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Fabrication and properties of short carbon fibers reinforced copper matrix composites

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Abstract Short carbon fibers (SCFs) reinforced copper matrix composites have been produced by a new electrodeposition plus cold press and sintering technique. SCFs were copperized directly by the new method, and the electrodeposit had a loose porous structure. The coating thickness is uniform, and can be controlled by appropriate parameters. A model representing the growth process of these electrodeposits was presented. SCFs were distributed homogeneously, and no defects were found in the Cu/SCFs composites. The effects of SCFs volume fraction on mechanical, physical, thermal, and tribological properties of the composites were discussed.

Introduction

Carbon fibers (CFs) possess high specific strength, specific modulus, low expansion coefficient, and high thermal and electric conductivity, which were widely used into resins and metals as reinforcements to fabricate high performance composites [1–3]. Cu/CFs composites are considered promising materials applied in the industry because of their outstanding properties of conductivity, thermal conductivity (TC), antifriction, wear resistance, and low thermal expansion [4–7]. However, perfect Cu/CFs composites were very difficult to fabricate, owing to the poor wettability of CFs and copper. Generally, Cu-coated CFs were obtained to solve this problem by surface treatments, such as electroless plating, electrodeposition, vapor deposition process etc. [5–8].

Many researchers studied the preparation processes and properties of Cu/CFs composites by using Cu-coated CFs. Erich et al. [8] investigated the properties of Cu/CFs composites by hot compaction of Cu-coated CFs, compared to, using bare CFs, the CFs were better distributed in the matrix, and the TC was increased by more than 20%. Šebo et al. [5] discussed three kinds of processing, and studied the physical properties of Cu composites with variously arranged CFs. Xu et al. [9] studied the wear behavior of Cu/CFs under low load, and indicated that the addition of CFs improved the wear resistance evidently. However, in these researches, the Cu-coated short carbon fibers (SCFs) were produced by electroplating or chopping Cu-coated CFs, which is uneconomical, and the fracture surface will lose the coating. Till now, there are no reports about improving conventional electrodeposition to metallize SCFs directly.

In this article, a new electrodeposition was presented to copperize SCFs directly with uniform coatings, and these Cu-coated SCFs were compacted to prepare Cu/SCFs composites by cold press and sintering. The mechanical, physical, thermal, and tribological properties of the Cu/SCFs composites were tested.

Experimental

Polyacrylonitrile (PAN)-based CFs (T300) used in this article, having a diameter of 7 μm and a density of 1.76 g/cm^3, were manufactured by Japan Toray Co., Ltd. The desized and chopped SCFs with the length of 1–2 mm were obtained from the fiber dealer. Prior to use, the SCFs

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were immersed into the acetone solution for about 40 min to clean off contaminants, and then mixed with surfactant (polyethylene glycol 0.05 g/L), and last agitated to uniformity by ultrasonic wave.

The Cu-plating bath was composed of 200 g/L $CuSO_4 \cdot 5H_2O$ and 70 g/L H_2SO_4. The concentration of short CFs in bath maintained constantly about 0.5 g/L. A pure Cu plate with an exposed surface of 20 cm^2(4 × 5 cm), and an electrolytic copper were used as the cathode and anode, respectively.

The composites were consolidated by cold press and sintering. The press pressure was 400 Mpa, and the sintering temperature was 850 °C, with hydrogen as protection gas. The repress pressure was 600 MPa, and the resintering temperature was 850 °C. The dimension of the die used in the experiments was 10.0 mm (width) × 50.0 mm (length). And pure Cu samples were prepared by the cold press and sintering using pure Cu powders.

The tensile strength of composites was measured at room temperature, using Zwick T1-FR020TN A50 test machine at a loading rate of 0.5 mm/min, the dimension of the tensile test samples was shown in Fig. 1. Microhardness tests were conducted on a Vicker's hardness tester using a load of 50 gf for 10 s. The density was measured using Archimedes' method with distilled water as the immersion medium. The dimension of the samples for electrical conductivity (EC) and TC tests was 5 mm × 5 mm × 35 mm, which was measured by FOR-7501 eddy current conductometer and TCT416 conductometer. The measurements of coefficient of thermal expansion were performed by TMA7 dilatometer in temperature range 293–493 K, at heating rate of 5 °C/min, the dimension of the samples was 5 mm × 5 mm × 2.5 mm. The friction and wear tests were evaluated using a ring-on-disk wear test machine (MMU-5G) under 100N with 50 r/min, the dimension of the samples was 6 mm × 7 mm × 16 mm. Scanning electron microscopy (SEM: S520) and optical microscope (Olympus B071) were used to observe the morphologies of the Cu-coated SCFs and the composites.

