

# Interfacial energy between Al melt and TiB<sub>2</sub> particles and efficiency of TiB<sub>2</sub> particles to nucleate α-Al

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## ABSTRACT

The interfacial energy between Al melt and TiB<sub>2</sub> particles is calculated based on the Gibbs adsorption isotherm. The efficiency of TiB<sub>2</sub> to nucleate α-Al is discussed. The interfacial energy between Al melt and TiB<sub>2</sub> remains almost constant while the efficiency of TiB<sub>2</sub> to nucleate α-Al depends on the solute Ti concentration ( $x_{Ti}$ ) in Al melt. When  $x_{Ti}$  is less than  $1.78 \times 10^{-4}$  at%, TiB<sub>2</sub> cannot nucleate α-Al. With the increase of  $x_{Ti}$ , the efficiency of TiB<sub>2</sub> to nucleate α-Al increases until a complete wetting of TiB<sub>2</sub> particles by solid Al in the environment of liquid Al is achieved.

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Inoculation has become a common practice to achieve a fine equiaxed grain structure in the industrial production [1–6]. Al-Ti-B master alloys are widely used as the grain refiners for aluminium alloys [7,8]. Much work has been done to investigate the inoculant effect of the Al-Ti-B master alloys. Models have been proposed in the last decades to explain the mechanism by which the Al-Ti-B master alloys refine the α-Al grains [9–13]. But none of them can explain all the experimental observations. Especially the exact role of TiB<sub>2</sub> particles during the nucleation process of α-Al is still under dispute.

In fact, the efficiency of TiB<sub>2</sub> particles to nucleate α-Al is closely related to the interfacial energies among the Al melt, TiB<sub>2</sub> particles and α-Al. It can be judged by a dimensionless parameter  $v_\gamma = \frac{\gamma_{Al(L)/TiB_2(S)} - \gamma_{\alpha-Al(S)/TiB_2(S)}}{\gamma_{Al(L)/\alpha-Al(S)}}$  with  $\gamma_{Al(L)/TiB_2(S)}$ ,  $\gamma_{\alpha-Al(S)/TiB_2(S)}$  and  $\gamma_{Al(L)/\alpha-Al(S)}$  being the interfacial energies between Al melt and TiB<sub>2</sub> particles, between α-Al and TiB<sub>2</sub> particles and between Al melt and α-Al, respectively.

The interfacial energies  $\gamma_{Al(L)/\alpha-Al(S)}$  and  $\gamma_{\alpha-Al(S)/TiB_2(S)}$  have been reported [8,14]. Up to date, there exists no reports on  $\gamma_{Al(L)/TiB_2(S)}$ . The measurement of  $\gamma_{Al(L)/TiB_2(S)}$  is, if possible, quite difficult especially due to the enrichment of solute Ti in the Al melt at the interface [15]. This work will first theoretically calculate  $\gamma_{Al(L)/TiB_2(S)}$  based on the Gibbs adsorption isotherm and then discuss the efficiency of TiB<sub>2</sub> particles to nucleate α-Al under the solute Ti effect based on the interfacial energies.

For an aluminium alloy melt with the presence of TiB<sub>2</sub> particles and solute Ti,  $\gamma_{Al(L)/TiB_2(S)}$  satisfies [15–17]:

$$\Gamma_{Ti} = -\frac{d\gamma_{Al(L)/TiB_2(S)}}{d\mu_{Ti}^i} = -\frac{d\gamma_{Al(L)/TiB_2(S)}}{d\mu_{Ti}} \quad (1a)$$

$$\Gamma_{Ti} = \frac{x_{Ti}^i - x_{Ti}}{\omega_{Al(L)/TiB_2(S)}} \approx \frac{x_{Ti}^i}{\omega_{Al(L)/TiB_2(S)}} \quad (1b)$$

