

## Optimization of SiCp Surface and Interface Structure of SiCp/A390 Composites

Ai-qin Wang<sup>a 1,2,\*</sup>, Hui-dan Guo<sup>b 1,2</sup>, Min Li<sup>c 3</sup>, Jing-pei Xie<sup>d 1,2</sup>, and Dou-qin Ma<sup>e1,2</sup>

<sup>1</sup>College of Material Science and Engineering, Henan University of Science and Technology, Luoyang 471023, China,

<sup>2</sup>Collaborative Innovation Centers of Non-Ferrous Materials, Henan Province, Luoyang 471023, China,

<sup>3</sup>Shine Tech CO., LTD Zhejiang Province, Zhejiang Province, Jiaxing 314000, China.

<sup>a</sup>aiqin\_wang888@163.com

\*Corresponding author

**Keywords:** Composite Materials, Surface Modification, Powder Metallurgy Method, Interface Structure, Interface Reaction

**Abstract:** SiCp/A390 (SiC particle reinforced Al matrix) composites before and after SiC particles surface modification were manufactured respectively by powder metallurgy, and the mass fraction of SiCp is 20%. The surface morphology of SiCp and the interface morphology of SiC/Al and SiC/Si of composites were characterized by TEM. The chemical state of interface material of SiCp/A390 composites was tested by XPS. The effect of surface modification of SiCp on interface structure of composites and thermodynamic principle of mechanism of interface formation of SiCp/A390 were researched. The results show that SiCp morphology was changed though surface optimization treatment, the dense SiO<sub>2</sub> oxide layer on the surface of SiCp was formed when SiC particles were roasted at 1000°C, which thickness membrane is about 50 nm. Before SiC particles surface modification, the interface of SiC/Al of composites is clear, clean interface, and discovered a small amount of amorphous layer interface of SiC/Al. While, after SiC optimization, the interface of SiC/Al of composites is an amorphous layer between two phases, and there is no Al<sub>4</sub>C<sub>3</sub> in SiCp/A390 composites. Surface modification treatment of SiCp can increase chemical reaction degree of the interface of composites, and effectively improve the interface bonding of SiC and Al.

### Introduction

SiCp reinforced Al metal matrix composites present a remarkable combination of outstanding advantages, such as low density and good dimensional stability, high elastic modulus, and are widely applied in spacecrafts, military industry and electronic components as lightweight structural materials [1]. Over the last two decades, the medium volume fraction SiCp/Al composites have become a hot spot research [2-3]. The composition and microstructure of composite materials decide materials performance. As a carrier of load, the interface between reinforced particles and matrix in composite materials has played a vital role on the performance of the composite material. The interface characteristics of the specific component composite materials would be affected by the morphology of reinforced particle, surface properties, preparation methods of composite materials and heat treatment process, etc. In order to control harmful interface reaction, SiC reinforced particles were preprocessed by some methods, when SiCp/Al composite material was prepared using liquid phase or semi-solid method. In several pretreatment methods of SiCp, the effects of dilute HCl wash and high temperature oxidation were better, and the reports about them were more. Guo Jian[4] et al. have studied the effect of pre-heating processing of SiC particles on porosity of SiCp/Al composites, which are manufactured by stirring casting composition means, by heating SiCp at 600 °C and heat preservation for 3 h. And they found that SiCp after oxidation treatment is uniform distributed in SiCp/Al composites, interfaces divide into two kinds: clean

interface and mild reaction interface, meanwhile avoiding the generation of harmful interface product Al<sub>4</sub>C<sub>3</sub>. Wang Chuan-ting [5] et al. studied the influence of SiCp oxidation on the wettability and interface bonding of composite material which are prepared by casting, and found that When SiCp is heated at 800-1100 °C, a certain thickness layer of SiO<sub>2</sub> forms on its surface. And interface reaction will form between melt aluminum and oxide layer under high temperature, which can improve the interfacial wettability, make the interface combination to be better. Meanwhile, MgAl<sub>2</sub>O<sub>4</sub> and Mg<sub>2</sub>Si generate near the interface, and no harmful product Al<sub>4</sub>C<sub>3</sub> founded.

