THERMODYNAMIC ANALYSIS OF INTERFACIAL REACTION SiN SiC/Mg MATRIX COMPOSITES

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Abstract
Gibbs free energy of chemical reactions between SiC particles and the Mg matrix at the different temperature has been calculated based on the Gibbs-Helmholtz equation and thermodynamic equilibrium of chemical reactions. The thermodynamic stability of Al_4C_3 and $MgAl_2O_4$ in the interface was investigated. The results showed that when the activity of Si on interface is more than a critical value of $\mathbf{A^0_{Si}}$. A stable Al_3C_4 cannot formed when $\mathbf{A_{Si}}$ is more than $\mathbf{A^0_{Si}}$, which is not a constant, increasing with the temperature. The mass fraction and distribution of SiO_2in the interface have directly effects on the reactions of SiO_2 with Mg and Al. There is a critical value of $\mathbf{A^0_{Mg}}$, $\mathbf{A^0_{Al}}$ and $\mathbf{A^1_{Al}}$, which increases with the temperature. When the mass fraction of Si in the interface is greater than a critical value, there is no interfacial reaction at a certain temperature. The interface reaction models have been proposed.

Keywords: magnesium matrix composites, interfacial reactions, $MgAl_2O_4$, Al_4C_3

1 Introduction

Particle reinforced magnesium matrix composites have a high specific strength and modulus of elasticity, good damping properties and low coefficient of thermal expansion, which have a great potential in aerospace, automotive and military fields. SiC has many excellent properties such as good thermal stability, low expansion coefficient and high hardness, making it widely used as a reinforcing phase in series of magnesium alloy [1-4]. More attentions have been paid on phase structure, mechanical properties and strengthening mechanisms in SiC particle reinforced magnesium matrix composites. The effect of the distribution of SiC particle size on magnesium matrix composites has illustrated that the reinforcing effect is optimal due to the particles completely distributed in grains [5]. It is found that the pulsed magnetic field has a significant influence on the solidification structure of SiC_p / AZ91D Composites [6]. In the SiC_p/AZ91D composites fabricated by vacuum pressure infiltration process, the SiC particles were homogenously distributed, the interface bonding of the particles and the matrix were favourable [7]. Reaction of Mg and Al with SiO_2 on the surfaces of oxidized SiC, leads to the formation of MgO and $MgAl_2O_4$ crystals, which act as diffusion barriers between Al and SiC at the interfaces [8].ASiO_2 layer is naturally present or artificially introduced at the SiC surface, which is presumed to modify the wettability and interfacial bonding between the reinforcement and the Al–Mg alloys

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[9-11]. A particle pull-out fracture will be the predominant mode if the particle strength is higher, while a tensile loading-induced SiC particles fracture will take place prior to interface failure if the interface strength is higher [12]. However, a thermodynamic analysis of interfacial reactions in SiC/Mg matrix composites has not been reported.

In the present work, the thermodynamic conditions of interface reactions in the SiC/Mg matrix composite, thermodynamic stability of Al_4C_3 and $MgAl_2O_4$ and the process of interfacial reactions have been investigated. The interface reaction models have been proposed.

2 Interfacial chemical reactions

There are many chemical elements such as silicon (Si), aluminium (Al), zinc (Zn), copper (Cu), oxygen (O) and carbon (C)in magnesium alloy. During the solidification processing of SiC/Mg composites, the possible reactions are shown in **Table 1**.

Table 1 Chemical reactions during the solidification processing of SiC/Mg composites

