 0.5	213.8 ± 2.6	45.0 ± 2.6	0.901 ± 0.010
6	96.6 ± 0.5	165.4 ± 2.2	75.1 ± 4.9	0.889 ± 0.012
10	97.7 ± 0.5	152.8 ± 1.9	117.0 ± 7.0	0.860 ± 0.011
16	100.0 ± 0.5	150.9 ± 2.3	164.0 ± 10.6	0.840 ± 0.013
24	100.1 ± 0.5	133.3 ± 2.4	220.0 ± 15.7	0.824 ± 0.014

in the centre of the grain for the ZK40-2Gd did not seem to enhance to corrosion resistance of the α -Mg matrix. In the particular case of ZK40-2Nd alloy, localised corrosion along the

Fig. 9. Nyquist diagrams obtained by EIS in 0.5 wt% NaCl solution after (a) 1 h; (b) 24 h; (c) Bode plots obtained by EIS in 0.5 wt% NaCl solution after 24 h; (d) measured and calculated Nyquist diagrams for the ZK40 alloy from EIS in 0.5 wt% NaCl solution after 24 h as well as the equivalent circuit for EIS analysis.

Fig. 10. First steps corrosion SE pictures after 4 h (a), (d), (g), 8 h (b), (e), (h) and 24 h (c), (f), (i) in 0.5 wt% NaCl for the ZK40 alloy (a)–(c), ZK40-2Gd (d)–(f) and ZK40-2Nd alloy (g)–(i).

intermetallic compounds also play a role (Fig. 10(c), (f), and (i)) on the corrosion mechanism. This effect was not observed for the ZK40 or the ZK40-2Gd. This result is unexpected as the SKPFM results for ZK40-2Nd alloy show that the Volta potential difference between the α -Mg matrix and the intermetallic compound was not large. The SKPFM measures the surface potential difference. It is expected that the highest the potential difference between the two surfaces results in a higher microgalvanic couple. The presence of microgalvanic couples can lead to microgalvanic corrosion. For the ZK40-2Nd, the localised corrosion of the α -Mg matrix along the intermetallic phase suggests that not only the nobility of the intermetallic phase played an important role during immersion in 0.5 wt% NaCl but other mechanisms of corrosion also contribute to the corrosion process. The chemical segregation for the ZK40-2Nd alloy was nearly absent. For the ZK40 and ZK40-2Gd alloys the grain boundary could act as cathodic areas related to the α -Mg matrix, prevent the grain boundaries to corrode. The absence of this effect for the ZK40-2Nd alloy could have enhanced the corrosion of the α -Mg matrix along the intermetallic compound;

- (ii) The barrier effect of second phases: As reported for AZ series magnesium alloys [45,46], the barrier effect due to the presence of a semi continuous network of intermetallic particles along the grain boundaries can prevent the advance corrosion front into the α -Mg matrix. However, the intermetallic particles along the grain boundary in ZE41 alloy did not behave as a barrier for the advance of corrosion [9]. Similar features were found in this work for the ZK40-2Nd alloy, without an important contribution of the second phase acting as a barrier. For the ZK40-2Gd the absence of localised corrosion along the grain boundary might have promoted the “barrier effect” of the semi continuous of $(\text{Mg}, \text{Zn})_3\text{Gd}_2$ intermetallic compound.

4. Conclusions

The addition of Gd and Nd modified the as-cast microstructure of the ZK40 alloy. There is no significant change in the yield and ultimate strengths with addition of Gd to ZK40 but elongation until fracture in tension increased with Gd addition. The corrosion resistance measured by impedance and hydrogen evolution was slightly enhanced for the ZK40-2Gd and very poor corrosion resistance was exhibited for the ZK40-2Nd. A complex series of localised corrosion at various microstructures features can explain the different corrosion behaviour:

- (1) Mg-Zn-Zr-Al-Fe impurities did not play an important role on corrosion;
- (2) The morphology of localised corrosion of the different alloys is associated to the presence of secondary phases and the chemical segregation for the different alloying elements in the α -Mg matrix;
- (3) Severe localised corrosion along the intermetallic particles along the grain boundaries was observed for the ZK40-2Nd alloy. The corrosion front propagated faster for this alloy.

The enhanced mechanical and corrosion properties observed in ZK40-2Gd alloy make the Mg-Zn-Zr-Gd an interesting magnesium alloy with for further development with a view for structural applications.

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References

- [1] K.U. Kainer, *Magnesium Alloys and Technology*, Wiley-VCH, Weinheim, 2003.
- [2] A.A. Luo, Wrought magnesium alloys and manufacturing processes for automotive applications, *SAE Trans.* 114.5 (2005) 411–421.
- [3] J. Zhang, J. Wang, X. Qiu, D. Zhang, Z. Tian, X. Niu, D. Tang, J. Meng, Effect of Nd on the microstructure, mechanical properties and corrosion behavior of die-cast Mg–4Al-based alloy, *J. Alloy. Compd.* 464.1 (2008) 556–564.
- [4] T. Zhang, G. Meng, Y. Shao, Z. Cui, F. Wang, Corrosion of hot extrusion AZ91 magnesium alloy. Part II: effect of rare earth element neodymium (Nd) on the corrosion behavior of extruded alloy, *Corros. Sci.* 53 (2011) 2934–2942.
- [5] G. Wu, Y. Fan, H. Gao, C. Zhai, Y.P. Zhu, The effect of Ca and rare earth elements on the microstructure, mechanical properties and corrosion behavior of AZ91D, *Mater. Sci. Eng. A* 408 (2005) 255–263.
- [6] R. Ambat, N.N. Aung, W. Zhou, Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy, *Corros. Sci.* 42.8 (2000) 1433–1455.
- [7] O. Lunder, M. Videm, K. Nisancioglu, Corrosion resistant magnesium alloys, *SAE Tech. Pap.* (1995) 950428.
- [8] M. Yamasaki, N. Hayashi, S. Izumi, Y. Kawamura, Corrosion behavior of rapidly solidified Mg–Zn–rare earth element alloys in NaCl solution, *Corros. Sci.* 49.1 (2007) 255–262.
- [9] M.C. Zhao, M. Liu, G.L. Song, A. Atrens, Influence of microstructure on corrosion of As-cast ZE41, *Adv. Eng. Mater.* 10 (1–2) (2008) 104–111.
- [10] W.C. Neil, M. Forsyth, P.C. Howlett, C.R. Hutchinson, B.R.W. Hinton, Corrosion of magnesium alloy ZE41–The role of microstructural features, *Corros. Sci.* 51.2 (2009) 387–394.
- [11] C. Ma, M. Liu, G. Wu, W. Ding, Y. Zhu, Tensile properties of extruded ZK60–RE alloys, *Mater. Sci. Eng. A* 349.1 (2003) 207–212.
- [12] T.E. Leontis, Magnesium and magnesium alloys–the room and elevated temperature properties of some sand cast magnesium-base alloys containing zinc, *Trans. AIME* 185 (1949) 327.
- [13] Q. Li, Q. Wang, Y. Wang, X. Zeng, W. Ding, Effect of Nd and Y addition on microstructure and mechanical properties of as-cast Mg–Zn–Zr alloy, *J. Alloy. Compd.* 427.1 (2007) 115–123.
- [14] Y.A.N.G. Mingbo, G.U.O. Tingzhang, Q.I.N. Caiyuan, P.A.N. Fusheng, Microstructure, tensile and creep properties of as-cast Mg–3.8 Zn–2.2 Ca–xCe (x=0, 0.5, 1 and 2 wt%) magnesium alloys, *J. Rare Earths* 30.2 (2012) 181–188.
- [15] N. Stanford, D. Atwell, M.R. Barnett, The effect of Gd on the recrystallisation, texture and deformation behaviour of magnesium-based alloys, *Acta Mater.* 58.20 (2010) 6773–6783.
- [16] H. Yu, Y. Hongge, C. Jihua, S. Bin, Z. Yi, S. Yanjin, M. Zhaojie, Effects of minor Gd addition on microstructures and mechanical properties of the high strain-rate rolled Mg–Zn–Zr alloys, *J. Alloy. Compd.* 586 (2014) 757–765.
- [17] M.M. Avedesian, H. Baker, *Magnesium and Magnesium Alloys*, ASM Speciality Handbook, ASM International, United States of America, 1999.
- [18] J. Luo, K. Ying, P. He, J. Bai, Properties of Savitzky–Golay digital differentiators, *Digit. Signal Process.* 15.2 (2005) 122–136.
- [19] G. Song, A. Atrens, Understanding magnesium corrosion—a framework for improved alloy performance, *Adv. Eng. Mater.* 5.12 (2003) 837.
- [20] G. Song, A. Atrens, D. StJohn, An hydrogen evolution method for the estimation of the corrosion rate of magnesium alloys, *Magn. Technol.* 2001 (2001) 254–262.
- [21] M.L. Huang, H.X. Li, H. Ding, Z.Y. Tang, R.B. Mei, H.T. Zhou, R.P. Ren, S.M. Hao, A ternary linear compound T 2 and its phase equilibrium relationships in Mg–Zn–Nd system at 400 °C, *J. Alloy. Compd.* 489.2 (2010) 620–625.
- [22] M. Nonnenmacher, M.P. o’Boyle, H.K. Wickramasinghe, Kelvin probe force microscopy, *Appl. Phys. Lett.* 58.25 (1991) 2921–2923.
- [23] N. Pebere, C. Riera, F. Dabosi, Investigation of magnesium corrosion in aerated sodium sulfate solution by electrochemical impedance spectroscopy, *Electrochim. Acta* 35 (1990) 555–561.
- [24] C.B.G. Baril, N. Pebere, AC impedance spectroscopy in characterizing time-dependent corrosion of AZ91 and AM50 magnesium alloys characterization with respect to their microstructures, *J. Electrochem. Soc.* 148 (2001) B489–B496.
- [25] K. Hladky, L.M. Callow, J.L. Dawson, Corrosion rates from impedance measurements: an introduction, *Br. Corros. J.* 15.1 (1980) 20–25.
- [26] G.J. Brug, A.L.G. Van Den Eeden, M. Sluyters-Rehbach, J.H. Sluyters, The analysis of electrode impedances complicated by the presence of a constant phase element, *J. Electroanal. Chem. Interfacial Electrochem.* 176.1 (1984) 275–295.
- [27] S.J. Liu, G.Y. Yang, S.F. Luo, W.Q. Jie, Microstructure and mechanical properties of sand mold cast Mg–4.58 Zn–2.6 Gd–0.18 Zr magnesium alloy after different heat treatments, *J. Alloy. Compd.* 644 (2015) 846–853.
- [28] G.-L. Song, *Corrosion of Magnesium Alloys*, Woodhead Publishing, Oxford, 2011.
- [29] H.B. Yao, Y. Li, A.T.S. Wee, An XPS investigation of the oxidation/corrosion of melt-spun Mg, *Appl. Surf. Sci.* 158 (2000) 112–119.
- [30] J.H. Nordlien, S. Ono, N. Masuko, K. Nisancioglu, A. TEM, Investigation of naturally formed oxide films on pure magnesium, *Corros. Sci.* 39.8 (1997) 1397–1414.
- [31] R. Arrabal, A. Pardo, M.C. Merino, M. Mohedano, P. Casajús, K. Paucar, G. Garcés, Effect of Nd on the corrosion behaviour of AM50 and AZ91D magnesium alloys in 3.5 wt% NaCl solution, *Corros. Sci.* 55 (2012) 301–312.
- [32] G.-L. Song, A. Atrens, M. Dargusch, Influence of microstructure on the corrosion of diecast AZ91D, *Corros. Sci.* 41 (1999) 249–273.
- [33] M.C. Zhao, M. Liu, G. Song, A. Atrens, Influence of the β -phase morphology on the corrosion of the Mg alloy AZ91, *Corros. Sci.* 50 (2008) 1939.
- [34] M.C. Zhao, M. Liu, G. Song, A. Atrens, Influence of homogenization annealing of AZ91 on mechanical properties and corrosion behaviour, *Adv. Eng. Mater.* 10 (2008) 93–103.
- [35] M.C. Zhao, M. Liu, G. Song, A. Atrens, Influence of microstructure on corrosion of As-cast ZE41, *Adv. Eng. Mater.* 10 (2008) 104–111.
- [36] M.C. Zhao, M. Liu, G.-L. Song, A. Atrens, Influence of pH and chloride ion concentration on the corrosion of Mg alloy ZE41, *Corros. Sci.* 50 (2008) 3168–3178.
- [37] J. Chang, X. Guo, S. He, P. Fu, L. Peng, W. Ding, Investigation of the corrosion for Mg–xGd–3Y–0.4 Zr (x=6, 8, 10, 12 wt%) alloys in a peak-aged condition, *Corros. Sci.* 50 (2008) 166–177.
- [38] L.M. Peng, J.W. Chang, X.W. Guo, A. Atrens, W.J. Ding, Y.H. Peng, Influence of heat treatment and microstructure on the corrosion of magnesium alloy Mg–10Gd–3Y–0.4 Zr, *J. Appl. Electrochem.* 39 (2009) 913–920.
- [39] M. Yamasaki, N. Hayashi, S. Izumi, Y. Kawamura, Corrosion behavior of rapidly solidified Mg–Zn–rare earth element alloys in NaCl solution, *Corros. Sci.* 49 (2007) 255–262.
- [40] Y. Song, D. Shan, R. Chen, E.H. Han, Effect of second phases on the corrosion behaviour of wrought Mg–Zn–Y–Zr alloy, *Corros. Sci.* 52 (2010) 1830–1837.
- [41] Y. Lisitsyn, G. Ben-Hamu, D. Eliezer, K.S. Shin, Some particularities of the corrosion behaviour of Mg–Zn–Mn–Si–Ca alloys in alkaline chloride solutions, *Corros. Sci.* 52 (2010) 2280–2290.
- [42] Y. Lisitsyn, G. Ben-Hamu, D. Eliezer, K.S. Shin, The role of Ca microalloying on the microstructure and corrosion behavior of Mg–6Zn–Mn–(0.5–2) Si alloys, *Corros. Sci.* 51 (2009) 776–784.
- [43] Y. Song, D. Shan, R. Chen, E.H. Han, Corrosion characterization of Mg–8Li alloy in NaCl solution, *Corros. Sci.* 51 (2009) 1087–1094.
- [44] N. Birbilis, M.A. Easton, A.D. Sudholz, S.M. Zhu, M.A. Gibson, On the corrosion of binary magnesium–rare earth alloys, *Corros. Sci.* 51 (2009) 683.
- [45] A.E. Coy, F. Viejo, P. Skeldon, G.E. Thompson, Susceptibility of rare-earth–magnesium alloys to micro-galvanic corrosion, *Corros. Sci.* 52.12 (2010) 3896–3906.
- [46] I. Apachitei, L.E. Fratila-Apachitei, J. Duszczek, Microgalvanic activity of an Mg–Al–Ca-based alloy studied by scanning Kelvin probe force microscopy, *Scr. Mater.* 57.11 (2007) 1012–1015.

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1. INTRODUCTION

Due to their specific mechanical properties and biocompatibility, Mg alloys have great potential to be used for a variety of applications. The yield strength, elongation to failure, creep resistance and corrosion resistance are important properties that need to be further enhanced for the wide application of these alloys. The most commonly used alloying additions in Mg alloys can be listed as: Al, Zn, Ca, Y, Zr, Mn, Si, and rare earth (RE). The impact of individual additions to the mechanical and corrosion properties has been investigated but for most cases it is not fully elucidated. Additionally, the combined effect of alloying additions on the microstructure, mechanical properties and corrosion behaviour has been studied only for a small number of systems. Significant advances are made in the development of creep resistant alloys (eg. Mg-Al-Sr-Ca alloys), wrought alloys (often AZ and ZK alloys), alloys for degradable biomaterials (eg. Mg-Ca and Mg-Gd alloys).

The enhanced yield stress exhibited by the ZK (Mg-Zn-Zr) alloys and satisfactory mechanical properties exhibited by the ZE41 (Mg-4Zn-0.6Zr-1RE(*mischmetal*)) alloy suggest that the Mg-Zn-Zr-RE system is suited for further development. The impact of individual rare earth (RE) elements (Gd, Nd and Y) and Ca on the microstructure, mechanical properties and corrosion resistance of the ZK40 alloy is investigated in the present work. Ca was added in the form of CaO which is cheaper compared to pure Ca. Ca addition has positive effects on the castability by decreasing the flammability. Therefore, the aims of this work are to investigate :

- i) the effect of individual additions of Ca, Gd, Nd and Y on the ZK40 microstructure, with consideration to phase evaluation and phase transformation;
- ii) Investigate the tensile and compressive mechanical properties at room temperature for the ZK40 alloy modified with Ca, Gd, Nd or Y;

- iii) The corrosion resistance of ZK40 alloys with additions of Ca, Gd, Nd and Y in 0.5 wt.% NaCl naturally aerated water solution.

The microstructures of ZK40 (Mg-4.5Zn-0.6Zr), ZK40 with 2 wt.% of CaO, Gd and Nd and 1 wt.% Y (ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y, respectively) were investigated with optical, scanning (SEM), transmission electron microscopy (TEM) and synchrotron radiation diffraction (SRD). The grain morphology, grain size, volume fraction of intermetallic phases and their morphology were investigated. TEM and SRD were used to identify the intermetallic phases of each alloy. Scanning Kelvin Probe Force Microscopy (SKPFM) was performed in order to evaluate the surface potential difference between the α -Mg matrix and impurities and the intermetallic phases.

