

The microstructures of in-situ synthesized TiC by Ti-CNTs reaction in Cu melts

Xuexia Xu^{1,2,*}, Yong Wang^{1,2}, Qing Wang^{1,2}, Guozhen Dong^{1,2}, Wenbin Li^{1,2}, Guowei Li^{1,2}, YaDong Lv^{1,2}, Jin Zhang³, Haimin Ding³

¹State Grid Hebei Electric Power Research Institute, Shijiazhuang 050021, PR China

²State Grid Hebei Energy Technology Service Co., Ltd, Shijiazhuang 050021, PR China

³School of Energy, Power and Mechanical Engineering, North China Electric Power University, Baoding 071003, PR China

In order to study the influence of the carbon nanotubes (CNTs) as a source of carbon on the microstructure of in-situ synthesized TiC in Cu melts, CNTs and Ti powders were introduced into melted Cu to prepare TiC-reinforced Cu matrix composites. The influence of Ti/C ratio and Si on the microstructures and properties of the composites were also examined. It is found that CNTs can be effectively wetted through the Ti-C reaction and successfully introduced into Cu melt to synthesize TiC. In examining the changes in Ti/C ratio, it was found that an increase in the Ti content may result in the decrease of TiC agglomeration and improvement of TiC dispersion, while simultaneously causing an increase in the TiC particle size. Besides, while the addition of Si into Ti-CNTs mixture can also improve the distribution of TiC, the effect is weak compared with that of increasing the content of Ti. It was also found that the highest hardness (238.8 HV) is achieved by the Cu-Ti-C composite with the highest Ti/C ratio, while the electrical conductivities of all the prepared composites are relatively low, which should be due to the insufficient reaction between Ti and CNTs.

Keywords: *Cu matrix composites, microstructures, TiC, CNTs*

1. Introduction

Due to its high modulus, high hardness, and high melting points, TiC has been widely used as reinforcement in the preparation of metal matrix composites. Zhang et al. [1] added TiC into FeCoNiCu2.0 by induction melting method, and found that the ultimate tensile strength of 10 vol.%TiC/FeCoNiCu 2.0 composite reached 698 MPa, which was 47.6% higher than that of the matrix. Radhakrishnan et al. [2] found that the mechanical performance of the Ti/TiC composite deposits can be improved using techniques that promote complete dissolution of the original TiC. Lu et al. [3] found that the yield strength of Ti-Mo-Al-TiC composites increased steadily with the increase of TiC content. TiC-reinforced Cu matrix composites, which can have good electrical and thermal conductivity as well as excellent mechanical properties, have attracted much

attention in recent years. Dudina et al. [4] obtained a TiC-Cu composite with a compressive strength of 920 MPa after spark plasma sintering (SPS) the mechanically ground TiC-C-3Cu reaction mixture. Wang et al. [5] prepared Ti-coated diamond particles, reinforced Cu/diamond composites by gas pressure infiltration, and by adjusting the thickness of the interfacial TiC layer, the maximum thermal conductivity of $811 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ was obtained at the 220 nm Ti-coating layer. Several studies in the literature have successfully prepared the TiC-reinforced Cu matrix composites using various methods. Shen et al. [6] prepared Cu-TiC-composites by combining mechanical alloying with hot isostatic pressing. Besterici et al. [7] prepared TiC dispersive Cu-TiC composites using powder metallurgy and analyzed the strain and fracture mechanisms. Palma et al. [8, 9] also successfully prepared Cu-TiC composites by combining reactive ball milling with extrusion molding. The prepared Cu-5 vol.%TiC composites have not only high hardness and strength but also ex-

* E-mail: xuxuexia2008@163.com

cellent electrical conductivity that reaches 76.9% International Annealed Copper Standard (IACS) [8]. Rathod *et al.* [10] prepared Cu-TiC composites with high TiC content by self-propagating reaction method (SHS) and systematically analyzed their reaction synthesis path, and the volume fraction of the TiC synthesized could reach 11%–13%. Wang *et al.* [11] prepared Cu-TiC composites by two-step ball milling, with the tensile strength and yield strength of 602 MPa and 572 MPa, respectively, and an electrical conductivity of 78.6% IACS. By further optimizing the above preparation process, Wang *et al.* [12] also prepared the self-generated nano-TiC-reinforced copper matrix composite, which has a higher tensile strength and electrical conductivity of 712 MPa and 72% IACS, respectively.

However, it is noticed that, at present, powder metallurgy is still the main method for preparing the TiC-reinforced Cu matrix composites; few studies have used the melting cast method, which is more suitable for industrial production. In the previous study [13], it has been reported that it was very difficult to effectively introduce TiC into Cu melt due to the poor wettability between TiC and Cu, which limited the preparation of TiC-reinforced Cu matrix composites by casting method. It has been found that some elemental carbon or carbon containing compounds, such as graphite, diamond, and SiC, can be introduced into Cu melts by reaction wetting method, especially by the Ti-C reaction wetting [14, 15]. In addition, when Si source is added to Ti-C system, Ti_5Si_3 can be formed, which is helpful for improving the wettability and dispersion of TiC in liquid copper [16]. In those cases, TiC can be synthesized in-situ in Cu melts, and thus the TiC-reinforced Cu matrix composites can be obtained. However, it is also found that the microstructures of the synthesized TiC are closely related to the type of carbon source.

Carbon nanotubes (CNTs) are one-dimensional tubular structures composed of sp^2 hybridized carbon atoms mixed with sp^3 hybridized carbon [17], which can be regarded as an improved version of sheet graphene. It has excellent intrinsic properties of graphite, such as good mechanical properties, self-lubrication, excellent electrical and ther-

mal conductivity, etc. [18–20]. Therefore, in this work, CNTs are chosen as the carbon source and introduced into Cu melts by Ti-C reaction to prepare TiC-reinforced Cu matrix composites. The influence of Ti/C ratio and Si on the microstructures of TiC is also examined.