Number	Chemical equations	Enthalpy changes in reactions ΔG^0(J/mol)
①	$SiO_2(s)+2Mg(l)=2MgO(s)+Si(s)$	-326570.4+35.42T
②	$2Mg(l)+Si(s)=Mg_2Si(s)$	—
③	$3SiC(s)+4Al(l)=Al_4C_3(s)+3Si(s)$	103900-16.48T
④	$3SiO_2(s)+4Al(l)=2Al_2O_3(s)+3Si(s)$	-719292.24+83.903T
⑤	$2SiO_2(s)+2Al(l)+Mg(l)=MgAl_2O_4(s)+2Si(s)$	-558519.12+56.689T
⑥	$MgO(s)+Al_2O_3(s)=MgAl_2O_4(s)$	—
⑦	$2MgO(s)+4Al(l)+3SiO_2(s)=2MgAl_2O_4(s)+3Si(s)$	—
⑧	$3Mg(l)+4Al_2O_3(s)=3MgAl_2O_4(s)+2Al(l)$	—
⑨	$3Mg(l)+Al_2O_3(s)=2Al(l)+3MgO(s)$	—
⑩	$SiC(s)=Si(l)+C(s)$	123470-37.57T
⑪	$Al_4C_3(s)=4Al(l)+3C(s)$	266520-92.3T

The calculation formula for the constant pressure and heat capacity is defined as [13]:

$$\Delta C_p = \Delta a + \Delta b \times 10^{-3}T + \Delta c \times 10^{5}T^{-2} + \Delta d \times 10^{-6}T^{2} \quad (1.)$$

Equation (1) is integrated to obtain a reaction process that function relationship is between ΔH^{θ} and temperature,

$$\Delta H^{\theta} = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} \times 10^{-3}T^{2} - \Delta c \times 10^{5}T^{-1} + \frac{\Delta d}{3} \times 10^{-6}T^{3} \quad (2.)$$

The equation (1) is divided by **T**, integrated, and multiplied by the temperature T, the obtained formula is subtracted by Equation (2). ΔG^{θ} is a function of temperature during the reaction.

$$\Delta G^{\theta} = \Delta H_0 + \Delta aT - \Delta aTlnT - \frac{\Delta b}{2} \times 10^{-3}T^{2} - \frac{\Delta c}{2} \times 10^{5}T^{-1} - \frac{\Delta d}{6} \times T^{3} \quad (3.)$$

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Here, ΔH_0 is the integral constant. The thermodynamic parameters a, b, c, d can be obtained from inorganic thermodynamic data sheet. The temperature of solidification processing SiC/Mg composites is generally between 700 - 1000K. Therefore, thermodynamics parameters a, b, c, d arechosen in the range of 700 -1000K.

3 Thermodynamics of interfacial products

3.1 Thermodynamic stability analysis of interfacial $MgAl_2O_4$

Reaction equations (5)-(8) show the possible way to generate$MgAl_2O_4$on the interfaces.
Equation (1) is satisfied the reaction equilibrium:

$$2\ln A_{MgO} - 2\ln A_{Mg} = -\Delta G_1^{\theta}/RT - \ln A_{Si} + \ln A_{SiO_2} \quad (4.)$$

Equation (5) is satisfied the reaction equilibrium:

$$\ln A_{MgAl_2O_4} - \ln A_{Mg} - 2\ln A_{Al} = -\Delta G_5^{\theta}/RT - 2\ln A_{Si} + 2\ln A_{SiO_2} \quad (5.)$$

$A_{MgAl_2O_4}$, A_{MgO}, A_{SiO_2} and A_{Al} are regarded as 1[14],and the following equations are referred as:

$$-2\ln A_{Mg} = -\Delta G_1^{\theta}/RT - \ln A_{Si} \quad (6.)$$

$$-\ln A_{Mg} = -\Delta G_5^{\theta}/RT - 2\ln A_{Si} \quad (7.)$$

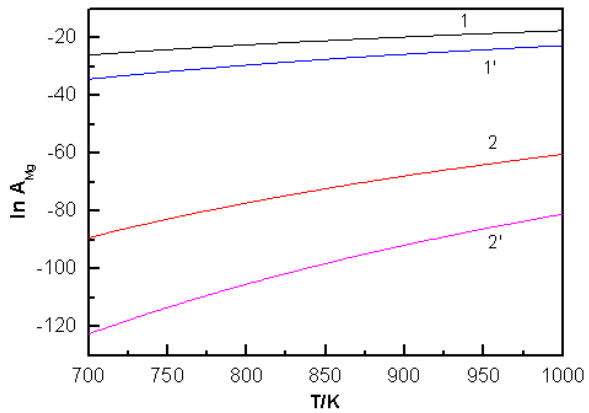

Fig. 1 Variations of the $\ln A_{Mg}$ value vs. the temperature as the maximum and the minimum A_{Si} in the interface