Many investigations about the pretreatment technology of SiCp have been reported. However, the research about microstructure change and phase composition of SiCp surface before and after oxidation and interface microstructure evolution of SiCp/Al-Si composite by powder metallurgy have been rarely reported [6]. In this article, the morphology and the surface phase chemical composition of SiCp under different processing methods have been characterized by TEM and XPS, and the interface materials chemical state of SiCp/A390 composites was also tested by XPS. In those contexts, the influence of SiCp surface optimization on interface structure of SiCp/A390 composites and the principle forming the thermodynamic mechanism of composite interface have been studied deeply. Overall, the aim of this paper is to provide the theoretical basis engineering application and technical support for lightweight, low expansion and high strength aluminum matrix composites.

## Materials and Methods

The matrix alloy used in this investigation is A390 (wt19.3% Si, 1.2% Cu, Mg, 0.8% Mg, 0.5% Ni) and reinforcement is SiC particle. The average particle size of A390 alloy power and SiC particles is 10 μm and 5μm, respectively. The volume fraction of SiC particles in the composites is 20%. After water washing processing, in order to remove impurity (instance water vapor and carbon element), SiCp would be heated to 650 °C and kept for 2 h, and then weighed. SiC particles were calcinated at a temperature of 1000 °C in a high temperature oxidation furnace, with a heating rate of 10°C/min, holding time of 6 h. To ensure the high temperature oxidation reaction conduct adequately, furnace would be opened for oxygenating every half hour during roasting. Then, used the QM - BP type planetary ball mill, the A390 alloy power and SiC particles were ball-mixed in a high-speed planetary mill for 4 h with the rotation speed of 250 rpm, and the weight ratio of ball and powder was 2:1. Then the mixtures (about 100 g) were pressed by employing TTD32 four-column hydraulic, with a pressure of 200 MPa, holding time of 50 min, unloading time of 20 min. First, the semi-finished products were sintered in the nitrogen protection furnace by furnace cooling, with a heating rate of 2 °C/ min, holding temperature of 560 °C, holding time of 3 h. Next, the sintered lumps were extruded by XJ-500 metal profile extrusion machine, with an extrusion ratio of 15:1, extrusion temperature of 480 °C, extrusion speed of 1 mm/s. At last the SiCp/Al composite materials were dealt with annealing treatment at the temperature of 400 °C for 2 h. Microstructure was observed by transmission electron microscopy (TEM) and the material phase chemical state of SiCp surface before and after oxidation and composite material interface structure was studied by X-ray photoelectron spectroscopy (XPS). Analyses on the surface optimization of SiC particles and its effect of interface structure of SiCp/A390 composites were carried out.

## Results and Discussion

### Microstructure and Chemical State Analysis of SiC Particle Surface

TEM images and the corresponding diffraction pattern of original and treated SiC particle surface are shown in Fig.1. It can be seen that the original SiC particle surface was clean, with relatively obvious edges and corners. Its contrasts obvious and is the typical crystal structure, seen Fig.1 (a). The original state SiCp diffraction pattern was calibrated as close the six-party α-SiC, space group as P63mc (186), the lattice constant for  $a = 3.081 \text{ \AA}$ ,  $c = 15.120\text{\AA}$ , each (001) crystal plane containing six stacking, its orders for ABCACB, each stacking interplanar spacing as 0.25 nm.

Another diffraction pattern of SiCp in the test was the cubic system  $\beta$ -SiC, space group for F - 43 m (216), the lattice constant for  $a = 4.359 \text{ \AA}$ , stacking order for ABCABC..... The treated SiC particle surface is smoother compared with that of original SiC particle surface, as shown in Fig.1 (b). And a thickness of 50 nm material is generated on the particle's surface, and its diffraction spot is dizzy ring, indicating that the material is amorphous, which convicted preliminary to be  $\text{SiO}_2$  according to the thermodynamic information of SiCp.