2. Experimental procedure

Ti powders (30 μm), CNTs [outer diameter (OD): 10–20 nm, length: 0.5–2.0 μm] produced by Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, Si powders (1 μm), and high purity electrolytic Cu (99.9%) were used as raw materials. The singular microstructures of CNTs are shown in Figure 1. It can be seen from Figure 1 that the CNTs have combined into agglomerates with the size of 5–15 μm . CNTs shown in Figure 1 have not undergone any pre-treatment and were directly added to the molten Cu for the synthesis of TiC. According to the ideal stoichiometry of TiC, when the mass ratio of Ti:C is 4:1, theoretically, Ti can completely react with carbon sources to form TiC. Therefore, three kinds of Cu-Ti-C composites with nominal compositions of Cu-4 wt.%Ti-1 wt.%CNTs, Cu-6.67 wt.%Ti-1 wt.%CNTs, and Cu-4 wt.%Ti-1 wt.%CNTs-1 wt.%Si were prepared. They will be designated as Cu-4Ti-1C, Cu-6.67Ti-1C, and Cu-4Ti-1C-1Si, respectively, in the following sections. The preparation processes are as following: first, the mixed powders were evenly mixed in a three-dimensional mixer for 2 h, and then cold-pressed into cylindrical pellets with a diameter of 20 mm under a pressure of 20 MPa; then, the compact was added to the Cu melt in the quartz crucible in a high-frequency induction heating furnace at 1,150–1,250°C; finally, after holding for 3 min, the melts were cast into the graphite mold to obtain the composite.

The as-cast samples were then ground and polished through standard routines, and the microstructures of the samples were investigated using scanning electron microscopy (SEM) with X-ray energy dispersion spectroscopy (EDS), where a Japanese electron scanning electron microscope (JSM-IT500, Japan, JEOL) was used for SEM. The accelerating voltage used was 20 kV, the work-

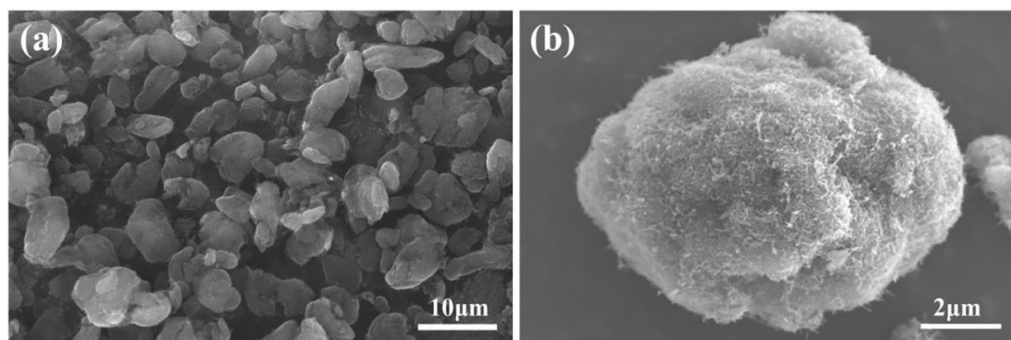


Fig. 1. The microstructures of the used CNTs (a) Low magnification microstructure; (b) High magnification microstructure. CNTs, carbon nanotubes

ing distance was 10 mm, and the probe current was 40A. Furthermore, the as-cast composites were etched in 18% phosphoric acid solution for 30 s under the current of 5 A to corrode the Cu matrix in order to better observe the morphology of the reactants, and then the corroded sample was analyzed using an SEM. In addition, the corrosion solution (10 vol.%H₂SO₄ + 30 vol.%H₂O₂) was also used to corrode the Cu matrix, and the extracted reaction products were analyzed by X-ray diffraction analysis (XRD; D8 advance, Bruker AXS, Germany). Test conditions were the following: Cu target, K α rays, wavelength $\lambda = 0.1540$ nm, 40 kV/40 mA, and scanning speed of $10^\circ \cdot \text{min}^{-1}$. The XRD results were analyzed by Jade. Furthermore, the mechanical properties of three kinds of composites were also tested. Among them, the hardness was measured by the digital display microhardness tester (HVS-1000, Shanghai Lianer Experimental Equipment Co., Ltd). The test force value was 0.5 KGF. The loading, load retention, and unloading time were all 15 s. The electrical conductivity of polished sample surface was measured by a conductivity tester (SMP350, Nantong Fisher Testing Instrument Co., Ltd). In the process, different areas were measured on the same sample surface. After removing the maximum and minimum values, the average value was taken as the final sample hardness and conductivity value.

In order to analyze the distribution and size of TiC, the volume fraction (which was approximately estimated by the area ratio of TiC particles in the SEM image) and size of TiC were analyzed using

Image-Pro Plus software. In the process, it was ensured that SEM images with the same magnification were used, and TiC were selected and calibrated using software or manually. After marking all objects, the area and size information of particles were automatically calculated using software. Five different areas of each sample were selected for measurement to ensure the reliability of test data, and finally the average values were obtained.

3. Results and discussions

3.1. The distribution and morphology of TiC in the Cu-4Ti-1CNTs samples

The as-cast microstructures of Cu-4Ti-1C are shown in Figure 2. It can be seen from Figure 2a that a new phase, which is gray in the Cu matrix, has been synthesized. The magnified microstructure shown in Figure 2b indicates that some of the synthesized phases are particlelike with a size of 1–3 μm . The EDS point analysis result shown in Figure 2c demonstrates that these synthesized particlelike phases are constituted by Ti and C, indicating that TiC has been synthesized as an outcome of the experimental procedure, and that these phases are chemically indistinguishable from TiC. It also can be seen that there are many agglomerations that are formed by small particles. The EDS point analysis result shown in Figure 2D confirms that these small particles also mainly contain Ti and C, demonstrating they are TiC agglomerations.