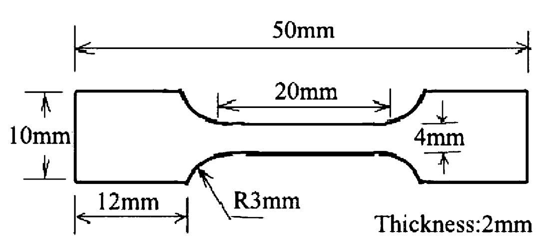

Fig. 1 Shape of the tensile test sample

Results and discussion

Direct electrodeposition of SCFs

Under the same experimental conditions, the various thickness of Cu-coated SCFs were obtained at various experimental parameters. Figure 2a and b, c, and d are the morphologies of electrodeposits prepared at 2.5 A/dm^2 and 40 min, 4.0 A/dm^2 and 60 min, respectively. All images show that the SCFs are well covered by uniform Cu coatings, and there are no bare SCFs appeared. The average coating thickness of the two electrodeposits can be measured from the photographs of cross-section, which is about 8.8 μm and 15.9 μm, respectively.

The growth process of the electrodeposits of Cu-coated SCFs is sketched in Fig. 3. In the bath, all SCFs were homogeneously dispersed by virtue of surfactant before plating, as shown in Fig. 3a. Some SCFs that contacted the substrate were coated preferentially, and then they were buried in Cu coating gradually. Subsequently, due to lapping with the buried SCFs, other SCFs were deposited by Cu as the substrate (Fig. 3b). At the same time, the SCFs in the bath migrated to the cathode slowly for the effect of agitation, and they twisted together. Finally, all SCFs coated by Cu and loose porous electrodeposit were formed (Fig. 3c).

The aspect ratio of the SCFs used in this paper was about 143–286. It is well known that the fibers are difficult to co-deposit, except those parallel to the substrate plane, so there are a few fibers buried in the substrate. And these fibers were very important to the process, because the inlayed ones offered other SCFs more opportunity to contact the cathode. Figure 4 is the SEM image about the situation of substrate at the intermediate stage of electrodeposition (at 2.0 A/dm^{-2}, 20 min). It shows clearly that fiber A is inlayed to the substrate in a parallel direction. From the arrows B, C, and D, it is seen that Cu coatings grow and fill the gap of the fiber A between the substrate gradually. In the electrodeposit, fiber E was an outer SCF, and apart from the substrate, which was lifted by other intertwisted SCFs. Figure 5 indicates the typical morphology of electrodeposit, prepared at 2.5 A/dm^{-2} for 40 min. The Cu-coated SCFs is uniform, they lap each other, and form the loose porous structure.

CFs are good conductors. If SCFs contact substrate or lap the inlayed ones, which means that they turn into an extended cathode, and will be copperized like the substrate. The conductivity of SCFs in the electrodeposit is different, nearer is the distance from the cathode, better is the conductivity of SCF. As the electrodeposition proceeded, the outer SCFs coated by copper gradually and the conductivity increased. The outer SCFs acted as a protective screen to the inner fibers, so the metal deposit rate of inner

