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Chemical reaction in Al matrix composite reinforced with SiC_p coated by SnO_2

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Reducing the extent of interfacial reaction in Al matrix composite reinforced with SiC particles during remelt-recycling is critical to its commercialization and sustainable-development. In this article, the remelting behavior of the composite with SnO_2 coating on SiC particles during the remelting was investigated by Differential Scanning Calorimeter (DSC) and the thermodynamic calculations. The results showed that SnO_2 coating could reduce the reaction during remelting of composites, but the effect was not obvious with remelting time increasing. In addition, the equilibrium Si content was predicted from Wilson equation and the result of prediction was consistent with the experiment. *© 2004 Kluwer Academic Publishers*

1. Introduction

Discontinuously reinforced metal matrix composites (DRMMCs) are very attractive in aerospace and automotive industry for their properties, such as high specific modulus, high specific stiffness, low coefficient of thermal expansion and good wear resistance [1–3]. Recently, there has been a growing interest in the recycling of metal matrix composites, due to the environmental factors [4, 5]. But unfortunately, all the theoretical and technological difficulties encountered in the manufacture and recycling of these materials are not solved entirely. For example, chemical interaction is still a major problem to be considered when these materials are recycled by remelting processing at high temperature.

SiC_p/Al DRMMCs fabricated by liquid phase methods are likely to be cost-effective in comparison with metal matrix composites produced by solid state processing [6, 7]. However, aluminum reacts with SiC to form aluminum carbide (Al_4C_3) based on the reaction as follows:

$$4Al + 3SiC = Al_4C_3 + 3Si \qquad (1)$$

The carbide (Al_4C_3) is water-soluble [8] and does great harm to the properties of the composites. Many investigations have been made to prevent the interfacial reaction [9–11]. As a result, fabrication and recycling of SiC_p/Al composites devoid of Al_4C_3 has been long one of the major concerns.

Among the solutions for the reduction of Al_4C_3 formation, surface treatment is likely to be an effective method, because this technique has some advantages as following [12]: low process cost, low temperature of heat treatment, high evenness of the films and widely possibility to vary film properties by changing the composition of solution and improving the wetting between SiC and liquid Al.

SnO_2 coating has many excellent properties such as chemical and thermodynamic stability [13, 14]. In addition, in comparison with other oxide coating, the coefficients of thermal expansion between SiC substrate and SnO_2 coating is very close, which are respectively $5.4 \times 10^{-6} \cdot K^{-1}$ and $4.0 \times 10^{-6} \cdot K^{-1}$ [15]. Therefore, it can be selected as a suitable coating for SiC reinforcement substrate.

However, the surface treatments on SiC particles are also dependent on the adequate combination of processing parameters during remelt-recycling, such as remelt-recycling temperature, holding time etc. Accordingly, knowledge of chemical reactions between surface treated reinforcement and the liquid matrix alloy is important for the recycling of SiC_p/Al composites.

The aims of the present work are to determine the chemical evolution during remelting and to emphasize the SnO_2 coating of SiC reinforcement upon the chemical reaction above the liquidus during remelting by means of Differential Scanning Calorimeter (DSC), Scanning Electron Microscopy (SEM), and thermodynamic calculations.

2. Experimental procedure

2.1. SnO_2 coating preparation

Sb:SnO_2 thin coating (the content of Sb is very low) obtained by sol-gel process has been given in previous papers [16, 17] and we only describe the main steps here. The solution was prepared by dissolving 16.74 g of $SnCl_2 \cdot 2H_2O$ in 200 ml absolute ethanol.

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The antimony solution was simultaneously obtained from a small amount of $SbCl_3$ dissolved in 40 ml absolute ethanol. Both mixtures were separately stirred and heated in a closed vessel, then the vessels were opened, and the solution was stirred and heated again, until the solvents were completely evaporated. We finally obtained two powders that were mixed in 100 ml of absolute ethanol. The doped mixture was finally stirred and heated at 50°C for 2 h.

The SiC particles were added into 100 ml absolute ethanol and stirred for homogenization. Then, they were mixed with the solution and stirred for 5 min. The particles coated with SnO_2 gel were obtained through filtering. Separating the agglomerate particles, the loose particles were first dried in air for 40 min at 150°C and then heated for 1 h at 500°C in air for densification. The coating is characterizd by the X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.2. Composite preparation

SiC_p/pure Al composites with 15 vol% uncoated and SnO_2 coated SiC particles were fabricated using Vacuum-high Pressure Infiltration Processing. The dominant phase of SiC_p as reinforcement was α-SiC and the average size was about 7 μm.