The EDS mapping analysis results shown in Figure 3 further confirm that the agglomerations

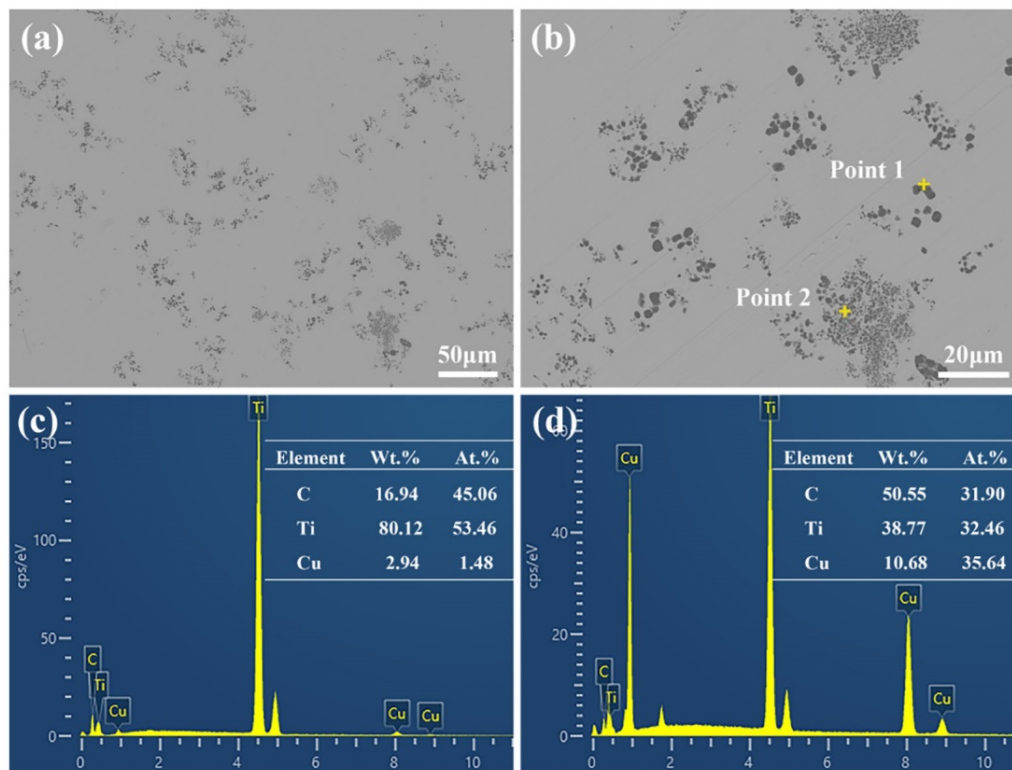


Fig. 2. Microstructures of the as-cast Cu-4Ti-1CNTs sample (a, b) Microstructures; (c, d) EDS analysis results of points 1 and 2 shown in (b). CNTs, carbon nanotubes; EDS, energy dispersion spectroscopy

mainly contain Ti and C elements, indicating they consist of TiC particles.

In addition, the XRD result in Figure 4a indicates the formation of TiC. These results demonstrate that CNTs have been effectively introduced into the Cu melts, and have reacted with Ti to form TiC. Considering that it is difficult to exclusively add CNTs into the Cu melts, the reaction between Ti and CNTs, which will improve the wettability between CNTs and Cu melts, should be the reason for the successful addition of CNTs into Cu melts.

Then, in order to better analyze the distribution of TiC in the Cu matrix, the as-cast Cu-4Ti-1C sample was electrolytically etched in the phosphoric acid solution to remove Cu from the surface and expose the TiC. The microstructures of the deeply etching sample are shown in Figure 5. It can be more clearly observed from Figure 5a that most of the TiC particles have been aggregated into clusters of different sizes. The magnified microstructure of one agglomeration is shown in Figure 5b.

It is found that the size of the TiC in the agglomerations is generally smaller than that of the surrounding relatively uniformly distributed TiC, and that the range of particle size distribution is also narrow. The microstructures of another agglomeration, shown in Figures 5c and 5d, further confirm the above results. It is also can be seen from Figure 5d that some TiC particles merged and grew larger.

On the other hand, it is found from the deeply etching sample that there are some relatively dense shells that are also formed by TiC particles, as shown in Figure 6a. The results shown in Figure 6b further confirm the formation of TiC shells. Since the TiC shell assumes the shape of a hollow cylinder or sphere, the mode of its formation may be considered as the adhesion of Ti-CNTs on the surface of the CNTs aggregate, followed by the separation of the shell from the aggregate. It is deduced that the formation of these dense TiC shells may prevent the unreacted CNTs inside the sample from

