# Preparation of titanium carbide nanosheet and tribological properties of copper matrix composites

*Maoquan Xue* ✉

*Changzhou Institute of Industry Technology, Changzhou, Jiangsu 213164, People's Republic of China*
✉ *E-mail: xuemaoq@163.com*

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TiC nanosheets with a thickness of about 50 nm were successfully prepared via solvent thermal etching $Ti_3AlC_2$ in hydrofluoric acid solution at 120°C. TiC reinforced copper-matrix composites with a content of 3, 5, 7, 9, 10, and 12 wt% were prepared by powder metallurgy with copper powder and TiC nanosheet as raw materials. The friction and wear behaviours of copper matrix composites were tested on a ball on disc under dry sliding conditions. The results showed that TiC particles were evenly distributed on the substrate and had a good combination with the substrate. The friction coefficient and wear scar widths of the composites gradually decreased with the increase of TiC nanosheet content, the maximum reduction of friction and wear was achieved under the content of 7 wt% for the TiC nanosheets. The increase in load causes the increase of friction coefficient and wear scar widths. The wear of pure copper is mainly adhesive wear and peel wear. The addition of TiC nanosheets improves the bearing capacity of copper matrix composites, and the wear mechanism is mainly abrasive wear.

**1. Introduction:** The metal matrix composites have attracted extensive attention and a wide range of applications because of their outstanding comprehensive physical and chemical properties when combined with the high abundance of particles, fibres, whiskers, and nanometres reinforcements [1]. These factors suggested that materials can be suitable for meeting the demand of transport vehicles and aerial equipment [2]. With the rapid development of the high-speed railway, the urban public transport trolley and other industries, such as copper alloys have good characterising, not only for mechanical and electrical conductivity but also for wear resistance and high-temperature softening resistance [3–5]. The methods of strengthening copper alloy are composite strengthening and alloying. Among them, alloying is to add a small amount of Al or Cr and other elements in the copper matrix to precipitate the hard second phase at a lower temperature [6]. One of the disadvantages of this alloy is that its strength will be seriously reduced at a high temperature above 500°C. However, the composite strengthening method of granular-reinforced copper matrix composites is an important development direction. At present, the literature reports that ceramic and intermetallic compounds such as carbides, borides, nitride, and oxides are used as reinforced particles for copper matrix composites, and the preparation methods have various kinds. Powder metallurgy has become one of the important methods to prepare particle reinforced composites with low cost, high efficiency, and wide applicability [7, 8]. As the hardest metal carbide, TiC is a very stable compound with a high melting point, high hardness, high Young's modulus, high chemical stability, wear resistance and corrosion resistance, and has become one of the best materials for particle reinforcement [9, 10].

Chandrakanth *et al.* have prepared copper matrix strengthened with TiC and graphite particles through microwave processing, and discovered that the prepared copper alloy composites display uniform distribution of reinforcements in the copper matrix, exhibited higher relative density, sintered density, and hardness compared with conventionally sintered ones [11]. Bagheri has fabricated copper matrix composites reinforced with different amounts of titanium carbide particles by mechanical milling and in situ formation of reinforcements. The reinforced composites showing a higher TiC percentage led to better mechanical and unfavourable physical properties [12]. Wang *et al.* have manufactured nanoscale TiC-reinforced copper alloys by a self-developed two-step ball-milling process on Cu, Ti, and C powders. The nanoscale TiC particles mainly located along the grain boundaries exhibited the promising trait of blocking grain boundary migrations, which leads to super-stabilised microstructures up to approximately the melting point of copper (1223 K) [13]. Narayanasamy *et al.* have prepared TiC reinforced magnesium matrix composites and found that the uniform distribution of TiC has greatly improved the density, hardness, and wear resistance of Mg composites [14].