2.3. Remelting of SiC_p/pure Al composites

Silicon formed in the interfacial reaction gives rise to an Al—Si alloy and the resultant system of Al—C—Si can be approximated with the binary subsystem Al—Si below 1100°C. As indicated in Equation 1, the amount of Si released from the reaction is proportion to the extent of reaction of SiC particles. Silicon content can be determined by measuring the melting point from thermal analysis curves to evaluate the reaction of SiC particles. DSC is used to measure the liquidus temperature. The samples were cut into the disc of $\phi 4 \times 4$ mm and the composite samples were remelted in a high purity alumna pan in Netsch DSC404 instrument. Multiple runs were carried out at a heating rate 20°C/min from ambient to 850°C, holding 0 min, 10 min, 20 min, respectively, then cooling to ambient temperature at 20°C/min under dynamic high purity argon atmosphere(80 ml/min), and high purity corundum was used as a reference. All DSC thermograms were normalized to the actual amount of metal (at.%) in each composite.

3. Results and observations

Fig. 1 shows a XRD profile of coated SiC particles. It is shown that the phase of SnO_2 was formed successfully by means of the sol-gel method mentioned above. The result also indicates that the amount of SnO_2 is very low and it cannot affect the liquidus temperature during later remelting.

Fig. 2 shows SEM micrograph of SnO_2-coated SiC particles and corresponding X-ray elemental images of Si and Sn, which indicates the distribution of SnO_2 on SiC surface. As seen in Fig. 2c, Sn is distributed evenly and sparsely on the surface of SiC and its content is very low. From the result of Terrier [16], the thickness of SnO_2 coating is about 100 nm by this sol-gel method.

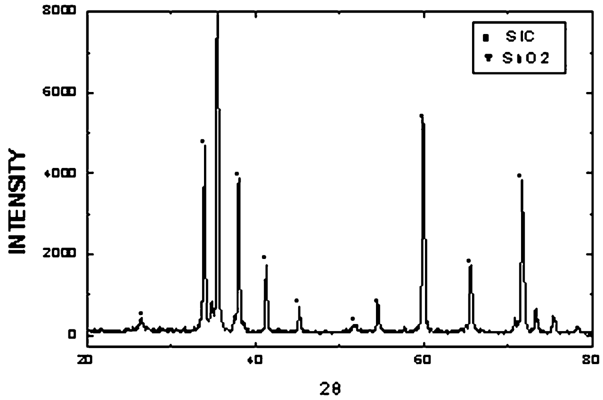

Figure 1 The XRD profile of SnO_2 coated SiC particles.

Fig. 3 shows the microstructures of the composites fabricated by Vacuum-high Pressure Infiltration process. The result indicates that the SiC particles were distributed evenly in the Al matrix. The result shows that in general, SiC particles in the Al matrix is well distributed. Hence, it also can be deduced that the liquidus temperatures of SiC_p/Al composites during later remelting will not be influenced by the reinforcement conglomeration.

Fig. 4 shows the heating curves of uncoated and SnO_2 coated SiC/Al composites during remelting at 850°C. As seen in Fig. 4, only one peak, which is the melting of primary aluminum, occurs in each curve. Two curves begin at 627°C, 632°C, respectively, and end at 702°C, 705°C. The matrix alloys become completely molten at 666 and 676°C, which is the temperature that the melting of alloy reaches its maximum. It is well known that the melting point of aluminum is 660°C, while the eutectic temperature is 577°C in binary Al—Si system and maximum solubility of Si in solid is 1.65 at.%. Both the results indicate whether SiC particles are coated with SnO_2 or not, the chemical reaction between SiC and Al is less serious.