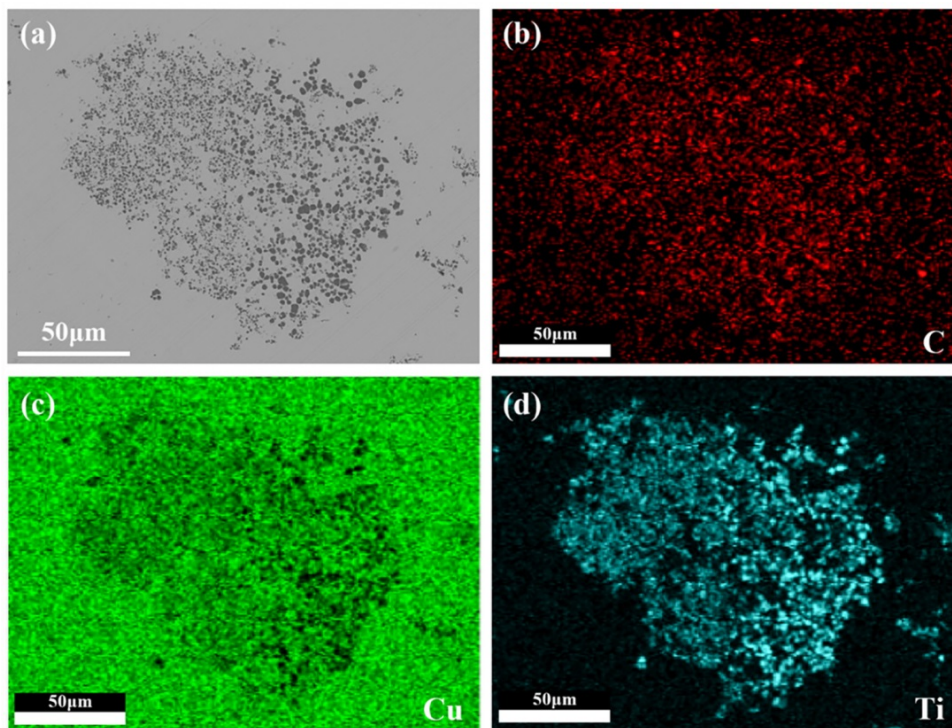


Fig. 3. EDS analysis of the as-cast Cu-4Ti-1C sample (a) SEM image; (b–d) mapping micrographs for the elements C, Cu, and Ti. EDS, energy dispersion spectroscopy; SEM, scanning electron microscopy

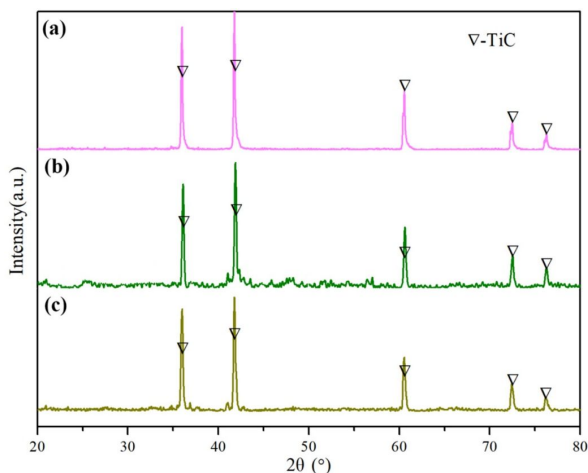


Fig. 4. The XRD results of the powders extracted from (a) Cu-4Ti-1C; (b) Cu-6.67Ti-1C; (c) Cu-4Ti-1C-1Si. XRD, X-ray diffraction analysis

coming into contact with the Ti that is present on the surface, ultimately resulting in the incomplete reaction of CNTs, as demonstrated in the insert figure shown in Figure 6d.

In order to further study the TiC and its agglomerations, the as-cast Cu-4Ti-1C sample was also put into the sulfuric acid and hydrogen peroxide aqueous solution (10 vol.%H₂SO₄ + 30 vol.%H₂O₂) to absolutely dissolve the Cu matrix, and then the synthesized TiC particles were extracted from the solution. The morphologies of the TiC agglomerations are shown in Figures 6C and 6D. It can be noticed from Figures 6C and 6D that the TiC agglomerations are spherical in three dimensions and their morphologies are almost the same as that of the original CNTs agglomerations shown in Figure 1b. These results indicate that the TiC is synthesized by the diffusion of Ti into CNTs. It has been reported that the TiC are formed by the dissolution–precipitation mechanism in the preparation of TiC by SHS method [10]. In this case, both Ti and C are dissolved in the liquid and then are constituted into TiC after saturation. In this work, the size of the formed particle-like TiC is uniform, which demonstrates that TiC should also be synthesized by Ti-CNTs in Cu melts through the dissolution–

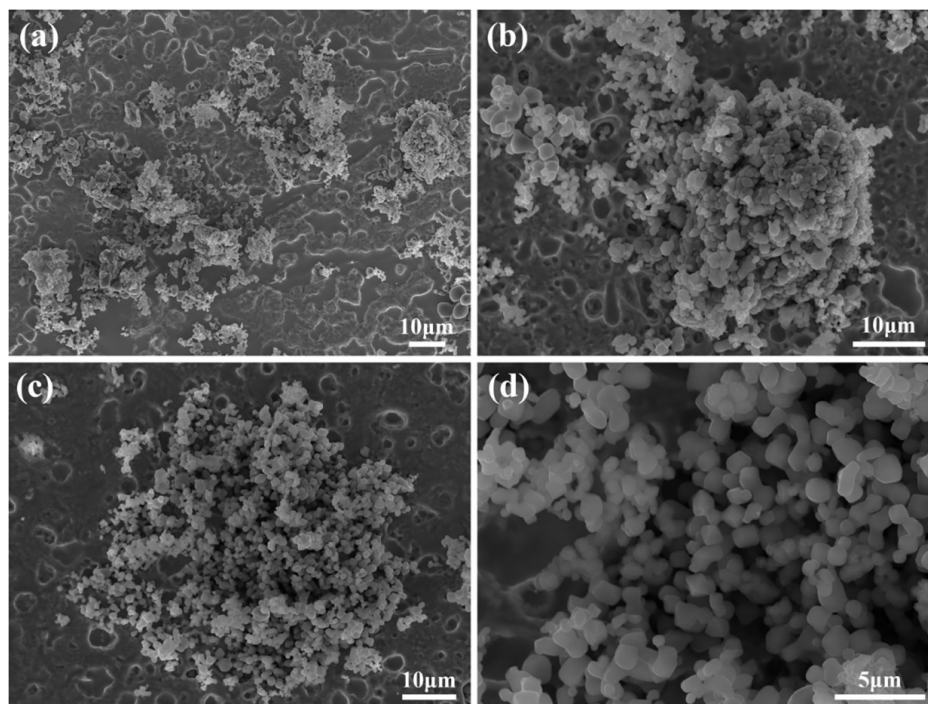


Fig. 5. Microstructures of the electrolytic etching Cu-4Ti-1C sample (a) Low magnification microstructure; (b–d) High magnification microstructures of the TiC agglomerations