where  $\Gamma_{Ti}$  is the interfacial excess of solute Ti,  $x_{Ti}$  and  $x_{Ti}^i$  are respectively the mole fractions of solute Ti in the Al melt and at the Al(L)/TiB<sub>2</sub>(S) interface,  $\omega_{Al(L)/TiB_2(S)} = \sqrt{\omega_{Al(L)}\omega_{Ti(L)}}$  is the molar area of the Al(L)/TiB<sub>2</sub>(S) interface [16],  $\omega_{Al(L)} = f \cdot (N_a)^{1/3} \cdot V_{Al(L)}^{2/3}$  and  $\omega_{Ti(L)} = f \cdot (N_a)^{1/3} \cdot V_{Ti(L)}^{2/3}$  are respectively the molar areas of the Al and the Ti melt [18],  $N_a$  is the Avogadro's number,  $V_{Al(L)}$  and  $V_{Ti(L)}$  are respectively the molar volumes of the Al and the Ti melt,  $\mu_{Ti}$  and  $\mu_{Ti}^i$  ( $\mu_{Ti} = \mu_{Ti}^i$  under the equilibrium conditions) are the chemical potentials of solute Ti in Al melt and at the Al(L)/TiB<sub>2</sub>(S) interface, respectively.

Using the relation  $\mu_{Ti}^i = \mu_{Ti}^0 + \Omega_{Al-Ti}(1 - x_{Ti}^i)^2 + R_g T \ln x_{Ti}^i$ , Eq. (1) can be rewritten as:

$$-d\gamma_{Al(L)/TiB_2(S)} = \frac{x_{Ti}^i}{\omega_{Al(L)/TiB_2(S)}} \left[ 2\Omega_{Al-Ti}(x_{Ti}^i - 1) + \frac{R_g T}{x_{Ti}^i} \right] dx_{Ti}^i \quad (2)$$

where  $\mu_{Ti}^0$  is the standard chemical potential of bulk Ti,  $\Omega_{Al-Ti}$  is the interaction energy parameter between the Al and Ti atoms in Al-Ti melt,  $R_g$  is the gas constant and  $T$  is the thermodynamic temperature.

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Integrating Eq. (2) using the boundary condition  $\gamma_{\text{Al(L)/TiB}_2(\text{S})}|_{x_{\text{Ti}}^i=0} = \gamma_{\text{Al(L)/TiB}_2(\text{S})}^0$ , one has:

$$\gamma_{\text{Al(L)/TiB}_2(\text{S})} = -\frac{2\Omega_{\text{Al-Ti}}}{3\omega_{\text{Al(L)/TiB}_2(\text{S})}} \left(x_{\text{Ti}}^i\right)^3 + \frac{\Omega_{\text{Al-Ti}}}{\omega_{\text{Al(L)/TiB}_2(\text{S})}} \left(x_{\text{Ti}}^i\right)^2 - \frac{R_g T}{\omega_{\text{Al(L)/TiB}_2(\text{S})}} x_{\text{Ti}}^i + \gamma_{\text{Al(L)/TiB}_2(\text{S})}^0 \quad (3)$$

where  $\gamma_{\text{Al(L)/TiB}_2(\text{S})}^0$  is the interfacial energy between the pure Al melt and  $\text{TiB}_2$  particles.

$x_{\text{Ti}}^i$  depends on  $x_{\text{Ti}}$  according to the following equation (see Appendix A) [16]:

$$\ln \left[ \frac{\left(x_{\text{Ti}}^i / (1 - x_{\text{Ti}}^i)\right)}{\left(x_{\text{Ti}} / (1 - x_{\text{Ti}})\right)} \right] = \frac{2\Omega_{\text{Al-Ti}}}{Z} \left[ Z_L (x_{\text{Ti}}^i - x_{\text{Ti}}) - Z_1 (x_{\text{Ti}} - 0.5) \right] + \frac{(\Delta S_m^{\text{Al}} - \Delta S_m^{\text{Ti}}) T}{R_g T} - \frac{\omega_{\text{Al(L)/TiB}_2(\text{S})} (\gamma_{\text{Ti(L)/TiB}_2(\text{S})}^0 - \gamma_{\text{Al(L)/TiB}_2(\text{S})}^0)}{R_g T} \quad (4)$$