The synthesis methods of titanium carbide powder mainly include the direct carbonisation method, gas phase method, and carbon thermal reduction method. Rahaei *et al.* synthesised nano-TiC powder by the mechanochemical reaction of titanium and graphite starting materials during milling and found that the mean size of TiC particles was decreased towards nanoscale with increasing milling time [15]. Sen *et al.* prepared TiC powders through carbothermal reduction of titania/charcoal under vacuum and found that fine TiC powders with low impurities were obtained at 1450°C for 8 h when the system pressure was about 1–60 Pa [16]. Hong *et al.* have prepared nano-sized TiC powders by a very high speed planetary ball milling, and found that liquid process control agent effectively refined the particles by heat dissipation [17].

Recently, a large family of two-dimensional titanium carbide nanomaterial (MXene) was successfully prepared by etching Al from $Ti_3AlC_2$ in Hydrofluoric acid solution (HF) at room temperature [18–21].

In this experiment, we successfully fabricated TiC nanosheets by immersing $Ti_3AlC_2$ powders in hydrofluoric acid assisted hydrothermal reaction at 120°C, TiC particles reinforced copper matrix composites were prepared by powder metallurgy with copper powder and TiC powder as raw materials, and their microstructure and tribological properties were studied to obtain experimental data. Therefore, the aim of the work is to prepare a new two-dimensional TiC nanosheet and explore the tribological properties of TiC nanosheet reinforced copper matrix composites, the basic data supplied will be beneficial in its potential application in various vehicles, various space devices, and other industries in the future.

**2. Experimental**

2.1. Materials and physical techniques: All starting reagents, including titanium powder, aluminium powder, graphite powder, and hydrofluoric acid solution were purchased from Sinopharm

(Shanghai) Chemical Reagent Co., Ltd and used as received. X-ray powder diffraction (XRD) measurements were performed using a D8 advance (Bruker-AXS) diffractometer with Cu–Kα radiation ($\lambda = 1.5416$ A°). X-ray data were analysed with the Jade software. The samples were characterised by using a scanning electron microscope (SEM) JEOL JXA-840A and an energy-dispersive spectrometer (EDS). The friction coefficient was recorded automatically by a computer. The microstructure and wear scar of copper matrix composites were observed using an optical microscope.

2.2. Synthesis: According to the method in [22], $Ti_3AlC_2$ was prepared by sintering Ti, Al, C, and Sn mixed powder in the Ar atmosphere by using the pressure less sintering method. In brief, powders in the appropriate proportion were magnetically stirred in anhydrous alcohol at 70°C. After being dried, shifted and cold-pressed at 30 MPa, then heated in a tubular furnace under Ar atmosphere at 1400°C for 30 min, cooled to room temperature and then taken out. The obtained $Ti_3AlC_2$ was crushed and sieved through a 300 mesh sieve.

The exfoliation process was as follows: 2 g $Ti_3AlC_2$ powder was slowly added into a 70 ml 40% concentrated HF solution, then transferred into the sealed Teflon-lined stainless steel autoclave and reacted at 120°C for various times, after naturally cooled to room temperature. The resulting suspension was filtered and washed several times with distilled water and anhydrous ethanol. Finally, the titanium carbide nanometre sheet was obtained by drying at 70°C for 12 h.

The samples of Cu/ TiC composites were fabricated through powder metallurgy. The copper powders were mechanically mixed with TiC nanosheets at the weight ratio of 100:0, 97:3, 95:5, 93:7, 91:9, 90:10, and 88:12. The mixed powder was cold-pressed at 200 MPa and sintered at 850°C for 2 h in an Ar atmosphere. After cooling to ambient temperature, the copper matrix composites were obtained.

2.3. Tribological tests procedure: Tribological properties were evaluated with a NANOVEA Micro Tribometer under dry conditions and in an air atmosphere. The balls used were 440C stainless steel had a 10.0 mm in diameter with a hardness of 62 HRC. The disc specimens were Cu/ TiC composite disc (Ø 30 mm × 5 mm). The applied load was 1–7 N, and the sliding speed was 0.17 m/s. The wear scar widths were measured by a common optical microscope.