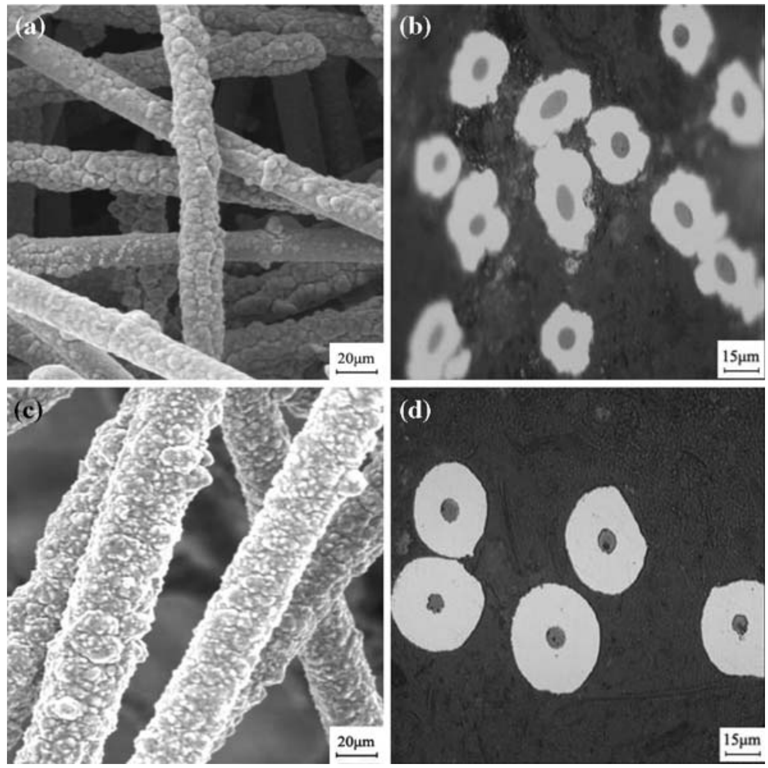

Fig. 2 Morphologies of the Cu-coated SCFs prepared at: (**a**) and (**b**), 2.5 A/dm^2 for 40 min; (**c**), and (**d**) 4.0 A/dm^2 for 60 min

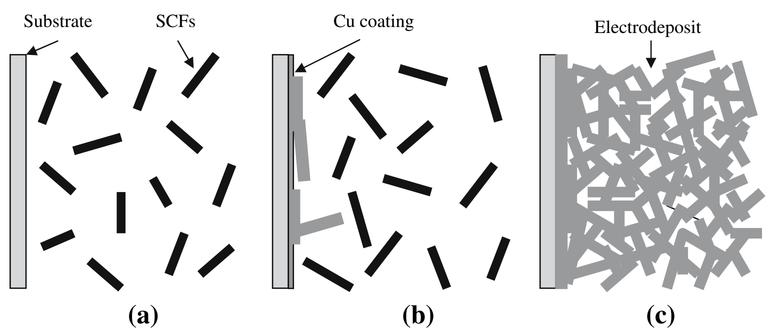

Fig. 3 Schematic of the growth process of the loose porous electrodeposits. (**a**) SCFs suspended uniformly in the bath. (**b**) Some SCFs near the substrate were buried by Cu coating, and they lapped with other SCFs. Cu deposited on the surface of the SCFs as on the substrate. (**c**) SCFs twisted, and coated to be a porous composite

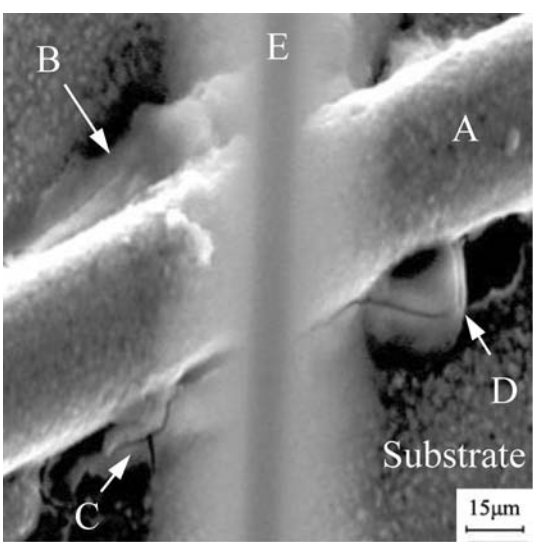

Fig. 4 SEM image about the SCFs buried into the substrate, and some of them lapped together (2.0 A/dm^2, 20 min)

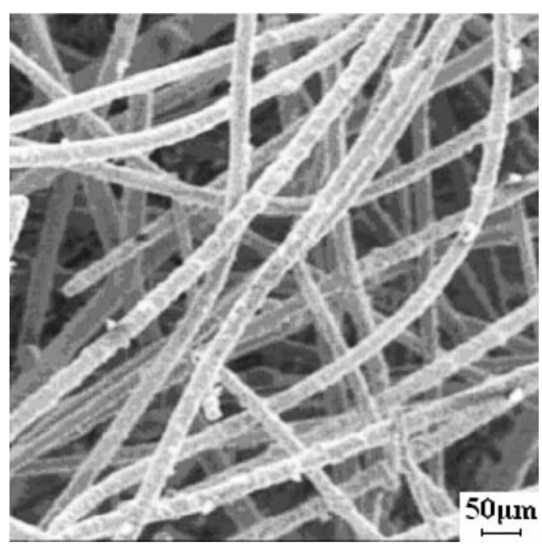

Fig. 5 SEM image of the electrodeposit (2.5 A/dm^2, 40 min)