The mechanical properties were investigated with compressive and tensile tests at room temperature. In order to understand the impact of the microstructure on the mechanical tensile properties, the fracture surfaces were analysed. The effect of the intermetallic phases in altering the load transfer was verified by examination of the nature of the fracture surfaces.

Electrochemical Impedance Spectroscopy, hydrogen evolution and weight loss in 0.5 wt.% NaCl solution were used to evaluate the corrosion resistance. Immersion tests for 4 h, 8 h and 24 h were also performed to investigate the initiation of corrosion. The corrosion behaviour was correlated with the microstructure. The present work shed lights on the effect of rare earth and Ca on the properties of ZK40 alloy.

2. LITERATURE REVIEW

Mg alloys have a high potential for use as lightweight structural materials due to the satisfactory strength/weight ratio. However, one of the main obstacles that impede the use of magnesium alloys is their low corrosion resistance and the poor absolute strength [1]. However, to become widely accepted for in structural applications research is still needed on Mg processing, alloy development, joining, surface treatment, corrosion resistance and mechanical properties improvement. The control of the microstructure and the understanding of the effect of its components in the materials properties are of importance in order to design high performance Mg alloys.

a. Natural resources and refining methods

Mg is the 8th highest abundant element in the surface layer of the Earth, corresponding to 2.3 wt.%, 2.0 mol% or 0.3 vol.% [2]. The raw ores of Mg are dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) and magnesite (MgCO_3). In addition, Mg is the second most abundant metal in seawater, following Na. North America is the main consumer followed by the western part of Europe and Japan [3]. The price in the international market of magnesium has been decreased in the last five years. It was 3.20 USD/kg in 2010 and currently it trades at 2.03 USD/kg [4], which is slightly more expensive compared with Al (1.55 USD/kg) [5]. Most of the Mg produced, approximately 40%, is at present used for alloying Al and about 34% is used for Mg parts, which can be divided into casting applications (33.5%) and wrought materials (0.5%) [6].

There are two methods for extracting Mg: electrolysis [7] and thermal reduction (Pidgeon process) [8]. Electrolysis consists in extracting MgCl_2 from seawater and then reduce the Mg to the metallic form by electrolysis. The Pidgeon process consists of extracting MgO from Mg ores by adding a reducing agent to it (usually silicothermic reduction) and refining it by heating it to a high temperature under reduced pressure.

Mg alloy casting are performed by liquid or semi-solid molding processes, with available and commonly used processes include high and low pressure die casting, thixomoulding, squeeze casting and gravity casting. Extrusion, rolling and forging are the widely used process for wrought alloy. [9] Currently, 95% of the Mg alloys used are manufactured by high pressure die casting, sand and permanent mold casting processes [10].

b. Mg and Mg alloys

Currently, Mg alloys do not satisfy the property profiles required for many structural applications or they contain large amounts of expensive rare earths (RE) elements. Thus, it is important to develop new alloys suitable for room and elevated temperature applications both for the as-cast and thermo-mechanically processed (eg. hot rolled or extruded) products.

The impurities such as Fe, Ni, Cu need to be below critical levels as increased additions of these elements are detrimental for corrosion resistance [11]. Al and Zn in combination has been reported to reduce the harmful effects of these impurities. Most commonly used alloying elements are Al and Zn while recently alloys containing RE (Gd, Y, Ce and Nd), Ca, Si have been investigated. Mn is added to Al containing alloys to trap impurities such as Fe, Ni [12]. Zr is added to Al free Mg alloys to refine the as-cast grain size. A small amount of Be is added at the point of refinement of Mg from ore to prevent oxidation [13]. Recently, Ca addition was shown to enhance the oxidation resistance of Mg melt [14,15].

The AZ series alloys contain Al, Mn and Zn and are the most common alloying elements for room temperature applications. These additions result in good castability and a minimum tendency for hot cracking. When the alloys are die cast, microporosity is a problem for these alloys. Creep properties, ductility and impact strength deteriorate with the increased Al addition. Due to the satisfactory mechanical properties and relative low cost as-cast AZ91

is the most widely used alloy in commercial applications. To improve the strength, castability, workability, corrosion resistance and weldability it is necessary to control the concentration of Al. The solid solution strengthening caused by Al (12.6 at.% Al are soluble in the Mg matrix at 437 °C) improves the strength of these alloys [16]. The microstructures of these alloys contain α -Mg matrix and eutectic structure containing $Mg_{17}Al_{12}$ eutectic along the grain boundaries. Solution treatment dissolves the $Mg_{17}Al_{12}$ phase into Mg matrix and after ageing treatment coarsely dispersed Al precipitates are formed and they contribute to hinder grain boundary migration and creep deformation. In terms of practical applications, AZ91 is used in car parts, notebooks, PCs, portable telephones and cases for other products. However, at temperatures above 100 °C the alloy undergoes creep deformation and the maximum application temperature is set at 125 °C [15]. AZ31 have high formability and weldability and is often used in materials for plates, pipes, rods and other products.

Mg-Al-Mn (AM) alloys are also commonly used Mg-Al based alloys. The majority of high pressure die casting consisted of this alloy system. AM60 has a typical elongation of 6% in the as-cast condition. AM50 and AM60 have satisfactory ductilities and impact resistance and are used for steering wheel cores. Another Mg-Al based system is the AS based alloys, which contain Si as a secondary alloying element. The AS41 was developed to provide improved elevated temperatures properties (creep resistance) and was used in the crank-case of air cooled engines [17].

Mg-Al-Sr system (or AJ series alloys) shows improved creep resistance compared with Mg-Al-RE and Mg-Al-Si systems and exhibits superior salt-spray corrosion resistance than some commercial alloys, such as AM60B, AS41 and AE42 [18]. The AJ series alloys contain intermetallic phases containing Al-Sr-(Mg) and the AJ62 (Mg-6Al-2Sr) shows significantly improved tensile properties, castability and higher resistance to hot tearing when prepared according to the strict casting protocols for die casting applications.

Table 1 - Common Mg alloys and their application [19-27]

Alloy	Application	Properties
AZ91	General casting alloy	Good castability, good mechanical properties at $T < 150\text{ }^{\circ}\text{C}$
AM60	High-pressure die-casting alloy	Greater toughness and ductility than AZ91, slightly lower strength. Often preferred for automotive structural applications.
AM50	General casting alloy	Good strength, ductility, energy absorption properties and castability.
AE44	General casting alloy	Better creep behaviour and castability than AE42
AE42	General casting alloy	Low castability, good creep behaviour
AS41	General casting alloy	Better creep resistance than AZ91 at elevated temperatures but lower strength
ZE41	Special casting alloy	Rare earth addition improves creep strength at elevated temperatures.
AZ31	Wrought alloy	Good extrusion alloy
AM20	Casting alloy	High ductility, toughness, poor die-castability
MRI153M	Casting alloy	For high temperature applications up to $150\text{ }^{\circ}\text{C}$
MRI230D	Casting alloy	For high temperature applications up to $190\text{ }^{\circ}\text{C}$
AS21	Casting alloy	For use at temperatures in excess of $120\text{ }^{\circ}\text{C}$
AJ62	High pressure die-casting (HPDC)	Good thermal and mechanical strength, superior castability, corrosion resistance and creep behaviour

Mg-Ca alloys are an alternative system to the high cost Mg-Al-Sr alloys. Small additions of Ca to Mg provides large increase in room temperature tensile and compressive yield strength and comparable creep resistance of alloys with Sr or RE additions [28]. ACM522 (Mg-5Al-2Ca-2Ce-1Mn) was developed by Honda and provides creep resistance similar to A384 in the temperature range of 150-200 °C. AXJ alloys also represents recent developments on Mg alloys. General Motors R&D Center developed a Mg-5Al-0.2Sr-(1.7-3.3)Ca, which also exhibits good creep resistance [22].

The Mg-Zn system is precipitate hardenable and the addition of Zr (ZK system) refines the grain size improving the yield strength and ductility. The ZK60A alloy has a higher hot-workability than other materials. Th or Ce is added to improve strength at the temperatures of 260 °C to 370 °C. Table 1 shows a list of the typical commercial Mg alloys and their applications.

c. Corrosion of Mg and Mg alloys

Corrosion of Mg alloys can be controlled with the use of coatings [29]. Corrosion resistance of Mg alloys under environmental conditions with appropriate coating is comparable or better than that of mild steel. Insufficient corrosion resistance is attributed to poor design, surface contamination, flux inclusions, incorrectly applied or inadequate surface protection and galvanic couples. The Fe, Ni and Cu impurities are usually present in the inclusions, and localized corrosion is enhanced in their vicinity [30]

The corrosion resistance can be improved via controlled alloying addition. The overall effect of an alloying element on corrosion behaviour depends on whether it is uniformly distributed through the microstructure or dissolved in the Mg matrix [29]. The corrosion layer is affected by the alloying additions. The presence of Fe, Mn, Al, Ca and Sr on the corrosion products and the corrosion resistance is not fully understood. Al in concentrations above 4% can increase the corrosion resistance [29]. Nordlein *et al.* [31]

investigated the influence of Al on MgO passive film. The increase in the activation energy for ion movement in the presence of Al ions is the main reason behind the improved corrosion [30,32]. Additionally, with the increase of Al content the corrosion products dehydrate and become enriched in Al oxide. During immersion, the Al containing alloys also exhibit enhanced corrosion resistance. When the $\text{Mg}_{17}\text{Al}_{12}$ phase forms a continuous network along the grain boundaries, it acts as a barrier preventing the propagation of the corrosion front [149].

Figure 1: Pourbaix (Potential-pH) diagram for the system Mg and water at 25 °C. Corrosion, immunity and passivation domains are shown [33].

The Pourbaix (potential-ph) diagram (Figure 1) shows the possibility of protection of Mg at high pH values, which can be attributed to Mg(OH)_2 formation during corrosion reactions. The following equations are considered for the E-pH diagram.

The corrosion potential of Mg is slightly more negative than -1.5 V in a dilute chloride media or neutral solution with respect to the standard H electrode. It is higher than the -2.37 V Mg standard electrode potential at 25 °C due to the polarization of the formed Mg(OH)_2 film [29]. Most common environments are not sufficiently alkaline for Mg self-passivate. However, the protective of MgO is susceptible to chloride, sulfate, or nitrate anions. Chlorides are very detrimental and a small amount is sufficient to break the protective film. On the other hand, chromates, vanadates, phosphates and other oxidants can promote the formation of a protective layer, preventing corrosion [34].

Corrosion in Mg and Mg alloys in natural atmospheres are typically localized and galvanic corrosion plays an important role. The corrosion morphology is usually

influenced by the phases distribution, conductivity, electrolyte properties, temperature, ionic species, differential aeration and alloy composition and homogeneity. [29]

The oxide layer that forms when Mg is exposed to air is composed of $\text{Mg}\cdot\text{H}_2\text{O}$. The oxide layer thickness on pure Mg was reported to be 2.2 ± 0.3 nm after ~ 10 s exposure in the air and it increases linearly with the logarithm of exposure time [30]. When Mg is exposed to ambient air for a period of 15-60 min a film thickness of 20-50 nm forms. If it is exposed to humid air with $\sim 65\%$ relative humidity for 4 days a layer of 100-150 nm forms [31]. If Mg is exposed to humid air or water a thicker hydrated film forms. The quasi-passive hydroxide film on Mg is significantly less stable than the passive films that forms on Al or stainless steels [35,36].

After 48 h immersion in distilled water, the morphology and structure of the oxide films on Mg was reported to be consist of a three-layer structure: an inner cellular structure (0.4-0.6 μm); a dense intermediate region (20-40 nm); and an outer layer with a platelet like morphology (~ 2 μm) [37].

In aqueous media, the corrosion layer consisted mainly of $\text{Mg}(\text{OH})_2$. The hydroxide film has a hexagonal layered structure, alternating between Mg and hydroxide ions. Theoretically, the $\text{Mg}(\text{OH})_2$ is unstable in an acidic, neutral or alkaline media (Pourbaix diagram, Figure 1). Therefore, it offers limited protection to Mg. The kinetics process of film formation and dissolution can explain the differences in corrosion behavior observed in different aqueous solutions. After the corrosion starts it is difficult for the surface film to repair itself [38]. $\text{Mg}(\text{OH})_2$ does not necessarily deposit on the Mg surface and the H_2 bubbles can prevent the corroding areas from being covered by the $\text{Mg}(\text{OH})_2$ [38]. Agitation or any other means of preventing or destroying the corrosion layer will accelerate the corrosion. The corrosion of Mg alloys in pure water increases significantly with temperature.

The intergranular corrosion is not observed in Mg alloys because the grain-boundary constituent is always cathodic to the α -Mg matrix [29]. The grain boundary is not only more resistant to attack but also always cathodically protected by the neighbouring grains. However, the α -Mg matrix can be attacked during the early stages of immersion locally at the interface of cathodic intermetallic compounds and thus can be considered to be intergranular corrosion [29].

d. Mechanical properties of Mg and Mg alloys

Mg alloys exhibit low ductility and poor cold workability. The mechanical properties for Mg alloys are controlled by the relative hardening of slip and twinning systems. The anisotropy resulting from the low symmetry of the hcp structure plays an important role in determining the mechanical properties. Mg exhibits only basal slip at room temperature and requires twinning as another deformation mechanism, as one slip system does not satisfy the von Mises criterion for uniform plastic deformation in polycrystalline material. Von Mises criterion requires the operation of at least five independent slip systems [39]. At temperatures above 220 °C additional slip systems (pyramidal and prismatic) can be thermally activated [40].

The strength of Mg and Mg alloys can be enhanced by alloying due to solute drag effect caused by the substitutional alloying additions. Thermo-mechanical processes can also improve the strength of magnesium alloys. The heat treatments are another way of enhancing the mechanical strength. Ageing in the as-cast condition (T5) or ageing after the solid solution treatment (T6) can form fine precipitates improves the mechanical strength of Mg alloys with the precipitates forming as plates on prismatic or basal planes of Mg providing the largest increment in strength.

The impact of alloying additions on solid solution and strengthening coefficient of the Hall-Petch relationship is controlled by the atomic size and elastic misfit. The grain size

can be significantly reduced with elements that cause a deep eutectic (that is eutectic temperature is much lower than the liquidus temperature) and elements with high solid solubility. The grain size has an impact on the yield stress (through the Hall-Petch relationship). RE improves the yield strength and creep resistance due to solid solution and precipitation hardening [41].

e. Mg-Zn alloys

i. Binary Mg-Zn

Zn is a widely used alloying element for Mg alloys due to the low cost and the improvement of strength properties of both cast and wrought alloys [42]. During melting and casting, Zn improves the fluidity. However, it can induce micro-porosity [43]. Mg-Zn alloy shows promising age-hardening response in comparison to other Mg systems [44]. Zn also plays an important role combining with impurities such as Fe and Ni reducing the harmful effect of the presence of those elements [45].

ii. Effect of Ca addition

Among the investigated Mg alloy systems, ZK alloys are one of the highest strength cast alloys available commercially [46]. Recently, there are numerous attempts to enhance the strength and ductility through the modification of alloy chemistry with the addition of quaternary and quinary additions [47,48]. The effect of Ca additions in both commercial and experimental Mg alloys has been reported in literature. The mechanical properties [49], microstructure modification [50], and texture randomisation [51,52] caused by Ca additions were investigated.

The addition of Ca to Mg-Zn alloys refines the grain size, contributes to solid solution hardening and enhances the precipitation hardening response [53-55]. Ca also improves corrosion resistance due to formation of an oxide layer [56]. In addition, some Ca in wrought Mg alloys [57] show similar increase in hardness and yield strength or weakened deformation texture achieved in alloying using RE metals. The Ca addition is also attributed to improve ignition resistance of Mg alloys [58]. Wiese *et al.* [59] showed that CaO reduces to form MgO and Mg₂Ca during casting and solidification, which can provide an easier route to add Ca to Mg alloys. The formation of thermally stable secondary phases that stabilizes the microstructure during heat treatments and thermo-mechanical processes is of interest for applications at elevated temperatures [60]. The creep resistance was enhanced by addition of Ca to ZK series alloys. It is attributed to the refinement of the rod like β_1 and plate like β_2 precipitates [61]. Oh-ishi *et al.* investigated the Mg-Zn-Ca system with different Zn contents [62]. In tension [63] and compression [64] for the cast and heat treated Mg-Ca-Zn alloys the creep properties were enhanced. Mg-Zn-Ca alloys also show promising applications as biodegradable implants [65,66] because both Zn and Ca can be well metabolized by the human body. Jeong *et al.* [67] showed that for as-cast Mg-Ca alloys the increase of Ca additions significantly influenced the anodic and cathodic polarisation and the corrosion resistance decreased.

