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Effect of Fe on the properties of Cu/SiCp composite

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Abstract The copper matrix composites reinforced with SiC particulates (Cu/SiCp) were fabricated using a powder metallurgy method with the addition of 0.5, 1.5, 2.5, and 5 wt.% Fe. The microstructure and properties of the composites were studied. The results of this investigation revealed that the addition of Fe improved the interface bonding and mechanical and thermal physical properties of the composites. The fracture mechanism of the Cu/SiCp composites was found to change from interface de-bonding to matrix tearing due to the addition of Fe.

Introduction

Cu/SiCp composites are usually used as a heat sink material for fusion applications owing to the high-thermal conductivity of Cu and the low swelling of SiC ceramic under neutron irradiation [1–4]. However, relatively poor mechanical and thermal properties of Cu/SiCp were usually obtained due to non-wetting characteristics between the Cu and SiC [5]. Coating the SiC with Cu or Ni has been successful to some extent for enhancing the wetting characteristics [6–8]. One of the other methods for this purpose is to modify the nature of interface with the addition of interfacial active agent into Cu matrix. The most effective additives of elements are those which can concentrate on the interface and react with SiC. Iron is reported to be such an element. Completely insoluble and non-reactive systems do not provide adequate bonding for desired properties. A controlled interface reaction is of practical importance and therefore modification of completely non-reactive interface to promote bonding is essential. One method of achieving this is to reduce the surface energy thus enhance the reaction at the interface. The most logical approach would then be to alloy the matrix (or alternatively coat the particle) with small amount of an effective interface active agent that reduces the surface energy. Previous work has shown that the wetting and a reaction zone are developed in Fe/SiC composite [9]. Pelleg has enhanced the reaction at fiber–matrix interfaces in a Cu/SiC$_f$ composite with the addition of 2.5% Fe [10]. However, information related to the effect of Fe on the properties of particulate-reinforced Cu/SiC composite is very limited.

Accordingly, the present study focuses on the effect of Fe on mechanical and thermal properties of Cu/SiCp composite. The mechanism for the effect of Fe in Cu/SiCp composite is also explored.

Experimental details

Copper powders (with 99.9% of purity and 15μm of mean particle size) and SiC particles (with 15μm of mean particle size) and Fe powder (with 99.9% of purity and 10μm of mean particle size) were used as starting materials to prepare the composites. The weight ration for SiC/Cu is fixed to 10%, while the ones for Fe/Cu in composite is 0, 0.5, 1.5, 2.5, and 5%, respectively. The powders were mixed homogeneously for 36 h and compressed under 800 MPa in a steel die with 1% zinc stearate as a die lubricant. Sintering was performed at 1,173 K for 5 h in a hydrogen atmosphere. The microstructures were examined under using optical microscopy (OM) and scanning (SEM) and transmission electron microscopes (TEM) and the composition was determined by

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electron probe microanalysis (EPMA). Each data in the EPMA are the averaged values from five detecting points. Thermal analyses were conducted on DSC-5p analyzer. True density was measured by a method based on Archimedes' law. The three-point flexural strength test was carried out with a sample size with 3 × 4 × 36 mm on a Zwick T1-Fro20TN A50 materials tester. The coefficient of thermal expansion (CTE) was measured by a LK-02 CTE tester with a scanning rate of 5 K/s in the temperature range from 298 K to 473 K. In order to ensure the accuracy of the test, five samples were selected randomly for these tests and the mean value can be obtained. Specimen for TEM was cut from composites and prepared by stand methods involving mechanical grinding, polishing, and dimpling followed by ion milling to perforation. Morphological and structural studies were performed in an H-800 transmission electron microscope operating at 200 kV. The OM and SEM examination of the composites were conducted on MEF4 M optical metallurgy analyzer and SEM515 SEM.