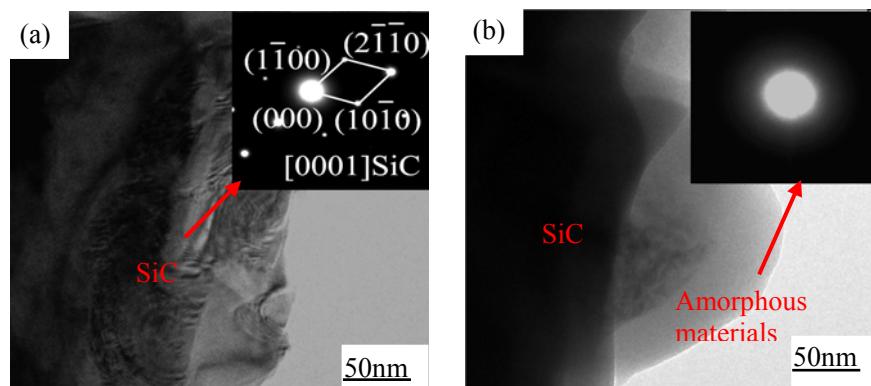


Fig.1 TEM of and diffraction pattern of SiC particles

(a) TEM original state SiC particles, (b) TEM and diffraction pattern of oxidized SiC particles

The material could not be detected by XRD when the content is less than a certain value, so XPS was carried out to identify the material compositions on the SiC particle surface. SiCp was analyzed all the components after vacuum treatment, then Si element was scanned accurately. XPS data was analyzed using Multipak peak software, correction data in a standard free C with the binding energy of 284.6 eV points, peaking and fitting each element separately again. Fig.2b shows the XPS survey spectrum of original SiC particulates. Three peaks were appeared in the full spectrum, peak 100.2 eV, 101.3 eV and 100.2 eV after data fitting. According to the NIST XPS Database, standard binding energy of SiC and Si are 100.1 eV and 101.3 eV, respectively. Thus, the original state of SiC surface has no  $\text{SiO}_2$ , which mainly existed in the form of SiC and handful instability SiO, shown as Fig. 1. Fig. 2b shows the XPS survey spectrum of original SiC particulates. By Si 2 p line of surface optimization SiCp, The binding energies of peaks are located at 101.5 eV and 103.6 eV, which correspond to the standard binding energy of SiC and SiO for 101.3 eV and 103.4eV. Therefore, it can be concluded that Si in the reaction layer mainly existed in the form of the SiO and  $\text{SiO}_2$ , and  $\text{SiO}_2$  peak area was biggest. From peaking and fitting analysis results, mole ratio of atom of  $\text{SiO}_2$  and the SiO was 96.31:3.69. So the reactant of surface optimization SiCp mainly was  $\text{SiO}_2$ .