The corrosion behaviour of Mg-Zn-Ca was investigated as well [68-70]. Rad *et al.* [68] showed that the addition of Zn for the Mg-Ca-Zn system alloys improved corrosion resistance and Lu *et al.* [71] showed that galvanic corrosion seems to play an important role on the corrosion resistance of Mg-3Zn-0.3Ca alloys. The additions of Ca on Mg-Zn-Ca alloys seems to form adherent and insoluble corrosion products that are more stable than the Mg(OH)₂ film [70].

iii. Effect of RE addition

Investigations on the effect of RE addition on Mg alloys is extensive. The influence of the RE elements on the mechanical properties [72] and corrosion behaviour [73] of Mg-Al alloy system has been reported. The addition of RE elements weakens the texture in wrought alloys [74-79], which can significantly improve ductility. The orientation spread of the basal planes in broader towards the sheets transverse direction (TD) compared with the rolling direction (RD) and recrystallization is attributed to be the main reason for the different behaviour.

Mg alloys with RE addition show potential for achieving improved strength and creep resistance compared with the AZ system and the most notable ones are based on the Mg-Gd, Mg-Gd-Y, Mg-Gd-Nd, and Mg-Y-Nd systems [80-86]. Among the Mg-Zn alloys, ZE41 (Mg-4Zn-1(RE *mischmetal*)) has been widely used in the aerospace industry in the as-cast condition. It has good castability and satisfactory mechanical properties and creep resistance. The corrosion resistance of ZE41 is lower than AZ91 and compared with the AZ alloys the eutectic structures in the ZE41 do not play the role of corrosion barrier hindering the corrosion front [87]. For ZE41 immersed in 1 N NaCl Zhao *et al.* [88] showed that the corrosion initiated as localised corrosion. Neil *et al.* [89] reported that segregation of Zr in the α -Mg matrix played a distinct role on the early stages of corrosion in the ZE41.

The addition of RE elements to the Mg-Zn-Zr (ZK system) alloys alters the microstructure and therefore can modify the mechanical properties and give satisfactory corrosion resistance. The RE elements includes the lanthanides, Sc and Y [90]. The addition of RE [91] resulted in enhanced castability and elevated temperature strength [92]. It is reported that the addition of RE and alkaline metals in Mg alloys has improved the corrosion resistance [93-95]. The RE additions are grain refiners, attributed mainly to the constitutional supercooling [96], which can lead to improved ductility at room temperature [97,98].

Additionally, when RE additions forms a disperse network of intermetallic compounds along the grain boundaries, it improved the mechanical strength [92].

The role of Y in Mg based alloys has been studied extensively. A systematic investigation on ternary Mg-Zn-Y phase diagram shows the presence of three equilibrium phases ($W\text{-Mg}_3\text{Zn}_3\text{Y}_2$; $Z\text{-Mg}_3\text{Zn}_6\text{Y}$; and $X\text{-Mg}_{12}\text{ZnY}$) [99]. The W-phase has a similar structure as AlMnCu_2 , the Z-phase is identified as an icosahedral quasicrystalline phase and X-phase is a long periodic structure with an 18R stacking sequence. The X-phase transforms to 14H upon annealing [100,101]. The ratio of Y/Zn modifies the microstructure and mechanical properties of Mg-Zn based alloys. Fine scaled LPSO (long period stacking ordered) structures are observed [102] when this ratio is large. Icosahedral phases containing Y and Zn as observed with intermediate ratios of Y/Zn, [103-105].

The yield anisotropy between compressive and tensile yield strengths was reduced in extruded alloys containing icosahedral phase, and the increased strength was attributed to increased load transfer between the matrix and the second phase [106]. Enhanced tensile yield strength and ultimate tensile strength without significant loss in ductility is reported with addition of Y to Mg-Zn alloys. Y is considered to be one of the most effective alloying additions which improves the mechanical properties at high temperatures for Mg alloys [107-110]. The addition of Zn to Mg alloys containing Y has significantly improved creep strength and it is proposed that Zn suppresses the non-basal slip through the formation of planar defects [111,112]. A high strength Mg-Zn-Y alloy was produced via rapidly solidified powder metallurgy [113,114]. Yield strength of 610 MPa and elongation of 5% was achieved.

The influence on corrosion behaviour and microstructure of Mg-Zn-Y alloy due to different solidification techniques with different cooling rates was investigated [115]. The effect of the Zn addition to the ZK60 have been extensively investigated [116,117] and

the addition of Y can enhance its mechanical properties at elevated temperature. The addition of Zn to a Mg-Nd-Zr alloy [118] increased the strength and decreased the plasticity at all test temperatures from ambient to 250 °C. However, strengthening caused by the Zn addition decreases with rising temperature. The effect of the Zn on the mechanical properties of a Mg-Gd-Y-Zr alloy was investigated [119]. Although the addition of Zn degrades the age-hardening response discontinuous precipitation of a 14H-type LPSO phase at grain boundaries and with grains in the over-aged condition, which enhances the maximum tensile elongation.

The role of the microstructure on the corrosion behaviour of Mg-Y-RE-Zr alloys was investigated by Ben-Hamu *et al.* [120] and the Zr distribution within the grain was attributed as the main reason in corrosion resistance for this alloys and it was shown that corrosion started between the grain centres and the grain boundary. Comparable corrosion behaviour was also reported by Song *et al.* [121] where filiform corrosion started in the central regions of α -Mg matrix for T6 Mg-5.8Zn-0.9Y-0.55Zr.

Gd was investigated due to the positive impact on the mechanical and corrosion properties. The creep resistance of binary Mg-Gd alloys improved, compared to the commercially used WE43, and QE22 alloys [122]. Microstructure, mechanical and corrosion properties of experimental alloys based on Mg-Gd-Y, Mg-Gd-Y-Nd, Mg-Gd-Zn, and Mg-Gd-Y-Zn systems have been investigated [123-128]. The Mg-Gd-Zn has a microstructure that consists of many different phases, such as I, W, X and laves phases, depending on the ratio of Zn to Gd contents, thus resulting in different mechanical behaviors [129]. The possibility of tailoring the mechanical properties of these alloys by altering the Zn and Gd contents make this an interesting system for investigation. Phase formation is defined not only by the alloy composition but also by heat treatments in the Mg-Zn-Gd system [127,129,130].

The effect of Gd on the microstructure and mechanical properties of a Mg-4.5Zn alloy was investigated by Yang *et al.* [131] and it is reported that only W phase was present in these alloy and the tensile properties were optimum at around 2 wt% Gd. W phase was also found in Mg-3Zn-xGd (x 1/4 1-3 wt.% Gd) alloys, maximum tensile strength occurred at 1-2 wt.% Gd whereas creep resistance improved remarkably with increase in Gd content [132]. For an extruded $\text{Mg}_{95.9}\text{Zn}_{3.5}\text{Gd}_{0.6}$ (at.%) alloy [129,133] I phase ($\text{Mg}_3\text{Zn}_6\text{Gd}$) was found and high elongation to failure after extrusion (94% at 200 °C) was observed. The addition of Gd to a ZK60 alloy led a reduction of the age-hardening response [42]. A Mg-Zn-Gd based alloy reported by Yuan *et al.* [134] exhibited better creep resistance compared with AE42 and improved room temperature mechanical properties compared with that of AZ91. Huang *et al.* [135] also reported for a double continuously extruded Mg-2.7Zn-0.47Gd (at.%) alloy high room temperature mechanical strength. Elongation to rupture of 22% was achieved for a high strain-rate rolled Mg-5.5Zn-0.6Zr-0.8Gd (wt.%) [98].

3. EXPERIMENTAL PROCEDURES

a. Materials

The alloys were prepared with pure Mg, Zn, CaO, Nd and master alloys Mg 10 wt.% Y, Mg 4 wt.% Gd and Mg-33 wt.%Zr (Zirmax[®]). Mg was molten in an electric resistance furnace as shown in Figure 2(a) and held at 750 °C and alloying elements were added to the melt and stirred for 10 min. The melt was then poured into a preheated thin walled steel mould held at 660 °C for 15 min, Figure 2(b). Then, the mould was immersed into water (shown by the red arrow in Figure 1(b)) at a rate of 10 mm.s⁻¹ until the top of the melt was in line with the cooling water. The ingots had a bottom diameter of 250 mm and the height of 300 mm. The indirect casting procedure was adopted to provide a homogeneous microstructure. Table 2 shows the actual compositions of the alloys prepared for this investigation measured with X-ray fluorescence (Zn and Gd) and spark analyser (Ca, Cu, Fe, Nd, Ni, Y, Zr).

Table 2: Chemical compositions of the investigated alloys measured with X-ray fluorescence (Gd and Ca) and spark analyser (Zn, Cu, Fe, Nd, Ni, Y, Zr).

Alloys	Zn wt.%	Zr wt.%	Ca wt.%	Gd wt.%	Nd wt.%	Y wt.%	Fe (ppm)	Cu (ppm)	Ni (ppm)
ZK40	5.00	0.53	-	-	-	-	11	14	13
ZK40- CaO	4.385	0.34	1.22	-	-	-	14	16	14
ZK40-Gd	4.50	0.55	-	1.70	-	-	7	29	<30
ZK40-Nd	4.70	0.55	-	-	2.46	-	11	15	28
ZK40-Y	4.10	0.33	-	-	-	1.12	4	29	<2

Figure 2: Furnaces used for preparing the investigated alloys: a) Narbertherm furnace with a capacity of 20 kg and operating temperature up to 1800 °C where the alloys were held at 750 °C; b) Second furnace used during the cast procedure, where the crucible is held for 15 min at 660 °C and then immersed into water at a rate of 10 mm.s⁻¹.

b. Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) measures the temperature difference between the sample under investigation and an inert reference as function of the temperature. Sample and reference material are heated at the same rate. The difference of the voltage to the sample and reference is measured and correlated to the difference in temperature. Any phase transformation/reaction that involves release of energy (exothermic reaction) or absorption of energy (endothermic reaction) is detected as an increase of temperature (exothermic reaction) or decrease of temperature (endothermic reaction).

DTA was performed using a DTA Perkin Elmer with 30-45 mg of Mg. The samples were placed in Mettler Toledo crucibles in Ar atmosphere. The heating and cooling

rate was 10 K/min in the temperature range of 300-700 °C. To ensure repeatability of the measurement three heating and cooling cycles were used for each alloy.

c. Metallographic specimen preparation and characterisation

Specimens for metallographic characterisation were cut from the ingots and embedded in Emotec 30 cold resin. The samples were then wet ground through successive grades of silicon carbide abrasive papers from P320 to P2500, followed by polishing in a 3 µm diamond suspension and then in OPS with 1 µm diamond suspension. The samples for hydrogen evolution, weight loss and impedance were not encapsulated and grounded to P2500, without polishing. The specimens analysed with optical microscopy (OM) were etched with an acetic picral acid solution and the composition is listed in Table 3 [136]. The analysis was performed using a reflected light microscope Leica DMI 5000. The AnalySIS Pro software and its extensions were used to determine the grain size using the intercepts method according to the standard ASTM E112-12. Samples without etching were examined with scanning electron microscopy (SEM) using a Zeiss FEG-SEM Ultra 55, an Inspect F50 and a Tescan Vega3 SEM using BSE and SE electron mode operating at 15 kV. The SEMs were equipped with Energy dispersive X-ray (EDX) microanalysis hardware.

Synchrotron Radiation diffraction (SRD) was used for phase characterization of the as-cast specimens using the facilities of P07 beamline of Petra III, DESY (*Deutsches Elektronen-Synchrotron*). A monochromatic beam with the energy of 100 keV ($\lambda=0.0124$ nm) and with a cross-section of 1.0 mm x 1.0 mm was used. Diffraction patterns were recorded with a Perkin Elmer 1622 flat panel detector with a pixel size of $(200 \mu\text{m})^2$, which was placed at a sample-to-detector distance of 1535 mm from the specimen (calibrated with a LaB_6 standard powder sample). In order to obtain information of possible phases the Pearson crystallographic database was used and CaRIne crystallographic software was used to simulate the theoretical diffraction patterns.

Table 3: Main constituents for the standard picral-acetic acid used for revealing the microstructure.

Constituent	Amount
Distillate water	30-40 ml
Acetic acid	6.5-7 ml
Ethanol	140 ml
Picric acid	25-40 g

Transmission electron microscopy (TEM) analysis were performed on the ZK40-Nd alloy. The sample preparation for TEM involved cutting 0.5 mm slices using a Struers Isomat precision saw and then wet ground to thickness of 150 μm using 500 grit SiC paper. 3 mm diameter discs were punched using a disc punch. The discs were electropolished to perforation using a Fischione twin jet electropolisher at -45 $^{\circ}\text{C}$ with a voltage of 50 V in solution of 1.5 vol.% Perchloric acid in ethanol. TEM analysis was conducted with a FEI CM 200 transmission electron microscope operating at 200 kV equipped with an Oxford EDAX Energy dispersive X-ray spectrometer (EDX) and quantitative composition measured using standards thin film technique.

d. Mechanical testing

Compressive and tensile specimens were cut from the cast ingots. The compressive and tensile specimen were manufactured according to DIN 50125 and an average of five samples per condition were tested. Both types of test were performed using a Zwick Z050 (Figure 3) with a strain rate of 0.001 mm/min at room temperature. Images of the fracture surfaces were taken via SE-SEM.

Figure 3: a) Mechanical test machine Zwick Z050 used for compression and tensile tests; b) View of the gages used for compression test.

e. Scanning Kelvin Probe Force Microscopy

The principle of Scanning Kelvin Probe Force Microscopy (SKPFM) involves scanning the surface in the tapping mode to determine the topography on a line-by-line basis. The metal coated or doped silicon cantilever is then lifted a fixed distance, typically 20-50 nm, and the tip is rescanned across the surface in the lift mode. On the rescan, the tapping piezo is turned off, but an ac voltage is applied to the tip which stimulates oscillation of the cantilever in the presence of an electric field. The magnitude of the oscillations, monitored by the AFM, is zeroed out on a point by point basis during the lift mode rescan by adding a dc voltage to the tip to balance it. [137]

SKPFM working in tapping mode was performed using a Nanoscope IIIa MultiMode microscope. Surface potential maps were obtained using a silicon tip with a

platinum coating of 20 nm thickness. The topographic and surface potential images were obtained simultaneously and the tip to sample distance was kept constant at 100 nm. The tested samples were metallographic prepared and polished to a OPS finish. All measurements were performed at room temperature and the relative humidity was in the range of 40-65%. SEM/EDS analyses were performed in the SKPFM-examined regions to identify the second phases.

f. Electrochemical measurements

Two electrochemical measurements were performed: electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves.

Electrochemical impedance consists of applying ac potential to an electrochemical cell and measuring the current through the cell. The response to this potential can be analysed as a sum of sinusoidal functions. Electrochemical impedance spectroscopy data are often represented in Nyquist and Bode plots. Nyquist plots consist of the imaginary impedance versus the real impedance of the cell. Bode plots represent the impedance magnitude and phase angle as a function of frequency. [138]

Equivalent circuit modeling of EIS data is used to extract physical properties of the electrochemical system. Resistors, capacitors and inductors are used in the model. Constant phase element (CPE) and Warburg element (Z_w) are also used to model systems that do not show ideal behaviour. Resistors represent conductive pathway for ion and electron transfer. Capacitors and inductors are associated with space-charge polarization regions.

Potentiodynamic polarization plot consists of the measured current versus the applied potential for a specimen that is immersed in an electrolyte, showing anodic polarization scan and cathodic polarization. In contact with a corrosive electrolyte, a metal will exhibit a potential relative to a reference electrode known as corrosion potential (E_{corr}). The cathodic polarization scan consists in polarise the specimen negatively to the E_{corr} and

measured the current produced and the cathodic reaction prevails (the metal is oxidised). The anodic polarization scan consists in polarize the sample positively to the E_{corr} and the anodic reaction prevails (hydrogen gas (H_2) is produced by the reduction of H^+).

A Gill AC computer-controlled potentiostat, as shown in Figure 4, was used for the electrochemical tests conducted in a stirred aqueous 0.5% NaCl solution at 22 ± 0.5 °C. A typical three-electrode cell was used with the specimen (V in Figure 4(b)) as the working electrode (0.5 cm^2 exposed area), a saturated Ag/AgCl electrode (III in Figure 4(b)) as the reference electrode, and a platinum mesh (IV in Figure 4(b)) as a counter electrode.

Polarization curves were measured in a stirred and un stirred aqueous 0.5% NaCl solution at 22 ± 0.5 °C. The polarization curves were obtained after 30 min of immersion, from -200 mV with respect to the open circuit potential (OCP) until a maximum potential of 500 mV . A minimum of three tests were conducted for each condition. The current density is estimated by Tafel extrapolation of the cathodic branch of the polarization curve.

EIS measurements were performed for immersion times ranging from 1h to 24 h at room temperature. The frequency range used was from 0.01 Hz to 30 kHz and 10 mV RMS with respect to the OCP with an amplitude of the sinusoidal potential signal was used. The impedance spectra were analysed using ZView[®] software. The errors for the individual parameters of the equivalent electrical circuits (such as CPE and R) were $<5\%$ and with values of the goodness of fit of the simulated spectra corresponded to $\chi^2 < 0.01$.

Figure 4: Equipment setup used for electrochemical tests: a) I: Electrochemical cell used for in the experiments and II) Gill AC potentiostat used for the measurements; b) detail of the cell used for the measurements: III) saturated Ag/AgCl electrode used as the reference electrode; IV) platinum mesh used as a counter electrode; V) specimen positioned as the working electrode with an exposed area of 0.5 cm²; VI) IKA magnetic stir base used to stir the solution during the test.

g. Hydrogen Evolution Test

The overall corrosion reaction of magnesium in aqueous solution is [139,140]:

Thus one mole of hydrogen gas corresponds to the dissolution of one mole of magnesium. Therefore, it is possible to monitor the weight loss of magnesium during the immersion corrosion experiments by measuring the volume of hydrogen gas evolution. Figure

5(a) shows the setups used for the hydrogen evolution tests. Figure 5(b) illustrates the basic principles involved in the hydrogen evolution setup.

