Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 59 (2011) 6176–6186
Acta MATERIALIA
www.elsevier.com/locate/actamat

Enhanced corrosion resistance of Mg alloy ZK60 after processing by integrated extrusion and equal channel angular pressing

D. Orlov [a,*], K.D. Ralston [a], N. Birbilis [a], Y. Estrin [a,b]

[a] ARC Centre of Excellence for Design in Light Metals, Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia
[b] CSIRO Division of Process Science and Engineering, Clayton South, Victoria, Australia

Received 29 April 2011; received in revised form 14 June 2011; accepted 18 June 2011
Available online 6 July 2011

Abstract

It was demonstrated in this work that the corrosion rate of Mg alloy ZK60 can be reduced through the use of an integrated process of extrusion and equal channel angular pressing concomitant with increased strength. The improvement in corrosion resistance, as measured by electrochemical experiments and immersion tests in NaCl electrolytes, was correlated with both grain refinement and the redistribution of Zn and Zr solutes within the microstructure. These microstructural changes impacted the relative anodic and cathodic reaction kinetics sustained by the alloy in a unique manner, whereby structural and chemical variations dictated the anodic reaction rates in the former and the cathodic rates in the latter. The observed decrease in the corrosion rate, combined with improved mechanical properties for ZK60, represents a scenario where two properties that are nominally inversely correlated can be improved simultaneously, offering an insight into how Mg can be unique in terms of its processing-property relationships.

Keywords: Magnesium; Corrosion; Severe plastic deformation; Grain refinement; Microstructure

1. Introduction

Mg alloys remain an increasingly attractive option for applications that demand lightweight materials, e.g. for energy or fuel conservation [1–4]. Among the key factors that currently limit a wider use of Mg products are:

(i) difficulties in processing of Mg alloys [1,2];
(ii) their relatively low strength and ductility at ambient temperatures [2,4,5]; and
(iii) extremely high reactivity, which leads to unacceptable levels of corrosion in many environments [6–8].

There are numerous studies that address the above issues in isolation with an objective to improve either mechanical or corrosion properties – without consideration for the impact the one will have on the other. However, both sets of properties are generally linked to alloy composition and microstructure (and hence to processing) and, as such, ideally need to be considered in parallel.

For most metals, improvements in mechanical properties can be effectively achieved through alloying and processing [2]. However, for Mg the solubility of many alloying elements is limited [1,3], which restricts the ability to improve mechanical properties solely through alloying. From a corrosion perspective, no element is soluble enough in Mg to allow an oxide to form on the surface that is more protective than Mg (as, for instance, Cr is able to do when added to Fe).

Commonly, Al, Zn, Mn and Zr are added to Mg to create alloys with relatively high strength (i.e. yield strength YS ~ 300 MPa). Improved strength is due to grain refinement (promoted by Zr) or the creation of a heterogeneous microstructure that contains a dispersion of chemically (and electrochemically) distinct intermetallic particles. In other instances, rare earth elements are added when creep

* Corresponding author. Tel.: +61 3 9905 5348; fax: +61 3 9905 4940.
E-mail address: dmytro.orlov@monash.edu (D. Orlov).

1359-6454/$36.00
doi:10.1016/j.actamat.2011.06.033

resistance is required, instead of Al or Zn (both of which can reduce operating temperature via low temperature eutectics). Furthermore, deformation processing involving severe plastic deformation (SPD) has also been found to be an effective method for improving the mechanical characteristics of Mg alloys [9–15]. These efforts have largely addressed the first two factors limiting the use of Mg described above; however, relatively little attention has been devoted to how SPD processing impacts corrosion, especially that of alloys based on Mg.

In addition to grain refinement, SPD processes cause a redistribution of solutes within the microstructure. Given that both microstructural features and small compositional changes can have a large impact on Mg corrosion [6,16,17], there is currently no detailed understanding of how SPD processing will impact the corrosion behavior of "real" engineering Mg alloys. A limited number of publications are available on the corrosion of Mg after equal channel angular pressing (ECAP) processing, and these have reported conflicting findings of decreased [18,19] or increased [20–22] corrosion rate for pure Mg, AZ31 and AZ91D. Amongst these studies, those reporting reduced corrosion were conducted in relatively non-aggressive electrolytes (0.1 M NaCl) as compared to studies that reported increased corrosion (3.5% NaCl). This may indicate the formation of partially protective films on materials with fine-grained microstructures, which nevertheless fail in high chloride content electrolytes.