In **Fig. 1** the line 1 and 2 represents the value of A_{Mg}in the equilibrium when A_{Si}= 1corresponding to the Equation (6) and (7)at the different temperatures, respectively. Line 1'and 2' represent the value of A_{Mg} whenA_{Si}isthe minimum value according to the Equation (6) and (7).It is shown that the interfacial reaction is controlled by the Equation⑤ at a certain temperature when the mass fraction of Mg in the interfaces is corresponded to a certain value and the corresponding activity is below A_{Mg}^0 which is related to the line 1'.When a fraction of Mg in the interface is more than a certain value and the corresponding activity is more than A_{Mg}^0, the interfacial reaction is controlled by the Equation ①.The interface products of Mg, Al and SiO_2 are largely dependent on the Mg

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content [15]. When the mass fraction Mg is below8%, the interfacial reaction is controlled by the Equation⑤. When the mass fraction Mg is more than8%, the interfacial reaction is controlled by the Equation ① [16]. It is consistent with the present theoretical thermodynamic analysis.
Equation (4) is satisfied the reaction equilibrium:

$$2\ln A_{MgO} - 2\ln A_{Mg} = -\Delta G_1^{\theta}/RT - \ln A_{Si} + \ln A_{SiO_2} \quad (8.)$$

$$2\ln A_{Al_2O_3} - 4\ln A_{Al} = -\Delta G_4^{\theta}/RT - 3\ln A_{Si} + 3\ln A_{SiO_2} \quad (9.)$$

In the Equation (9), A_{Mg} and A_{Al} meets the following equilibrium:

$$2\ln A_{Al} - 3\ln A_{Mg} = -\Delta G_9^{\theta}/RT - 3\ln A_{MgO} + \ln A_{Al_2O_3} \quad (10.)$$

The $A_{MgAl_2O_4}$, A_{MgO}, A_{SiO_2} and $A_{Al_2O_3}$ are considered as 1[14],and taking the Equation (10) into the Equation(5). It can be obtained

$$4\ln A_{Al} = \Delta G_4^{\theta}/RT + 3\ln A_{Si} \quad (11.)$$

$$\frac{3}{8}\ln A_{Al} = \Delta G_5^{\theta}/RT - \Delta G_9^{\theta}/3RT + 2\ln A_{Si} \quad (12.)$$

In **Fig. 2** the line 3 and 4 represent the value of A_{Al} in the equilibrium when A_{Si}=1 corresponding to the Equation (11) and (12) at the different temperatures, respectively. Line 3'and 4' represent the value of A_{Al} when $A_{Si}$is the minimum value according to the Equation (11) and (12).
It is shown that the interfacial reaction is controlled by the Equation ④when the activity of Al is below A_{Mg}^0 which is related to the line 4' in the interface. The interfacial reaction is controlled by the Equation⑤ when the activity of Al is more than A_{Mg}^0 which is related to the line 4'in the interface. When the value A_{Al} is in the range of A_{Al}^0 and A_{Al}^1, the Equation④ and ⑤ occurs simultaneously. Both of A_{Al}^0 and A_{Al}^1 are the function of temperature.

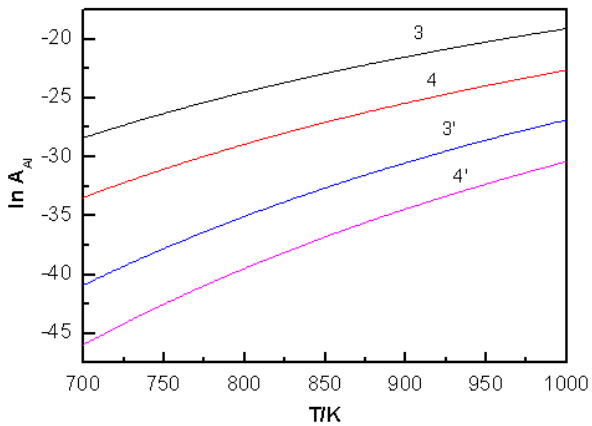

Fig. 2 Variations of theln A_{Al} value vs. the temperatures as the maximum and the minimum A_{Si} in the interface varies with temperatures