Fig. 5 shows the cooling curves of uncoated and SnO_2 coated SiC/Al composites during remelting at 850°C. Two peaks are observed in each curve. In the cooling curves, the first peak at about 590°C represents the melting of primary Al and the second peak at about 550°C is considered as the melting of Al—Si eutectic phase. From the Fig. 5, the liquidus temperature of uncoated SiC/Al is about 10°C lower than that of the SnO_2 coated SiC/Al, and the eutectic heat in the first cooling trace of uncoated SiC/Al is much greater than that of SnO_2 coated SiC/Al. Therefore, from the Al—Si alloys phase diagram, it is concluded that the Si content of SnO_2 coated SiC/Al composites is lower than that of uncoated SiC/Al composites after remelting at 850°C. Both the results suggest that the extent of interfacial reaction of uncoated SiC/Al composites is greater than that of SnO_2 coated SiC/Al composites.

Figs 6 and 7 show the cooling curves remelted at 850°C and holded for different times in uncoated

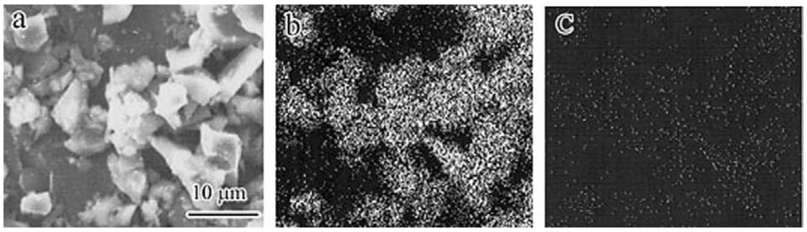

Figure 2 (a) SEM micrograph of second phases in SnO_2 coated SiC particles and corresponding X-ray elemental images of (b) Si; and (c) Sn.

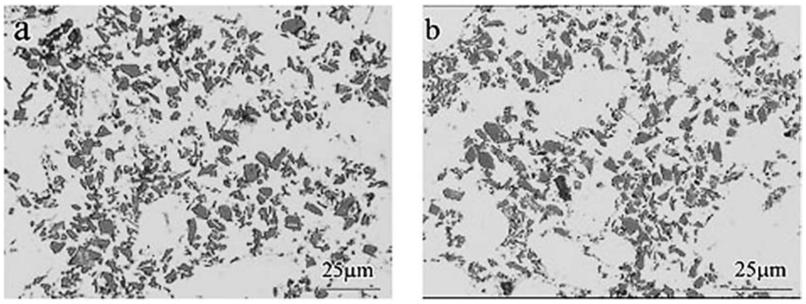

Figure 3 Metallograph of SiC_p/Al composites: (a) with uncoated SiC particles and (b) with SnO_2 coated SiC particles.

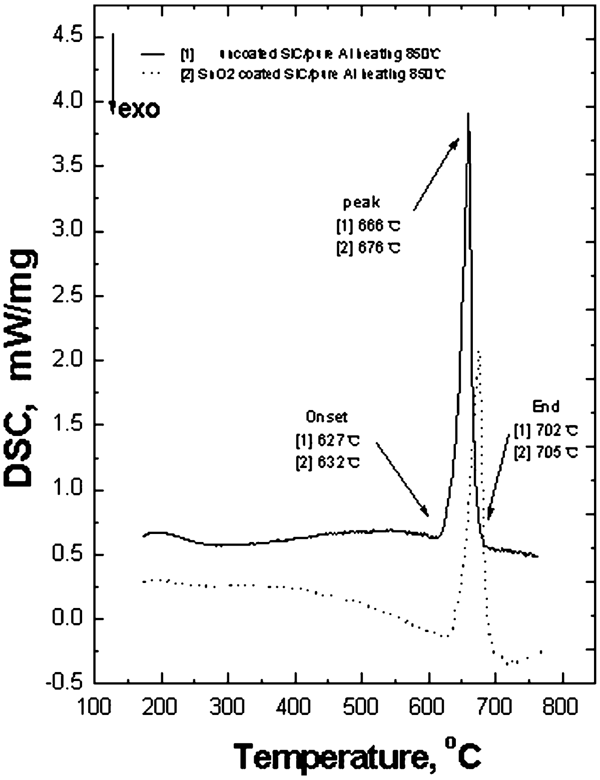

Figure 4 Dsc heating curve of uncoated and SnO_2 coated SiC/Al composites remelted at 850°C.

