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Correlation between thermal parameters, structures, dendritic spacing and corrosion behavior of Zn–Al alloys with columnar to equiaxed transition

A.E. Ares[a,b,*], L.M. Gassa[c], S.F. Gueijman[b], C.E. Schvezov[a,b]

[a]CONICET, Argentina
[b]University of Misiones, 1552 Félix de Azara Street, 3300 Posadas-Misiones, Argentina
[c]CONICET-INIFTA (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas), Universidad Nacional de la Plata, Diagonal 113 y 64, La Plata, Argentina

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Abstract

The columnar to equiaxed transition (CET) has been examined for many years and the significance of CET has been treated in several articles. Experimental observations in different alloy systems have shown that the position of the transition is dependent on parameters like cooling rate, velocity of the liquidus and solidus fronts, local solidification time, temperature gradients and recalescence. The dendritic structure in alloys results in microsegregation of solute species which affects significantly the mechanical properties of the material. The main parameters characterizing the microstructure and the length range of microsegregation is the spacing which is classified as primary, secondary and tertiary. Properties like mechanical resistance and ductility are influenced by the dimensions and continuity of the primary branches, while the secondary and tertiary branches permit the isolation of interdendritic phases which can deteriorate the mechanical behavior of the material. Since the morphology and dimensions of the dendritic structure is related to the solidification parameters mentioned above, for each type of alloy it is essential to correlate dimensions and solidification conditions in order to control the structure. The objective of the present research consists on studying the influence of solidification thermal parameters with the type of structure (columnar, equiaxial or with the CET); and with grain size and dendritic spacing (primary and secondary) in Zn–Al (ZA) alloys (Zn—4 wt%Al, Zn—16 wt%Al and Zn—27 wt%Al, weight percent). Also, correlate the thermal parameters, type of structure, grain size and dendritic spacing with the corrosion resistance of these alloys.

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1. Introduction

Among the group of zinc base alloys (ZA4, ZA8, ZA12, ZA27), the zinc–aluminum alloys (ZA or ALZEN) have gotten a lot of attention in the last years like substitute materials of aluminum base alloys, irons and brasses [1].

The ZA27 alloy (ASTM B669–82, 25–28%Al, 2.0–2.5%Cu, 0.01–0.02%Mg and Zn-balance) has a higher mechanical resistance, ductility and resistance to abrasive wear of the group [2].

In general, equiaxed grains grow ahead of the columnar dendrites and the columnar to equiaxed transition (CET) occurs when these equiaxed grains are sufficient in size and number to impede the advance of the columnar front. The authors determined in a previous research that the extent of the equiaxed zone is the result of competition between the columnar and the equiaxed grains [3–5]. Spittle recently

*Corresponding author. University of Misiones, 1552 Félix de Azara Street, 3300 Posadas-Misiones, Argentina. Tel.: +54 3752 434118; fax: +54 3752425414.
E-mail address: aares@fceqyn.unam.edu.ar (A.E. Ares).

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summarized and assessed the present level of understanding of the CET [6].

In the industrial production it is very important to increase the quantity of quality products and without defects, where the structural morphology can also play an important role in the corrosion behavior of the metallic alloys. Although it is well-known that, as much the quantity as the homogeneity in the distribution of second phases are important parameters that define the level of mechanical resistance of the alloys [7–11]. It is necessary to study in systematic form the relation between the thermal and structural parameters and the resistance to the corrosion.

Recently, Song et al. [12] and Osório et al. [13–16] have reported a direct correlation between the tensile yield strength and the corrosion resistance of AZ91D alloys, Zn–Al alloys, Al–Si alloys, Al–9%Si and Al–20%Sn alloys.

The results presented in this paper focus on the CET studies in ZA4, ZA16 and ZA27 alloys. In the investigation, we correlate the effect of several parameters, like thermal, structural and electrochemical parameters on the transition and the type of structure.