Results

Thermal physical and mechanical properties of Cu/SiCp with and without Fe element

Figure 1 shows the effect of Fe on the density, flexural strength, and CTE of Cu/SiCp composites with different Fe content. With the increase of Fe content from 0 to 5%, flexural strength increased from 246 MPa to 362 MPa, while relative density increased from 92% to 99%, while CTE of Cu/SiCp composite decreased from 13.43 ppm to 12.15 ppm after the addition of Fe.

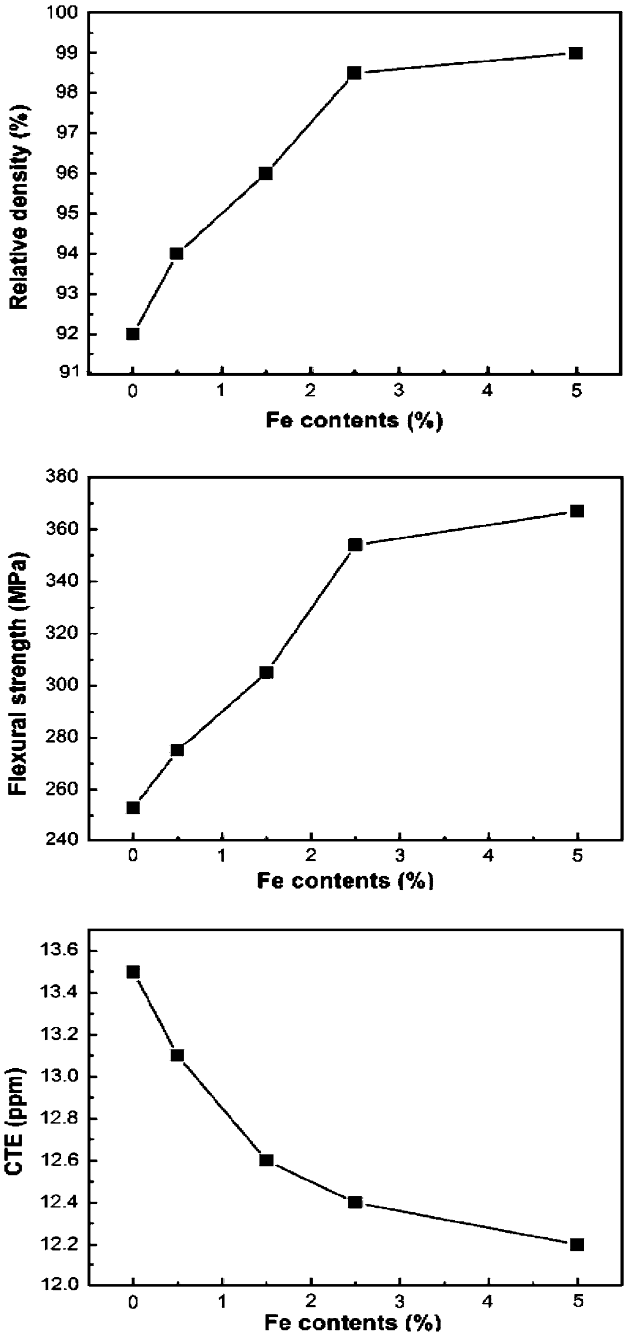

Fig. 1 Variation of relative density, flexural strength, and CTE with the iron content in the Cu/SiCp composite

Microstructure of Cu/SiCp composite

Comparing Fig. 2(a and b), SiC particles are all dispersed in the matrix uniformly. SiC particles are bonded with Cu matrix intimately in Fig. 2(b). Interface between Cu and SiC appear cleaner in Cu/SiCp composite with 5 wt.% Fe. However, A few defects can be seen at Cu/SiC interface in the Cu/SiCp composite without Fe additive.

Figure 3 shows the fracture surface of the Cu/SiCp specimens with and without Fe. Pulling out of SiC particles (A) and big hollows (B) with and without particles in them can be clearly seen on the fracture surface (as shown in Fig. 3(a)). The fracture appearance (as shown in Fig. 3(b) of the Cu/SiCp composite with 5 wt.% Fe is much different from former one. Pulling out of SiC particles from the copper matrix is not obvious on the fracture surface. Most of SiC particles distributing homogeneously remains in copper matrix. Small dimples can also be seen in copper matrix.

