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Acta Materialia 53 (2005) 3261–3270
Acta MATERIALIA
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Crystallography of grain refinement in Mg–Al based alloys

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Received 5 January 2005; received in revised form 24 March 2005; accepted 24 March 2005
Available online 10 May 2005

Abstract

An edge-to-edge matching model has been used to analyze the crystallographic features between magnesium matrix and three commonly accepted heterogeneous nucleants for magnesium grains, Al_4C_3, Al_2CO and $Al_8(Mn,Fe)_5$. Although certain orientation relationships between magnesium and each of these compounds have been predicted, the potency of each of these three compounds as nucleating substrates for magnesium grains is different. Based on calculated interatomic spacing misfits along matching directions and d-value mismatches between matching planes, the model has predicted that Al_2CO is the most effective nucleant of the three compounds assessed for Mg grains and is probably responsible for the grain refinement in both the superheating and carbon inoculation processes. Al_4C_3 can be a nucleant for Mg grains, but it is not as effective as Al_2CO. This prediction is consistent with most experimental results reported recently. The $Al_8(Mn,Fe)_5$ intermetallic compound is predicted to have the lowest efficiency as a nucleant for magnesium grains. The model may be used to provide theoretical guidance for selection of new and more powerful grain refiners for Mg–Al based alloys.

Keywords: Crystallography; Grain refinement; Magnesium alloys; Orientation relationship; Edge-to-edge matching

1. Introduction

Grain refinement is an important practice in the magnesium industry that is used to improve the mechanical properties of magnesium alloys and the relevant research work dates back to the 1930s [1]. It has been well demonstrated that Zr is an extremely potent grain refiner for Mg alloys, and this appears to be a result of the significant similarities between the crystal structures of Zr and Mg [2–4]. However, Zr cannot be used in Mg alloys that contain Al, Mn, Si, etc., as Zr forms stable compounds with these alloy elements [2,5]. Over the past decades, several grain-refining techniques have been developed for Mg–Al based alloys, of which, superheating and carbon inoculation are the two most effective. Formation of Al_4C_3 and Al_2CO particles, which subsequently nucleate magnesium grains, is generally regarded [2,6–10] as the primary reason for grain refinement obtained by the superheating and carbon inoculation processes. Another grain-refining method developed for Mg–Al based alloys is the Elfinal process, which involves the addition of anhydrous ferritic chloride ($FeCl_3$) to a molten Mg alloy. The process was reported to give rise to obvious grain refinement in the presence of Mn [11] and of more than 3% of Al [12]. Emley [2] and Nelson [11] suggested that the cause of grain refinement in the Elfinal process is the formation of Al_4C_3 due to the liberation of some carbon from mild steel crucibles, arising from chemical attack by the HCl fume that resulted from the use of $FeCl_3$. Although, controversial results have been reported that Fe is an inhibiting element for grain refinement of magnesium alloys [13], Cao et al. [14] have recently confirmed that Fe

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1359-6454/$30.00
doi:10.1016/j.actamat.2005.03.030

is a grain refiner for Mg–Al based alloys when introduced in the form of anhydrous $FeCl_3$. They observed Al- and Fe-enriched intermetallic particles in the central regions of many magnesium grains and proposed that these particles are probably responsible for the grain refinement observed in the Elfinal process. However, no more specific information was given about these compounds. Another recent study [15] has suggested that the $Al_8(Mn,Fe)_5$ compound is an effective heterogeneous nucleation site for primary Mg and a method for manufacturing of AZ91 alloy slurries for semi-solid forming has accordingly been developed. Other studies [2,7,16] have indicated that the similarities between Al_4C_3 and Mg, or Al_2CO and Mg, in terms of both crystal structure and lattice parameter, make both Al_4C_3 and Al_2CO highly potent nucleants for Mg and, therefore, both play an important role in grain refinement of Mg–Al based alloys [2,13]. However, no actual crystallographic studies have been reported. Using a recently developed edge-to-edge matching crystallographic model [17–20], the present work examines the crystallographic features of each of the three proposed nucleants for magnesium, Al_4C_3, Al_2CO and $Al_8(Mn,Fe)_5$, and the orientation relationships between magnesium and each of them. The aim is to establish the relationship between the potency of each of these compounds as nucleating substrates for Mg and their crystallographic characteristics. This may form useful theoretical guidance for seeking new grain refiners for Mg–Al based alloys.

2. Introduction to the edge-to-edge matching model

The edge-to-edge matching model developed by Zhang and Kelly [17–21] is used for examination of actual atom matching across an interface between any two phases. It is capable of predicting orientation relationships (OR) between any two phases from first principles, using data including crystal structure, lattice parameters and atom positions. The model is based on the assumptions that the crystallographic relationships between any two phases are governed by minimization of the strain energy of the interface and that the necessary and sufficient conditions for minimization of the strain energy are the matching of rows of atoms in the two phases [22]. To achieve the maximum matching, it requires that the matching atom rows are along the close-packed or nearly close-packed directions and that the interatomic spacing misfit along each of these directions is less than 10% [19–21]. These directions are termed matching directions. These matching atom rows can be either straight or zigzag rows [19,21]. It is easy to understand the straight atom rows but the zigzag rows need to be further explained. Let us assume that atoms A, B and C form a part of the zigzag row and r is the radius of the atoms, as shown in Fig. 1. For zigzag atom rows to be matching directions, the following conditions have to be satisfied:

- At least two atoms (atoms A and C) should be touching and the other two (atoms C and B) either be nearly touching or touching.
- Angle α between AC and AB must be equal to or smaller than 30°.
- Angle γ between CA and CB must be equal to or greater than 120°.
- Distance CD must be equal to or smaller than the atom radius r.

The model requires that straight rows match with straight rows and zigzag rows with zigzag rows.

As an additional requirement, in order to maximize the atom matching across the interface, the d-value mismatch between the planes that contain the matching directions should be less than 6% [19,21]. These planes are normally the close-packed or nearly close-packed planes in both phases and are called matching planes. According to the model, the matching planes must contain the matching direction. An approximate OR can be predicted by combining the direction pair and the plane pair. This OR needs to be further refined using the **Δg** conditions [23,24]. **Δg** is a displacement vector of the two **g**'s in reciprocal space for the two sets of planes that forms an intersection plane. Previous studies [23–25] have demonstrated that when two sets of planes in two different phases overlap, the intersection plane is always parallel to the Moiré plane and is perpendicular to **Δg**. The refinement of the OR keeps the matching directions parallel and will specify the rotation angle of the matching planes relative to each other about the matching directions. At one particular rotation angle, there are at least two **Δg**'s that are parallel to each other. A simple computer program has been written to perform this task [19–21]. Normally, if the d-value mismatch of the matching planes is less than or equal to 6%, the rotation angle is small and often the matching planes are nearly parallel to each other. In the case that the minimum d-value mismatch between matching planes in a given system is greater than 6%, say up to 15%, certain ORs may still exist between these two phases, although, in most cases, it will be accompanied by a large angle rotation of the matching planes.

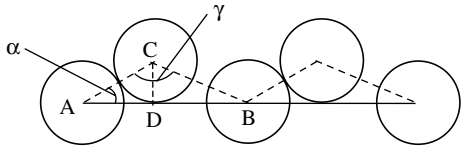

Fig. 1. Schematic illustration of the conditions for zigzag atom rows to be matching directions.