Hydrogen evolution measurements were performed in 0.5 wt.% NaCl naturally-aerated solution for up to 10 days for the ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y alloys. Due to the fast corrosion of the ZK40-Nd the experiments were interrupted after 4 days. After the corrosion tests, the cross-section of the specimens were characterized by SEM in order to investigate the distribution, morphology and composition of the corrosion products.

Figure 5: a) Hydrogen evolution setups used for the measurements; b) Principle of hydrogen evolution: at the start the air is sucked out of the column (indicated by the red arrows) and the external part is filled with water. Bubbles of H_2 are generated during the corrosion in 0.5 wt.% NaCl. They go through the central part of the column and the increase of the internal pressure pushing the water down (black arrows). The displaced volume of water is taken as the volume of H_2 gas generated.

h. Immersion testing

Immersion tests were performed for 4 h, 8 h and 24 h in 0.5 wt.% NaCl naturally-aerated solution in order to investigate the initiation of corrosion process. The surface analysed was prepared metallographically to the final polishing step using OPS suspension. This procedure was adopted to avoid the sample preparation imperfections, such as scratches from influencing the initiation of corrosion. Finally, the corroded surface was investigated with SEM after the removal of the corrosion products by cleaning in a solution containing 200 g/L CrO_3 at room temperature for 5-10 min following the ASTM standard G1-90, Designation C5.2.

Weight loss was measured after immersion for 10 days for the ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y and for 7 days for the ZK40-Nd. These times were adopted to compare the corrosion rates with the hydrogen evolution test. The specimens were weighed before and after the tests using a Sartorius Ax224 balance with a resolution of 0.001 g. The total area of the specimens was measured before the experiment. The metal loss measured by weighing the specimens after removing the corrosion products, and was used to calculate the average corrosion rate. The specimens were also cleaned in a solution containing 200 g/L CrO_3 at room temperature for 5-10 min.

4. RESULTS

a. Microstructure

The optical (OM) and scanning electron (SEM) micrographs showing the as-cast microstructure are illustrated in Figures 6 and 7, respectively. A relatively uniform microstructure was observed for all alloys, except the ZK40-Gd which consist of a bimodal grain structure (Figure 6(c)). ZK40-Nd, Figure 6(d) has shown the most pronounced dendritic microstructure. ZK40 has the most uniform grain size distribution. The average grain size of the ZK40 was $72.4 \pm 2.5 \mu\text{m}$, $75.9 \pm 5.0 \mu\text{m}$ for the ZK40- CaO. The coarse and fine grained ZK40-Gd gives rise to two different grain distribution with a global average of $46.1 \pm 9.1 \mu\text{m}$. The average size of the fine grains is $30.1 \pm 4.2 \mu\text{m}$ while coarse grains were $81.9 \pm 9.2 \mu\text{m}$. The ZK40-Nd had an average grain size of $67.1 \pm 5.4 \mu\text{m}$. and the ZK40-Y $86.1 \pm 4.5 \mu\text{m}$.

Figure 6: Optical micrographs of the as-cast alloys: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

The SEM micrographs, illustrating the volume fraction and distribution of the intermetallic particles, are shown in Figure 7. The volume fraction of second phases is

1.6 $\pm$ 0.5%, 6.5 $\pm$ 0.9%, 5.7 $\pm$ 1.0%, 7.3 $\pm$ 0.6% and 3.1 $\pm$ 0.5% for ZK40, ZK40-CaO, ZK40-Gd, ZK-Nd and ZK40-Y, respectively. In the unmodified ZK40 alloy, discrete particles of intermetallic phase were observed randomly at triple points and grain boundaries (Figure 8(a)) and within the grains (Figure 8(b)). In addition, segregation of Zn was observed from the centre of grains to the intermetallic area as illustrated by the brighter regions close to the grain boundaries, Figure 7(a). The ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y alloys contain a semi-continuous distribution of intermetallic particles along the grain boundaries. In the ZK40-CaO and the ZK40-Nd the interconnectivity is larger than the other alloys. A lamellar morphology of the second phases was observed for the ZK40-CaO (Figure 8(c)) and the ZK40-Gd (Figure 8(d)) alloys. For the ZK40-Nd (Figure 8(e)) and ZK40-Y (Figure 8(f)) continuous intermetallic particles were observed.

Figure 7: SEM micrographs of the as-cast alloys: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

The synchrotron radiation diffraction (SRD) line profiles (Figure 9) from the three alloys show that they consisted of α -Mg and intermetallic phases. The composition of the intermetallic phase was alloy dependent. The ZK40 alloy contained MgZn_2 phase,

Figure 9(a). The ZK40-CaO (Figure 9(b)) and ZK40-Gd (Figure 9(c)) contained $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and $(\text{Mg,Zn})_3\text{Gd}_2$. The ZK40-Y (Figure 9(e)) contained and $\text{Mg}_3\text{Y}_2\text{Zn}_3$. Due to the large number of peaks observed in the XRD line profile of the ZK40-Nd the intermetallic phases were analysed with TEM, Figure 10. Only one phase was detected with the composition 71.8 ± 7.2 at% Mg 20.3 ± 5.2 at% Zn and 7.9 ± 2.0 at.% Nd, Figure 10(b). The crystal structure could be indexed according the C centred orthorhombic phase reported by Huang *et al.* [141]. Figure 10(c,d,e) shows the diffraction patterns for the (001), (101) and (110) zone axes, respectively, with $a = 0.97$ nm, $b = 1.12$ nm and $c = 0.95$ nm, designated as $\text{Mg}_{75}\text{Zn}_{20}\text{Nd}_5$.

Figure 8: Secondary electrons (SE) images of the intermetallic phases observed in the microstructure of: a,b) ZK40; c) ZK40-CaO; d) ZK40-Gd; e) ZK40-Nd; f) ZK40-Y.

The DTA curves show an exothermic peak during cooling from 700 °C at 636-638 °C attributed to the formation of α -Mg, Figure 11. Table 4 summarizes the peak temperatures for the formation of the intermetallic phase. For the ZK40-Nd alloy two peaks

were detected. The SRD and TEM analysis show only one phase ($\text{Mg}_{75}\text{Zn}_{20}\text{Nd}_5$), which suggests that solid state transformation may happen during cooling in ZK40-Nd.

Figure 9: Synchrotron Radiation X-ray linescan profiles for the as-cast alloys: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

Figure 10: TEM analyses for the ZK40-2Nd alloy: a) the bright field image of the intermetallic phase; b) EDX line profile; Diffraction patterns for the (c) (001), (d) (101) and (e) (110) zones axes.

Figure 11: Differential Temperature Analysis (DTA) plots for the investigated alloys during cooling.

The surface potential differences between micro constituents of the as-cast alloys were investigated using scanning kelvin probe force microscopy (SKPFM). Surface potential maps and potential profiles are shown in Figure 12 for the alloys investigated. The

potential profiles show the surface potential difference between the intermetallic phase and the α -Mg matrix. The intermetallic phases found in the investigated alloys were cathodic with respect to the α -Mg matrix. For the ZK40, ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y alloys the potential difference between the intermetallic phases and the α -Mg matrix was 50 ± 20 mV, 50 ± 10 mV, 170 ± 20 mV, 35 ± 10 mV and 65 ± 10 mV, respectively.

Figure 13 illustrates the surface potential maps, potential profiles and chemical composition for the impurities particles in the ZK40-Gd alloy (Figure 13(a)) and for the ZK40-Nd alloy (Figure 13(b)). These impurities particles contain Mg, Zn, Zr, Fe and Al and are cathodic with respect to the α -Mg matrix (430 ± 50 mV for the ZK40-2Gd alloy and 140 ± 30 mV for the ZK40-2Nd alloy).

Table 4: Temperature of formation of the second phases for the investigated alloys obtained from DTA.

Alloys	Formation Temperature (°C)		
	α -Mg	1 st peak	2 nd peak
ZK40	638.5	337.7	-
ZK40-CaO	631.4	390.0	-
ZK40-Gd	635.3	496.4	-
ZK40-Nd	638.0	487.8	466.3
ZK40-Y	638.2	499.3	-

Figure 12: Surface potential maps and potential profiles in selected areas of (b,e) ZK40, (b,g) ZK40-CaO, (c,h) ZK40-Gd, (d,i) ZK40-Nd and (e,j) ZK40-Y ZK alloys.

Figure 13: Surface potential maps (a,d), composition (b,e) and potential profiles (c,f) in selected areas of (a,b,c) ZK40-Gd and (d,e,fe) ZK40-Nd.

b. Room temperature tensile and compression properties

The typical tensile and compressive curves of the alloys investigated are shown in Figure 14. The yield stress, maximum stress and total elongation are summarised in Table 5. There was no significant difference between compressive and tensile yield strengths of all five alloys. The maximum compressive strength and compression to failure did not show significant deviations for the investigated alloys.

ZK40-Gd exhibited the highest total elongation in tension, followed by the ZK40-Y alloy. The addition of Nd and Ca in the ZK40 for the as-cast condition decreased the total elongation (from $\sim 12\%$ to less than 4%) significantly. The maximum tensile stress was

comparable for the ZK40, ZK40-Gd and ZK40-Nd alloys and substantially lower for the ZK40-CaO and ZK40-Nd.

Figure 14: Room temperature stress-strain for the modified ZK40 alloys: a) tensile; b) Compressive deformation.

Table 5: Pertinent values recorded from the tensile and compressive stress-strain curves for the modified ZK40 alloy.

	Tensile properties			Compression properties		
	Yield Stress (MPa)	Maximum Stress (MPa)	Total elongation (%)	Yield Stress (MPa)	Maximum Stress (MPa)	Total elongation (%)
ZK40	101.8 ± 6.7	225.1 ± 15.2	12.8 ± 4.6	106.8 ± 2.9	365.2 ± 3.6	20.6 ± 1.2
ZK40-CaO	90.8 ± 3.1	125.8 ± 27.1	2.2 ± 2.0	99.1 ± 2.3	347.9 ± 3.6	20.7 ± 1.8
ZK40-Gd	99.8 ± 6.0	227.9 ± 6.5	17.9 ± 1.9	107.3 ± 2.7	360.9 ± 3.8	20.2 ± 1.5
ZK40-Nd	99.3 ± 2.7	147.5 ± 10.3	3.9 ± 1.0	109.3 ± 2.4	351.2 ± 2.3	22.3 ± 2.1
ZK40-Y	97.0 ± 3.2	220.1 ± 6.9	16.8 ± 6.0	99.1 ± 2.0	357.4 ± 2.5	22.36 ± 1.4

Figure 15: SEM Fractographies for the as-cast tensile specimens. a,c,e,g,i) Secondary electrons (SE) images; b,d,f,h,j) Backscattered electrons (BSE) images; a,b) ZK40; c,d) ZK40-CaO; e,f) ZK40-Gd; g,h) ZK40-Nd; i,j) ZK40-Y.

Figure 15 shows the fracture surfaces for the tensile specimens. Figure 15(a,c,e,g,i) illustrates the fractography using secondary electrons (SE), which provide more information on the topography of the fracture surface. Figure 15(b,d,f,h,j) shows the backscattered electrons (BSE) images for the fracture surface. The BSE mode can give information on the differences in chemical composition between the exposed area. For ZK40 (figure 15(a,b)), ZK40-Gd (Figure 15(e, f)) and ZK40-Y (Figure 15(i, j)) the fracture surfaces are comparable and characterised by near parallel cleavage fracture surfaces (better illustrated in the SE images). For ZK40-CaO and ZK40-Nd alloys the fracture surfaces were characterised by a globular cleavage surface. The BSE images show that the fracture surface was mostly constituted by the intermetallic phases (“brighter” surface) for the ZK40-CaO and ZK40-Nd alloys. For the ZK40, ZK40-Gd and ZK40-Y the grain was fractured, represented by the (“darker” surfaces). Thus, the fracture was inter-granular for the ZK40-CaO and ZK40-Nd alloys and typically intra-granular for the ZK40, ZK40-Gd and ZK40-Y alloys.

c. Corrosion Behaviour

Figure 16 shows the volume of hydrogen evolution of investigated alloys in 0.5 wt%. NaCl. ZK40-Nd alloy has a considerably higher hydrogen evolution volume compared with the other alloys. ZK40-Y showed a large hydrogen volume evolved in the first days of experiments but after 3 days the rate of evolution decreased and the volume is slightly higher than for the ZK40 alloy. The ZK40-CaO and ZK40-Gd alloys show slightly lower volume of hydrogen evolution. After one-day, the volume of hydrogen evolved for the ZK40 was 0.23 ± 0.01 ml/cm². For the ZK40-CaO and ZK40-Gd it was not detectable after 1 day. For the ZK40-Nd and ZK40-Y it was 1.07 ± 0.15 ml/cm² and 0.58 ± 0.01 ml/cm² respectively. The amount of hydrogen evolved for the ZK40-Nd was approximately 4 times that of the ZK40 and 2 times that of the ZK40-Y. After 7 days the volume of hydrogen evolved was 7.39 ± 0.19 ml/cm², 4.40 ± 0.30 ml/cm², 3.40 ± 0.66 ml/cm² and 8.09 ± 0.14 ml/cm² for the

ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y respectively. The amount of hydrogen evolved by ZK40-CaO was ~35% lower than that for the ZK40. The ZK40-Gd evolved ~39% less hydrogen gas compared with the ZK40.

Figure 16: Hydrogen evolution volume curves immersion in of 0.5 wt.% NaCl solution at room temperature for alloys investigated

The cross-section and the planar view micrographs recorded after the hydrogen evolution experiments shown in Figure 17 contain a corrosion layer with regions of localised corrosion (indicated by the “holes” in the plan view (Figure 17(h-i))) and it is more pronounced on the cross section of the ZK40 (Figure 17(a)) and ZK40-Nd (Figure 17(d)).

Figure 17: a,b,c,d,e) cross-section back scattered electron (BSE) images; f,g,h,i,j) plan view secondary electron (SE) images; a,f) ZK40; b,g) ZK40-CaO; c,h) ZK40-Gd; d,i) ZK40-Nd; e,j) ZK40-Y.

The corrosion rate calculated via weight loss measurement after immersion in 0.5 wt.% NaCl solution for 10 days (ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y) and after 4 days (ZK40-Nd) are shown in Figure 18. The ZK40-Nd exhibits the highest value of corrosion rate (0.0284 g/day). ZK40, ZK40-Gd and ZK40-Y show comparable values of corrosion rate and the ZK40-CaO shows the lowest.

Figure 18: Corrosion rate from weight loss measurement after 14 days (ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y) and 7 days (ZK40-Nd).

The polarization curves of ZK40, ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y alloys are shown in Figure 19. Significant differences between the polarization curves measured with stirred and un stirred solutions are observed are shown in Table 6. Compared with the ZK40 alloy, the addition of Ca, Gd, Nd or Y decreased the rate of cathodic reaction kinetics solution when the solution is stirred, leading to lower corrosion current density (i_{corr}). The ZK40-CaO and the ZK40-Gd exhibited slightly lower corrosion potential

(E_{corr}) values than the ZK40 alloy. In the un stirred solution, the ZK40-CaO and ZK40-2Nd alloys exhibited slightly higher rate of cathodic reaction kinetics compared with the ZK40 alloy. However, the differences are small and the electrochemical behaviours are comparable for the investigated alloys under the same experimental conditions.

Figure 19: Potentiodynamic polarization curves: a) measured with stirred solution of 0.5 wt.% NaCl at room temperature; b) measured with un stirred solution of 0.5 wt.% NaCl at room temperature.

Table 6: Pertinent points calculated from the Potentiodynamic Polarization Curves presented in Figure 19.

Alloy	Potential, E_{corr} [V]		Current density [mA/cm^2]	
	Stirred	Un stirred	Stirred	Un stirred
ZK40	-1.496 ± 0.006	-1.555 ± 0.014	0.116 ± 0.016	0.019 ± 0.004
ZK40-2CaO	-1.513 ± 0.004	-1.541 ± 0.004	0.064 ± 0.012	0.025 ± 0.005
ZK40-2Gd	-1.502 ± 0.025	-1.539 ± 0.043	0.049 ± 0.008	0.011 ± 0.004
ZK40-2Nd	-1.476 ± 0.01	-1.513 ± 0.015	0.042 ± 0.009	0.023 ± 0.010
ZK40-1Y	-1.481 ± 0.021	-1.530 ± 0.052	0.036 ± 0.004	0.012 ± 0.005

Figure 20: Equivalent circuit used to fit the electrochemical impedance spectroscopy data obtained for immersion in 0.5 wt% NaCl naturally aerated solution. Rel stands for electrolyte resistance; Rct stands for charge transfer resistance and CPEdl stands for the constant phase element of the dielectric layer.

Figure 21: Electrochemical spectroscopy Impedance (ESI) results after 1 h immersion in 0.5 wt% NaCl naturally aerated solution at room temperature: a,b) Measured Bode plots and Nyquist plots, respectively; c,d) Fitted Bode plots and Nyquist plots, respectively.