DSC analysis

Figure 4 shows DSC patterns of the composites without and with 5 wt.% Fe. At 1,086 K, an exothermic peak can be observed. While the composite without Fe addition has no such peak.

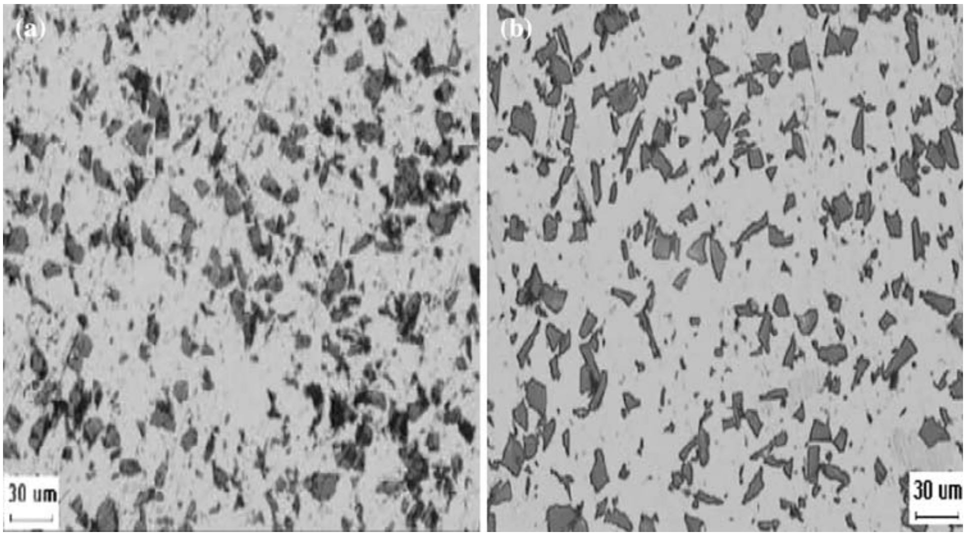

Fig. 2 OM-micrographs of Cu/SiCp composites: (**a**) without Fe; (**b**) with 5 wt.%Fe

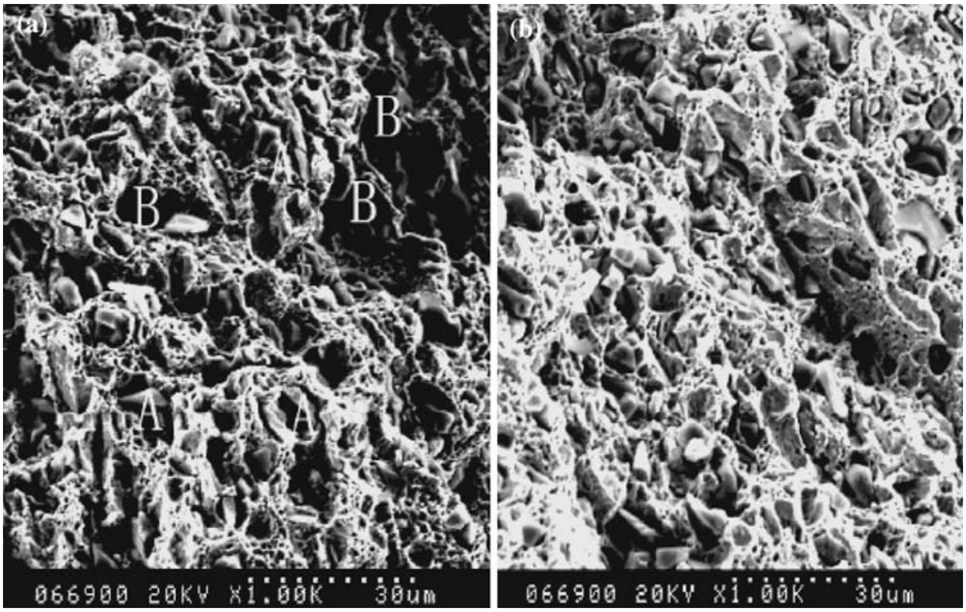

Fig. 3 SEM fractography of Cu/SiCp of three-point flexural specimens of Cu/SiCp composites (**a**) without Fe; (**b**) with Fe