3.2 Thermodynamic Stability Analysis of interface Al_4C_3

The Al_4C_3 is generated in the Equation③ in the **Table 1**. At a certain temperature, it meets the equilibrium:

$$\Delta G_3^{\theta} = -RT\left(\ln A_{Al_4C_3} + 3\ln A_{Si} - 3\ln A_{SiC} - 4\ln A_{Al}\right) \quad (13.)$$

The activity of $A_{SiC}$and $A_{Al}$is considered as 1, and then:

$$\ln A_{Al_4C_3} + 3\ln A_{Si} = -\Delta G_3^{\theta}/RT \quad (14.)$$

The main factors affecting the generation of Al_4C_3 are temperature T and the activity of A_{Si}. The enhancing of Si activity can obviously suppress the formation of harmful interface reaction product Al_4C_3 [17]. At a certain temperature, $\ln A_{Al_4C_3}$ and $\ln A_{Si}$ expressed as the linear relationship in double commonly logarithmic coordinates [14].
In the decomposition reaction ⑩ of SiC, it is satisfied by the equilibrium:

$$\ln A_C + \ln A_{Si} = -\Delta G_{10}^{\theta}/RT \quad (15.)$$

Fig. 3 is the magnitude of $A_C \times A_{Si}$at the different temperatures, which is corresponding to the value of A_{Si}as$A_C = 1$, the value of A_C as$A_{Si} = 1$, or the minimum A_{Si} or $A_C$in SiC at different temperatures.
In the Equation⑪, the equilibrium formula of $A_{Al_4C_3}$and $A_C$can be expressed as:

$$3\ln A_C + 4\ln A_{Al} - \ln A_{Al_4C_3} = -\Delta G_{11}^{\theta}/RT \quad (16.)$$

When A_{Al} is regarded as 1, $A_{Al_4C_3}$ and A_C can be expressed as the linear relationship in the double commonly logarithmic coordinates. When the silicon is rich in the interface, the minimum of A_C obtained by the Equation (15) issubstituted into the Equation (16), and then it can get the minimum activity of a stable Al_4C_3 in the interface. In **Fig.4** it is shown that the lines AA' is represented by the linear relationship of $A_{Al_4C_3}$ and A_{Si} determined by the Equation (6) in the double commonly logarithmic coordinates as the temperature is ranged from 700K to 1000K. The zero point is represented by the minimum $A_{Al_4C_3}$ when a stable Al_4C_3 forms in the corresponding temperature determined by the Equation (16). Similarly, it represents the maximum value A_{Si}^0 for $A_{Al_4C_3}^0$ and A_{Si}.

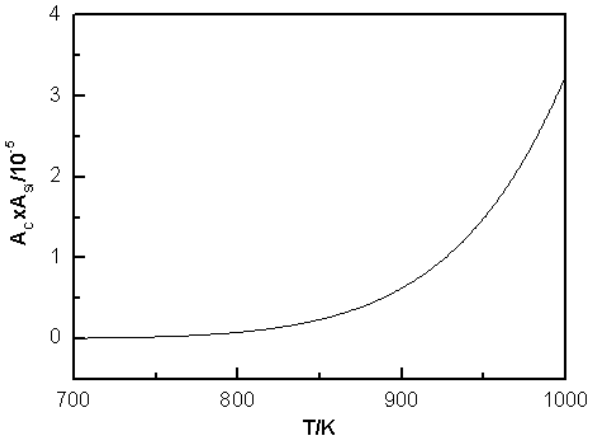

Fig. 3 The magnitude of $A_C \times A_{Si}$ with different temperatures

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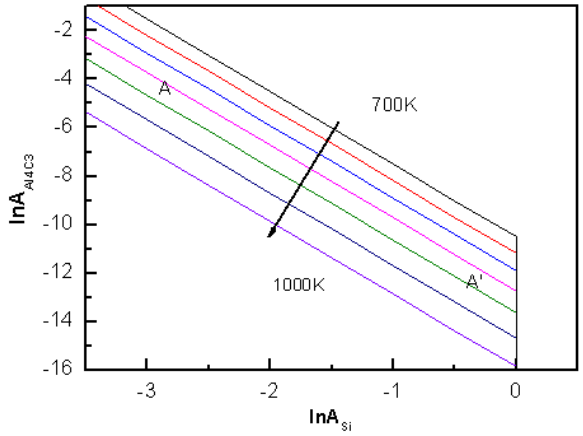

Fig. 4 The relationship of $\ln A_{Al_4C_3}$ and $\ln A_{Si}$ at the equilibrium temperatures

In the interfaces, there are several possible reaction models in the following.