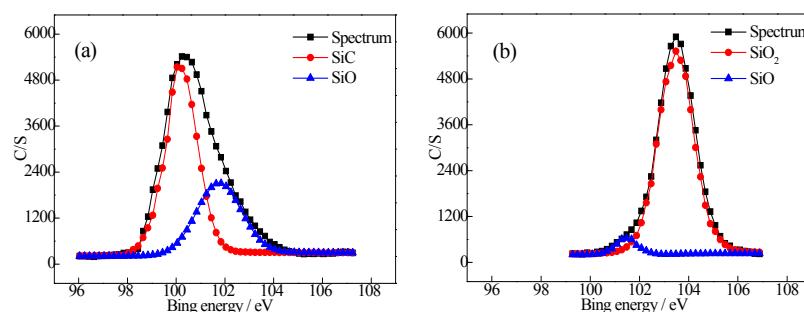


Fig.2 XPS analysis of SiC particles

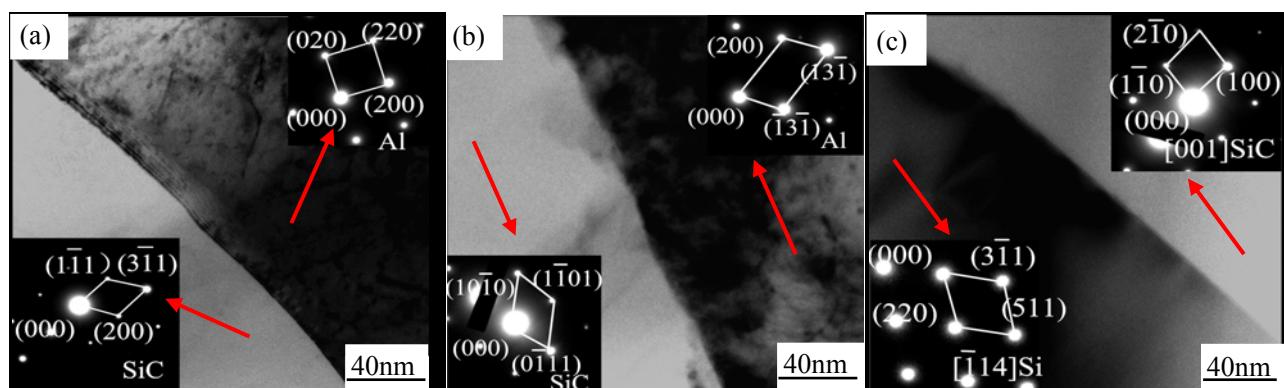
(a) Si2P peak of original SiC particles; (b) Si2P peak of oxidized SiC particles

## Influence of Surface Optimization of SiCp on Interface of SiCp/A390 Composite

The interface between the SiC and A390 of SiCp/A390 composites, which prepared by powder metallurgy with solid solution and aging treatment, was observed by TEM, shown as Fig.3. By plenty of observation showed that, there are two main types interface of the original state SiCp/A390 composite. The interface is clean and smooth, and there are no obvious interface chemical reaction and particle dissolution phenomena as well as cavity defects, seen Fig.3 (a). Fig.3 (b) shows another interface type is amorphous type interface, which existing several nanometers wide interface layer between the matrix and the reinforcement. The thermal expansion coefficient of SiCp and Al respectively were  $4.7 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  and  $25 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  at room temperature. Al matrix near SiCp has a high density of dislocations due to the vast different thermal expansion coefficient between the SiCp and Al. The thermal stress between matrix and strengthen body was produced because of large deformation, or large temperature difference from high temperature cooling to room temperature, during the preparation of composite materials. And dislocation loops are released to Al matrix, which forming a large number of dislocations, when thermal stress exceeded the yield strength of the matrix. Fig.3 (c) shows the clean interface of SiC/Si of original state composite. Si precipitation is precipitated when composite materials are sintered, which forming a large number of SiC and Si interface, and the interface is clean, flat and no obvious interface reaction, shown as Fig.3 (c). The diffraction patterns of  $\text{Al}_4\text{C}_3$  and  $\text{MgAl}_2\text{O}_4$  as described in the literature [7, 8] haven't been found in SiC/Al interface of original state SiCp/A390 composites. Maybe, this interface reaction can't occur because of low temperature during powder metallurgy process, or the matter content was less special. Therefore, that should go on further research.

Based on plenty of comparison and analysis, SiC/Al interface of SiCp/A390 composites are also divided into two types after interface optimization processing. The one is an amorphous layer interface, accounted for the vast majority in the surface optimization SiCp/A390 composites, which has about 5 nm interface thickness between Al and SiC, seen Fig.3 (d). Another is obvious reactive interface, which has about 10 nm reaction interfaces between Al and SiC, shown as Fig.3 (e). It is too difficult to select the appropriate area to diffract the analysis interface structure since the interface zone width is small. A density  $\text{SiO}_2$  layer is founded on the optimization surface of SiCp, and it can react with Al and Mg (which is easily gathered at the interface) to generate magnesium aluminum spine ( $\text{MgAl}_2\text{O}_4$ ), according to the research of LiuPei [9].

As shown in Fig.3 (f), the interface of SiC and Si in optimization SiCp/A390 composites is also clean interface type. Namely, the surface optimization of SiCp changes the interface structure type of SiCp/A390 composites. The clean interface of most of the original SiCp / A390 composites is converted into the amorphous interface of the oxidation state. The surface optimization of SiCp was less effect on the interface structure type of SiC and Si interface of SiCp/A390 composite. SiC particles stating in the optimum conditions have little effect on the interface in composite materials.