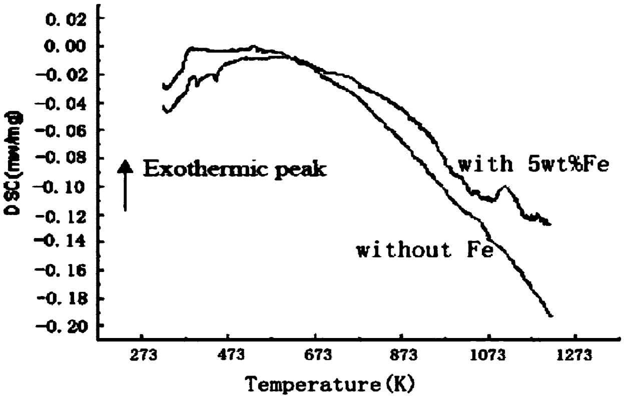

Fig. 4 DSC patterns of Cu/SiCp composite

Discussion

Mechanical and thermal properties

In the process of sintering, copper atoms will inter-diffuse to form sintering neck. Sintering neck grows up at high temperature to decrease porosity. However, SiC ceramic is very stable at the sintering temperature. So when the copper atom inter-diffusion is impeded by SiC particle, densification is difficult to complete. With the addition of Fe, most of the pores near the interface disappear. This shows the Fe addition can boost the Cu atoms inter-diffusion to decrease porosity. The reason for density is mainly due to the decrease of porosity near the interface (shown in

Fig. 2). There are several reasons for the enhancement of flexural strength: First, porosity decreases with the increase of Fe content, as shown in Fig. 1. The second, the improvement of bonding between Cu and SiC will increase mechanical properties, which can be observed apparently in Fig. 3. The third, the e strengthen effect of Fe element in copper matrix. On the basis of Cu–Fe phase diagram, about 0.5%wt Fe can be alloyed in Cu matrix at room temperature. The alloyed matrix has better mechanical properties. The redundant Fe element will dispersed in copper matrix as very fine particle. Fe element dispersion in Cu matrix will increase the flexural strength greatly. The decreased CTE of composites is related with the better interface adhesion and decreased porosity. Under higher temperature, metal matrix will expand. The ceramic particle can inhibit this expansion by interface due to its low CTE. Better interface adhesion will result in lower CTE.

Cu/SiC interface analysis

Proper quantity of the interfacial additive Fe is necessary to be considered. Although SiC has the crystal structure with steady covalent bond, when it reacts with transition metals such as Ti, Ni, and Fe, solid reaction will occurs easily above 1,073 K [11–13]. The DSC results (Fig. 4) showed that there is an exothermic peak at 1,086 K. It suggests that perhaps a reaction occurred in Cu/SiCp composite with Fe additive at 1,086 K. To prove this possibility, Interface of Cu/SiCp composite were observed by TEM.

Figure 5 shows the Cu/SiC interface morphology in Cu/SiCp composite without Fe. Although Cu/SiC interface bond intimately at some place, some cavities exist between SiC and copper matrix. The gaps width is about 50 nm. These gaps often can be seen in the TEM observation of the Cu/SiC composite. No reaction product was detected at Cu/SiC interface during TEM observation.