Table 1 Fiber volume fraction of the samples prepared at different electrodeposition parameters

Code of samples	A	B	C	D
Parameters of electrodeposition	4.0 A/dm^2 60 min	3.5 A/dm^2 60 min	3.0 A/dm^2 60 min	2.5 A/dm^2 40 min
Volume fractions of SCFs	9.3%	13.8%	17.9%	23.2%

fibers decreased gradually. Finally, to all SCFs in the electrodeposit, the metal coatings are uniform and no bare fibers left, as shown in Figs. 2 and 5.

Microstructures of the Cu/SCFs composites

The SCFs with various thicknesses of Cu coatings were used to prepare copper matrix composites by cold press and sintering. Four kinds of composites were fabricated in this article. Ethylenediamine tetraacetic acid (EDTA) titration analysis was used to measure the fiber volume fraction (V_f) in the samples, and the results are listed in Table. 1.

The typical morphologies of the Cu/SCFs composites are shown in Fig. 6, which is the sample D with V_f of 23.3%. It displays that the SCFs disperse uniformly, no aggregation, and no obvious defects appear in the matrix. The characteristic of SCFs in the two directions imply that the SCFs are apt to horizontal distribution in the press process, which accord with the reports that fibers prefer orientation in composites during the pressing process [10, 11].

The highly magnified images of the Cu/SCFs composites with various V_f are displayed in Fig. 7. Figure 7a and b represent sample A and sample D, respectively, which show fibers dispersed homogeneously, and no apparent pores or defects in the matrix. Figure 8 shows the interface between SCF, and the matrix was smooth and well-bonded. All of this illuminated that the parameters of cold press and sintering in this experiment are feasible. By the way, lots of micropores existed in matrix, which lead to bad compactibility, so we failed to obtain the higher V_f composite (more than 23.3%). The reason may be the increasing content of brittle phase (SCFs) in the matrix, and the irregular orientation of SCFs in electrodeposits, which were the adverse factors for consolidations.

Properties of the Cu/SCFs composites

Mechanical properties

Figures 9 and 10 show the microhardness and tensile strength of pure Cu and Cu/SCFs composites, respectively. The results indicate that the mechanical properties increase with the increase in V_f. The process of repress and resintering helps to enhance the properties of the composites.

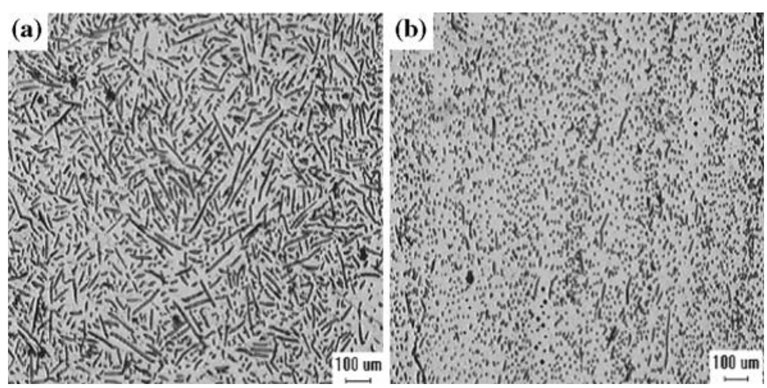

Fig. 6 Cross-sections of the sample D, (**a**) is in the vertical to press direction, (**b**) is parallel to press direction