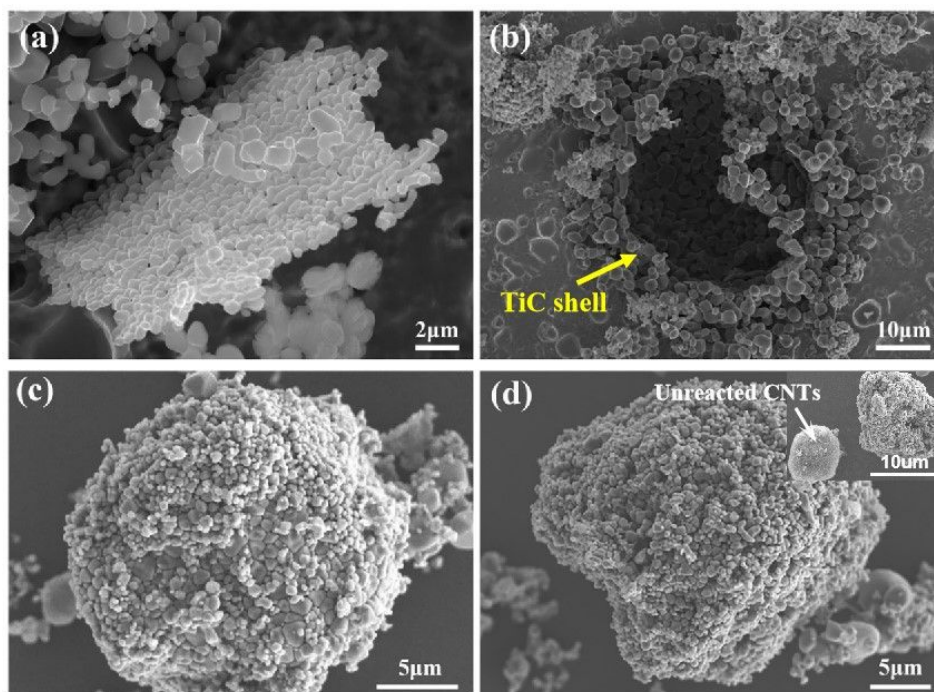


Fig. 6. The morphologies of TiC extracted from the Cu-4Ti-1C sample (a, b) The formed TiC shells; (c, d) The agglomerations of TiC; Insert figure in (d): Unreacted CNTs

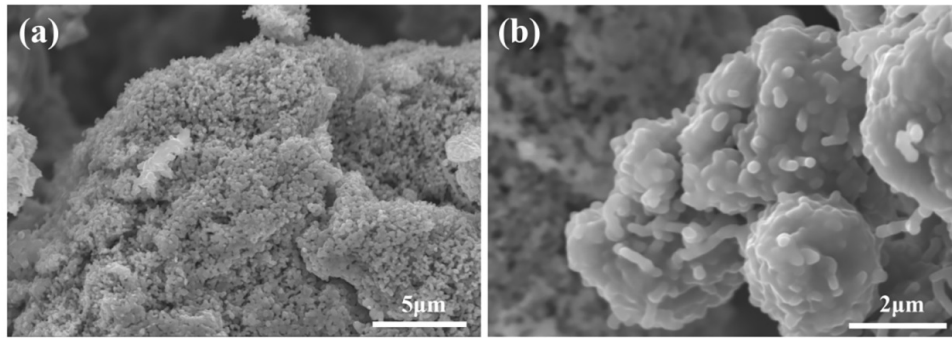


Fig. 7. The agglomerations of TiC in Cu-4Ti-1C (a) The synthesized TiC agglomeration with the surface morphology similar to that of the CNTs agglomeration; (b) The formed TiC with a certain aspect ratio. CNTs, carbon nanotubes

precipitation mechanism. Because both the diffusion ability and the solubility of C in Cu melts are very low, TiC prefer to be synthesized surrounding the original CNTs. Furthermore, due to the poor wettability between TiC and Cu melts, it is difficult to disperse the in-situ synthesized TiC in the Cu melts. As a result, TiC agglomerations are formed.

In addition, the surface morphology of a few synthesized TiC agglomerations is very similar to that of the original CNTs, and the formed TiC is not particle-like but a short rod with a more pronounced aspect ratio, as Figure 7 shows. This indicates that the direct reaction between liquid Ti and CNTs may also occur.

3.2. The influence of Ti/C ratio and Si content on the distribution and morphology of TiC

According to the above results, it is found that the CNTs can be introduced into Cu melts by Ti-C reaction and to form TiC, but most of the synthesized TiC particles are aggregated, which should be due to the poor wettability between TiC and Cu melts. It has been found that the wettability between TiC and Cu melts was effectively improved by the presence of the elements Ti and Si [14, 16, 21]. Therefore, during the addition of Ti-CNTs mixture into the Cu melts, more Ti and some Si are, respectively, added into the mixture to prepare Cu-6.67Ti-1C and Cu-4Ti-1C-1Si samples.

The microstructures of the prepared as-cast Cu-6.67Ti-1C samples are shown in Figure 8. It can be

seen from Figure 8a that the particle-like phase is also formed in the Cu matrix.

The EDS mapping analysis shown in Figure 9 confirms that the particles are synthesized TiC, while the XRD results in Figure 4b also prove the formation of TiC. Compared with the results shown in Figure 2, the distribution of TiC in the Cu matrix has been remarkably improved.

It can be seen from Figure 8 that although there are some small agglomerations, the reaction was sufficient and the overall distribution of synthesized TiC was relatively dispersed. The magnified microstructure shown in Figure 8b demonstrates that the synthesized TiC had two forms, agglomerated fine TiC particles and single larger TiC particles.

Subsequently, in order to better analyze the distribution of TiC in the Cu matrix, the as-cast Cu-6.67Ti-1C was also electrolytically etched in a 30% phosphoric acid solution to erode the Cu matrix on the surface of the sample and expose the synthesized TiC. The microstructures of the etched samples are shown in Figures 8c and 8d. It can be seen that the TiC is uniformly dispersed. In addition, in Figure 8d, it can be seen that the size of TiC in the TiC agglomeration is relatively small, in the range of 1–2 μm , while the size of TiC particles is relatively large, in the range of 2–5 μm . However, the size of TiC is very uniform, and the phenomenon of combined growth of TiC is found.