### 3. Results and discussions

3.1. Microstructure of TiC nanosheet: The structure and crystallographic phase of specimens were determined by XRD. Fig. 1*a* shows TiC (JCPDS Card No. 65-8808) was formed after the hydrothermal reaction at 120°C for 12 h. With some impurity phases, such as $AlF_3$, AlxTiy etc. The intensity of the XRD peaks of TiC is higher than those of impurity phases. Further prolonged reaction time to 24 h resulted in the formation of stronger TiC and weaker impurity phases [23]. The diffraction peaks of TiC clearly match with the cubic crystal structure with the *Fm*-3*m*(225) space group.

The morphological evolution of the specimens was analysed by SEM as displayed in Figs. 1*b* and *c*. It has been found that the nanosheets were composed of sheet-like nanostructures. The size of the sheets was ∼1 µm and thickness of about 50 nm and they were stacked to each other (Fig. 1*b*). The temperature had no significant effect on the morphology as seen from the similar shape and size of the nanosheets as shown in Fig. 1*c*. In addition, the elemental composition of these specimens was analysed by EDS and is shown in Fig. 1*d*. EDS analysis reveals that the nanosheets were composed of Ti, F, Al, and C, which is consistent with the XRD analysis.

3.2. Characterisation, conductivity and microhardness of copper matrix composites: Fig. 2*a* shows the XRD patterns of copper matrix composites prepared by P/M. It was found that the diffraction peaks primarily belonged to the Cu phase. Some other peaks except Cu were observed in the XRD patterns of Cu-base composites, such as TiC, $AlF_3$, AlxTiy etc. Figs. 2*b* and *c* reveal the microstructure of sintered copper and copper matrix composites, which was characterised by optical micrographs after metallographic preparation. It can be observed that the microstructure of pure copper is dense, the microstructures of TiC showed good bonding of Cu particles, the TiC particles embedded in the matrix.

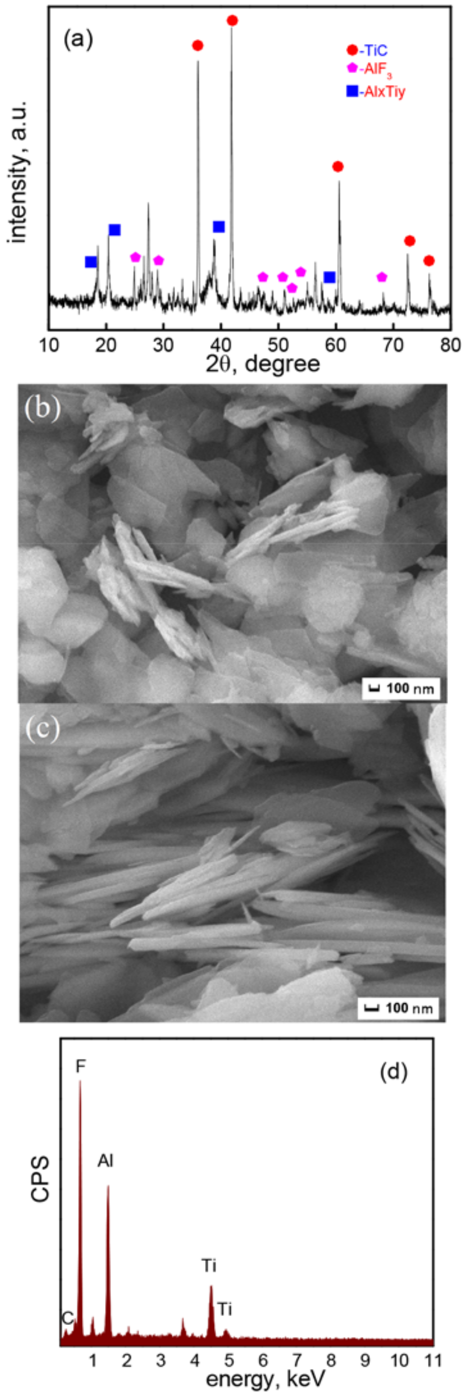


**Fig. 1** *The structure and crystallographic phase of TiC nanosheet obtained at 120°C for 12 h*
*a* X-ray diffraction (XRD) pattern
*b*, *c* SEM images
*d* EDS of TiC nanosheet

Conductivity was measured by using an FQR-7501A eddy current conductometer. A load of 100 N and the duration time of 15 s were employed for microhardness measurement. Five tests