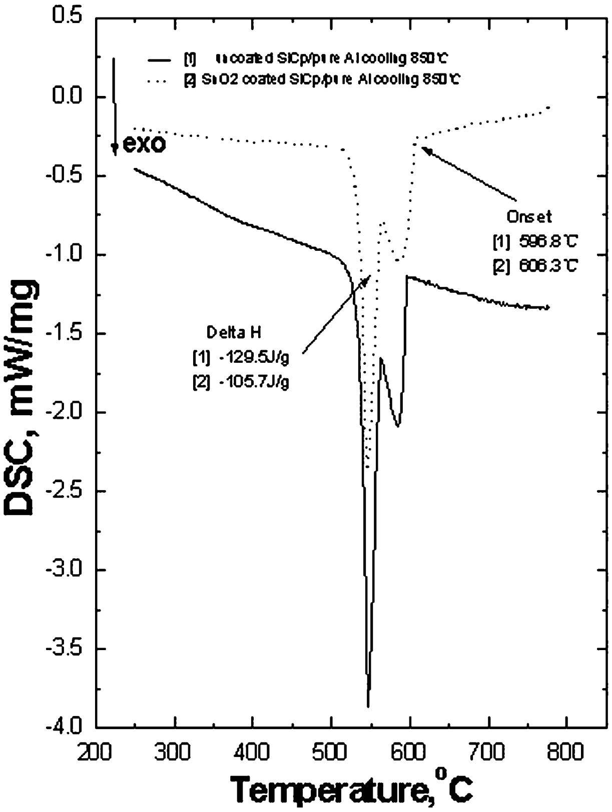

Figure 5 DSC cooling curve of uncoated and SnO_2 coated SiC/Al composites remelted at 850°C.

SiC/Al and SnO_2 coated SiC/Al composites, respectively. As indicated in Fig. 6, the liquidus temperatures of three cooling traces are 596.8, 592.2 and 587.5°C, respectively, and the eutectic heat increases from 129.5 J/g, 130.6 J/g to 150.2 J/g. As indicated in Fig. 7, the liquidus temperatures of three cooling traces of SnO_2 coated SiC/Al are 606.3°C, 598.1°C and 592.0°C, respectively. At the same time, the eutectic heat increases from 105.7 J/g, 156.6 J/g to 160.7 J/g, which indicates that the interfacial reaction is also serious and the eutectic heat of SnO_2 coated SiC_p/Al composites is more than that of uncoated composites with the remelting time increasing at 850°C. Therefore, it suggests that the reaction can exist as

$$Al + SnO_2 \rightarrow Al_2O_3 + Sn \qquad (2)$$

Fig. 8 shows the evolution of the interfacial reaction in uncoated SiC_p/Al and SnO_2 coated SiC_p/Al composites remelted at 850°C and holded for different times. The results indicate that the interfacial

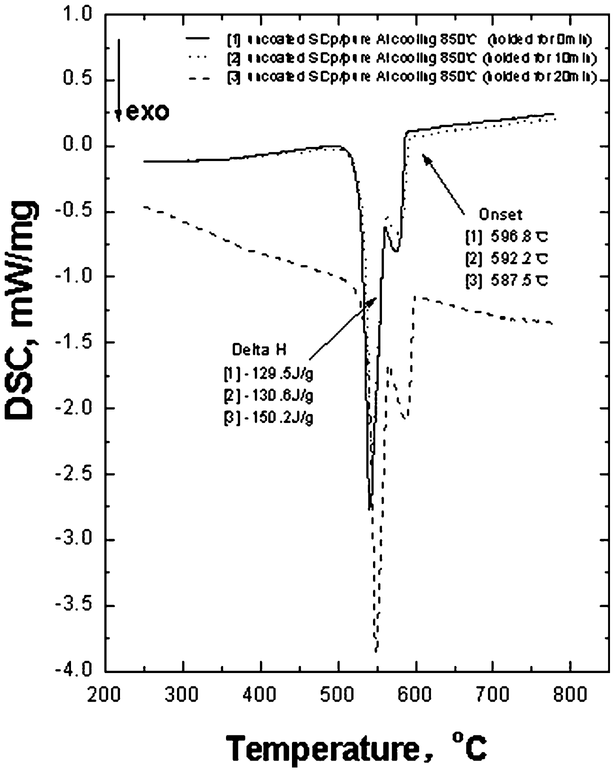

Figure 6 The cooling curve of uncoated SiC_p/Al composites remelted at 850°C and holded for different times.