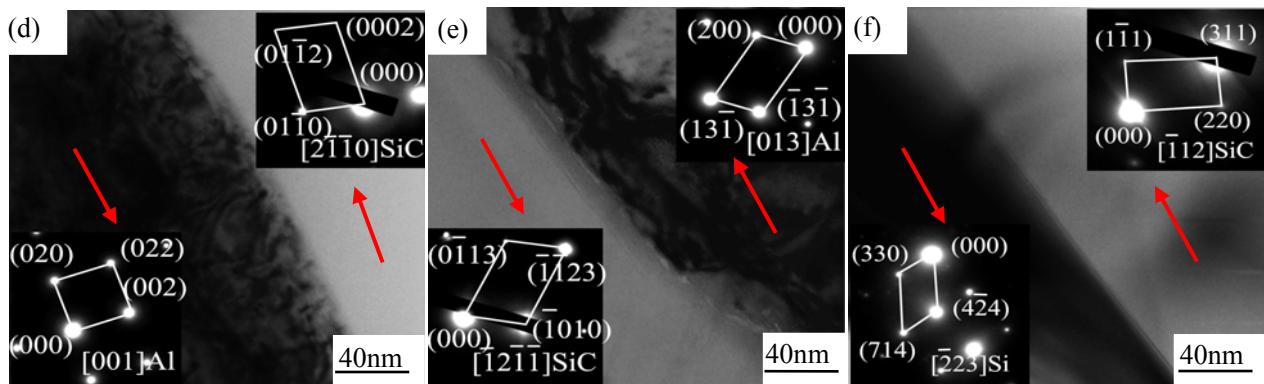


Fig.3 TEM of SiC/A390 composites;

(a) The clean interface of SiC/Al of original state composite; (b) The amorphous interface SiC/Al of original state composite; (c) The clean interface of SiC/Si of original state composite; (d) The amorphous interface of SiC/Al of oxidized state composite; (e) The reaction interface of SiC/Al of oxidized state composite; (f) The clean interface of SiC/Si of oxidized state composite

### **Effect of Surface Optimization Chemical Speciation of Interface Materials of SiCp/A390 Composites**

TEM analysis has certain limitations to test a small amount of interface material, so it is better use X-ray photoelectron spectroscopy (XPS) analysis to explore the formation mechanism of the interface microstructure and composite interface bonding mechanism [9]. Full spectrum diagram (Fig.4 (b)) of original state SiCp/A390 composites shows that element Al, Si and C, O exist on the fracture interface, Mg element is relatively small, and is not shown. From 2p points peak fitting chart of Al, there are two peaks at 72.8 eV and 74.6 eV, its corresponding the binding energy of Al (2p peak combined energy is 72.6 eV) and  $\text{Al}_2\text{O}_3$  (2p peak combined energy is 74.4 eV) according to the NIST XPS Database. XPS test on the material surface chemical state can qualitative analysis, content can be semi-quantitative analysis, shows the ratio of Al and  $\text{Al}_2\text{O}_3$  is 91:9. Brittle phase  $\text{Al}_4\text{C}_3$  (its 2p peak combined energy is 73.6 eV) in the spectrogram has not been found, probably because the sintering temperature in powder metallurgy method relative to the liquid phase method is low, and harmful interface reaction doesn't produce. Oxygen in the  $\text{Al}_2\text{O}_3$  may come from the substrate A390 alloy powders, not the interface enhancement and chemical reaction according to TEM (Fig.1 (a,b)) of the surface of original state SiCp, and a small amount of the amorphous interface in the composite (Fig. 3b) may be the  $\text{Al}_2\text{O}_3$  that formed by oxidation of matrix alloy. There are two peaks at 99.9 eV and 100.4 eV, respectively corresponding to the binding energy of Si (2p peak combined energy was 99.8 eV) and SiC (2p peak combined energy is 100.4 eV) by 2p points peak fitting chart of Si (Fig. 5(c)), namely, the existence form of Si are Si that separate out and SiC.

