

# A novel model to account for the heterogeneous nucleation mechanism of $\alpha$ -Mg refined with $\text{Al}_4\text{C}_3$ in Mg-Al alloy



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## ABSTRACT

To explore the heterogeneous nucleation mechanism of Mg-Al alloy refined by  $\text{Al}_4\text{C}_3$ , the valence electron structure and cohesive energy of  $\text{Al}_4\text{C}_3$  crystal were calculated using the empirical electron theory of solids and molecules. A novel model to account for heterogeneous nucleation process of  $\alpha$ -Mg on  $\text{Al}_4\text{C}_3$  is described. The weak bonds exist in the surface of  $\text{Al}_4\text{C}_3$  might leads to the replacement of atoms in  $\text{Al}_4\text{C}_3$  surface by Mg atoms in melt, which ultimately result in easily stacking of Mg atoms on the newly formed surface of  $\text{Al}_4\text{C}_3$ . This model also indicates that Mg-Al atom cluster preferentially occupies the atom vacancies on  $\text{Al}_4\text{C}_3$  surface in comparison to Mg-Mg atom cluster, which can decrease the refining efficiency of  $\text{Al}_4\text{C}_3$  in high Al containing magnesium alloys.

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## 1. Introduction

Grain refinement of as-cast Mg-Al serial alloys is contributed to improving the mechanical properties and broadening its applied range. However, being lack of understanding to the grain refinement mechanism, a reliable, efficient and environment-friendly commercial grain refiner is still not successfully developed for Mg-Al alloys [1–3]. Since Davis originally found the adding of C containing agent can refine Mg-Al alloy in 1945 [4], considerable efforts had been carried out to elucidate the grain refinement mechanisms of carbon inoculation over half-centuries. The  $\text{Al}_4\text{C}_3$  compounds was first proposed as a nucleating substrate for  $\alpha$ -Mg in 1948, then this hypothesis on the heterogeneous nucleation of  $\text{Al}_4\text{C}_3$  was supported by many investigators in terms of crystallographic characteristic [5–11], but there seems no direct convincing experimental data showing the existence of  $\text{Al}_4\text{C}_3$  particle in Mg-Al alloy. Although  $\text{Al}_2\text{OC}$ , of which lattice misfit with  $\alpha$ -Mg is smaller than that of  $\text{Al}_4\text{C}_3$ , appears to be a much more potent nucleating agent for  $\alpha$ -Mg than  $\text{Al}_4\text{C}_3$  [7], it is thermodynamically impossible to form Al-C-O compounds in Mg-Al melt [11]. In addition to  $\text{Al}_4\text{C}_3$  and  $\text{Al}_2\text{OC}$ , other C-containing compounds were also identified as a nucleating substrate. Huang [12] exactly found the existence of the ternary carbide  $\text{Al}_2\text{C}_2\text{Mg}$  in Mg-Al alloy inoculated by SiC, and the lattice constant of  $\text{Al}_2\text{C}_2\text{Mg}$  also has small misfit in comparison with that of primary Mg phase. Nonetheless, it is worthy to note in Huang's investigation that the adding amounts of SiC are large

enough, but it is probably still questionable whether  $\text{Al}_2\text{C}_2\text{Mg}$  nuclei can be formed or not under the condition of small amount of SiC, i.e. low C/Al ratio. Hence, the hypothesis of  $\text{Al}_4\text{C}_3$  heterogeneous nucleation to date is still the commonly accepted grain refining mechanism of C treatment method.

The popular theory of heterogeneous nucleation is the lattice matching between substrate and matrix. The lattice misfit between  $\text{Al}_4\text{C}_3$  and primary Mg is about 4%, but it is not certain to become potent nuclei for other particles, such as TiC,  $\text{TiB}_2$  and  $\text{AlB}_2$  being disable for refining aluminum [13–15], in spite of satisfying the condition of atomic arrangements misfit. Inversely, it also has been experimentally demonstrated that the particle with large lattice misfit to matrix can act as nucleating substrate [16]. Thus, it seems that lattice misfit criterion is not sufficient to the mechanism description of heterogeneous nucleation. Alternatively, the interfacial energy between the nucleating particle and matrix is considered as a direct factor to determine the occurrence of heterogeneous nucleation, which is only partly related to lattice misfit of the two phase. Li [17] and Wang [18] used density functional theory (DFT) to calculate the interfacial energy of Mg/ $\text{Al}_4\text{C}_3$ , Mg/ $\text{Al}_2\text{C}_2\text{Mg}$ , and the results indicate that both interfacial energy are lower to that of between  $\alpha$ -Mg and magnesium melts. Nevertheless, these works still cannot explain the effects of alloying component on the refining efficiency of heterogeneous particles, and the affecting mechanism needs to be further explored.