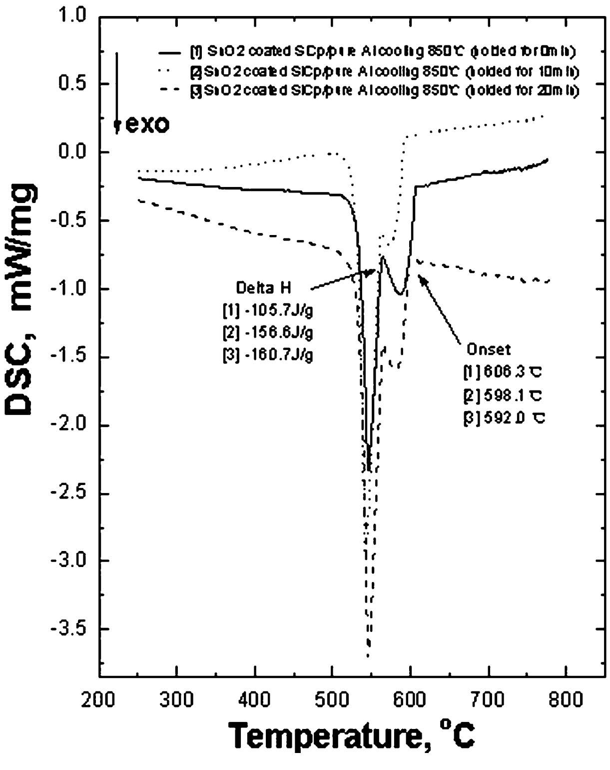

Figure 7 The cooling curve of SnO_2 coated SiC_p/Al composites remelted at 850°C and holded for different times.

reactions increase with the increasing of holding time both in uncoated SiC_p/Al and SnO_2 coated SiC_p/Al composites, but the SnO_2 coating can suppress the interfacial reaction, compared with SiC particles without coating.

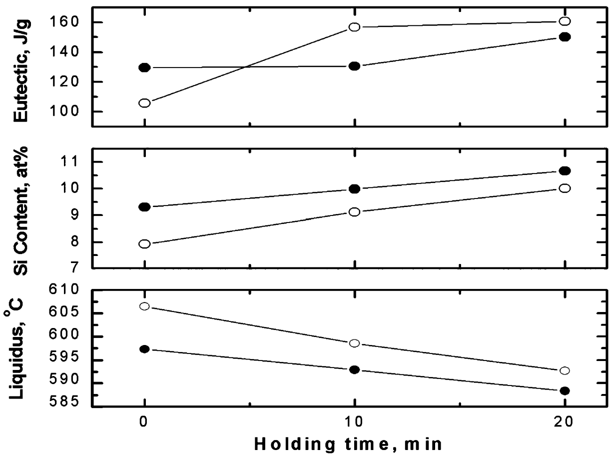

Figure 8 The evaluation of interfacial reaction in (●) uncoated and (○) SnO_2 coated SiC_p/Al composites remelted at 850°C and holded for different times.

4. Discussion

From the experimental result, it can be concluded that SnO_2 coating is effective on reducing the content of the interfacial reaction between SiC and Al when the remelting holds for some time. However, with the increase of holding time, the reaction extent obviously rises. The kinetic mechanism of this reaction with SnO_2 coating can be discussed here. When SnO_2 coated SiC/Al composite is remelted at 850°C, at the beginning stage the interface is considered as $Al/SnO_2/SiC$, and SnO_2 coating could make a thermodynamic barrier between SiC and molten Al. However, the molten aluminum can slowly diffuse through the SnO_2 coating and attack SiC particles. Hence, when the holding time for remelting increases, Al can break through SnO_2 barrier and become easier to react with SiC particles.

Si formed in the interfacial reaction is important to suppress the reaction and when the reaction reaches balance, the ultimate Si content can be determined by thermodynamic equilibrium.

The interfacial reaction given by Equation 1, when occurring at liquid state, can be rewritten in a general form as equation [18]

$$4\{\mathrm{Al}\}_{(\text{in Al alloy})} + 3\langle \mathrm{SiC}\rangle = \langle \mathrm{Al_4C_3}\rangle + 3\{\mathrm{Si}\}_{(\text{in Al alloy})} \tag{3}$$

where ⟨ ⟩ and { } denote the solid and the liquid phase.