Figure 21 and Figure 22 show Bode and Nyquist diagrams the of the EIS measurement and the fitted model after 1 h and 24 h of immersion in 0.5 wt.% NaCl solution, respectively. The equivalent circuit used for fitting of the electrical parameters is illustrated in Figure 20. The resistance caused by the electrolyte is represented by R_{el} . The resistance due to charge transfer is R_{ct} . The growth corrosion layer is similar to the capacitance effect, which is represented by a constant phase element CPE_{dl} . The calculated electrochemical parameters are presented in Table 7.

R_{el} values were comparable for the all alloys and were in the range between 80 and 100 $\Omega \cdot \text{cm}^2$. The diameter of the capacitive arc observed in the Nyquist diagram for 1 h immersion (Figure 21(b,d)) reaches the highest Z' values for the ZK40-Gd (around 1200 $\Omega \cdot \text{cm}^2$), followed by the ZK40-CaO ($\sim 1150 \Omega \cdot \text{cm}^2$). For the ZK40 the Z' values is $\sim 800 \Omega \cdot \text{cm}^2$, which is slightly higher than the ZK40-Y (750 $\Omega \cdot \text{cm}^2$). ZK40-Nd shows the lowest Z' values ($\sim 500 \Omega \cdot \text{cm}^2$). After 24 h, the calculated diameter of the capacitive arc observed in the Nyquist diagram also shows the same corrosion behaviour tendency: the ZK40-Gd has the highest Z' values ($\sim 550 \Omega \cdot \text{cm}^2$), followed by ZK40-CaO (around 535 $\Omega \cdot \text{cm}^2$), ZK40 ($\sim 500 \Omega \cdot \text{cm}^2$), ZK40-Y ($\sim 415 \Omega \cdot \text{cm}^2$) and ZK40-Nd ($\sim 235 \Omega \cdot \text{cm}^2$).

The values of the CPE_{dl} -T, the dielectric layer, increase with the increase in time and the highest values of was observed for the ZK40-Nd. It was approximately double the value of the other alloys (around 20 $\text{mF} \cdot \text{cm}^{-2}$) for 1 h immersion and approximately 3 times of the ZK40 and ZK40-Y (around 80 $\text{mF} \cdot \text{cm}^{-2}$) after 24 hours. The lowest values after 24 h immersion was for ZK40-CaO (59.2 $\text{mF} \cdot \text{cm}^{-2}$) followed by the ZK40-Gd (65.6 $\text{mF} \cdot \text{cm}^{-2}$).

The charge transfer resistance (R_{ct}) was significantly lower for the ZK40-Nd alloy for all the immersion times, and show a decreasing tendency with the increase in immersion time. A slight increase in the R_{ct} for 24 h immersion and in 16 h immersion for the ZK40-Y. The ZK40-Gd has the highest R_{ct} after 24 h immersion (485.5 $\Omega \cdot \text{cm}^2$) followed by

the ZK40-CaO ($451.3 \Omega \cdot \text{cm}^2$). The ZK40 has a Rct of $412.3 \Omega \cdot \text{cm}^2$ and the ZK40-Y a Rct of $329.1 \Omega \cdot \text{cm}^2$. The lowest value was measured for the ZK40-Nd ($133.3 \Omega \cdot \text{cm}^2$).

Figure 22: Electrochemical spectroscopy Impedance (ESI) results after 24 h immersion in 0.5 wt% NaCl naturally aerated solution at room temperature: a,b) Measured Bode plots and Nyquist plots, respectively; c,d) Fitted Bode plots and Nyquist plots, respectively.

Figure 23 shows the plan view of the corroded specimens after the removal of the corrosion products following 4 h immersion in 0.5 wt.% NaCl solution. Different types of localised corrosion were detected for the alloys:

- Micro “craters” of diameter $\sim 1 \mu\text{m}$ was observed within the grains for all alloys. These were more pronounced for the ZK40-Y as highlighted in the insert in Figure 23(e);

- Localised corrosion in the shape of “craters” in some grains was observed for all alloys. It is highlighted in the insert of Figure 23(b) for ZK40-CaO and the insert of Figure 23(c) for ZK40-Gd. These “craters” were more observed in the ZK40-CaO;
- Localised corrosion along the intermetallic phases was observed only for the ZK40-Nd as highlighted in the insert in Figure 23(d).

Table 7: Simulated parameters of the electrochemical impedance spectroscopy (EIS) data of the investigated ZK40, ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y alloys in immersion in 0.5 wt% NaCl naturally aerated solution up to 24 hours.

Time (h)	$R_{el} (\Omega)$	$R_{ct} (\Omega.cm^2)$	CPE-T (mF.cm ⁻²)	CPE-n
ZK40				
1	84.75 ± 0.47	702.9 ± 6.7	23.1 ± 0.7	0.880 ± 0.005
3	84.87 ± 0.46	581.2 ± 5.7	31.1 ± 1.0	0.892 ± 0.005
6	87.32 ± 0.55	525.0 ± 6.1	39.3 ± 1.6	0.893 ± 0.007
10	86.40 ± 0.46	494.6 ± 5.3	45.1 ± 1.6	0.909 ± 0.006
16	86.36 ± 0.41	452.0 ± 4.6	64.5 ± 2.1	0.877 ± 0.007
24	85.79 ± 0.43	412.3 ± 4.8	75.1 ± 2.7	0.876 ± 0.006
ZK40-CaO				
1	80.63 ± 0.48	1093.0 ± 10.6	22.4 ± 0.6	0.882 ± 0.005
3	82.19 ± 0.42	669.9 ± 6.0	26.1 ± 0.8	0.904 ± 0.006
6	82.31 ± 0.61	499.6 ± 5.8	29.1 ± 1.4	0.915 ± 0.008
10	85.36 ± 0.48	486.9 ± 4.5	41.4 ± 1.5	0.883 ± 0.006
16	84.01 ± 0.51	454.9 ± 5.4	49.8 ± 2.0	0.877 ± 0.007
24	83.66 ± 0.52	451.3 ± 5.1	59.2 ± 2.4	0.868 ± 0.007

ZK40-Gd				
1	84.67 ± 0.90	1131.0 ± 16.5	19.9 ± 1.0	0.868 ± 0.008
3	87.10 ± 0.52	677.5 ± 6.8	24.5 ± 0.8	0.904 ± 0.006
6	87.35 ± 0.51	627.2 ± 6.7	35.2 ± 1.2	0.905 ± 0.006
10	89.29 ± 0.49	594.3 ± 6.0	43.8 ± 1.4	0.906 ± 0.006
16	89.43 ± 0.63	458.7 ± 6.7	45.2 ± 2.1	0.927 ± 0.009
24	88.10 ± 0.45	485.5 ± 5.2	65.6 ± 3.4	0.892 ± 0.006
ZK40-Nd				
1	94.83 ± 1.03	413.2 ± 7.7	41.6 ± 3.3	0.831 ± 0.013
3	97.26 ± 0.52	213.8 ± 2.6	45.0 ± 2.6	0.901 ± 0.010
6	96.62 ± 0.50	165.4 ± 2.2	75.1 ± 4.9	0.889 ± 0.012
10	97.71 ± 0.46	152.8 ± 1.9	117.0 ± 7.0	0.860 ± 0.011
16	100.00 ± 0.50	150.9 ± 2.3	164.0 ± 10.6	0.840 ± 0.013
24	100.1 ± 0.51	133.3 ± 2.4	220.0 ± 15.7	0.824 ± 0.014
ZK40-Y				
1	81.36 ± 0.78	665.8 ± 9.2	23.2 ± 1.3	0.873 ± 0.009
3	82.23 ± 0.46	419.7 ± 3.9	29.9 ± 1.2	0.899 ± 0.006
6	82.88 ± 0.52	342.8 ± 4.2	39.7 ± 1.9	0.919 ± 0.008
10	84.16 ± 0.47	358.6 ± 4.1	50.8 ± 2.1	0.914 ± 0.008
16	85.42 ± 0.43	389.6 ± 4.5	65.0 ± 2.4	0.904 ± 0.007
24	83.95 ± 0.42	329.1 ± 3.8	80.8 ± 3.1	0.885 ± 0.007

Figure 23: First steps corrosion after 4 h immersion in 0.5 wt% NaCl naturally aerated solution at room temperature: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

The plan view of the corroded specimens after the removal of the corrosion products following 8 h immersion in 0.5 wt.% NaCl solution is shown in Figure 24. The grains were more severely corroded compared with the 4 h immersion. The initiation of corrosion followed the same tendency as 4 h immersion. Small “craters” of diameter $\sim 1 \mu\text{m}$ were present within the grain for all alloys and was more pronounced for the ZK40-Y alloy. A lower number of micro “craters” were observed for the ZK40-Nd alloy. Larger “craters” were also found within some grains for all investigated alloys. This is highlighted in the inserted

image for ZK40-CaO alloy. The localised corrosion was also only observed for the ZK40-Nd, where the α -Mg matrix corroded along the intermetallic compounds.

Figure 24: First steps corrosion after 8 h immersion in 0.5 wt% NaCl naturally aerated solution at room temperature: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

The plan view of the corroded specimens after the removal of the corrosion products after 24 h immersion in 0.5 wt.% NaCl solution is shown in Figure 25. For the ZK40 (Figure 25(a)) and ZK40-Gd (Figure 25(c)) the localised corrosion within the grain was more pronounced compared with 8 h immersion. The “microcraters” appears to start to coalesce for

the ZK40. No significant differences between 8 h and 24 h is observed for the ZK40-CaO alloy. Severe localised corrosion was observed for the ZK40-Nd (Figure 25(d)) and ZK40-Y (Figure 25(e)) alloys, while it was more pronounced for the ZK40-Nd alloy. In the case of the ZK40-Nd the corrosion front seems to have started at the grain boundary, and propagate toward the α -Mg matrix (inserted figure in Figure 25(d)). On the other hand, the corrosion front seems to propagate along the grain boundary, without deep corrosion of the α -Mg matrix for the ZK40-Y.

Figure 25: First steps corrosion after 24 h immersion in 0.5 wt% NaCl naturally aerated solution at room temperature: a) ZK40; b) ZK40-CaO; c) ZK40-Gd; d) ZK40-Nd; e) ZK40-Y.

5. DISCUSSION

The as-cast microstructure of the ZK40 alloy was modified with the addition of Ca, Gd, Nd and Y elements. The ZK40 alloy contains only a small volume fraction of intermetallic particles, mainly localised at the grain boundaries, especially at triple points. The intermetallic phase was identified as MgZn_2 . The ZK40 with addition of Ca, Gd, Nd and Y resulted in a semi-continuous network of intermetallic particles along the grain boundaries. Similar microstructures were reported for the ZE41 alloy [87,89]. The volume fraction of intermetallic particles was higher for the ZK40-Nd alloy. CaO was not observed in the as-cast microstructure, which agrees with Wiese *et al.* [59] who reported CaO dissociates during melting and solidification. The ZK40-CaO contained the $\text{Ca}_2\text{Mg}_3\text{Zn}_3$ phase and the ZK40-Gd the $(\text{Mg,Zn})_3\text{Gd}_2$ phase. Liu *et al.* [142] reported the $(\text{Mg,Zn})_3\text{Gd}_2$ intermetallic phase for a $\text{Mg-4.58Zn-2Gd-0.18Zr}$ alloy which has a composition similar to the ZK40-Gd alloy. For the ZK40-Nd the DTA analysis shows the presence of two exothermic peaks during solidification in addition to the peak for $\alpha\text{-Mg}$. This suggests the formation of two intermetallic phases during phase transformation. However, based on the TEM results and SRD only one intermetallic phase was observable in the microstructure, with chemical composition of 71.8 ± 7.2 at% Mg, 20.3 ± 5.2 at% Zn and 7.9 ± 2.0 at.% Nd, $\text{Mg}_{75}\text{Zn}_{20}\text{Nd}_5$. This suggests that it may be possible to have a solid-state transformation of the intermetallic phase subsequent to solidification. For the ZK40-Y the $\text{Mg}_3\text{Y}_2\text{Zn}_3$ phase was observed, as described by Padezhnova *et al.* [143].

The equiaxed dendrites were observed for the ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y. The ZK40-Nd had a dendritic microstructure. The grain size was highest for the ZK40-Y alloy (86.1 ± 4.5 μm). The ZK40, ZK40-CaO and ZK40-Nd alloys show comparable grain size (~ 70 μm). The ZK40-Gd shows a refined microstructure with a grain size of 46.1 ± 9.1 μm . In Figure 7 the brighter areas along the grain boundaries suggest that there is

segregation within the grains of the ZK40 alloy, where a higher amount of Zn can be seen in the brighter areas closer to the grain boundaries.

The compressive behaviour was similar between the alloys investigated. The tensile tests show that elongation was enhanced with Gd and Y additions, but it was severely compromised with Ca and Nd additions. The tensile yield stresses were similar for all alloys. The ultimate tensile stress was comparable for ZK40, ZK40-Gd and ZK40-Y alloys and the 50% and 35% lower for the ZK40-CaO alloy and ZK40-Nd alloy, respectively, compared with ZK40, Figure 14 and Table 5. The fracture surface images for the tensile samples (Figure 15) show for the ZK40 (Figure 15(a,b)), ZK40-Gd (Figure 15(e,f)) and for the ZK40-Y (Figure 15(i,j)) fracture cleavage occurred in planes approximately parallel to each other. This morphology is characteristic of intragranular fracture. Additionally, the BSE fractographies for these alloys (Figure 15(b) for the ZK40, Figure 15(f) for the ZK40-Gd and Figure 15(j) for the ZK40-Y) show that although the intermetallic phase was present fracture occurred within the α -Mg matrix via cleavage. This suggests that the presence of intermetallic compounds along the grain boundaries reinforced the grain boundary. The additional stress/strain that was accommodated by the semi-continuous network of intermetallic compounds and the strong bonding between the intermetallic phase and the α -Mg matrix can explain the enhanced elongation of the ZK40-Gd and ZK40-Y alloys. Similar effect was reported by Yu *et al.* [98] for a high strain-rate tests in the rolled Mg-5.5Zn-0.6Zr-xGd (x=0.2, 0.5 and 0.8 wt.%).

Fracture surfaces for the ZK40-CaO and ZK40-Nd alloys show cleavage surfaces mainly constituted by dimples. This is characteristic of intergranular fracture. The BSE images of the ZK40-CaO (Figure 15(d)) and the ZK40-Nd (Figure 15(h)) show that the dimple surface constituted mainly of intermetallic phase for the ZK40-Nd and for the ZK40-CaO the intermetallic phase was also found in the cleavage surface. For these alloy the shell of the grains can be seen, Figure 15(d). This indicates that the semi continuous network of

intermetallic phase along the grain boundary did not withstand the load during tension and fractured before any significant deformation of the α -Mg. Therefore, the reinforcement caused by intermetallic phases in the ZK40-CaO and ZK40-Nd only played a role at the initial stages of deformation.

The corrosion behaviour, based on weight loss, hydrogen evolution and impedance suggests that the addition of Ca and Gd to the ZK40 alloy improved its corrosion resistance. The weight loss shows the highest corrosion resistance for the ZK40-CaO. The ZK40, ZK40-Gd and ZK40-Y has comparable corrosion rates. The highest corrosion rate was reported for the ZK40-Nd. In the hydrogen evolution test the ZK40-Gd alloy has a slightly enhanced corrosion resistance compared with the ZK40. Additionally, the ZK40-CaO did not show significant corrosion resistance improvement as observed for the weight loss. The combination of non-complete removal of the corrosion products in regions deep localised corrosion and the removal of intermetallic particles during the cleaning with chromic acid solution are likely to be the main reasons for the differences in corrosion rates between the investigated methods.

Differences between the polarization curves measured with stirred and un stirred solutions are observed (Figure 19 and Table 6). The addition of Ca, Gd, Nd or Y slightly decreased the rate of cathodic reaction kinetics solution when the solution is stirred, leading to lower corrosion current density (i_{corr}). The ZK40-CaO and ZK40-Gd alloys exhibited the lowest corrosion potential (E_{corr}) values. For the un stirred solution, the ZK40-CaO and ZK40-Nd alloys exhibited the highest rate of cathodic reaction kinetics. ZK40 alloy exhibited the lowest corrosion potential (E_{corr}) values for the un stirred solution.

The corrosion resistance, based on hydrogen evolution and impedance, suggests that the addition of 2 wt.% of Nd to the ZK40 was detrimental to the corrosion resistance. The corrosion resistance was slightly improved by Gd and Ca additions. Hydrogen

evolution results reveal the kinetics along the immersion time was alloy dependent. At the initial stage of corrosion, an incubation period with a low rate of hydrogen evolution followed by a period of acceleration in hydrogen evolution after approximately 10 h for the ZK40-Nd alloy, 24 h for the ZK40-Y and 75 h for the ZK40, ZK40-CaO and ZK40-Gd alloys. After approximately 175 h exposure for the ZK40, ZK40-CaO, ZK40-Gd and ZK40-Y alloys the hydrogen evolution volume reached a near constant rate of increase, indicated by the linearity of curves. In ZK40-Nd alloy corrosion kinetics accelerated was observed, and after 4 days the volume of hydrogen was out of the range of the setup used. Two main factors are responsible for corrosion in the magnesium alloys:

- Microgalvanic corrosion due to: impurities; intermetallic compounds, segregation or microsegregation;
- Effectiveness of the corrosion layer: constitution and adhesion of the corrosion layer including its constituents, their morphology, and its cohesion.