In order to obtain the CET, the alloys were solidified directionally upwards in an experimental set up consisting of a heating unit, a temperature control system, a temperature data acquisition system, a sample moving system and a heat extraction system, with a set of thermocouples in the samples which permit to determine the time dependent profiles during growth. From these profiles and the location of thermocouples it was possible to calculate the cooling rates, growth velocities and the temperature gradients along the sample.

The primary and secondary spacings were measured and correlated with the solidification parameters. The corrosion study was realized by electrochemical impedance spectroscopy and polarization curves. The CET zone and the equiaxed structures presented a better corrosion resistance than the columnar zone.

2. Experimental procedure

ZA alloys of different compositions were prepared from zinc (99.998%) and aluminum (99.960%). The samples were directional solidified in alumina molds of 16.00 mm in diameter and 200 mm in length.

The alloy samples were melted and solidified directionally upwards in an experimental set up described elsewhere [3–5].

During the solidification process, temperatures at different positions in the alloy samples were automatically acquired using a data logger. The temperature measurements were performed using five K-type thermocouples (2 mm), which were protected with a refractory paste.

After solidification the samples were cut in the axial direction, were polished and the zinc–aluminum alloys were etched using concentrated hydrochloric acid for 3 s at room temperature, followed by rinsing and wiping off the resulting black deposit and for microstructures were etched with a mix containing chromic acid (50 g Cr_2O_3; 4 g Na_2SO_4 in 100 ml of water) for 10 s at room temperature [17]. Typical macrostructure and microstructures are shown in Fig. 1. The position of the transition was located by visual observation and optical microscopy and the distance from the chill zone of the sample was measured with a ruler. It is noted in Fig. 1(a) that the melted zone in the experiment starts at the region marked as zero on the macrostructure and the CET is not sharp, showing a zone where some equiaxed grains co-exist with columnar grains. The size of the transition zone is in the order of up to 10 mm. As previously reported [3,5] no effect of the set of the thermocouples in the transition was observed; either acting as nucleating sites or changing the solidification structure.

The equiaxed grain size is measured using the ASTM standard norm [18], at equally spaced intervals. The procedure for the columnar grains was as followed; the width was determined dividing the number of grains per unit length in the whole sample width. The columnar length was defined for all the grains in the longitudinal section and averaged.

The range of growth velocity and temperature gradients employed in the experiments were 0.10–0.28 cm/s and 1–20 °C/cm, respectively.

The correlation between the different dendrite spacings and the parameters were determined by measuring the spacings in the regions close to the position of the thermocouples. The microstructure was inspected by employing optical microscopy and using an image processing systems Neophot 32 and Leica Quantimet 500 MC. The spacings were measured by counting the number of branches; primary (λ_1) or secondary (λ_2) along a line of known length. The mean value of λ_1 and λ_2 was calculated from 15 measurements in each zone. In order to find the possible transformations taking place during solidification and to correctly determine the beginning and the end of the solidification, a DSC analysis was utilized.

For the electrochemical tests (polarization curves and electrochemical impedance spectroscopy technique, EIS), samples of 2 cm in length of each zone (columnar, equiaxed and CET) and for each concentration, were prepared as working electrodes cutting from the longitudinal sections, polished with sandpaper (from CSi #200 until #1200) and washed with desmineralized water and dried by natural flow of air.

All the electrochemical tests were conducted in a 300 ml of a 3% NaCl solution at room temperature using an IM6d ZAHNER® electrik potentiostat coupled to a frequency analyzer system, a glass corrosion cell kit with a platinum counter electrode and a sutured calomel reference electrode (SCE).

Polarization curves were obtained using a scanning rate in the range of $0.002\ V/s \leqslant v \leqslant 0.250\ V/s$ from open circuit potential until to 0.250 V. Impedance spectrums were registered in the frequency range of $10^{-3}\ Hz \leqslant f \leqslant 105\ Hz$ in open circuit.