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Preparation of a C/C–Cu composite with Mo_2C coatings as a modification interlayer

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ABSTRACT

To improve the wettability between molten copper and carbon and prepare C/C–Cu composites, Mo_2C layers were fabricated throughout the internal surface of a C/C preform in molten salt (NaCl–KCl) with ammonium paramolybdate. The Mo_2C layers obtained showed a thickness of approximately 1 μm and uniformly covered the internal pore surface of the C/C preform. Mo_2C layer formation transformed the non-wettable copper/carbon interface into Mo_2C/carbon and wettable Cu/Mo_2C interfaces. Good interfacial bonding was observed between Mo_2C/C and Cu/Mo_2C, and the carbon near the Mo_2C layer showed an evidently high degree of orientation. Compared with the C/Cu composite currently used, the C/C–Cu composite prepared in this work showed higher flexural and impact strengths, as well as electrical resistivity reaching the same order of magnitude as that of pure copper.

1. Introduction

Carbon/copper (C/Cu) composites for use as sliding electrical contact materials exhibit fine electrical and tribological properties [1]. Conventional graphite/Cu or carbon fiber-reinforced copper composites prepared by powder metallurgy commonly feature inhomogeneous microstructures attributable to a major density difference between carbon and copper. Achieving satisfactory mechanical properties are difficult because of the insufficient strengthening effect of graphite or short fibers. Moreover, C/Cu composites usually possess low electrical conductivity because of the discontinuity of copper [2].

Carbon/carbon (C/C) composites have attracted considerable research interest because of their low density, high strength, high modulus, excellent friction performance, and thermal shock resistance [3]. By introducing copper into C/C composite preforms, carbon and copper phases present a continuous distribution in the final C/C–copper(C/C–Cu) composites. These composites can showcase a good combination of the advantageous properties of both C/C and copper [4,5]. However, non-wettability between carbon and copper is a major limitation of the infiltration process [6]. A copper-wettable intermediate layer can contribute to copper infiltration into porous carbon preforms. Cr, Ti, V and their carbides have been used to reduce the contact angle of carbon and copper. However, these layers show obvious diffusion of metal atoms into copper which sharply decreases the thermal conductivity of copper. Mo_2C shows good wettability with copper and the solid solubility of Mo in copper is zero [7,8]. Plasma deposition, physical vapor deposition, and slurry technology have been applied to prepare the layers described above. These methods, however, cannot successfully fabricate uniform and integrated coatings throughout the internal pore surface of the porous carbon preform.

In the present study, copper-wettable Mo_2C layers were formed on the internal surface of C/C preforms through the molten salt method, and C/C–Cu composites were obtained via the pressureless infiltration method. The microstructure and properties of the resultant C/C–Cu composite were studied in detail.

2. Experimental procedure

Sample preparation: The C/C preform ($1.20\ g\ cm^{-3}$) was fabricated from integrated needled carbon fiber felts ($0.45–0.5\ g\ cm^{-3}$, T300, Toray, Japan) that had been densified by chemical vapor infiltration. A flux consisting of NaCl and KCl (molar ratio of 1:1) was mixed with 10 wt% ammonium paramolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$], here, the mass ratio of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and C was 1:2. The C/C preform was buried in the salt mixture in a lid-covered alumina crucible and heat-treated at 1273 K for 60 min to fabricate the Mo_2C coatings. The Mo_2C-coated C/C preform was infiltrated with pure copper (purity, 99.9%) at 1573 K in vacuum (Cu:preform volume ratio, 0.5:1).

Sample characterization: Densities were measured using Archimedes' principle. Flexural strengths were tested using the three-point bending fixture method on bar specimens (10 mm × 10 mm × 60 mm) with a span of 40 mm according to JB/T 8133.7-1999. Impact strength

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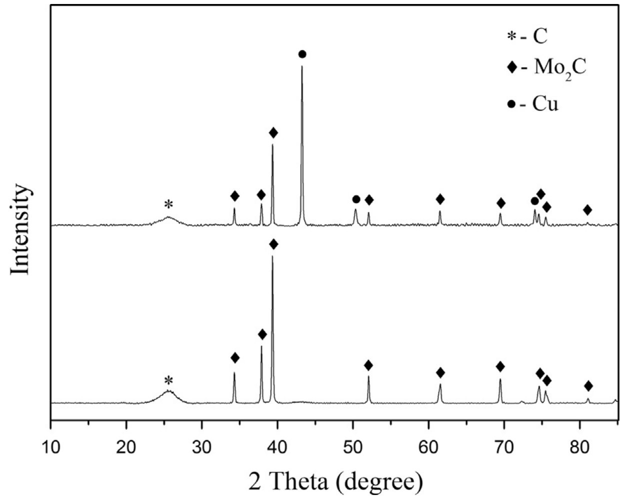

Fig. 1. XRD patterns of (a) the Mo_2C-coated C/C preform and (b) the C/C–Cu composite.

tests were performed on bar specimens (10 mm × 10 mm × 55 mm) using the Charpy method. Electrical resistance was tested on bar specimens (10 mm × 10 mm × 60 mm) by a DC resistance tester according to JB/T 8133.7-1999, and the electrical resistivity was calculated according to its definition. Thermal conductivity was measured by a Netzsch LFA447 at 298 K with wafer sample (ϕ12.5 mm × 2.5 mm).

Phase analysis was conducted by X-ray diffraction (XRD, RIGAKU-3014, Cu K_α radiation, 40 kV, 250 mA) over angles ranging from 10° to 85° at a scanning rate of 0.02°/s. Microstructures were characterized by scanning electron microscopy (SEM, Nova Nano SEM 230) and transmission electron microscopy (TEM, Tecnai G2 F20).