According to the Gil-Huf equation, the free energy change associated with the interfacial reaction can be expressed as

$$\Delta G = RT \ln \frac{\alpha_{\mathrm{Si}}^3}{\alpha_{\mathrm{Al}}^4} + \Delta G^{\mathrm{f}}_{\mathrm{Al_4C_3}} - 3\Delta G^{\mathrm{f}}_{\mathrm{SiC}} + 3\Delta G_{\mathrm{Si}}^{\mathrm{D}\to\mathrm{liquid}} \tag{4}$$

where α_{Al} and α_{Si} are the activities of Al and Si in the Al alloy matrix, and $\alpha = x\gamma$, x represents the atom ration and γ, the activity coefficient. $\Delta G^{\mathrm{f}}_{\mathrm{Al_4C_3}}$ and $\Delta G^{\mathrm{f}}_{\mathrm{SiC}}$ are the free energy change associated with the formation of α-SiC and Al_4C_3, $\Delta G_{Si}^{D\rightarrow liquid}$ is the free energy change associated with the phase transformation of the solid Si having a diamond crystallographic structure into the liquid phase.

Therefore, if the values of γ_{Al} and γ_{Si} are known, the relation of ΔG with the Si content can be obtained. The necessary thermodynamic data $\Delta G^{f}_{Al_4C_3}$, ΔG^{f}_{SiC} and $\Delta G_{Si}^{D\rightarrow liquid}$ can be obtained in the reference [18].

By Wilson equation [19], the activity coefficient of a component is determined as

$$\ln \gamma_i = -\ln\left(1 - \sum_j x_j A_{j/i}\right) + 1 - \sum_j \left[\frac{x_j(1 - A_{i/j})}{1 - \sum_k x_k A_{k/j}}\right] \quad (5)$$

where x_i = molar fraction of component i and $A_{i/j}$ is an adjustable parameter as

$$A_{i/j} = 1 - \frac{V_j}{V_i} e^{-(g_{ji} - g_{ii})/kT} \quad (6)$$

where V_j is molar volume of component j, g_{ij} is proportional to the interaction energy between atoms i and j, and $g_{ij} = g_{ji}$. In most cases, g_{ij} is a constant independent of the temperature. Therefore, when $(g_{ij} - g_{ii})$ and $(g_{ji} - g_{jj})$ are known, $A_{i/j}$ and $A_{j/i}$ at different temperatures can be determined.

In a binary alloy system, Equation 5 becomes, after rearrangement of terms

$$\ln \gamma_1 = -\ln(1 - A_{2/1}x_2) + x_2\left[\frac{x_2 A_{1/2}}{1 - A_{1/2}x_1} - \frac{x_1 A_{2/1}}{1 - A_{2/1}x_2}\right] \quad (7a)$$

$$\ln \gamma_2 = -\ln(1 - A_{1/2}x_1) + x_1\left[\frac{x_1 A_{2/1}}{1 - A_{2/1}x_2} - \frac{x_2 A_{1/2}}{1 - A_{1/2}x_1}\right] \quad (7b)$$

Therefore, the activity coefficient γ can be calculated when the values of $A_{1/2}$ and $A_{2/1}$ are known at some temperatures.

Tarby [20] has stated that the values of $A_{1/2}$ and $A_{2/1}$ for each binary system were that values which produced the minimum root-mean-square deviation between experimental and calculated activities.

As seen in Fig. 9, according to the available data about activities measured in the previous article [21], the fitting parameters $A_{Al/Si}$ and $A_{Si/Al}$ at 1427°C can be obtained as:

$$A_{Al/Si} = -3.2955$$

$$A_{Si/Al} = 0.9990$$

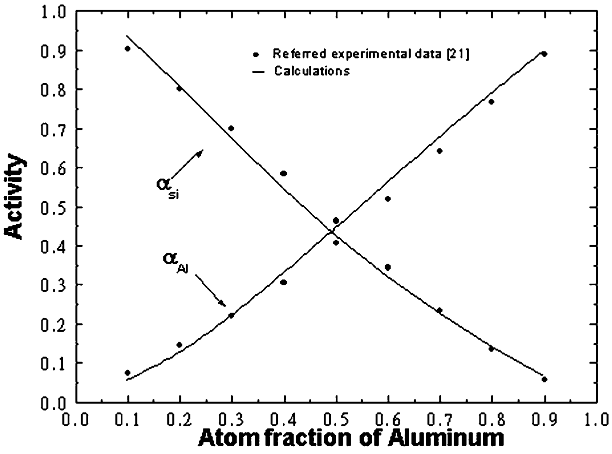

Figure 9 Activity in liquid Al—Si alloys at 1427°C.