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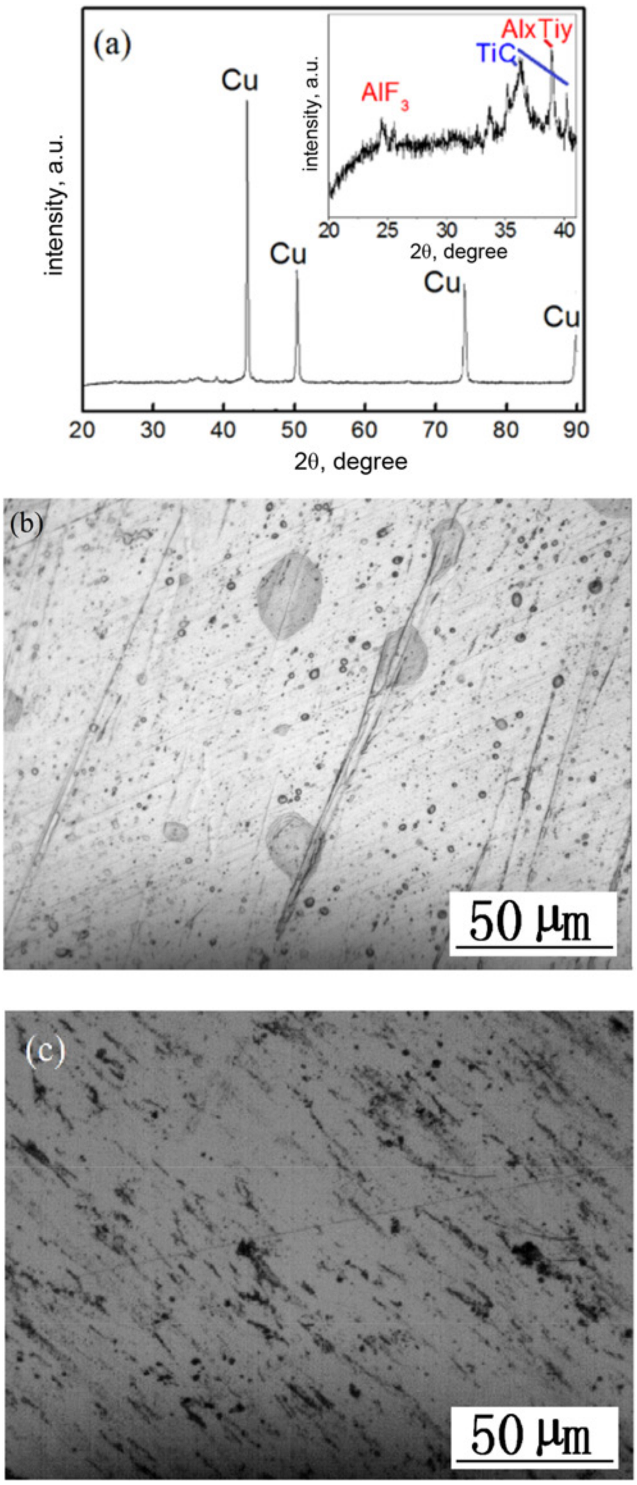


**Fig. 2** *The structure and crystallographic phase of copper matrix composites*
*a* XRD pattern
*b* Optical microscopy image of copper and
*c* Optical microscopy image of copper matrix composites with 7% TiC

were carried out at different places of composites and the mean value was given. The conductivity and microhardness of Cu–7% TiC-based composites is 26.7 MS/m and 108.4 Hv.

3.3. Friction and wear behaviour: The wear resistance of the composite materials can be discovered from two important properties and considered during the wear test: the wear scar width and the friction coefficient. Pin-on-disc is used to evaluate the wear and friction properties of the Cu–TiC composites. Fig. 3 shows the variation of wear scar width as a function of TiC reinforcement content under the fixed testing parameters of an applied load of 5 N, sliding time of 300 s and sliding velocity of 0.17 m/s. As the TiC particles are reinforced in the soft copper matrix material which enhances the hardness and hence the wear scar width decreases. The wear scar width of composites decreases with an increased TiC content of up to 7%. In higher content, TiC copper matrix composites exhibit TiC effects and result in a little higher wear scar width than that of Cu–7%TiC composites. Fig. 3 also presents the particulars of the friction coefficient of the composites. As can be seen from Fig. 3, the friction coefficient of Cu–TiC composites slowly decreases with the increase of TiC content and then rises gradually with the continuous increase of TiC content. The results of this study clearly indicate that adding appropriate TiC particles could improve the overall tribological response of copper.