Figure 6(a) shows the interface morphology of Cu/SiC composite with 5 wt.%Fe. SiC particle and Cu matrix combined tightly, some products occurred at the Cu/SiC interface. The product is of fine spherical shape (100 nm) and mainly exists at the interface. Combined with the DSC result we believe that it is the reaction product of Fe and SiC. Figure 6(b) shows the other place of Cu/SiC interface in Cu/SiCp composite with Fe addition. There is no apparent reaction product in Cu/SiC composite interface. Cu/SiC interface also bond intimately and SiC particle interlock with copper matrix. To further know the distribution of Fe, Fe element was detected by EPMA. Table 1 shows the EPMA result.

From Table 1, the change of Fe concentration at Cu/SiC interface can be observed. Fe concentration appears near the interface. The Fe content near the interface is 6.4 wt.% in the sintered composite. It means that Fe/Cu ratio near the interface in the composites is 6.8%. 3.2 wt.% Fe was detected in copper matrix. However, no Fe content can be detected in SiC particle. Based on the results, we can know most of Fe element concentrated at the interface. Only few of Fe exists in copper matrix. Based on the study above, we can conclude that some reaction occurred at intimately bonded Cu/SiC interface in Cu/SiCp composite. Fe element concentrates near the Cu/SiC interface. Combined with the improved properties and the fracture surface morphology, we believe the reaction product and the Fe concentration near interface will improve the Cu/SiC interface adhesion.

Table 2 shows the enthalpy and entropy of the reactant and probable Fe/SiC reaction products. The energy barrier of the SiC decomposition is very high, which is the chief

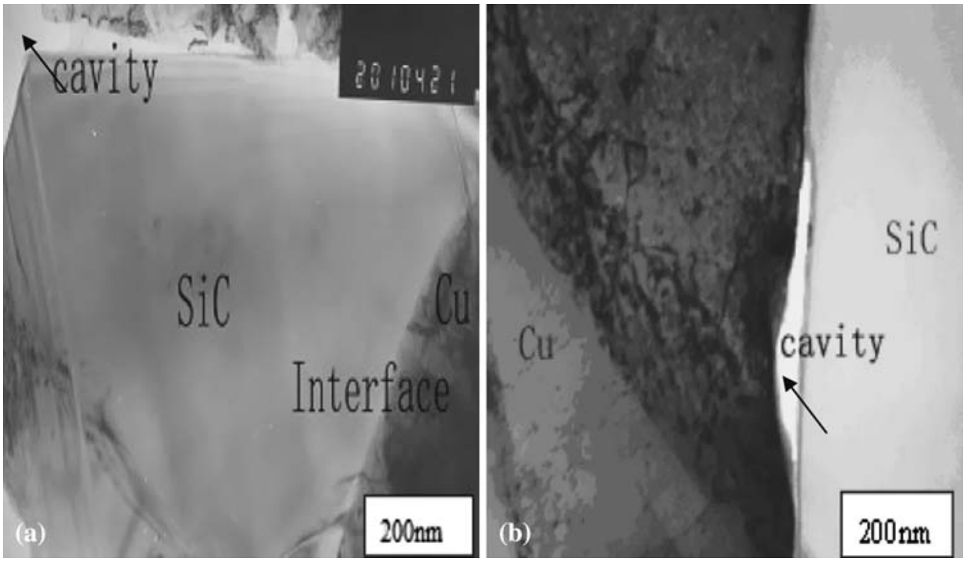

Fig. 5 TEM micrographs of the interface (Cu/SiC composite without Fe)