Obviously, compared with Cu-4Ti-1C, the reaction of Cu-6.67Ti-1C shows greater completion,

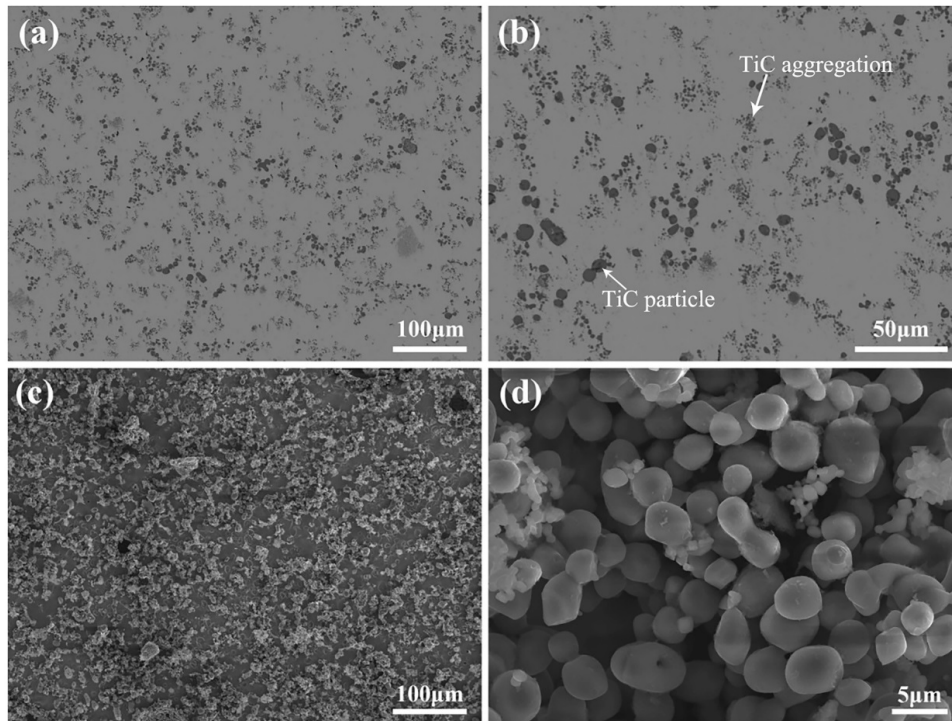


Fig. 8. Microstructures of the Cu-6.67Ti-1C sample (a, b) as-cast sample; (c, d) electrolytic etching sample

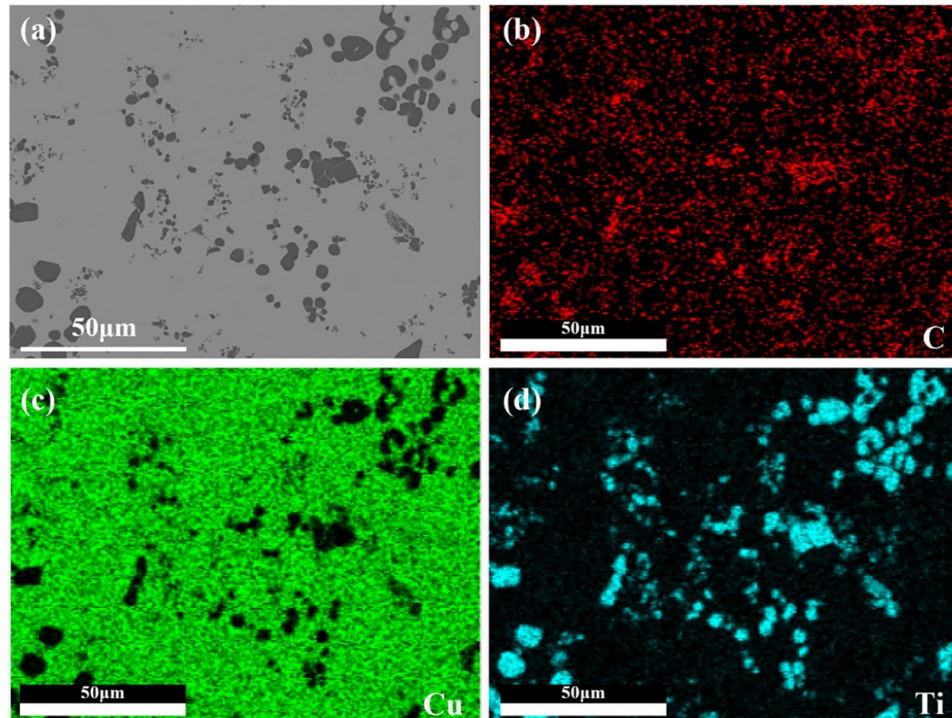


Fig. 9. EDS analysis of the as-cast Cu-6.67Ti-1C sample (a) SEM image; (b–d) mapping micrographs for the elements C, Cu, and Ti. EDS, energy dispersion spectroscopy; SEM, scanning electron microscopy