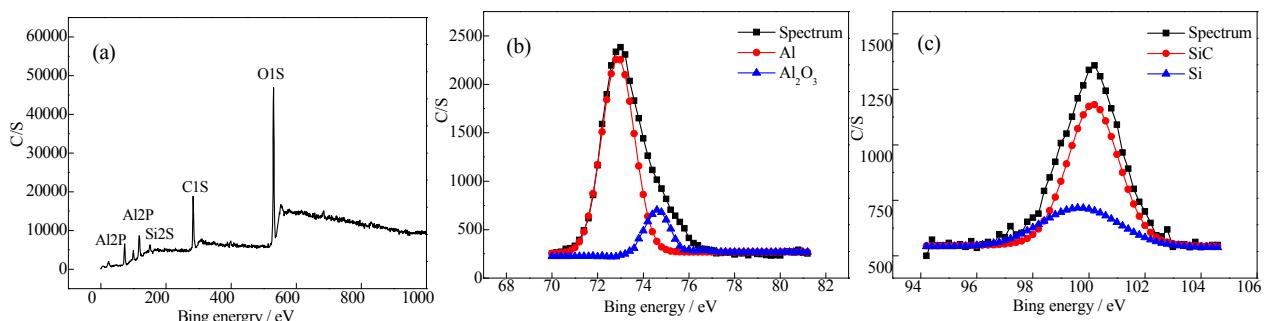


Fig.4 XPS analysis of interface materials of the original SiCp/A390 composites

- (a) spectrum of the original SiCp/A390; (b) Al2P peak of original SiCp/A390; (c) Si2P peak of original SiCp/A390; (d) Mg2P peak of original SiCp/A390

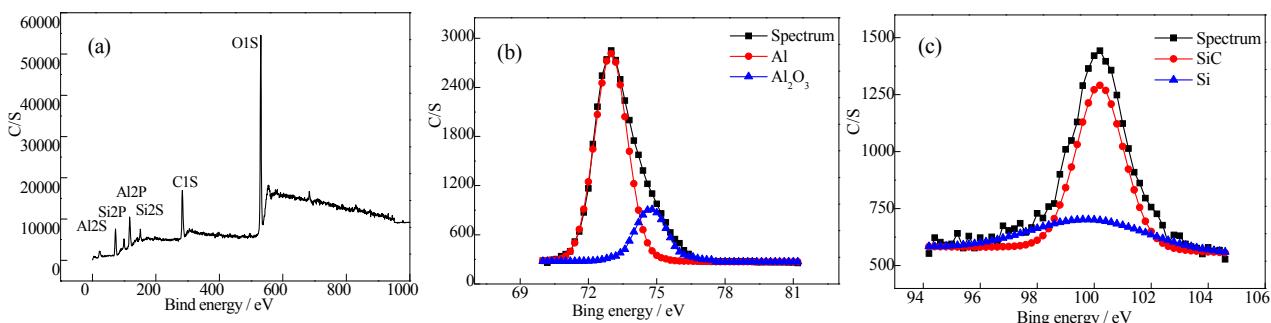


Fig.5 XPS analysis of interface materials of the oxidation SiCp/A390 composites

(a) spectrum of the oxidation SiCp/A390; (b)Al2P peak of oxidation SiCp/A390; (c) Si2P peak of oxidation SiCp/A390;  
 (d)Mg2P peak of oxidation SiCp/A390

Fig.5 shows the interface of surface modification composites analyzed by XPS. The interface main element of the SiCp/A390 composites that surface modification are Al, Si and C, O by all the component spectra (Fig.5(a)). The spectral peaks are 74.8 eV and 73.0 eV by 2p spectral line of Al (Fig.5b), contrast NIST XPS Database, the standard binding energy of Al in Al<sub>2</sub>O<sub>3</sub> was 74.4 eV, and the 2p standard binding energy of Al is 72.6 eV, then the existence form of Al element at the interface for SiCp/A390 composites after surface modification are Al and Al<sub>2</sub>O<sub>3</sub>. The content ratio of Al and Al<sub>2</sub>O<sub>3</sub> content on the interface is 83:17 through semi-quantitative analysis. So the quantity of Al<sub>2</sub>O<sub>3</sub> increases obviously at the interface through contrast the strength of the peak shown as Fig. 5(b) and Fig.5 (b), and the process of surface modification of SiCp made the obviously chemical reaction at the interface, which will be conducive to the combination of reinforced particles and matrix, increased the strength of composite material interface. Interface reactant MgAl<sub>2</sub>O<sub>4</sub> (2p peak combined energy is 75.7 eV) has not been found in Fig.5 (b), because the content is too little compared with Al and Al<sub>2</sub>O<sub>3</sub>, and it can't be detected by XPS. Fig. 6 (c) shows the 2P accurate scanning lines of Si in SiCp/A390 composites, the corresponded binding energy values of two peaks are 100.5 ev and 99.9 ev. The corresponded value of standard spectrum peak and the 2 p standard spectrum peak of Si in the SiC are 100.4 eV and 99.8 eV, respectively. Si exists mainly as SiC and elemental Si, which can be obtained by Fig.5(c). So the oxide layer on surface modification SiCp is fully participated in interfacial chemical reaction, forming Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub>.