At present, all the mechanism about heterogeneous nucleation have focused on the nucleating criterion, none have thought the initial process of heterogeneous nucleation, i.e. the atoms interactions between nucleating particle and matrix liquid. But due to the

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limitation on the experimental facilities, there is no direct evidence at atomic level for exploring the atom mechanism of  $\text{Al}_4\text{C}_3$  heterogeneous nucleation. Therefore, the present study used the empirical electron theory (EET) of solids and molecules to calculate the valence electron structure of  $\text{Al}_4\text{C}_3$ . Based on analysis of calculation results, a new model of  $\alpha$ -Mg heterogeneously nucleating on  $\text{Al}_4\text{C}_3$  was proposed to clarify the essence of heterogeneous nucleation insightfully by paying specific attention to the atom interactions between the liquid Mg-Al and the  $\text{Al}_4\text{C}_3$  particle.

## 2. Calculation method

EET, established by Yu in 1978 [19], is based on Pauling's valence bond theory and Hume-Rothery's electron concentration theory. After decades of continuous efforts, EET was better improved to deal with the two main problems of multi-solutions and calculation accuracy by using equal probability principle [20] and the self-consistent bond length difference (SCBLD) method [21,22], respectively. Now the developed EET is widely used in many fields such as solid solutions, compounds, mechanical properties, strengthening mechanisms and phase transformations [23–28]. In this paper, it is therefore possible to calculate the bonds energy and cohesive energy for  $\text{Al}_4\text{C}_3$  using EET.

### 2.1. Calculations of valence electron structure (VES) of $\text{Al}_4\text{C}_3$

The VES in EET usually includes the covalent bonds formed by atoms, the electron distribution on covalent bonds, and the atomic states. Fig. 1 shows the VES analysis model. There are three models used in this paper, initial pure  $\text{Al}_4\text{C}_3$  (Fig. 1(a)),  $\text{Al}_4\text{C}_3$  doped Mg atom i.e. C1 atom on  $\text{Al}_4\text{C}_3$  surface replaced by Mg (Fig. 1(b)),  $\text{Al}_4\text{C}_3$  doped Mg-Al atom cluster. It is noted that the position of

alloy atom Al in Mg-Al cluster is random and indeterminate. Therefore, in the light of the calculation models supposed in our previous investigations [25,26], we consider that a kind of mixing atom that is composed of  $(1-x)$  Mg and  $x$ Al atoms ( $x = 3, 6, 9$ , at.%) occupies the lattice points of C1 atoms, as shown in Fig. 1(c).

The VES parameters for  $\text{Al}_4\text{C}_3$ ,  $\text{Al}_4\text{C}_2$ -Mg, and  $\text{Al}_4\text{C}_2$ -(Mg- $x\%$ Al) can be calculated with the SCBLD method which is developed from the bond length difference (BLD) method [21,22] in EET, respectively. Taken pure  $\text{Al}_4\text{C}_3$  structure unit as an example, the detail calculation steps of the VES of  $\text{Al}_4\text{C}_3$  are given as follows.

$\text{Al}_4\text{C}_3$  has the non-close packed hexagonal lattice and its lattice constants are  $a = b = 0.333$  nm,  $c = 2.489$  nm, each unit cell contains 9 carbon atoms and 12 aluminum atoms, the atom position are listed in Table 1.