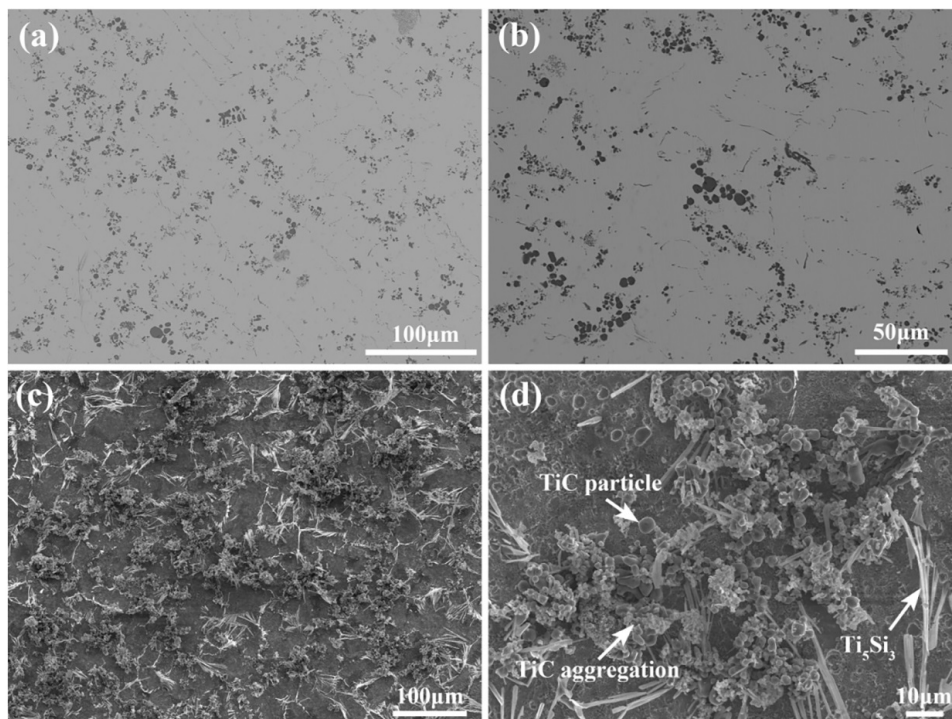


Fig. 10. Microstructures of the Cu-4Ti-1C-1Si sample (a, b) as-cast sample; (c, d) electrolytic etching sample

and more TiC are formed. The aggregation degree of TiC was less and the dispersion of TiC was significantly improved. This indicates that the increase of Ti content can effectively improve the wettability between TiC and Cu melt, and improve the dispersion of TiC. However, the increase of Ti content makes the reaction more intense, which promotes the growth of TiC particles.

The microstructures of the prepared as-cast Cu-4Ti-1C-1Si samples are shown in Figure 10. It can be seen from Figure 10a that the particle-like phase is also formed in the Cu matrix. The EDS mapping and point analysis shown in Figure 11 confirm that the particles are synthesized TiC. Compared with the results shown in Figure 2, the distribution of TiC in the Cu matrix has been remarkably improved. However, compared with the results shown in Figure 8, it can be found that the dispersion of TiC is relatively poor and there are relatively more agglomerations.

It can be seen from Figure 10b that in addition to the granular TiC phase, there is also a needle-like phase. In order to more clearly show the mor-

phology of the generated phase and analyze the distribution of TiC in the Cu matrix, the as-cast Cu-4Ti-1C-1Si samples were electrolytically etched in phosphoric acid solution to remove the surface Cu. The microstructures of the electrolytically etching sample are shown in Figures 10c and 10d. It can be observed that most of the TiC particles have been congregated into clumps with different sizes. It also can be seen from Figure 10d that the size of TiC in agglomerations is generally smaller than that of TiC particles distributed around, and the size distribution range is smaller.

Apart from the granular TiC, a needle-like phase is also found. EDS point analysis in Figure 12 shows that the needle-like phase mainly contains the elements Ti and Si, and is determined to be Ti_5Si_3 after considering the insights offered by a previous study [22]. Besides, the XRD result in Figure 4c shows that TiC is formed, but the Ti_5Si_3 is not detected, which may be owing to its presence in trace amounts only.

Obviously, compared with Cu-4Ti-1C, Cu-4Ti-1C-Si reacted more vigorously and more TiC was

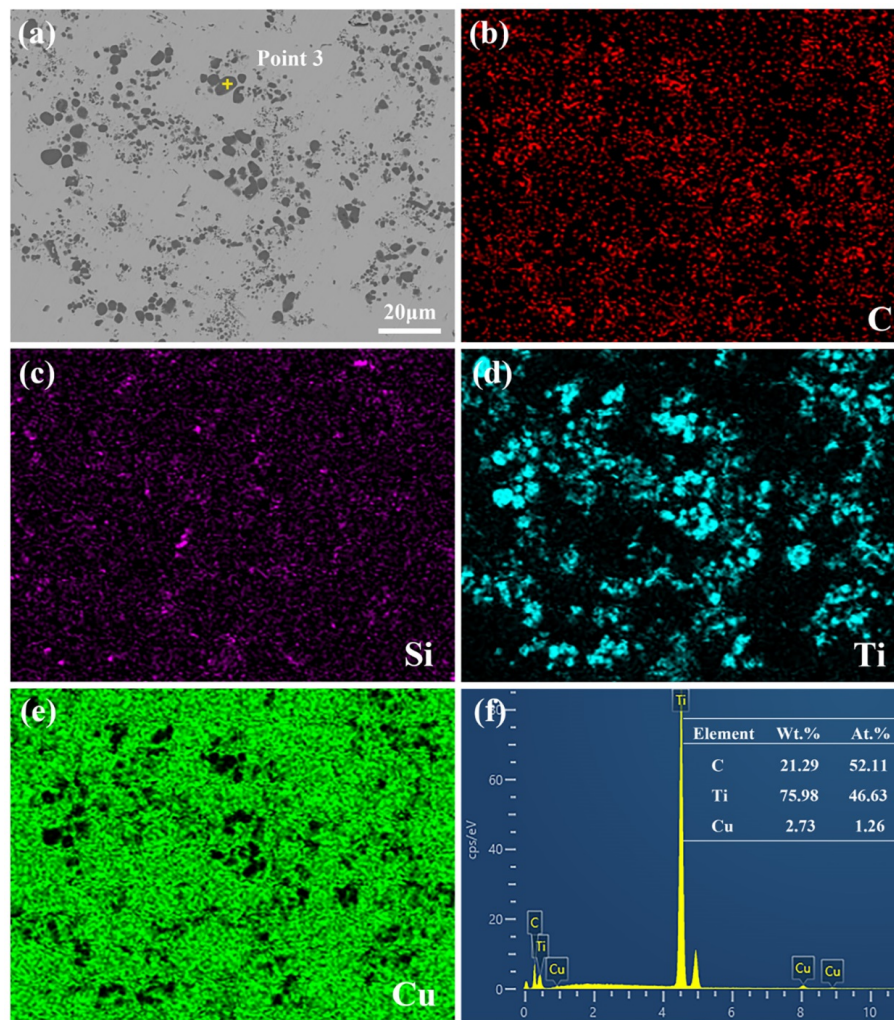


Fig. 11. EDS analysis of the as-cast Cu-4Ti-1C-1Si sample (a) SEM image; (b-e) mapping micrographs for the elements C, Si, Ti, and Cu. (f) EDS point analysis result of point 3 in (a). EDS, energy dispersion spectroscopy; SEM, scanning electron microscopy