### Interface Formation Mechanism of Surface Modification Composites

SiCp was preceded by 1000 °C and 6 h high temperature oxidation treatment to reach surface modification, and the particles surface arise SiO<sub>2</sub> oxide layer, which is about 50nm. The weighing method and formulas calculate the oxygen contents in the oxidation process. The oxygen contents before oxidation is 99.1327 g and after oxidation is 101.2891g. Oxygen ration of SiCp after surface modification can calculate according to the molecular weight SiC, SiO<sub>2</sub> and O<sub>2</sub> is 40.99 g/mol, 60.08 g/mol and 32 g/mol, respectively. The calculation process is  $(101.2891 - 99.1327) \times 32 / (60.08 - 40.99) / 101.2891 \times 100 = 3.5687\%$ .

Table 1 Possible chemical reactions in the interface between SiC and Al [12]

Chemical reaction equations	Enthalpy changeΔG <sup>0</sup> (J/mol)	ΔG <sup>0</sup> (J/mol) 833.15K
(1) 3SiO <sub>2</sub> (s) + 2MgO(s) + 4Al(l) = 2Mg Al <sub>2</sub> O <sub>4</sub> (s) + 3Si(l)	-790467+77.96T	-725514.63
(2) 2SiO <sub>2</sub> (s) + 2Al(l) + Mg(l) = MgAl <sub>2</sub> O <sub>4</sub> (s) + 2Si(l)	-558519+56.69T	-511287.85
(3) 3SiO <sub>2</sub> (s) + 4Al (l)=2Al <sub>2</sub> O <sub>3</sub> (s) + 3Si(l)	-719292+83.90T	-649390.96
(4) SiO <sub>2</sub> (s) + 2Mg(l) = 2MgO(s) + Si(l)	-326570+35.42T	-297060.23
(5) Si(l)=Si(s)	-50630+30.08T	-25568.85
(6) SiC(s)=Si(l)+C(s)	123470-37.57T	92168.55
(7) 3SiC(s)+4Al(l)=Al <sub>4</sub> C <sub>3</sub> (s)+3Si(l)	103900-16.48T	90169.69

The composite materials' sintering temperature is 560°C which closes to the solidus temperature, which makes preparation process presenting a small amount of liquid. According to the analysis of infiltration and diffusion principle, the chemical reaction between Mg, which appear in the boundary, SiO<sub>2</sub>, which present in the surface of SiCp, and Al matrix. The chemical reaction equation Gibbs free enthalpy and reaction process are shown in Table 1. Those reactions are possible since the gibbs free enthalpy of reaction equation (1-5) is negative. The gibbs value of reactions (6 and 7) is positive, so those reactions are impossible. There is no Al<sub>4</sub>C<sub>3</sub> found by XRD and TEM test, which also verify that these reactions can't be carried out. The gibbs free energy of reaction equation (1-4) under the experiment condition is -725.5KJ/mol and -511.2KJ/mol, -649.4KJ/mol and -297.1KJ/mol, respectively. If MgO exist on interface, chemical reaction (1) will preferentially occur, then the chemical reaction (2-3) follow. Meanwhile, the presence of reactive interface is confirmed from the perspective of thermodynamics. SiCp surface is covered a SiO<sub>2</sub> oxide layer after surface modification. During the preparation process, Al element and Mg element diffusion and enrichment on the surface of SiCp, which with SiO<sub>2</sub> layer can promote the good combination between Al matrix and SiCp. The O<sub>2</sub> content is 0.7137 g for SiCp/A390 composites (SiCp is 20%) after surface modification, only requires O<sub>2</sub> 0.1338 g. It is indicated that the oxide film on the surface of reinforced particles in composite materials can fully reflect off under ideal conditions, and there is no SiO<sub>2</sub>, shown as Fig.5 (c).