I. When A_{Al} is less than a certain value of A^0_{Al} and A_{Mg} is more than a certain value of A^0_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid; Mg and Al are adsorbed and forms the MgO, Al_2O_3 and Si in the interface. Finally, MgO, Al_2O_3 are transformed into $MgAl_2O_4$, it will be desorbed from the interface.

II. When A_{Al} is greater than a certain value of A^1_{Al} and A_{Mg} is less than a certain value of A^0_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid. Mg and Al are formed into $MgAl_2O_4$, and Si will be desorbed from the interface.

III. When A_{Al} is greater than a certain value of A^1_{Al} and A_{Mg} is less than a given value of A^1_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid. Mg is adsorbed and reacted into MgO and Si in the interface, and then MgO and Al are reacted into $MgAl_2O_4$.

IV. When A_{Al} is less than a certain value of A^0_{Al} and A_{Mg} is more than a given value of A^0_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid. Al is adsorbed and reacted into Al_2O_3 and Si in the interface, then Al_2O_3 and Mg are reacted into $MgAl_2O_4$ and it will be desorbed from the interface.

V. When the value of A_{Al} is between A^0_{Al} and A^1_{Al}, A_{Mg} is greater than a certain value of A^0_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid. Mg and Al are adsorbed and reacted into MgO, Al_2O_3 and Si in the interface, and then MgO and Al will reacted into $MgAl_2O_4$.

VI. When the value of A_{Al} is between A^0_{Al} and A^1_{Al}, A_{Mg} is less than a certain value A^0_{Mg}, Mg and Al are diffused to the interface of SiO_2 and the liquid. Mg and Al are reacted into $MgAl_2O_4$ and Si in the interface and will desorb from the interface. At the same time, Al is adsorbed and reacted into MgO and Si.

The $MgAl_2O_4$ spinel phase can improve the bonding strength of the interface characteristics of Al-Mg-Si/SiC composites [18]. The interfacial reaction at the SiC/Al interface involved with the elements Mg, Al and O can be identified as $MgAl_2O_4$ spinel [11,19]. The case of oxidized SiC particles covered with a layer of SiO_2 is of advantage to control the formation of $A1_4C_3$ [20]. In the solidification processing of SiC/Al composites, SiO_2 generated by oxidative treatment of SiC surface will reacted into the spinel, Si, oxidation of Al and Mg, which can not only improve interfacial wettability of the SiC/Mg composite, but also the formation of Si can suppress the

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generation of Al_4C_3. Because the percentage of Si increases with the formation of Mg, Al oxide and spinel, it is difficult for the related react of Mg and Al in the interface.

4 Conclusions

1) When a stable Al_3C_4 forms in the interface, which is significantly dependent on $\mathbf{A_{Si}}$.There is a critical value of $\mathbf{A_{Si}^0}$.A stable Al_3C_4 cannot formed when $\mathbf{A_{Si}}$ is more than $\mathbf{A_{Si}^0}$. $\mathbf{A_{Si}^0}$ is not a constant, it increases with the temperature.
2) The mass fraction and distribution of SiO_2 in the interface have directly effects on the reactions of SiO_2 with Mg and Al. The reactions process and the ratio of products are greater affected by the interface activity of Mg and Al. There is a critical value of $\mathbf{A_{Mg}^0}$,$\mathbf{A_{Al}^0}$ and $\mathbf{A_{Al}^1}$, which increases with the temperature.
3) When the mass fraction of Si in the interface is greater than a critical value, there is no interfacial reaction at a certain temperature.

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