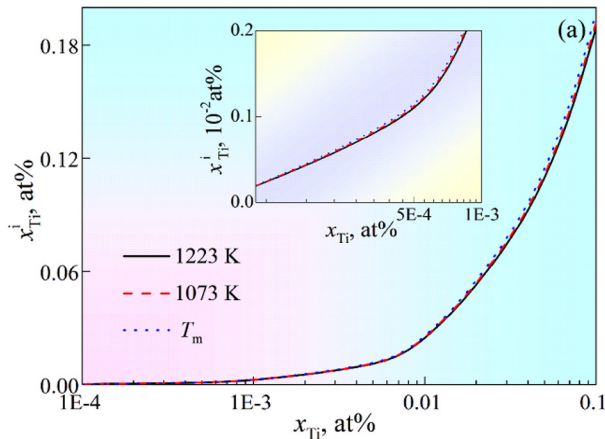
where  $Z$  is the coordination number of an atom in the pure Al melt,  $Z_L$  is the coordination number of an atom in the interfacial monolayer within the interfacial monolayer,  $Z_1$  is the coordination number of an atom in the interfacial monolayer to one of the adjacent layers,  $\Delta S_m^{\text{Al}}$  and  $\Delta S_m^{\text{Ti}}$  are respectively the entropies of fusion of Al and Ti [16],  $\gamma_{\text{Ti(L)/TiB}_2(\text{S})}^0$  is the interfacial energy between the pure Ti melt and  $\text{TiB}_2$  particles [19].

$\gamma_{\text{Al(L)/TiB}_2(\text{S})}^0$  can be calculated by (see Appendix B) [18]:

$$\gamma_{\text{Al(L)/TiB}_2(\text{S})}^0 = \frac{0.364(2\Omega_{\text{Al-B}} + \Omega_{\text{Al-Ti}} - \Delta_f H_{\text{TiB}_2}) + 0.310f \cdot f_b^{1/3} (\Delta_m H_{\text{Ti}} + 2\Delta_m H_{\text{B}})}{3} + (3.5 \pm 1) T \omega_{\text{Al(L)/TiB}_2(\text{S})} \quad (5)$$

where  $\Delta_f H_{\text{TiB}_2}$  is the heat for the formation of  $\text{TiB}_2$ ,  $\Delta_m H_{\text{Ti}}$  and  $\Delta_m H_{\text{B}}$  are the enthalpis of fusion of Ti and B, respectively,  $f_b$  is the bulk packing factor [20]. The unit of the constant  $(3.5 \pm 1)$  is  $\text{J}/(\text{mol} \cdot \text{K})$ .  $\Omega_{\text{Al-B}}$  is the interaction energy parameter between the Al and B atoms in Al-B melt, which can be calculated using the relation  $\Omega_{\text{Al-B}}(1 - x_{\text{B}})^2 = R_g T \ln \gamma_{\text{B}}$  [20,21].  $\gamma_{\text{B}}$  is the activity coefficient of solute B in Al melt. It can be determined by using the Wilson equation  $\ln \gamma_{\text{B}} = 1 - \ln(1 - x_{\text{Al}} A_{\text{Al/B}}) - \frac{x_{\text{B}}}{1 - x_{\text{Al}} A_{\text{Al/B}}} - \frac{x_{\text{Al}}(1 - A_{\text{B/Al}})}{1 - x_{\text{B}} A_{\text{B/Al}}}$ .  $A_{\text{Al/B}} = 0.0016T - 3.2795$  and  $A_{\text{B/Al}} = -0.0004T + 1.1121$  are the Wilson parameters [21].  $x_{\text{Al}}$  and  $x_{\text{B}}$  are the mole fractions of solvent Al and solute B, respectively.

Fig. 1a shows  $x_{\text{Ti}}^i$  as a function of  $x_{\text{Ti}}$  calculated using Eq. (4) with the thermo-physical parameters listed in Table 1. It demonstrates that  $x_{\text{Ti}}^i$  increases with  $x_{\text{Ti}}$  and the temperature of the melt has a very weak effect



**Table 1**  
Thermo-physical parameters used in the calculations.

Symbol	Value	Unit	Reference
$R_g$	8.314	$\text{J}/(\text{mol} \cdot \text{K})$	-
$N_A$	$6.02 \times 10^{23}$	1/mol	-
$\Omega_{\text{Al-Ti}}$	-120,000	J/mol	[22]
$V_{\text{Al}}$	$1.13 \times 10^{-5}$	$\text{m}^3/\text{mol}$	[23]
$V_{\text{Ti}}$	$1.16 \times 10^{-5}$	$\text{m}^3/\text{mol}$	[23]
$\Delta_m H_{\text{Ti}}$	14,146	J/mol	[24]
$\Delta_m H_{\text{B}}$	50,200	J/mol	[24]
$\Delta_f H_{\text{TiB}_2}$	-323,842	J/mol	[25]
$f_b$	0.74	-	[20]
$f$	1.06	-	[18]
$\gamma_{\text{Ti(L)/TiB}_2(\text{S})}^0$	0.164	$\text{J}/\text{m}^2$	[19]
$\Delta S_m^{\text{Al}}$	11.48	$\text{J}/(\text{mol} \cdot \text{K})$	[16]
$\Delta S_m^{\text{Ti}}$	7.29	$\text{J}/(\text{mol} \cdot \text{K})$	[16]
$Z$	12	-	-
$Z_L$	6	-	-
$Z_1$	3	-	-