## Conclusions

- 1) Before SiC particles surface modification, the interface of SiC/Al of composites is clear, clean, flat, no hole defect, and discovered a small amount of amorphous layer interface of SiC/Al. Surface modification treatment not only can change the surface morphology of SiCp, but also make the dense SiO<sub>2</sub> layer formed on the surface, which is about 50nm. Very little SiO but no SiO<sub>2</sub> can be observed on the surface of the original state SiCp.
- 2) Surface modification made SiC/Al surface based amorphous type interface that obvious interface layers, and there is no Al<sub>4</sub>C<sub>3</sub> in SiCp/A390composites. Surface modification treatment of SiCp has little influence on the type of SiC/Si surface.
- 3) Surface modification treatment of SiCp can increase chemical reaction degree of the interface of composites, and effectively improve the interface bonding of SiC and Al.

## Acknowledgement

This work is supported by the Education Department of Henan Province (grant no. 13A430262)

## References

- [1] L.H. Zou, J.Z. Fan, T. Zuo, et al. High-cycle fatigue behavior of 15%SiCp/2009Al composite prepared by powder metallurgy process[J].The Chinese Journal of Nonferrous Metals, 20 (2010) 1955 -1961.
- [2] D. Mandal, S. Viswanathan. Effect of heat treatment on microstructure and interface of SiC particle reinforced 2124 Al matrix composite [J]. Materials Characterization, 85 (2013) 73-81.
- [3] A. Bahrami, M.I. Pech-Canul, C.A. Gutierrez, N. Soltani. Effect of rice-husk ash on properties of laminated and functionally graded Al/SiC composites by one-step pressureless infiltration, 2015, Journal of Alloys and Compounds, 644 (2015) 256-266.
- [4] J. Guo, X.B. Liu. Effect of pre-heating processing of SiC particles on porosity of SiCp/Al composites [J].Transactions of Materials and Heat Treatment, 27 (2006) 20-22.
- [5] C.T. Wang, L.Q. Ma, M.Y. Yin, Z.Y. Liu, Y. Ding, H. Zhang, Y.G. Chen. Effects of SiC Particles oxidation on the wettability and interfacial bonding of SiC-p/Al composites [J].Special Casting & Nonferrous Alloys, 30 (2010) 1062-1065.

- [6] Z.Q. Yu, G.H. Wu, L.T. Jiang. Effect of surface modification of sub-micron Al<sub>2</sub>O<sub>3</sub> particles by rare-earth on interfacial wettability of Al matrix composites [J]. *The Chinese Journal of Nonferrous Metals*, 15 (2005) 1087-1091.
- [7] N.P. Cheng, S.M. Zeng, Z.Y. Liu. Preparation, microstructures and deformation behavior of SiCP/6066Al composites produced by PM route [J]. *Journal of Materials Processing Technology*, 202(2008) 27–40.
- [8] T.X. Fan, D. Zhang, G. Yang, T. Shibayanagi, M. Naka, T. Sakata, et al. Chemical reaction of Al-SiC composites during multiple remelting[J]. *Compos A* 34 (2003) 291-299.
- [9] P. Liu, A.Q. Wang, S.M. Hao, J.P. Xie. The interfacial condition of SiCp/Al composites [J]. *Journal of Chinese Electron Microscopy Society*, 33 (2014) 306-312.
- [10]W.M. Wang, F.S. Pan, etal. Avance in research on interfacial reaction in SiCp/Al composites [J]. *Journal of Chongqing University (NaturalScience Edition)*, 27 (2004) 108-113.