Therefore, according to Equation 6, $(g_{Al-Si} - g_{Al-Al})$ and $(g_{Si-Al} - g_{Si-Si})$ can be calculated:

$$g_{Al-Si} - g_{Al-Al} = -19.965 \text{ KJ/mol}$$

$$g_{Si-Al} - g_{Si-Si} = 163.330 \text{ KJ/mol}$$

Then, at 850°C, the values of $A_{Al/Si}$ and $A_{Si/Al}$ can be calculated as:

$$A_{Al/Si} = -7.1872$$

$$A_{Si/Al} = 1.0000$$

Hence, according Equations 4 and 7, the relation of ΔG with Si molar fraction during remelting of SiC_p/Al composites at 850°C can be obtained as seen in Fig. 10. It indicates that the Si content is 10.9 at.% when the interfacial reaction reaches the equilibrium ($\Delta G = 0$). Although the result was a little higher than that (10.3 at.%) of the experiment, considering that the remelting time was not enough, it was in good agreement with the experiment.

Several studies [2, 22–26] have been made to predict the meta-equilibrium silicon content under different temperature, but obviously they were not in completely good agreement with each other, as seen in Fig. 11. From present work, the equilibrium Si content can be obtained as a function of remelting temperature as seen in Fig. 11.

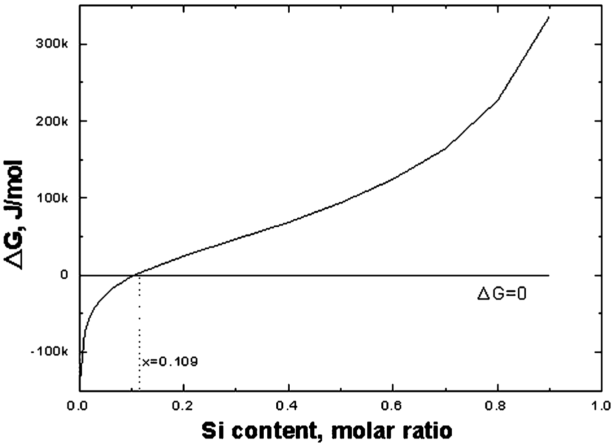

Figure 10 The relation of Gibbs free energy with the Si molar fraction In SiC_p/Al composites at 850°C.

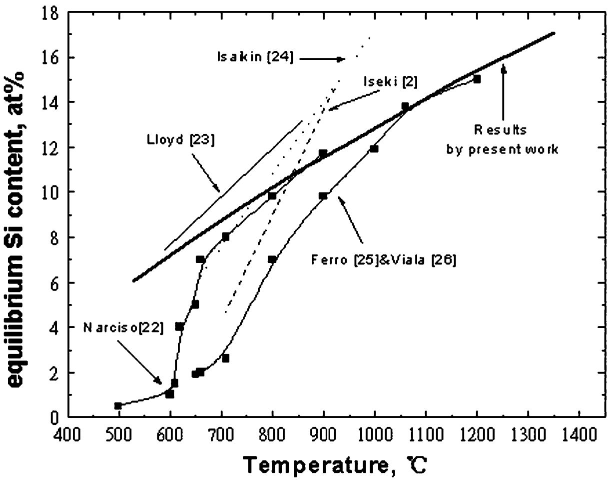

Figure 11 Variation in the equilibrium Si content in SiC/Al composites plotted as a function of temperature.

5. Conclusions

Compared with the uncoated SiC_p/Al composites, when the remelting time is short, SnO_2 coating on SiC particles by the so-gel process can effectively reduce the interfacial reaction during the remelting of the composites at 850°C. However, with the remelting time increasing, the effect of SnO_2 coating is not obvious.

The Gibbs free energy of interfacial reaction can be calculated with the variation of the Si contents, and therefore the equilibrium Si content can be known when the reaction reaches balance ($\Delta G = 0$). Further, the equilibrium silicon content can be predicted as the function of remelting temperature.

Acknowledgements

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