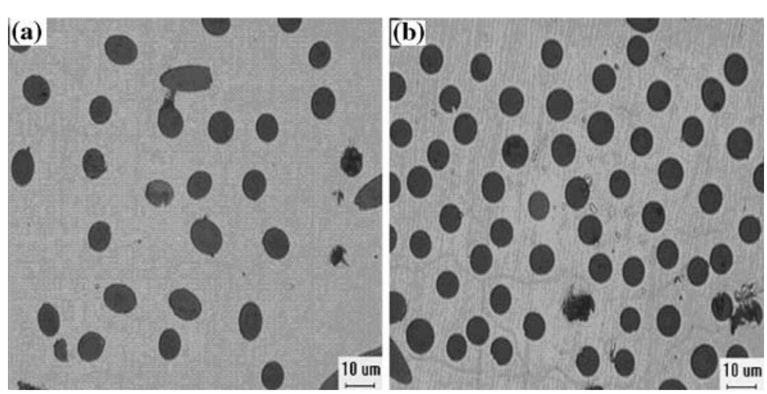

Fig. 7 Micrographs of the Cu/short CFs composites with various V_f, (**a**) is the image of sample A, (**b**) is the image of sample D

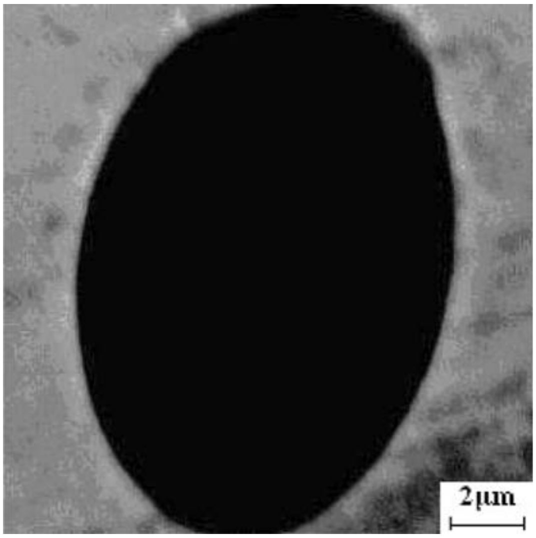

Fig. 8 SEM micrograph of the interface between SCF and the matrix

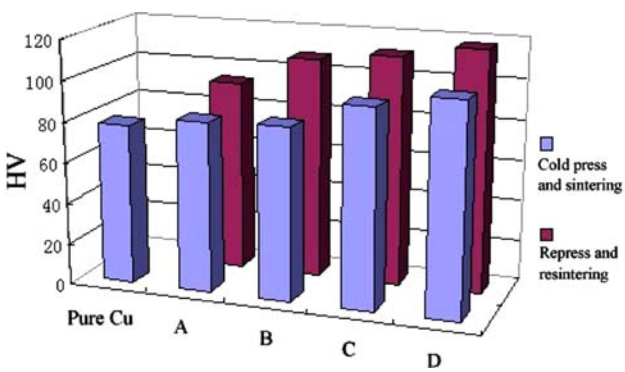

Fig. 9 Microhardness of the Cu/SCFs composites

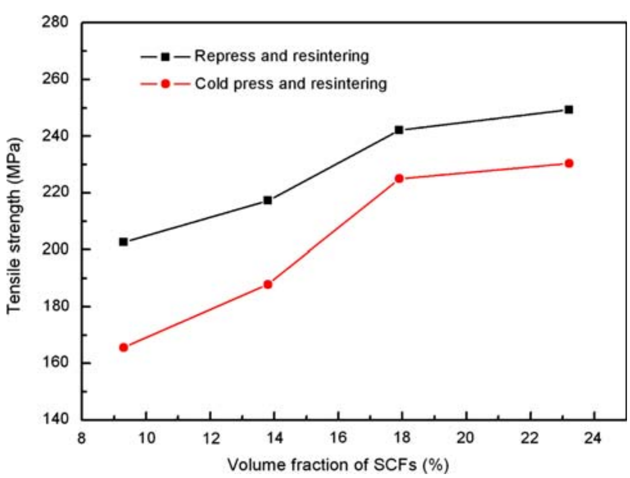

Fig. 10 Tensile strength of the Cu/SCFs composites

CFs are brittle material having poor briquettability, which result in the compacts occurring spring back, so the lower V_f composites have higher relative density. As shown in Fig. 11, with the V_f increasing, the relative density of the composites decreased. The relative density of the composites may be responsible to the mechanical test results. Low relative density means the high pores exist in the compacts. Under stress, the pores in composites will induce stress concentration and form crack sources, thereby decreasing mechanical properties. Repress and resintering is the common process to obtain high density compacts in powder metallurgy [12, 13], and according to Fig. 11, the relative density of all samples is enhanced by the process, so they have higher mechanical properties than those samples of cold press and sintering.