on the dependence of  $x_{\text{Ti}}^i$  on  $x_{\text{Ti}}$ . The temperature effect on the segregation of solute Ti to the interface is thus neglected in the following discussion especially considering that the nucleation of  $\alpha$ -Al may only occur in a narrow temperature region below the melting point of Al  $T_m = 933$  K.

$x_{\text{Ti}}$  may vary in a range determined by the solubility products of  $\text{TiB}_2$  ( $K_{\text{TiB}_2}^0$ ),  $\text{TiAl}_3$  ( $K_{\text{TiAl}_3}^0$ ) and  $\text{AlB}_2$  ( $K_{\text{AlB}_2}^0$ ) in Al melt [26] (see Eqs. (6a), (6b), and (6c)), as shown by the shadowed area in Fig. 1b for the melt at  $T_m$ .

$$x_{\text{Ti}} \cdot x_{\text{B}}^2 \leq K_{\text{TiB}_2}^0 \quad (6a)$$

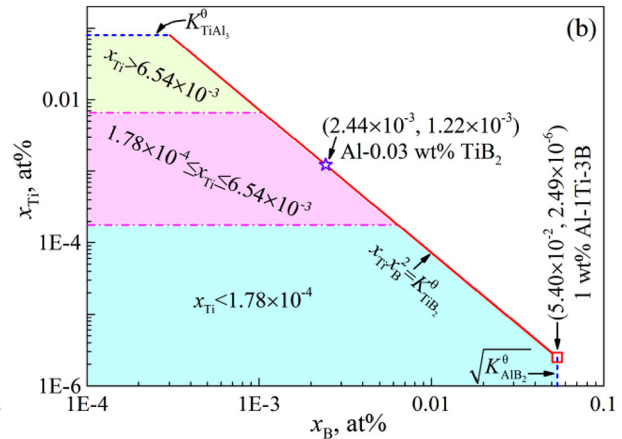
$$x_{\text{Ti}} \leq K_{\text{TiAl}_3}^0 \quad (6b)$$

$$x_{\text{B}} \leq \sqrt{K_{\text{AlB}_2}^0} \quad (6c)$$

The calculated  $\gamma_{\text{Al(L)/TiB}_2(\text{S})}$  is plotted in Fig. 2 as a function of  $x_{\text{Ti}}^i$  at  $T_m$  together with  $\gamma_{\alpha\text{-Al(S)/TiB}_2(\text{S})}$  [14] and  $v_\gamma$ . The results demonstrate that  $\gamma_{\text{Al(L)/TiB}_2(\text{S})}$  remains almost constant while  $\gamma_{\alpha\text{-Al(S)/TiB}_2(\text{S})}$  decreases dramatically with  $x_{\text{Ti}}^i$ .

Figs. 1b and 2 indicate that the value of  $v_\gamma$  and the efficiency of  $\text{TiB}_2$  particles to nucleate  $\alpha$ -Al vary with  $x_{\text{Ti}}^i$  (or  $x_{\text{Ti}}$ ):

- (1) when  $x_{\text{Ti}}^i < 3.50 \times 10^{-4}$  at% (or  $x_{\text{Ti}} < 1.78 \times 10^{-4}$  at%) (blue areas in Figs. 1b and 2),  $v_\gamma < -1$  and  $\text{TiB}_2$  particles cannot nucleate  $\alpha$ -Al and no grain refinement of  $\alpha$ -Al can be achieved.



**Fig. 1.** (a) Solute Ti concentration in the Al melt at the  $\text{Al(L)/TiB}_2(\text{S})$  interface vs the solute Ti concentration in the bulk Al melt at different temperatures; (b) Concentration of solutes Ti and B in the bulk Al melt at  $T_m$ .

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