In EET, the head and tail states of C are given as

$$\begin{array}{l} \text{h state: } s^2p^2 \\ \text{t state: } s^1p^3 \end{array} \quad \begin{array}{c} s \\ \Phi \\ \underline{\quad} \end{array} \quad \begin{array}{c} \overline{p} \\ \bullet \quad \bullet \quad \circ \\ \bullet \quad \bullet \quad \bullet \end{array}$$

From the above hybridization states, we can obtain  $l = 2$ ,  $m = 2$ ,  $n = 0$ ,  $\tau = 0$ ;  $l' = 1$ ,  $m' = 3$ ,  $n' = 0$ ,  $\tau' = 1$ ,  $R(1)_h = 0.0763$  nm,  $R(1)_t = 0.0763$  nm.

For Al element, the hybridization two-states are given as

$$\begin{array}{l} \text{h state: } s^2p^1 \\ \text{t state: } s^1p^2 \end{array} \quad \begin{array}{c} s \\ \Phi \\ \bullet \end{array} \quad \begin{array}{c} \overline{p} \\ \bullet \quad \circ \quad \circ \\ \bullet \quad \bullet \quad \bullet \quad \circ \end{array}$$

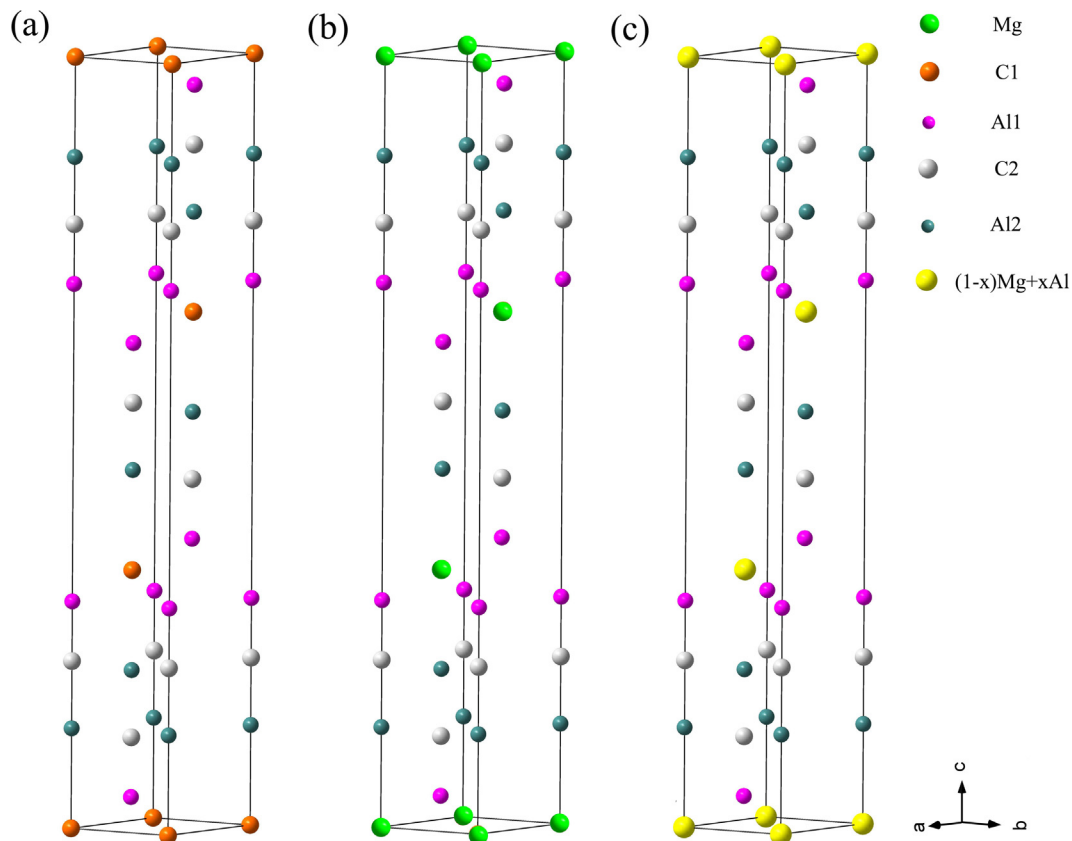


Fig. 1. VES analysis models of hcp-structured  $\text{Al}_4\text{C}_3$  (a)  $\text{Al}_4\text{C}_3$  structure unit; (b)  $\text{Al}_4\text{C}_3$  doped Mg structure unit; (c)  $\text{Al}_4\text{C}_3$ -doped (Mg- $x$ Al) structure unit.

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