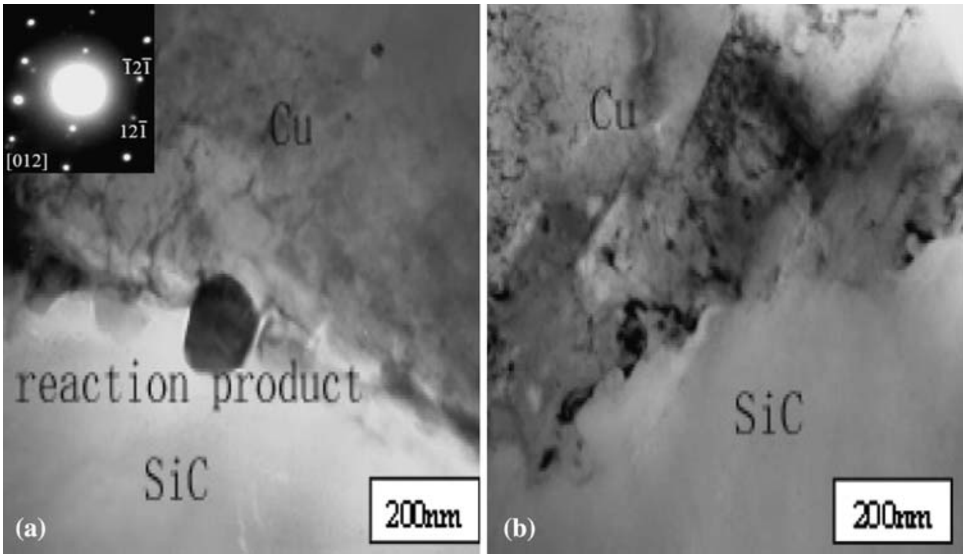

Fig. 6 TEM micrographs of the interface (Cu/SiC composite with 5 wt.% Fe)

Table 1 Results of electron probe analysis for Cu/SiCp composite with 5 wt.% Fe

	On Cu near interface	On Cu far from interface	On SiC
Cu	93.6	96.8	0
Fe	6.4	3.2	0
Si	0	0	43.8
C	0	0	56.2

Table 2 Some thermodynamic data of Fe silicides, SiC, Fe, and C [14]

	ΔH_{298K} (KJ/mol)	S^0 (J/mol.deg)	$\Delta H_{298K,\ \mathrm{Fe\ silicides}} - \Delta H_{298K,\ \mathrm{SiC}}$
Fe_3Si	−93.7	103.8	−30.9
FeSi	−73.6	46.0	−10.8
$FeSi_2$	−81.2	55.6	−18.4
SiC	−62.8	16.5	–
Fe	0	27.3	–
C(graphite)	0	7.3	–

resistance for the happen of Fe/SiC solid reaction. So enough energy should be supplied for the Fe/SiC reaction. As shown in Table 2, the Fe silicides formation can supply thermodynamic driving force to finish Fe/SiC solid reaction.

When the reaction product is Fe_3Si, the reaction heat is the highest. It means that under the same condition of energy barrier in Fe/SiC reaction, the Fe_3Si can form easily. When Fe reacts with SiC, Fe_3Si is probably the reaction product. The reaction equation is as following:

$$\mathrm{SiC} + 3\mathrm{Fe} = \mathrm{Fe_3Si} + \mathrm{C_{Gr}}. \tag{1}$$

$$\Delta G_T \approx \Delta H_{298\mathrm{K}} - T\Delta S_{298\mathrm{K}} = -30900 - 12.7T. \tag{2}$$

$$\Delta G_{1173\mathrm{K}} = -45\ \mathrm{kJ}$$

Based on thermodynamic calculation of the reaction of Fe and SiC (Table 2 and Eqs. (1, 2)), we can know that thermodynamic requirement of reaction of Fe and SiC above 1,103 K can be satisfied enough. The probable reaction product is Fe_3Si. Combined with the results above, we can obtain that the proper reaction and the Fe concentration near the Cu/SiC interface can reduce the surface energy between Cu and SiC, which results in the better bonding of Cu/SiC.

Conclusions

(a) The addition of Fe into the copper matrix can accelerate the densification of Cu/SiC composite and increase its density.
(b) The flexural strength and the CTE of Cu/SiCp composite sintered at 1,173 K increased and decreased respectively with the addition of Fe.
(c) With the addition of Fe, the fracture mechanisms of Cu/SiC composite change from de-bonding of SiC particle to SiC particle fracture and some matrix tearing character.
(d) The proper reaction and the concentration of Fe at the Cu/SiCp interface can modify the Cu/SiCp interface adhesion.

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