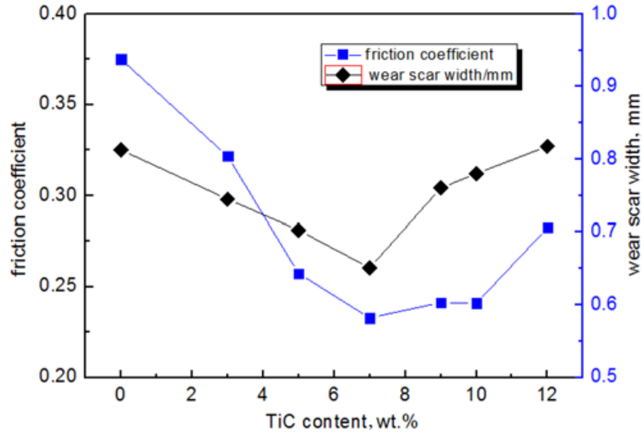


**Fig. 3** *Effect of TiC reinforcement content on wear scar width and the friction coefficient*

Meanwhile, as can be seen from Fig. 3, with the increase of TiC content up to 7 wt%, the wear scar width of copper matrix composites decreased significantly. However, when the TiC content continues to increase, the wear scar width of copper matrix composites increased. In other words, under the conditions of this experiment, the addition of 7 wt% TiC could effectively improve the wear resistance of copper matrix composites. During the test process, the stainless steel ball slides continuously on the surface of the copper matrix composite. Copper matrix is worn off firstly, then TiC is squeezed on to the worn surface, which greatly weakens the plough cutting effect of the friction ball, and bearing most of the main applied load to reduce its damage to the copper matrix. In addition, TiC will form a protective film on the wear surface under the action of continuous contact stress, effectively reducing the direct contact area between friction pairs and further reducing the wear of copper matrix. Moreover, the good interface between TiC and copper matrix is conducive to the stress transfer and dispersion of the friction contact surface.

Fig. 4 shows the effect of load on the friction coefficient and wear scar width of Cu–7% TiC composites. As can be seen from the figure, with the increase of the applied load, the friction coefficient and wear scar width of the copper matrix composite showed a trend of increase gradually. The increase of load will destroy the smoothness of the friction surface, make the friction surface rough, and cause friction coefficient to rise. Also, with the increase of the applied load, the wear scar width increases monotonously. Generally, in the friction and wear process, with the increase of the load, the wear scar width and depth of the copper matrix composite will also increase, resulting in the direct contact area between the stainless steel ball and the copper matrix composite increases. At the same time, the high load will increase the temperature between the sliding surfaces, eventually leading to serious wear.