The effectiveness of the corrosion layer it is related to the capability of the surface oxide film to repair itself [38]. After immersion in an aqueous solution, a film of MgO that forms in air transform into a film consisting mainly of $\text{Mg}(\text{OH})_2$. The volume expansion from MgO to $\text{Mg}(\text{OH})_2$ disrupts the surface film [144] and explain the porous nature of the $\text{Mg}(\text{OH})_2$ layer in the surface film. The initial incubation period observed during hydrogen evolution attributed to the initial formation of $\text{Mg}(\text{OH})_2$ and the breakdown of the MgO surface film until cracks are produced on the corrosion film. However, once the corrosion film starts breaking down and corrosion initiates in a localised region (localised corrosion) repairing the corrosion film is relatively difficult. Although the dissolved Mg^{2+} can react with OH^- and deposit $\text{Mg}(\text{OH})_2$ on the Mg surface, the loosely deposited $\text{Mg}(\text{OH})_2$ film does not necessarily cover the cracks. Simultaneously, the hydrogen bubbles generated in the corroding areas can cause localised disruptions to the deposited $\text{Mg}(\text{OH})_2$ prevents the corroding areas

from being fully covered by the $\text{Mg}(\text{OH})_2$. The accelerating hydrogen evolution is attributed to the intense localised corrosion activity. During this period the area of the corrosion front increases significantly and the corrosion is enhanced. Finally, due to the increase in pH (intrinsically related to the redox reactions of Mg, which produce OH^- as one of the products), and the thermodynamic stability of the magnesium corrosion products under high pH [35,145,146], the effectiveness of the corrosion layer is enhanced and the corrosion front is hindered in a way that the volume of hydrogen produced during this period tend to increase linearly. The relatively high volume of hydrogen evolved in the investigated alloys in 0.5 wt.% NaCl indicates that the effectiveness of the corrosion layer is low.

The breakdown of the corrosion layer is not the only phenomena that could explain the corrosion behaviour of these alloys. The presence of impurities, intermetallic phases and localised segregation of alloying elements play an important role on the corrosion behaviour of Mg alloys. Significant amount of intermetallic phases is more noble and more stable than the α -Mg matrix, as reported for AZ alloys [147-151], ZE41 [87-152], Mg-xGd-3Y-0.4Zr (x= 6, 8, 10, 12%) [153], Mg-10Gd-3Y-0.4Zr [154], Mg-Zn-Mn-Si-Ca [155,156], Mg-8Li [157] and Mg-RE (0.5-5% La, 0.5-5% Ce, 0.5-4% Nd) [158]. For AZ system alloys [159-164] the intermetallic phases act as galvanic cathodes and accelerate the corrosion rate of the Mg if the volume fraction of the second phases is small. However, if the amount of second phase is significantly high and it forms a continuous network along the grain boundary they can act as a barrier to the corrosion of the alloy. The immersion tests (4 h, 8 h and 24 h in 0.5 wt.% NaCl) show the initiation of the corrosion and each alloy show differences in the mechanism that control the initiation of corrosion.

In ZK40, localised corrosion occurs within the grain, mainly as “microcraters” of $\sim 1 \mu\text{m}$ diameter. Additionally, “craters” are observed within a few grains where there is

severe localised corrosion. With increased immersion times from 4 h to 8 h and then from 8 h to 24 h the localised corrosion due to “microcraters” became more pronounced.

In ZK40-CaO, localised corrosion occurs through “microcraters” was also pronounced. More grains show “crater” type of localised corrosion compared with the ZK40. The area near the intermetallic phase was generally unaffected by the initial stages of corrosion for this alloy.

In ZK40-Gd, localised corrosion as “microcraters” plays an important role. The area near the intermetallic along the grain boundaries were unaffected by corrosion. In comparison with the ZK40-CaO the amount of grain with severe localised corrosion as “craters” was smaller.

For ZK40-Nd not only “microcraters” and “craters” in some grains were observed but also intensive corrosion of the α -Mg matrix along the interface with the intermetallic compounds along the grain boundaries was observed. After 24 h immersion, severe localised corrosion is observed. In this case, the corrosion seems to start at the grain boundary and propagate toward the interior of α -Mg grains.

For ZK40-Y intensive localised corrosion occurs as “microcraters”. As with the ZK40, ZK40-CaO and ZK40-Gd the grain boundaries were preserved for 4 h and 8 h immersion. In 24 h immersion, severe localised corrosion was observed and the corrosion front seems to propagate along the grain boundary. The corrosion front, though, does not seem to propagate as fast as in the ZK40-Nd toward the α -Mg matrix.

The immersion tests reveal that corrosion initiate locally. The main difference between the alloys is the kinetics of the localised corrosion within the grain and the corrosion resistance offered by the grain boundaries. For the ZK40, ZK40-CaO and ZK40-Gd alloys the grain boundaries seems to hinder the corrosion front. For the ZK40-Y, when severe localised

corrosion starts, the corrosion front seems to propagate along the grain boundaries (Figure 25(e)). The corrosion front, though, does not propagate fast toward the α -Mg matrix. The ZK40-Nd show a different behaviour. Localised corrosion of the α -Mg matrix at the interface of the intermetallic phase along the grain boundary was observed after 4 h and 8 h of immersion. After 24 h, when severe localised corrosion is pronounced, the corrosion front seems to start at the grain boundaries and propagate fast into the grains. So the corrosion front propagates faster in the ZK40-Nd compared with the other alloys, which could explain its poor corrosion resistance.

The electrochemical impedance spectroscopy (EIS) is also an effective method to characterize the corrosion behaviour [165,166] and it shows (Figure 21 and Figure 22) comparable tendency for the corrosion behaviour of the investigated alloys as the mass loss and hydrogen evolution techniques. The Nyquist diagrams show a capacitive arc at high and intermediate frequencies (HF and MF), which can be attributed to the charge transfer reaction of the magnesium corrosion process and the diameter decreases with time. The equivalent circuit (Figure 20) shows one time constant related to the corrosion process that can be described by the double layer capacitance on the electrolyte/metal interface (CPE_{dl}) and the charge transfer resistance (R_{ct}). Constant phase elements (CPE) is used instead of capacitances in order to account for non-ideal behaviour of the system [167]. The R_{ct} decreased for all alloys as the immersion time increased, similar to behaviour reported by Arrabal *et al.* [168]. The high R_{ct} of the ZK40-CaO alloy indicates the improved corrosion resistance. CPE_{dl} values of the dielectric layer of ZK40-Nd are approximately 2.5 times larger than those of the ZK40 alloy and the ZK40-Gd alloy. CPE_{dl} values of the dielectric layer of ZK40-Y are slightly higher than those of ZK40. This may be attributed to a larger active area in ZK40 Nd and ZK40-Y alloy that is exposed to the electrolyte, since roughness increases with the progression of the corrosion attack. The lowest values were observed by the

ZK40-CaO followed by the ZK40-Gd alloy. The highest CPE-n value was observed for the ZK40-Gd alloy and the lowest for the ZK40-Nd alloy. This suggests that there is an increased heterogeneity of the surface due to the corrosion process in ZK40-Nd alloy.

Based on the present work, the corrosion resistance of the modified ZK40 alloys could be attribute to:

- (i) Micro-galvanic corrosion between the α -Mg matrix and second phases and between the α -Mg matrix and the impurities. The SKPFM analysis (Figure 12 and 13) indicates that for the ZK40-Gd and ZK40-Nd the impurities have a higher Volta surface potential compared with the matrix, and it is higher than the potential difference between the intermetallic compounds and the matrix. However, during the first steps corrosion (Figure 23, Figure 24 and Figure 25) there no evidence conclusively to support the hypothesis that microgalvanic corrosion due to these impurities influenced the corrosion process of this alloy up to 24 h immersion in 0.5 wt.% NaCl. Thus, the impurities particles can act as initiation points of corrosion but it does not play an important role during the development of corrosion within the α -Mg matrix. The corrosion started within the grain (“craters” and “micro craters”) in all investigated alloys. A similar phenomenon was observed for the ZE41 alloy [89]. The amount and distribution of these localised corrosion “micro craters” is attributed to be due to the different alloying elements in the α -Mg matrix on the corrosion film formation. Localised corrosion of the α -Mg along the intermetallic phases also plays an important role in the ZK40-Nd alloy. This is an unexpected result as the SKPFM maps for ZK40-Nd alloy show that the Volta potential difference between the α -Mg matrix and the intermetallic phase is not very large. It is expected that the highest the potential difference between the two surfaces

results in a higher microgalvanic couple, as the microgalvanic couples can lead to microgalvanic corrosion. For the ZK40-Nd, the localised corrosion of the α -Mg matrix along the intermetallic compounds suggests that not only the nobility of the intermetallic phases play an important role during immersion in 0.5 wt.% NaCl but other mechanisms of corrosion also contribute to the corrosion process. In this case, the immersion tests suggest that the corrosion front propagates faster in this alloy.

- (ii) As reported for AZ series magnesium alloys [169,170], the barrier effect due to a semi continuous network of intermetallic particles along the grain boundaries can prevent the advance of the corrosion front into α -Mg matrix. However, the intermetallic compounds along the grain boundary in ZE41 alloy does not behave as a barrier for the advance of corrosion [87]. In the ZK40-Nd alloy, the corrosion of the α -Mg matrix along the semi continuous network of intermetallic particles with no significant corrosion of the intermetallic particles indicates that it also does not act as a corrosion barrier. In this case corrosion started at the grain boundary and propagated into the α -Mg matrix. In the ZK40-Y, corrosion did not start at the grain boundaries, but the corrosion front seems to propagate in this region. For the ZK40, ZK40-CaO and ZK40-Gd, the absence of localised corrosion along the grain boundary seems to promote the “barrier effect” due to semi continuous network intermetallic particles. In this case, the volume fraction of intermetallic particles, grain size and distribution of the intermetallic particles are the main factors that contribute to corrosion behaviour. The larger the grain size, the more α -Mg is attacked in the corrosion front. The higher the volume fraction of intermetallic particles and the uniform distribution provide better protection through the

barrier effect. The smaller grain size and high volume fraction of intermetallic particles that were semi-continuously distributed along the grain boundaries contributed to the enhanced corrosion resistance observed in the ZK40-Gd. Comparable behaviour was observed in ZK40-CaO. In this case, the larger grain size and the slightly higher activity of the localised corrosion in the ZK40-CaO, as indicated by the initiation of corrosion due the higher amount of “craters”, explains the slightly lower corrosion resistance observed in comparison to the ZK40-Gd alloy.

6. CONCLUSIONS

As-cast microstructures of ZK40 (Mg-4.5Zn-0.6Zr), ZK40 with 2 wt.% of Ca, Gd and Nd and 1 wt.% Y (ZK40-CaO, ZK40-Gd, ZK40-Nd and ZK40-Y, respectively) were investigated with optical, scanning (SEM), transmission electron microscopy (TEM) and synchrotron radiation diffraction (SRD). TEM and SRD were used to identify the intermetallic phases of each alloy. Scanning Kelvin Probe Force Microscopy (SKPFM) was performed in order to evaluate the surface potential difference between the α -Mg matrix and impurities and the intermetallic phases. The mechanical properties were investigated with compressive and tensile tests at room temperature. In order to understand the impact of the microstructure on the mechanical tensile properties, the fracture surfaces were analysed. Electrochemical Impedance Spectroscopy, hydrogen evolution and weight loss in 0.5 wt.% NaCl solution were used to evaluate the corrosion resistance. Immersion tests for 4 h, 8 h and 24 h were also performed to investigate the initiation of corrosion.

The addition of Ca, Gd, Nd and Y modified the as-cast microstructure of the ZK40 alloy. CaO was not detected in the as-cast microstructure of the ZK40-CaO alloy. Elongation was slightly improved with Y addition due to the reinforcement of the matrix with its particular Mg-Zn-Y intermetallic phase. The corrosion resistance measured by three different techniques was slightly enhanced for the ZK40-CaO and slightly inferior for the ZK40-Y. The detrimental effect of Nd addition on the ZK40 alloy is attributed to micro galvanic corrosion. The difference in corrosion behaviour between the ZK40-CaO and the ZK40-Y alloys can be explained in terms of the prevalence of either the barrier effect either the micro galvanic corrosion. For the ZK40-CaO, the semi-continuous network of intermetallic compounds along the grain boundary hinders the corrosion (barrier effect) and improved the corrosion properties. For the ZK40-Y alloy, the amount of intermetallic compounds is inferior compared with the ZK40-CaO and the barrier effect does not play an

important role, leading to a decrease on the corrosion resistance. An increase on the Y containing could not only lead to enhanced corrosion properties with the formation of a well-established net of intermetallic compounds along the grain boundaries but also improve the mechanical properties, making the Mg-Zn-Zr-Y an interesting Mg alloy system for development for commercial applications.

Tensile elongation improves with Gd addition. The corrosion resistance measured by three different techniques was enhanced for the ZK40-2Gd and very poor corrosion resistance was exhibited for the ZK40-2Nd. The detrimental effect of Nd addition on the ZK40 alloy attributed to microgalvanic corrosion. Therefore, the enhanced properties exhibited for the ZK40-2Gd alloy make the Mg-Zn-Zr-Gd an interesting magnesium alloy series for development for commercial applications.

7. SUGGESTIONS FOR FUTURE RESEARCH

This work shed lights on the effect of CaO, Gd, Nd and Y on the mechanical properties and corrosion resistance of ZK40 alloys. It was found that the additions of Gd and Y have improved the tensile elongation at room temperature, whereas the addition of CaO and Gd have improved the corrosion resistance. In this way the development of Mg-Zn-Zr-Gd alloys seems to be promising for producing alloys for industrial applications. In order to achieve the optimum relation corrosion resistance – mechanical properties different ratios of Zn/Gd should be tested. Another suggestion for future work would be the production of ZK40 with 1 wt.% and the comparison with ZE41 alloy in terms of creep resistance, tensile and compression behaviour and corrosion resistance (typically evaluated with salt spray testing) in order to compare the feasibility of producing in industrial scale Mg-Zn-Zr-Gd alloys.

Regarding the mechanical properties, still it is not clear what is the exact cause for the differences in elongation observed in this work. It is attributed to the effect of the reinforcement caused by presence of different intermetallic compounds in the different alloys. However, as suggestion for further investigations experiments that could analyse separately the mechanical properties (i.e. yield stress, young modulus and elongation till fracture) of intermetallic compounds and α -Mg matrix could not only elucidate such differences in mechanical behaviour but also help to create a database of mechanical properties of usual intermetallic compounds that are found in magnesium alloys.

In terms of corrosion properties, techniques that can measure the dissolution of the different ions (i.e. different chemical elements) for different immersion times could improve the understanding of the corrosion behaviour of the investigated alloys.

8. REFERENCES

- [1] Kainer, K.U. (Ed.). (2003). **Magnesium alloys and technology**.
- [2] RAILSBACK, L.B. (2006). **Some fundamentals of mineralogy and geochemistry**. On-line book, quoted from: www.gly.uga.edu/railsback.
- [3] International Magnesium Association: (annual Report 2001)
- [4] <http://www.infomine.com/investment/metal-prices/magnesium/5-year/>. Accessed on the 19th of April 2016.
- [5] <http://www.infomine.com/ChartsAndData/ChartBuilder.aspx?z=f&gf=110569.USD.lb&dr=5y&cd=1>. Accessed on the 19th of April 2106.
- [6] KAMMER, C. (2001) **Magnesium Taschenbuch, Aluminium-Verlag**. ISBN 3–87017-264-9.
- [7] RAO, D. Bhogeswara et al. Extraction processes for the production of aluminum, titanium, iron, magnesium, and oxygen and nonterrestrial sources. 1979.
- [8] BARCZA, Nicholas A.; SCHOUKENS, Albert FS. **Thermal production of magnesium**. U.S. Patent n. 4,699,653, 13 out. 1987.
- [9] EDGAR, Robert L. (2000) Global overview on demand and applications for magnesium alloys. **Magnesium Alloys and their Applications**, p. 1-8.

- [10] JASCHIK, C.; HAFERKAMP, H.; NIEMEYER, M. (2000) New magnesium wrought alloys. **Magnesium Alloys and their Applications**. p. 41-46.
- [11] SONG, G., ATRENS, A. (2003). Understanding magnesium corrosion—a framework for improved alloy performance. **Advanced Engineering Materials**. v.5, n.12, p. 837-858.
- [12] ZHU, S. et al. (2013). Effect of rare earth and Mn elements on the corrosion behavior of extruded AZ61 system in 3.5 wt% NaCl solution and salt spray test. **Journal of Magnesium and Alloys**. v.1, n.3, p. 249-255.
- [13] LUO, A., PEKGULERYUZ, M. O. (1994). Cast magnesium alloys for elevated temperature applications. **Journal of Materials Science**. v.29, n.20, p.5259-5271.
- [14] POLMEAR, I. J. in: AVEDESIAN, M.M. and BAKER, H. (ed.). (1999) **Magnesium and Magnesium Alloys**. ASM International. p. 3
- [15] STALMANN, A. et al. (2001). Properties and processing of magnesium wrought products for automotive applications. **Advanced Engineering Materials**. v.3, n.12, p. 969-974.
- [16] HILLIS J. E., Proc. of 40th Annual Conf. of Metallurgists of CIM, (2001), PP.3-26
- [17] MILLER, W.K., RYNTZ, E. F. Jr. (1984) Magnesium for Automotive Applications. A State-of-the-Art Assessment, Localized Corrosion. **Society of Automotive Engineers**. Warrendale. p. 2.524-2.542.