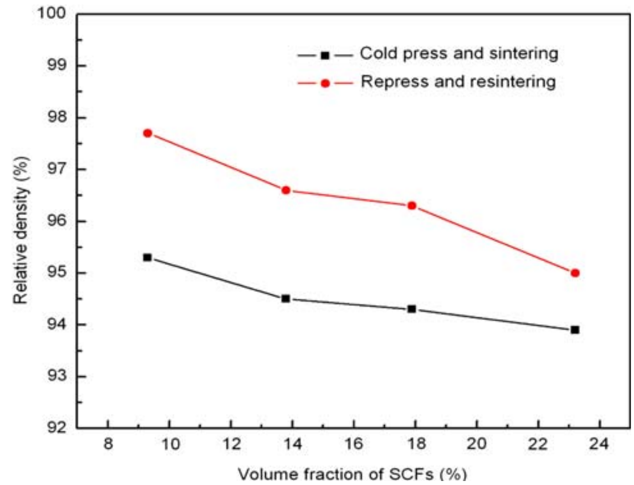

Fig. 11 Relationships between V_f and relative density of the Cu/SCFs composites

Physical and thermal properties

The physical and thermal properties were tested, as Table 2 listed. It shows that the properties of the Cu/SCFs composites decreased with the increase in V_f. T300 CFs have excellent coefficient thermal expansion (CTE), the CTE of axes direction is -0.41×10^{-6} °C, however, as compared to pure Cu, the properties of TC and EC are only 10.5 w/m K and 0.06 m/Ω mm^2, which is the main reason for the low

Table 2 Effect of fiber contents on physical and thermal properties

Code of sample	Fiber content (vol.%)	Coefficient thermal expansion ($\times 10^{-6}$/°C)	Thermal conductivity (W/m K)	Electrical conductivity (m/Ω mm2)
Pure Cu	0	17.8	398	56.5
A	9.3	15.1	286.2	50.2
B	13.8	13.9	248.5	46.7
C	17.9	12	193.2	40.3
D	23.2	10.8	157.4	29.8

Table 3 Effect of fiber contents on friction and wear behavior

Code of sample	Fiber content/vol.%	Friction coefficient	Wear weight loss/mg m^{-1}
Pure Cu	0	0.38	1.63×10^{-2}
A	9.3	0.27	1.54×10^{-3}
B	13.8	0.20	7.38×10^{-3}
C	17.9	0.17	2.91×10^{-4}
D	23.2	0.12	6.47×10^{-4}

properties of the composites. Furthermore, abundant interfaces and microdefects in the composites prevent expanding, weaken heat transfering, and cause electron scattering, which result in the decrease of physical and thermal properties.

Tribological properties

The results of tribological tests are listed in Table 3. It shows that, compared with pure Cu, the wear resistance of Cu/SCFs composites are greatly improved, and the friction coefficient and wear weight loss of the composites are decreased obviously with the increase in V_f. CFs consist of small crystallites of turbostratic graphite, which result in low coefficient [3]. And CFs reinforced the matrix and improved the microhardness evidently, which can hinder the deformation of matrix during the sliding process. On the other hand, CFs are very stable at high temperature, so the composites can bear the high local temperature during the wear test. In short, the addition of SCFs is helpful for the improvement of tribological properties.

Conclusions

By studying the fabrication and properties of SCFs reinforced copper matrix composites, the following conclusions could be drawn: (1) The new and simple method of electrodeposition can copperize SCFs directly. During the process, SCFs aggregated in the cathode, and coated uniformly by copper to form the loose porous electrodeposits. (2) The Cu/SCFs composites, V_f, ranged form 9.3% to 23.3%, were prepared successfully using the various thickness coatings of electrodeposits by cold press and sintering. SCFs distributed in the composites homogeneously and no obvious defects existed in matrix. (3) With the increase in V_f, the Cu/SCFs composites have higher mechanical properties, which can be significantly improved by repress and resintering. (4) The addition of SCFs results in the low physical and thermal properties, and with the increase in V_f, the properties are decreased in a wide-range. (5) As compared to pure Cu, the Cu/SCFs composites have better tribological properties with the contributions of SCFs.

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