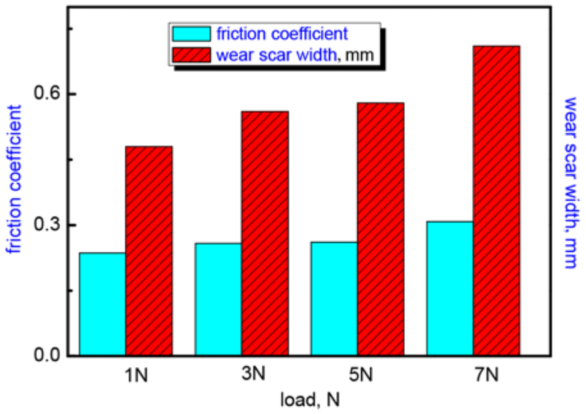


**Fig. 4** *Friction coefficient and wear scar width of Cu–7% TiC composite sliding under different applied loads*

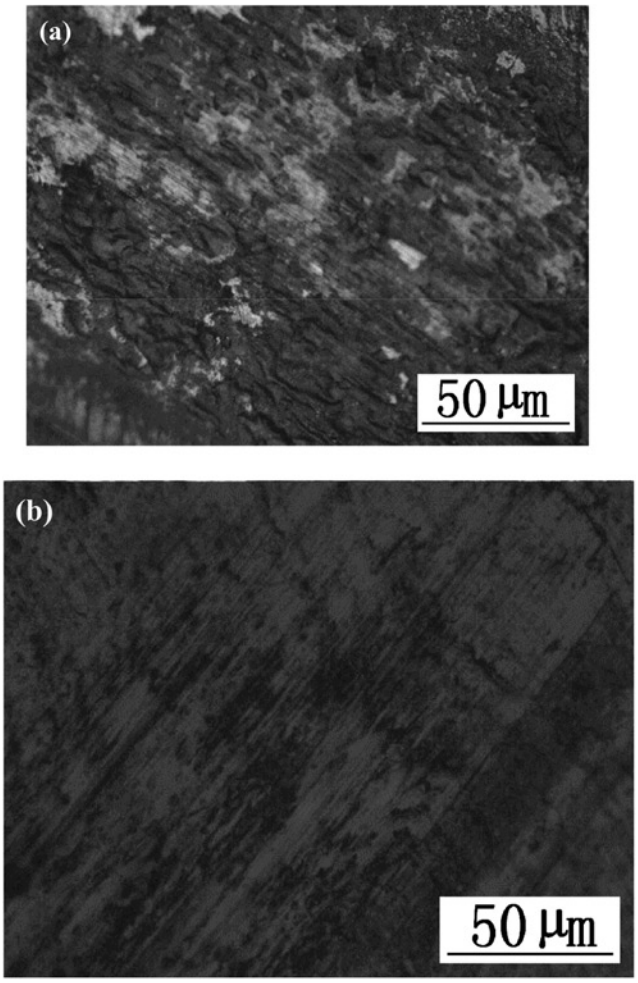


**Fig. 5** *Wear surfaces of*
*a* Pure Cu
*b* Cu matrix composites reinforced by 7% TiC

Fig. 5 shows the wear surface morphologies of pure copper and TiC particle reinforced copper matrix composites. As can be seen from the figure, the wear mechanism of pure copper is mainly adhesive wear and stripping wear. The wear of TiC nanosheet reinforced copper matrix composites is mainly abrasive wear. The hardness of pure copper is low, when it is rubbed against the higher hardness stainless steel ball, the surface will produce serious plastic deformation, and lead to adhesive wear and peeling wear. Exposed TiC particles and furrows can be seen on the worn surface of the composite. The hardness of TiC is higher than that of the matrix, and its addition can play a role of bearing load, effectively relieving the plastic deformation of the copper matrix, so as to improve the wear resistance of the material [24]. A small number of exfoliated TiC particles can act as 'ball bearings' on the worn surface, thereby reducing the friction coefficient. As the TiC content increases, the carrying area of TiC particles increases, and the pressure assigned to individual particles decreases. Thus, the higher the TiC content, the higher the load that will change from slight wear to severe wear. Moreover, the more TiC particles on the friction surface, the more obvious the 'ball bearing' effect they play on the friction surface, so the more obvious their anti-grinding effect is. Therefore, the wear resistance of TiC particle reinforced copper-based composite increases with the increase of TiC content. However, when the TiC content reaches a certain value, especially under a large load, its ploughing action on the copper substrate will also be enhanced, aggravating the plastic damage of the copper substrate, which will increase the wear of the copper substrate, thus showing a reduction in wear resistance.

**4. Conclusion:** TiC nanosheets were successfully prepared by facile immersing $Ti_3AlC_2$ powders in hydrofluoric acid assisted hydrothermal reaction at 120°C.

During the sliding process, TiC nanosheets would be transferred to the friction surface to form the tribofilm, which greatly resisted the plastic deformation of counterpart to avoid the serious damage of copper matrix composites, so, the tribological behaviours of copper can be improved by adding an appropriate number of TiC nanosheets.

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