- [18] PEKGULERYUZ, M., BARIL, E. (2001) Development of Creep Resistant Mg-Al-Sr Alloys. In: Magnesium Technology 2001, HRYN, J. (ed.). **The Minerals, Metals & Materials Society**. p. 119-25.
- [19] DAVIES, G. (2003) Magnesium. Materials for automotive bodies, **Elsevier**, G. London, pp 91, 158, 159.
- [20] KUO, J.L., SUGIYAMA, S., HSIANG, S.H., YANAGIMOTO, J. (2006) Investigating the characteristics of AZ61 Magnesium alloy on the hot and semi-solid compression test. **International Journal of Advanced Manufacture Technology**. v.29, n.(7–8), pp. 670–677.
- [21] FRIEDRICH, H., SCHUMANN, S. (2001) Research for a “new age of magnesium” in the automotive industry. **Journal of Materials Processing Technology**. v.117, p. 276–281
- [22] PEKGULERYUZ, M.O., KAYA, A.A. (2003) Creep resistant magnesium alloys for powertrain applications. **Advancing Engineering Materials**. v.5, n.12, p. 866–878.
- [23] BARIL, E., LABELLE, P., PEKGULERYUZ, M.O. (2003) Elevated temperature Mg-Al-Sr: Creep resistance, mechanical properties, and microstructure. **Jom-Journal of the Minerals Metals & Materials Society**. v.55, n.11, p. A34–A39.
- [24] AGHION, E., BRONFIN, B., VON BUCH, F., SCHUMANN, S., FRIEDRICH, H. (2003) Newly developed magnesium alloys for powertrain applications. **Jom-J Miner Metals Mater Society**. v.55, n.11, p. A30–A33.

- [25] PEKGULERYUZ, M.O., BARIL, E., LABELLE, P., ARGO, D. (2003) Creep resistant Mg-Al-Sr alloys. **Journal of Advancing Materials**. v.35, n.3, p. 32–38.
- [26] HUANG, Z.H., GUO, X.F., ZHANG, Z.M. (2006) Effects of alloying on microstructure and mechanical property of AZ91D magnesium alloy. **Rare Metal Materials Engineering**. v.35, n.3, p. 363–366.
- [27] GARMO, E.P.D., BLACK, J.T., KOHSER, R.A. (1997) **Magnesium and magnesium alloys. Materials and processes in manufacturing (8th Edition)**. Wiley, USA, pp 182–184.
- [28] LUO, A.A., POWELL, B.R., BALOGH, M.P. (2002) Creep and microstructure of magnesium-aluminum-calcium based alloys. **Metallurgical and Materials Transactions A**. v.33, n.3, p. 567-574.
- [29] GHALI, E., DIETZEL W., KAINER, K.U. (2004) General and localized corrosion of magnesium alloys: a critical review. **Journal of Materials Engineering and Performance**. v.13.1, p. 7-23.
- [30] N.S. MCINTYRE, N.S., CHEN, C. (1998) Role of Impurities on Mg Surfaces Under Ambient Exposure Conditions. **Corrosion Science**. v.40, n.10, p. 1697-1709.
- [31] NORDLIEN, J.H., NISANCIOGLU, K., ONO, S., MASUKO, N. (1996) Morphology and Structure of Oxide Films Formed on MgAl Alloys by Exposure to Air and Water. **Journal of Electrochemical Society**. v.143, n.8, p. 2654-72.

- [32] CHEN, C., SPLINTER, S.J., DO, T., MCINTYRE N.S. (1997) Measurement of Oxide Film Growth on Mg and Al Surfaces Over Extended Periods Using XPS. **Surface Science**. v.382, p. L652-L657.
- [33] POURBAIX M. (1974) Atlas of Electrochemical Equilibria in Aqueous Solutions. **National Association of Corrosion Engineers**. P. 139.
- [34] HAWKE, D.L., HILLIS, J.E., PEKGULERYUZ, M., I. NAKATSUGAWA, I. (1999) Corrosion Behavior in Magnesium and Magnesium Alloys. AVEDESIAN, M.M., BAKER, H. (ed.). **ASM International**. Materials Park, OH. 1999, p. 194-210.
- [35] SONG, G.L., ATRENS A. (1999) Corrosion Mechanisms of Magnesium Alloys. **Advanced Engineering Materials**. v.1, n.1, pp. 11-33.
- [36] SONG, G.L., ATRENS A., DARGUSCH, M. (1999) Influence of Microstructure on the Corrosion of Diecast AZ 910. **Corrosion Science**. v.41, p. 249-73.
- [37] FROATS, A.F., AUNE, T.Kr., HAWKE, D., UUNSWORTH, W., HILLIS, J. Corrosion of Magnesium and Magnesium Alloys. In: Metals Handbook, 9th (ed). **Corrosion ASM International**, Materials Park, OH, 1987, Vol. 13, pp. 740-54.
- [38] SONG, G.L. (Ed.). (2011). Corrosion of magnesium alloys. **Elsevier**.
- [39] MISES, R.V. (1928) Mechanik der plastischen Formänderung von Kristallen. **Zeitschrift für Angewandte Mathematik und Mechanik**. v.8, p. 161-185.

- [40] YANG, H.S. et al. (1992) High temperature deformation of a magnesium alloy with controlled grain structures. **Materials Science and Engineering: A**. v.158, n.2, p. 167-175.
- [41] GAO, L., CHEN, R.S., HAN, E.H. (2009) Microstructure and strengthening mechanisms of a cast Mg–1.48 Gd–1.13 Y–0.16 Zr (at.%) alloy. **Journal of materials science**. v.44, n.16, p. 4443-4454.
- [42] HE, S.M., et al. (2006). Comparison of the microstructure and mechanical properties of a ZK60 alloy with and without 1.3 wt.% gadolinium addition. **Materials Science and Engineering: A**. v. 433, n.1, p. 175-181.
- [43] Emley E.F. (1966) Principles of Magnesium Technology. **Pergamon Press**, London.
- [44] ROBERTS, C.S. (1960) Magnesium and its Alloys. **Wiley**.
- [45] ASM International. Handbook Committee. (1999). *Magnesium and magnesium alloys*. AVEDESIAN M.M., BAKER H. (Eds.). **ASM International**.
- [46] WU, A., XIA, C., WANG, J. (2006) Distribution, evolution and the effects of rare earths Ce and Y on the mechanical properties of ZK60 alloys. **Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material**. v.13.5, p. 424-428.
- [47] HOMMA, T., MENDIS, C.L., HONO, K., KAMADO, S. (2010). Effect of Zr addition on the mechanical properties of as-extruded Mg–Zn–Ca–Zr alloys. **Materials Science and Engineering: A**. v.527, n.9, p. 2356-2362.

- [48] CHANG, S.Y., TEZUKA, H., KAMIO, A. (1997). Mechanical properties and structure of ignition-proof Mg–Ca–Zr alloys produced by squeeze casting. **Materials Transactions, JIM**, v.38, n.6, p. 526-535.
- [49] SUZUKI, A., et al. (2008) Precipitation strengthening of a Mg–Al–Ca–based AXJ530 die-cast alloy. **Metallurgical and Materials Transactions A**. v.39, n.3, p. 696-702.
- [50] HOFSTETTER, J., et al. (2015). Processing and microstructure–property relations of high-strength low-alloy (HSLA) Mg–Zn–Ca alloys. **Acta Materialia**. v.98, p. 423-432.
- [51] CHINO, Y., et al. (2011). Effects of Ca on tensile properties and stretch formability at room temperature in Mg–Zn and Mg–Al alloys. **Materials transactions**. v.52, n.7, p. 1477-1482.
- [52] ZHANG, B., et al. (2012). Effects of calcium on texture and mechanical properties of hot-extruded Mg–Zn–Ca alloys. **Materials Science and Engineering: A**. v.539, p. 56-60.
- [53] GENG, L., et al. (2009). Microstructure and mechanical properties of Mg–4.0 Zn–0.5 Ca alloy. **Materials Letters**. v.63(5), p. 557-559.
- [54] SOMEKAWA, H., MUKAI, T. (2007) High strength and fracture toughness balance on the extruded Mg–Ca–Zn alloy. **Materials Science and Engineering: A**. v.459, n.1, p. 366-370.
- [55] SUN, Y., et al. (2012). Preparation and characterization of a new biomedical Mg–Zn–Ca alloy. **Materials & Design**. v.34, p. 58-64.

- [56] YANG, M., CHENG, L., PAN, F. (2009). Comparison about effects of Ce, Sn and Gd additions on as-cast microstructure and mechanical properties of Mg–3.8 Zn–2.2 Ca (wt%) magnesium alloy. **Journal of materials science**. v.44, n.17, p. 4577-4586.
- [57] STANFORD, N. (2010). The effect of calcium on the texture, microstructure and mechanical properties of extruded Mg–Mn–Ca alloys. **Materials Science and Engineering: A**. v.528, n.1, 314-322.
- [58] SEONG-HO, H.A., et al. (2006). Behavior of CaO and Calcium in pure Magnesium. **Rare Metals**. v.25, n.6, 150-154.
- [59] WIESE, B., et al. (2015). CaO dissolution during melting and solidification of a Mg–10wt.% CaO alloy detected with in situ synchrotron radiation diffraction. **Journal of alloys and compounds**. v.618, p. 64-66.
- [60] HRADIOVÁ, M., et al. (2013). Structural and mechanical characteristics of Mg–4Zn and Mg–4Zn–0.4 Ca alloys after different thermal and mechanical processing routes. **Materials Science and Engineering: A**. v. 586, p. 284-291.
- [61] BETTLES, C. J., GIBSON, M.A., VENKATESAN, K. (2004) Enhanced age-hardening behaviour in Mg–4 wt.% Zn micro-alloyed with Ca. **Scripta Materialia**. v.51, n.3, p. 193-197.
- [62] OH-ISHI, K., et al. (2009) Age-hardening response of Mg–0.3 at.% Ca alloys with different Zn contents. **Materials Science and Engineering: A**. v.526, n.1, p. 177-184.

- [63] GAO, X.S.M.Z., et al. (2005) Precipitation-hardened Mg–Ca–Zn alloys with superior creep resistance. **Scripta materialia**. v.53, n.12, 1321-1326.
- [64] KATSARAU, L., et al. (2015). MICROSTRUCTURE AND PROPERTIES OF MAGNESIUM ALLOY Mg-1Zn-1Ca (ZX11). **Magnesium Technology 2015**. p. 419-423.
- [65] SEONG, J.W., KIM W.J. (2015) Development of biodegradable Mg–Ca alloy sheets with enhanced strength and corrosion properties through the refinement and uniform dispersion of the Mg₂Ca phase by high-ratio differential speed rolling. **Acta biomaterialia**. v.11, p. 531-542.
- [66] GUNDE, P., et al. (2011). High-strength magnesium alloys for degradable implant applications. **Materials Science and Engineering: A**. v.528, n.3, p. 1047-1054.
- [67] JEONG, Y. S., KIM W. J. (2014) Enhancement of mechanical properties and corrosion resistance of Mg–Ca alloys through microstructural refinement by indirect extrusion. **Corrosion Science**. v.82, p. 392-403.
- [68] RAD, Bakhsheshi et al. (2012) Characterization and corrosion behavior of biodegradable Mg-Ca and Mg-Ca-Zn implant alloys. **Applied Mechanics and Materials**. Trans Tech Publications. p. 568-572.
- [69] LU, Y. et al. (2015) Effects of secondary phase and grain size on the corrosion of biodegradable Mg–Zn–Ca alloys. **Materials Science and Engineering: C**. v. 48, p. 480-486.

- [70] MANDAL, M. et al. (2014) Corrosion behavior of Mg–2.4 Zn alloy micro-alloyed with Ag and Ca. **Corrosion Science**. v. 78, p. 172-182.
- [71] LU, Y. et al. (2015) Effects of secondary phase and grain size on the corrosion of biodegradable Mg–Zn–Ca alloys. **Materials Science and Engineering: C**. v.48, p.480-486.
- [72] ZHANG, J. et al. (2008) Effect of Nd on the microstructure, mechanical properties and corrosion behavior of die-cast Mg–4Al-based alloy. **Journal of Alloys and Compounds**. v. 464, n. 1, p. 556-564.
- [73] ARRABAL, R., et al. (2015). Role of alloyed Nd in the microstructure and atmospheric corrosion of as-cast magnesium alloy AZ91. **Corrosion Science**. v.97, p. 38-48.
- [74] BOHLEN, Jan et al. (2007) The texture and anisotropy of magnesium–zinc–rare earth alloy sheets. **Acta Materialia**. v. 55, n. 6, p. 2101-2112.
- [75] MACKENZIE, L. W. F.; PEKGULERYUZ, M. O. (2008) The recrystallization and texture of magnesium–zinc–cerium alloys. **Scripta Materialia**. v. 59, n. 6, p. 665-668.
- [76] HANTZSCHE, K. et al. (2010) Effect of rare earth additions on microstructure and texture development of magnesium alloy sheets. **Scripta Materialia**. v. 63, n. 7, p. 725-730.
- [77] STANFORD, N. (2010) Micro-alloying Mg with Y, Ce, Gd and La for texture modification - a comparative study. **Materials Science and Engineering: A**. v. 527, n. 10, p. 2669-2677.

- [78] STANFORD, N., BARNETT, M. (2008) Effect of composition on the texture and deformation behaviour of wrought Mg alloys. **Scripta materialia**. v. 58, n. 3, p. 179-182.
- [79] STANFORD, N., BARNETT, M.R. (2008) The origin of “rare earth” texture development in extruded Mg-based alloys and its effect on tensile ductility. **Materials Science and Engineering: A**. v. 496, n. 1, p. 399-408.
- [80] GAO, X. et al. (2006) Microstructure evolution in a Mg–15Gd–0.5 Zr (wt.%) alloy during isothermal aging at 250 C. **Materials Science and Engineering: A**. v. 431, n. 1, p. 322-327.
- [81] HONMA, T. et al. (2005) Chemistry of nanoscale precipitates in Mg–2.1 Gd–0.6 Y–0.2 Zr (at.%) alloy investigated by the atom probe technique. **Materials Science and Engineering: A**. v. 395, n. 1, p. 301-306.
- [82] NIE, J. F., MUDDLE, B. C. (2000) Characterisation of strengthening precipitate phases in a Mg–Y–Nd alloy. **Acta Materialia**. v. 48, n. 8, p. 1691-1703.
- [83] ANTION, C. et al. (2003) Hardening precipitation in a Mg–4Y–3RE alloy. **Acta Materialia**. v. 51, n. 18, p. 5335-5348.
- [84] APPS, P.J. et al. (2003) Precipitation reactions in magnesium-rare earth alloys containing yttrium, gadolinium or dysprosium. **Scripta Materialia**. v. 48, n. 8, p. 1023-1028.
- [85] ANYANWU, I. A., KAMADO, S., KOJIMA, Y. (2001) Platform Science and Technology for Advanced Magnesium Alloys. Aging

- Characteristics and High Temperature Tensile Properties of Mg-Gd-Y-Zr Alloys. **Materials Transactions**. v. 42, n. 7, p. 1206-1211, 2001.
- [86] SMOLA, B. et al. (2004) Significance of stable and metastable phases in high temperature creep resistant magnesium–rare earth base alloys. **Journal of Alloys and Compounds**. v. 378, n. 1, p. 196-201.
- [87] ZHAO, M.-C. et al. (2008) Influence of Microstructure on Corrosion of As-cast ZE41. **Advanced Engineering Materials**. v. 10, n. 1-2, p. 104-111.
- [88] ZHAO, M.-C. et al. (2008) Influence of pH and chloride ion concentration on the corrosion of Mg alloy ZE41. **Corrosion Science**. v.50, n.(11), p.3168-3178.
- [89] NEIL, W. C. et al. (2009) Corrosion of magnesium alloy ZE41–The role of microstructural features. **Corrosion Science**. v. 51, n. 2, p. 387-394.
- [90] *Edited by N G Connelly and T Damhus (with R M Hartshorn and A T Hutton), ed. (2005). Nomenclature of Inorganic Chemistry: IUPAC Recommendations 2005 (PDF). Cambridge: RSC Publ. ISBN 0-85404-438-8. Archived from the original (PDF) on 2008-05-27. Retrieved 2012-03-13.*
- [91] LEONTIS, T. E. (1949) Magnesium and Magnesium Alloys-The Room and Elevated Temperature Properties of Some Sand Cast Magnesium-base Alloys Containing Zinc. **Transactions of the Metallurgical Society of AIME**. v. 185, p. 327.

