Electrochemical behavior of Zn-rich Zn–Cu peritectic alloys affected by macrosegregation and microstructural array

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ABSTRACT

The aim of this experimental investigation is to evaluate the electrochemical behavior of an as-cast Zn-rich Zn–Cu peritectic alloy as a function of both the solute macrosegregation profile and the microstructure cellular spacing. A directional solidification apparatus was used to obtain the as-cast samples. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization techniques and an equivalent circuit analysis were used to evaluate the corrosion resistance in a 0.5 M NaCl solution at 25 °C. It was found that both copper content and cell spacing are significantly affected by the position along the casting length from the cooled bottom of the casting. These parameters play interdependent roles on the resulting corrosion behavior. Samples which are closer to the casting cooled surface are more affected by the solute inverse segregation, i.e. have a Cu content that is higher than the alloy nominal composition. This is shown to be a driving-force leading to a decrease in the corrosion resistance. However, for other samples with similar Cu content and close to the nominal alloy composition, the cell spacing seems to be the driving-force associated with the corrosion resistance and for these cases finer microstructures are shown to be related to higher corrosion resistance.

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1. Introduction

Zn-based alloys have been widely used in many industrial applications, e.g. mobile phone antennae, portable computers, electronic connectors, chassis and frames for handheld telecoms and computing components and a number of other electrical and electronic applications [1,2]. Zn–Cu peritectic alloys have recently been drawn more attention in a number of experimental studies [1–6]. Due mainly to cost advantages favoring Zn alloys over, for instance, copper-based alloys and cast iron, they emerge as attractive substitutes in many structural and pressure tight applications [1]. Besides, their corresponding strength, hardness, electrical properties indicate that they could also be interesting alternatives to machined, pressed, stamped and fabricated components [1,2].

It is well-known that a Zn-rich Zn–Cu peritectic alloy involves a solid phase (ε) reacting with a liquid phase (L) and inducing the growth of a second solid phase (η) when solidification take place at 425 °C [2,5,7]. The peritectic reaction is commonly observed in systems that include components with dissimilar melting points, e.g. Pb–Bi, Sn–Sb, Sn–Cd, Ni–Al, Zn–Ag, Fe–Ni, etc. [2,6,8–10].

The microstructure of a Zn-rich Zn–Cu peritectic alloy depends strongly on the growth conditions from the melt. A number of investigations used a Bridgman-type furnace (a typical steady-state directional solidification apparatus) with a view to characterizing the resulting microstructures and validating theoretical growth models [1–6]. The Zn-rich Zn–Cu peritectic alloys were shown to exhibit four distinct microstructural solidification arrays for Bridgman growth conditions [2,5]: (i) Regular (or plate-like) cells of a single phase η; (ii) primary dendrites of ε in a matrix of η; (iii) regular cells of η with intercellular ε with (or without) dendrites of primary ε; and (iv) plate-like cellular η with intercellular ε with (or without) dendrites of primary ε phase. They can also be formed by coupled growth structures such as lamellar and banding structures for higher growth rates, including laser surface remelting [4–6]

Kaya et al. [3] reported that the microhardness increases with the increase in alloy Cu content of Zn-rich Zn–Cu peritectic alloys. Ma et al. [5] correlated the Vickers microhardness (HV) of an as-cast peritectic Zn–3.37 wt.% Cu alloy processed by continuous CO_2 laser surface remelting – LSR (with power density of 480 W mm^{-2}) with the corresponding intercellular spacing (λ). The experimental results have shown that the microhardness of the LSR sample (140 HV) is about 1.5 times higher than that of as-cast Zn–Cu alloy (90 HV).

The literature is scarce on reports dealing with the effects of microstructural features on the corrosion resistance of Zn–Cu alloys. Moreover, segregation is a phenomenon that can occur during solidification of Zn–Cu alloys and that affects the mechanical strength [3] and can also have a role on the corrosion resistance. In

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spite of the importance of the simultaneous action of microstructural parameters and segregation on the electrochemical corrosion behavior of Zn–Cu alloys, studies dealing with the analysis of both features cannot be found in the literature. The present study aims to evaluate the combined effects of Cu macrosegregation and cell spacing on the resulting electrochemical corrosion resistance of an as-cast Zn–2.2 wt.% Cu peritectic alloy. The analysis was carried out on samples which were collected along the length of a unidirectionally solidified casting. This experimental technique permitted samples having quite different segregation severity and cell spacing to be obtained. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves and an equivalent circuit analysis were used to evaluate the electrochemical parameters in a naturally stagnant 0.5 M NaCl solution at room temperature.

2. Experimental procedure

A directionally solidified Zn–2.2 wt.% Cu alloy casting was used to obtain the samples. This solidification set-up was designed in such way that heat was extracted only through the water-cooled bottom, promoting vertical upward directional solidification, as previously reported [11–15]. This experimental technique permits samples with quite different cell spacing and segregation severity to be obtained along the casting length.