3. Results and discussions

Composition and microstructure of the Mo_2C-coated C/C perform: Fig. 1(a) shows the XRD pattern of the Mo_2C-coated C/C preform; here, only C and Mo_2C phases were identified. According to the results of DSC–TG analysis (Fig. S1 in the supplementary data) and the literature [8,9], the reactions of ammonium paramolybdate and C occur as follows: gasification of water, decomposition of ammonium paramolybdate, reduction of MoO_3 to MoO_2, and carbonization of MoO_2 to Mo_2C.

Fig. 2(a) and (b) shows cross-sectional micrographs of the Mo_2C-coated C/C preform. Continuous Mo_2C coatings are found throughout the internal pore surface of the C/C preform [Fig. 2(a)]. Molybdenum oxide molecules dissolve in molten NaCl–KCl and infiltrate into the porous C/C preform. Fig. 2(b) shows that the pyrolytic carbon (PyC) around carbon fibers (C_f) reacts with molybdenum oxides to generate Mo_2C, which protected the fibers from damage. The coatings were approximately 1 μm thick.

Microstructure and mechanical properties of the C/C–Cu composite: Fig. 1(b) shows the XRD patterns of the C/C–Cu composite; here, C, Mo_2C, and Cu phases can be identified. The obtained C/C–Cu composite was composed of 26.83 wt% C, 8.47 wt% Mo_2C, and 64.70 wt% Cu as calculated from the result of chemical analysis. Fig. 2(c) shows a micrograph of the C/C–Cu composite at low magnification; here, bright and dark phases corresponding to copper and carbon, respectively, may be observed. Formation of Mo_2C interlayers transforms the non-wettable copper/carbon interface into Mo_2C/carbon and wettable Cu/Mo_2C interfaces, which contribute to the sufficient penetration of copper into the preform. The copper and preform exhibit an interconnected net-like distribution. Fig. 2 (d) shows a micrograph of the C/C–Cu composite at high magnification; here, a clear interface between the copper and Mo_2C layers can be observed.

Table 1 shows properties of the C/C–Cu composite. The flexural and impact strengths of the C/C–Cu composite were remarkably higher than those of C/Cu composites (42 MPa, 1.2 J cm^{-2}) currently used as contact strip pantographs [4]. The interconnected net-like structure of the C/C–Cu composite takes full advantage of the strengthening effect of the preform. The high strength obtained could also be attributed to suitable interface bonding. The Mo_2C layer changes the bonding type at the C/Cu interface from mechanical bonding to chemical/metallurgical bonding, which is beneficial for effective load transfer. Mo_2C layers also induce relatively low bonding strength between carbon and copper [10] and prevent brittle fractures caused by strong interfacial bonding [4]. Fig. 2(e) and (f) shows the fracture morphologies of the composite. Pulling-out of carbon fibers as well as holes from the drawn fibers of PyC may be seen, and copper presents a typical ductile fracture characteristic. Fig. 2(f) demonstrates that the fracture surfaces of the carbon fiber, PyC, and Mo_2C layers are not in the same plane; thus, the presence of PyC and Mo_2C layers could lead to increases in fracture crack propagation paths. This configuration also confirms the moderate interfacial bonding between carbon and copper caused by Mo_2C layers.

Fig. 3 shows TEM micrographs of the interfaces in the C/C–Cu composite. Fig. 3(a) demonstrates that the Mo_2C layer is composed of Mo_2C particles with sizes ranging from hundreds of nanometers to 1 μm. Combined with the HRTEM images in Fig. 3(b) and (c), good interfacial bonding may be observed between fcc-Cu and hcp-Mo_2C, as well as between Mo_2C and PyC. Comparing the SAED patterns at positions ③ and ④, PyC near the Mo_2C layer may be observed to show a diffraction spot for the 002 plane, which reflects a high degree of orientation. By contrast, the PyC away from the interface shows an arc-like diffraction that reflects low orientation. $(NH_4)_6Mo_7O_{24}$ or molybdenum oxides are reportedly able to catalyze carbon graphitization at relatively low temperatures. This ability is endowed by molten molybdenum oxides dissolving the disordered carbon up to the solubility limit, after which graphite crystals precipitate [11,12]. Stress originating from differences in thermal expansion results in stress graphitization [13]. Thus, the high degree of PyC orientation at the interface may result from both catalytic effects and stress graphitization. The improved graphitization degree of PyC can facilitate lubricant friction film formation because the carbon matrix softens and presents increased ductility [14].

Thermal, physical, and electrical properties of the C/C–Cu composite: After copper infiltration, the thermal conductivity of the preform increases from 11.9 W m^{-1} K^{-1} to 148.9 W m^{-1} K^{-1}. The Mo_2C interlayer between copper and graphite fibers has been reported to exert a significant influence on improving the thermal conductivity of composites by up to 40% because of extensive bonding at the interface [15]. The thermal conductivity of the C/C–Cu composite is just slightly lower than 153.7 W m^{-1} K^{-1} as calculated based on the "rule of mixtures" for composites [8]. Fig. 3(b) and (c) shows good interfacial bonding between Cu/Mo_2C and Mo_2C/PyC, which is beneficial for reducing phonon backscattering at the interface. Improvements in the order degree of PyC could induce scattering of lattice waves caused by the disordered arrangement of carbon atoms [16].

The electrical resistivity of the C/C–Cu composite was markedly lower than 17.846 μΩ m, as calculated according to the same rule of mixtures, and even reached the same order of magnitude as that of pure copper (0.017 μΩ m). In the C/C–Cu composite, good interfacial bonding and high PyC orientation could induce scattering of the current carrier caused by interface resistance effects and lattice defects, respectively. Moreover, the interconnected structure of the C/C–Cu composite leads to a unique electrical conductive mechanism called network conduction [17], in which electrical conduction occurs