- [92] LI, Qiang et al. (2007) Effect of Nd and Y addition on microstructure and mechanical properties of as-cast Mg–Zn–Zr alloy. **Journal of Alloys and Compounds**. v. 427, n. 1, p. 115-123.
- [93] ZHANG, Tao et al. (2011) Corrosion of hot extrusion AZ91 magnesium alloy. Part II: Effect of rare earth element neodymium (Nd) on the corrosion behavior of extruded alloy. **Corrosion Science**. v. 53, n. 9, p. 2934-2942, 2011.
- [94] FAN, Y., WU, G., ZHAI, C. (2006) Influence of cerium on the microstructure, mechanical properties and corrosion resistance of magnesium alloy. **Materials Science and Engineering: A**. v. 433, n. 1, p. 208-215.
- [95] WU G. et al. (2005) The effect of Ca and rare earth elements on the microstructure, mechanical properties and corrosion behavior of AZ91D. **Materials Science and Engineering A**. v.408, p. 255–263.
- [96] MINGBO, Y. A. N. G. et al. (2012) Microstructure, tensile and creep properties of as-cast Mg-3.8 Zn-2.2 Ca-xCe (x= 0, 0.5, 1 and 2 wt.%) magnesium alloys. **Journal of Rare Earths**. v. 30, n. 2, p. 181-188.
- [97] STANFORD, N., ATWELL, D., BARNETT, M.R. (2010) The effect of Gd on the recrystallisation, texture and deformation behaviour of magnesium-based alloys. **Acta Materialia**. v. 58, n. 20, p. 6773-6783.
- [98] YU, H. et al. (2014) Effects of minor gd addition on microstructures and mechanical properties of the high strain-rate rolled Mg–Zn–Zr alloys. **Journal of Alloys and Compounds**. v. 586, p. 757-765.

- [99] LUO, Z. P.; ZHANG, S. Q. (2000) High-resolution electron microscopy on the X-Mg₁₂ZnY phase in a high strength Mg-Zn-Zr-Y magnesium alloy. **Journal of Materials Science Letters**. v. 19, n. 9, p. 813-815.
- [100] ITOI, T. et al. (2004) Long period stacking structures observed in Mg₉₇Zn₁Y₂ alloy. **Scripta Materialia**. v. 51, n. 2, p. 107-111.
- [101] MATSUDA, M. et al. (2005) Variation of long-period stacking order structures in rapidly solidified Mg₉₇Zn₁Y₂ alloy. **Materials Science and Engineering: A**. v. 393, n. 1, p. 269-274.
- [102] YOSHIMOTO, S., YAMASAKI, M., KAWAMURA, Y. (2006) Microstructure and mechanical properties of extruded Mg-Zn-Y alloys with 14H long period ordered structure. **Materials transactions**. v. 47, n. 4, p. 959-965.
- [103] SINGH, A. et al. (2004) Microstructure and strength of quasicrystal containing extruded Mg-Zn-Y alloys for elevated temperature application. **Materials Science and Engineering: A**. v. 385, n. 1, p. 382-396.
- [104] XU, D. K. et al. (2007) Effect of microstructure and texture on the mechanical properties of the as-extruded Mg-Zn-Y-Zr alloys. **Materials Science and Engineering: A**. v. 443, n. 1, p. 248-256.
- [105] KAWAMURA, Y., YAMASAKI, M. (2007) Formation and mechanical properties of Mg₉₇Zn₁RE₂ alloys with long-period stacking ordered structure. **Materials Transactions**. v. 48, n. 11, p. 2986-2992.

- [106] CHINO, Y., SASSA, K., MABUCHI, M. (2009) Texture and stretch formability of a rolled Mg–Zn alloy containing dilute content of Y. **Materials Science and Engineering: A**. v. 513, p. 394-400.
- [107] AGNEW, S. R.; YOO, M. H.; TOME, C. N. (2001) Application of texture simulation to understanding mechanical behavior of Mg and solid solution alloys containing Li or Y. **Acta Materialia**. v. 49, n. 20, p. 4277-4289.
- [108] AGNEW, S.R., SENN, J.W., HORTON, J.A. (2006) Mg sheet metal forming: lessons learned from deep drawing Li and Y solid-solution alloys. **Jom**. v. 58, n. 5, p. 62-69.
- [109] DATTA, A., WAGHMARE, U.V., RAMAMURTY, U. (2008) Structure and stacking faults in layered Mg–Zn–Y alloys: A first-principles study. **Acta Materialia**. v. 56, n. 11, p. 2531-2539.
- [110] GAO, L.; CHEN, R. S.; HAN, E.H. (2009) Solid solution strengthening behaviors in binary Mg–Y single phase alloys. **Journal of Alloys and Compounds**. v. 472, n. 1, p. 234-240.
- [111] SUZUKI, M. et al. (2004) Effects of zinc on creep strength and deformation substructures in Mg–Y alloy. **Materials Science and Engineering: A**. v. 387, p. 706-709.
- [112] SUZUKI, M., MARUYAMA, K. (2010) Effects of Stacking Faults on High Temperature Creep Behavior in Mg-Y-Zn Based Alloys. In: **Materials Science Forum**. Trans Tech Publications, 2010. p. 1602-1607.

- [113] KAWAMURA, Y. et al. (2001) Rapidly Solidified Powder Metallurgy Mg97Zn1Y2Alloys with Excellent Tensile Yield Strength above 600 MPa. **Materials Transactions**. v. 42, p. 1171-1174.
- [114] INOUE, A. et al. (2001) Novel hexagonal structure and ultrahigh strength of magnesium solid solution in the Mg–Zn–Y system. **Journal of Materials Research**. v. 16, n. 07, p. 1894-1900.
- [115] IZUMI, S., YAMASAKI, M., KAWAMURA, Y. (2009) Relation between corrosion behavior and microstructure of Mg–Zn–Y alloys prepared by rapid solidification at various cooling rates. **Corrosion Science**. v. 51, n. 2, p. 395-402.
- [116] WANG, C.Y. et al. (2007) Processing maps for hot working of ZK60 magnesium alloy. **Materials Science and Engineering: A**. v. 464, n. 1, p. 52-58.
- [117] SOMEKAWA, H., MUKAI, T. (2006) Fracture toughness in an extruded ZK60 magnesium alloy. **Materials transactions**. v. 47, n. 4, p. 995-998.
- [118] ROKHLIN, L.L. (2003) **Magnesium alloys containing rare earth metals: structure and properties**. CRC Press.
- [119] HONMA, T. et al. (2007) Effect of Zn additions on the age-hardening of Mg–2.0 Gd–1.2 Y–0.2 Zr alloys. **Acta Materialia**. v. 55, n. 12, p. 4137-4150.
- [120] BEN-HAMU, G. et al. (2007) The relation between microstructure and corrosion behavior of Mg–Y–RE–Zr alloys. **Journal of Alloys and Compounds**. v. 431, n. 1, p. 269-276.

- [121] SONG, Y. et al. (2010) Effect of second phases on the corrosion behaviour of wrought Mg–Zn–Y–Zr alloy. **Corrosion Science**. v. 52, n. 5, p. 1830-1837.
- [122] MORDIKE, B. L. (2002) Creep-resistant magnesium alloys. **Materials Science and Engineering: A**. v. 324, n. 1, p. 103-112.
- [123] LI, J. P. et al. (2007) Microstructures of extruded Mg–12Gd–1Zn–0.5 Zr and Mg–12Gd–4Y–1Zn–0.5 Zr alloys. **Scripta materialia**. v. 56, n. 2, p. 137-140.
- [124] YAMASAKI, Michiaki et al. (2007) Formation of 14H long period stacking ordered structure and profuse stacking faults in Mg–Zn–Gd alloys during isothermal aging at high temperature. **Acta Materialia**. v. 55, n. 20, p. 6798-6805.
- [125] LIU, Yong et al. (2006) Stable icosahedral phase in Mg–Zn–Gd alloy. **Scripta materialia**. v. 55, n. 10, p. 919-922.
- [126] ZHANG, S. et al. (2011) The relationship between (Mg, Zn) 3 RE phase and 14H-LPSO phase in Mg–Gd–Y–Zn–Zr alloys solidified at different cooling rates. **Journal of Alloys and Compounds**. v. 509, n. 8, p. 3515-3521.
- [127] WU, Y. J. et al. (2009) The microstructure evolution with lamellar 14H-type LPSO structure in an Mg 96.5 Gd 2.5 Zn 1 alloy during solid solution heat treatment at 773K. **Journal of Alloys and Compounds**. v. 477, n. 1, p. 193-197.
- [128] YUAN, Guangyin et al. (2008) Effect of quasicrystal and Laves phases on strength and ductility of as-extruded and heat treated Mg–Zn–Gd-

- based alloys. **Materials Science and Engineering: A**. v. 472, n. 1, p. 75-82.
- [129] LIU, Yong et al. (2008) Effects of Zn/Gd ratio and content of Zn, Gd on phase constitutions of Mg alloys. **Materials transactions**, v. 49, n. 5, p. 941-944.
- [130] WU, Y. J. et al. (2010) Formation of a Novel X Phase in Mg–Gd–Zn–Zr Alloy. In: **Materials Science Forum**. Trans Tech Publications, 2010. p. 623-626.
- [131] YANG, Jie et al. (2008) Microstructures and mechanical properties of the Mg–4.5 Zn–xGd (x= 0, 2, 3 and 5) alloys. **Journal of Alloys and Compounds**. v. 459, n. 1, p. 274-280.
- [132] KIM, J. M.; PARK, J. S. (2013) Microstructure and tensile properties of Mg–Zn–Gd casting alloys. **International Journal of Cast Metals Research**.
- [133] LIU, Yong et al. (2008) The role of nanoquasicrystals on the ductility enhancement of as-extruded Mg–Zn–Gd alloy at elevated temperature. **Journal of materials science**. v. 43, n. 16, p. 5527-5533.
- [134] YUAN, G. et al. (2005) Excellent creep properties of Mg–Zn–Cu–Gd-based alloy strengthened by quasicrystals and Laves phases. **Journal of materials research**. v. 20, n. 05, p. 1278-1286.
- [135] HUANG, H. et al. (2013) Microstructure and mechanical properties of double continuously extruded Mg–Zn–Gd-based magnesium alloys. **Materials Science and Engineering: A**. v. 560, p. 241-248.

- [136] AVEDESIAN, M.M. et al. (Ed.). (1999) **ASM specialty handbook: magnesium and magnesium alloys**. ASM international.
- [137] BLÜCHER, D.B. et al. (2004) Scanning Kelvin Probe Force Microscopy A Useful Tool for Studying Atmospheric Corrosion of MgAl Alloys *In Situ*. **Journal of The Electrochemical Society**. v. 151, n. 12, p. B621-B626.
- [138] BARSOUKOV, E., MACDONALD, J.R. (Ed.). (2005) **Impedance spectroscopy: theory, experiment, and applications**. John Wiley & Sons.
- [139] GODARD, H.P. (1967) **The corrosion of light metals**. John Wiley & Sons Inc.
- [140] MAKAR, G.L., KRUGER, J. (2013) Corrosion of magnesium. **International Materials Reviews**.
- [141] HUANG, M.L. et al. (2010) A ternary linear compound T2 and its phase equilibrium relationships in Mg–Zn–Nd system at 400° C. **Journal of Alloys and Compounds**. v. 489, n. 2, p. 620-625.
- [142] LIU, S. J. et al. (2015) Microstructure and mechanical properties of sand mold cast Mg–4.58 Zn–2.6 Gd–0.18 Zr magnesium alloy after different heat treatments. **Journal of Alloys and Compounds**. v. 644, p. 846-853.
- [143] PADEZHNOVA, E. M.; MELNIK, E. VI; MILIEVSKII, R. (1982) Investigation of the Mg-Zn-Y System. **Russ. Metall.**, n. 4, p. 185-188.

- [144] YAO, H.B., LI, Y., WEE, A.T.S. (2000) An XPS investigation of the oxidation/corrosion of melt-spun Mg. **Applied Surface Science**. v. 158, n. 1, p. 112-119.
- [145] NORDLIEN, J. H. et al. (1997) A TEM investigation of naturally formed oxide films on pure magnesium. **Corrosion science**. v. 39, n. 8, p. 1397-1414.
- [146] NORDLIEN, J.H. et al. (1995) Morphology and structure of oxide films formed on magnesium by exposure to air and water. **Journal of the Electrochemical Society**. v. 142, n. 10, p. 3320-3322.
- [147] SONG, G., ATRENS, A., DARGUSCH, M. (1998) Influence of microstructure on the corrosion of diecast AZ91D. **Corrosion science**. v. 41, n. 2, p. 249-273.
- [148] SONG, G. et al. (1998) Corrosion behaviour of AZ21, AZ501 and AZ91 in sodium chloride. **Corrosion science**. v. 40, n. 10, p. 1769-1791.
- [149] ZHAO, M.-C. et al. (2008) Influence of the β -phase morphology on the corrosion of the Mg alloy AZ91. **Corrosion Science**. v. 50, n. 7, p. 1939-1953.
- [150] SONG, G., BOWLES, A.L., STJOHN, D.H. (2004) Corrosion resistance of aged die cast magnesium alloy AZ91D. **Materials Science and Engineering: A**. v. 366, n. 1, p. 74-86.
- [151] ZHAO, M.-C. et al. (2008) Influence of homogenization annealing of AZ91 on mechanical properties and corrosion behavior. **Advanced Engineering Materials**. v. 10, n. 1-2, p. 93-103.

- [152] ZHAO, M-C et al. (2008) Influence of pH and chloride ion concentration on the corrosion of Mg alloy ZE41. **Corrosion Science**. v. 50, n. 11, p. 3168-3178.
- [153] CHANG, J. et al. (2008) Investigation of the corrosion for Mg-xGd-3Y-0.4 Zr (x= 6, 8, 10, 12wt%) alloys in a peak-aged condition. **Corrosion Science**, v. 50, n. 1, p. 166-177.
- [154] PENG, L.-M. et al. (2009) Influence of heat treatment and microstructure on the corrosion of magnesium alloy Mg-10Gd-3Y-0.4 Zr. **Journal of Applied Electrochemistry**. v. 39, n. 6, p. 913-920.
- [155] LISITSYN, V. et al. (2010) Some particularities of the corrosion behaviour of Mg-Zn-Mn-Si-Ca alloys in alkaline chloride solutions. **Corrosion Science**. v. 52, n. 7, p. 2280-2290.
- [156] LISITSYN, V. et al. (2009) The role of Ca microalloying on the microstructure and corrosion behavior of Mg-6Zn-Mn-(0.5-2) Si alloys. **Corrosion Science**. v. 51, n. 4, p. 776-784.
- [157] SONG, Y. et al. (2009) Corrosion characterization of Mg-8Li alloy in NaCl solution. **Corrosion Science**. v. 51, n. 5, p. 1087-1094.
- [158] BIRBILIS, N. et al. (2009) On the corrosion of binary magnesium-rare earth alloys. **Corrosion Science**. v. 51, n. 3, p. 683-689.
- [159] AMBAT, R., AUNG, N.N., ZHOU, W. (2000) Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy. **Corrosion science**. v. 42, n. 8, p. 1433-1455.
- [160] LUNDER, O. et al. (1989) The role of Mg₁₇Al₁₂ phase in the corrosion of Mg alloy AZ91. **Corrosion**. v. 45, n. 9, p. 741-748.

- [161] LUNDER, O., NISANCIOGLU, K., HANSEN, R.S. (1993) **Corrosion of die cast magnesium-aluminum alloys**. SAE Technical Paper.
- [162] LUNDER, O., VIDEM, M., NISANCIOGLU, K. (1995) **Corrosion resistant magnesium alloys**. SAE Technical Paper.
- [163] NISANCIOGLU, K., LUNDER, O., AUNE, T.R. (1990) Corrosion mechanism of AZ 91 magnesium alloy. In: **Past to Future: 47 th Annual World Magnesium Conference**. p. 43-50.
- [164] UZAN, P. et al. (2000) The Role of Composition and Second Phases on the Corrosion Behaviour of AZ Alloys. In: **Proceedings of the 2nd Israeli International Conference on 'Magnesium Science and Technology', Magnesium**. p. 285.
- [165] PEBERE, N., RIERA, C., DABOSI, F. (1990) Investigation of magnesium corrosion in aerated sodium sulfate solution by electrochemical impedance spectroscopy. **Electrochimica Acta**. v. 35, n. 2, p. 555-561.
- [166] BARIL, G., BLANC, C., PÉBÈRE, N. (2001) AC impedance spectroscopy in characterizing time-dependent corrosion of AZ91 and AM50 magnesium alloys characterization with respect to their microstructures. **Journal of the Electrochemical Society**. v. 148, n. 12, p. B489-B496.
- [167] BRUG, G. J. et al. (1984) The analysis of electrode impedances complicated by the presence of a constant phase element. **Journal of electroanalytical chemistry and interfacial electrochemistry**. v. 176, n. 1, p. 275-295.

- [168] ARRABAL, R. et al. (2012) Effect of Nd on the corrosion behaviour of AM50 and AZ91D magnesium alloys in 3.5 wt.% NaCl solution. **Corrosion Science**. v. 55, p. 301-312.
- [169] COY, A. E. et al. (2010) Susceptibility of rare-earth-magnesium alloys to micro-galvanic corrosion. **Corrosion Science**. v. 52, n. 12, p. 3896-3906.
- [170] APACHITEI, I., FRATILA-APACHITEI, L.E., DUSZCZYK, J. (2007) Microgalvanic activity of an Mg–Al–Ca-based alloy studied by scanning Kelvin probe force microscopy. **Scripta Materialia**. v. 57, n. 11, p. 1012-1015.