Simultaneous improvement of disparate properties is somewhat unique – as is the case with strength and corrosion – and such situations can be exploited to shift materials to more favorable property space. This manuscript details such a circumstance for SPD-processed Mg ZK60. Significant improvements in both the strength and ductility (Table 1) of 4 m long Mg ZK60 rods were achieved previously [15] through a single-pass integrated extrusion and ECAP. The improvement of mechanical properties was demonstrated using standard ASTM samples and testing procedures, and the properties observed were correlated with microstructure, texture and processing variables. The present study builds on this prior work with a focus on the corrosion properties. The primary objective is to characterize the corrosion resistance of Mg alloy ZK60 in NaCl electrolyte and correlate the observed behavior with the microstructural evolution during processing by integrated extrusion and ECAP. Furthermore, this work aims to determine whether the grain size or the chemical composition is the predominant factor controlling the corrosion response, and to what extent the corrosion resistance of alloy ZK60 can be altered by SPD processing.

2. Experimental material and methods

2.1. Material and extrusion processing

Commercial Mg alloy ZK60 with a nominal composition Mg–6Zn–0.5Zr (wt.%) was used for this study. Inductively coupled plasma–atomic emission spectroscopy analysis of the as-received alloy revealed a Zr content of 0.44 wt.%, close to the lower limit for alloys with this denomination, and the presence of Fe at a level of approximately 45 ppm (which is below the tolerance limit for Mg alloys). Whilst surface Fe contamination may be possible from SPD processing involving steel dies, this effect was not explored in the present study. The billets (70 mm in diameter and ~250 mm in length) were extruded in a single pass through a specially designed die to obtain bars with a diameter of 16 mm and a length of $\geqslant$4000 mm. The die, shown schematically in Fig. 1, consists of two parts: (i) a conical section, where conventional extrusion takes place; and (ii) a section with two parallel channels (PC), where two consecutive ECAP events occur. In the conical section, the aforementioned reduction in the billet diameter produced an equivalent strain of $\varepsilon_c = 3.4$. In the PC section, the bar experienced two consecutive shearing events without any change in the cross-sectional dimensions, analogous to route C of ECAP, which imparted on the billet an additional equivalent strain of $\varepsilon_{pc} = 2$ to produce a total equivalent strain of $\varepsilon = 5.4$. Further details regarding the processing parameters can be found in Ref. [15]. The locations of sampling along the processing route are indicated in Fig. 1. The states of the specimens extracted from the as-received bar, the section between the conical and PC sections of the die, and after the final stage of processing are referred to as "initial", "intermediate" and "SPD-processed" conditions, respectively. The principal directions on the processed bars have been designated the extrusion direction (ED), the normal direction (ND; orthogonal to ED, and lying in the drawing plane in Fig. 1), and the transverse direction (TD; orthogonal to both ED and ND) [15]. Specimens were sectioned and their corrosion behavior was assessed both on the bar transverse section orthogonal to ED and longitudinal section orthogonal to TD. The TD, or ND–ED plane, is the most representative one for the plastic flow during processing, and therefore it was used for the observation of microstructure evolution.

Table 1
Mechanical properties of magnesium alloy ZK60 after the processing by integrated extrusion + ECAP [15].

σ_{YS} (MPa)	σ_{UTS} (MPa)	δ_f (%)	ψ_f (%)	HV,ND–TD	HV,ND–ED	Material condition
222	264	7.4	3.5	59.9	71.9	Initial
310	351	17.1	42.5	89.1	79.1	SPD-processed

σ_{YS} = yield strength, σ_{UTS} = ultimate tensile strength, δ_f = elongation to failure, ψ_f = reduction in area at failure, and HV = Vickers Hardness. 'ED', 'ND' and 'TD' denote extrusion direction, normal direction and transverse direction, respectively.