Commercially pure grade (c.p.): Zn (99.97 wt.%) and electrolytic grade Cu (99.992 wt.%) were used to prepare the peritectic Zn–2.2 wt.% Cu alloy. The mean impurities detected were: Fe (0.015 wt.%), Pb (0.012 wt.%), Si (0.003 wt.%) and other less than 0.001 wt.% for c.p. grade Zn, and Pb (0.002 wt.%) and Fe (0.007 wt.%) for electrolytic Cu grade. These chemical compositions were obtained by an X-ray fluorescence technique, and are average values which are based on measurements carried out in three different alloy samples.

The samples for metallography and corrosion tests were extracted from both longitudinal and transversal sections of the unidirectionally solidified casting. The samples were further ground with silicon carbide papers up to 1200 mesh, polished and etched with the Palmerton's reagent (40 g CrO_3; 1.5 g Na_2SO_4 and 200 ml of distilled and deionized water) to reveal the microstructure.

Microstructural characterization was performed by an optical microscope associated with an image processing system Neophot 32 (Carl Zeiss, Esslingen, Germany) and a scanning electron microscope (SEM, Jeol JXA 840A). A Shimadzu EDX-720 X-ray fluorescence spectrometer was used to estimate the segregation of the samples considering an area of 100 mm^2.

Fig. 1 indicates the positions along the casting length from where transversal samples were extracted for the electrochemical corrosion tests. These samples were selected at these specifics positions in order to permit quite different samples in terms of microstructure and segregation to be obtained. Finer cell spacings and higher Cu content are associated with positions closer to the cooled bottom of the casting (higher solidification cooling rates). The cell spacing increases and the Cu content decreases (tending to the nominal Cu composition of the alloy) with increasing distance from the bottom of the casting.

In order to permit the samples to have a similar surface roughness, all samples were further ground with silicon carbide papers up to 1200 mesh before the corrosion tests. The Zn–Cu alloy samples constituting the working electrodes were positioned at the glass corrosion cell kit, leaving a circular 1 cm^2 metal surface in contact with a naturally aerated and stagnant 500 cm^3 of a 0.5 M NaCl solution at 25 ($\pm$2) °C and with a 6.98 ($\pm$0.4) pH.

EIS measurements began after an initial delay of 10 minutes for the sample to reach a steady-state condition. Although open-circuit potential measurements (OCP) had not been carried out, there were experimental evidences that after 10 min the potential steady-state condition had been reached. A potentiostat coupled to a frequency analyzer system, a glass corrosion cell kit with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the EIS tests. The potential amplitude was set to 10 mV; peak-to-peak (AC signal) in open-circuit, with 5 points per decade and the frequency range was set from 100 mHz to 100 kHz.
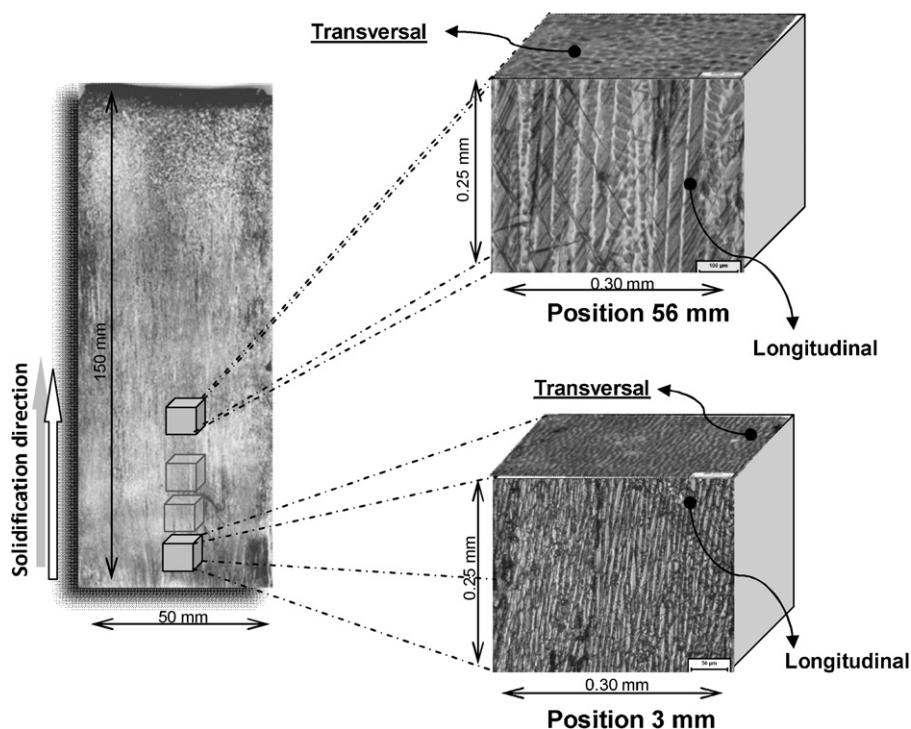

Fig. 1. (a) Typical macrostructure of a Zn–2.2 wt.% Cu peritectic alloy, (b) representation of transverse and longitudinal microstructures.