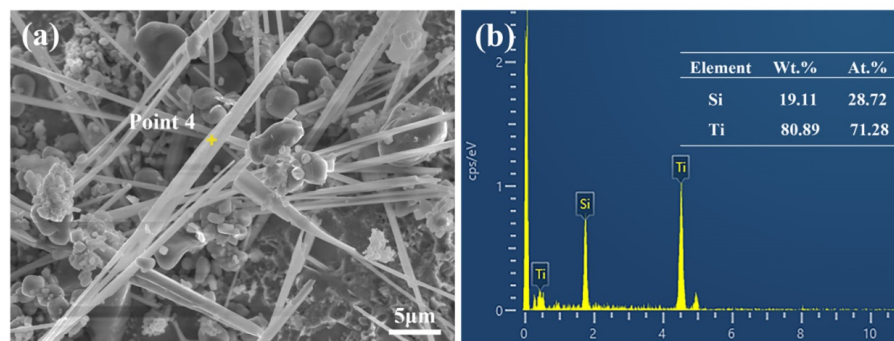


Fig. 12. EDS analysis of the electrolytic etching Cu-4Ti-1C-1Si sample (a) SEM image; (b) EDS point analysis result of point 4 in (a). EDS, energy dispersion spectroscopy; SEM, scanning electron microscopy

formed. The dispersion of TiC increased perceptibly while the agglomeration decreased. However, it can be seen from Figures 8 and 10 that the content of TiC in Cu-4Ti-1C-1Si composite is less than that of Cu-6.67Ti-1C, and there are more TiC agglomerates in Cu-4Ti-1C-1Si composite. This indicates that the addition of Si is helpful to improve the wettability of TiC and Cu melt, and improves the dispersion of TiC. However, since the solubility of Si in Cu solution is higher than in CNTs, Ti reacts with Si first to form Ti_5Si_3 , which makes the reaction more intense and leads to the faster growth of TiC particles.

The distribution and size of the synthesized TiC particles were analyzed using SEM images with the same magnification as indicated in Figures 8 and 10. The volume fractions of the different composites are shown in Figure 13. It can be seen that the volume fraction of TiC in Cu-4Ti-1C is only 4.59% while it increases to 9.35% in Cu-6.67Ti-1C and to 7.59% in Cu-4Ti-1C-1Si. The results further confirm that the increasing of the Ti/C ratio and addition of Si can promote the synthesis of TiC and improve its distribution.

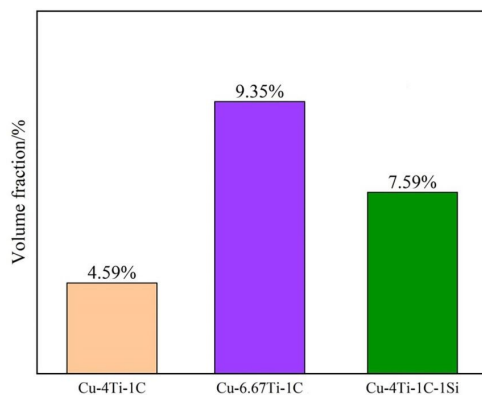


Fig. 13. The volume fraction of TiC in the different composites

The size distribution of TiC in the different composites is shown in Figure 14. According to Figure 14a, the size of TiC in Cu-4Ti-1C is mainly in the range of 0.5–1.0 μm and its average particle size is about 0.79 μm . However, the size of TiC in Cu-6.67Ti-1C is mainly in the range of 1–5 μm , with the larger ones having a size of 5–10 μm also

being synthesized, as shown in Figure 14b. Accordingly, the average size in this instance increases to about 2.46 μm . When Si is added, the size of TiC decreases to 0.5–2.0 μm and the average size is about 1.23 μm , as shown in Figure 14c.

Therefore, it is concluded that it is during Cu-4Ti-1C reaction that the size of TiC particles is smallest and the TiC content lowest. In addition, the most TiC agglomerations are formed since the worst dispersion of TiC. This is due to the poor wettability between TiC and Cu melt. It is difficult to separate TiC from the reaction interface during agglomeration or layer formation. In Cu-6.67Ti-1C, more TiC are synthesized, and the aggregation degree of TiC is perceptibly reduced, which result in an improvement in the dispersion of TiC. However, TiC particles are larger. Since the maximum number of TiC agglomerations/particles is formed when the dissolution-precipitation mechanism is involved, when the content of Ti increases, more Ti will come into contact with CNTs and bring about an intense reaction, which increases the growth rate of TiC, eventually resulting in the formation of large particles. On the other hand, for the Cu-4Ti-1C-1Si composites, Ti will react with Si first to form Ti_5Si_3 and completely promote the synthesis of TiC. In this case also, the reaction is intense and makes TiC easily proliferate.

In addition, the hardness and conductivity of the as-cast composites were also tested. As can be seen from Figure 15a, the hardness of the composite obtained by Cu-4Ti-1C is 161.1 HV. When the content of Ti increased, the hardness of the Cu-6.67Ti-1C composite is significantly increased to 238.8 HV. However, the hardness of the Cu-4Ti-1C-1Si composite decreases to 121.6 HV. In this work, the hardness of the in-situ synthesized Cu composites is related to the content of TiC and the solid solubility of Si and residual Ti. Then, in order to clarify whether it is the change of matrix that leads to the hardness change, the hardness of the Cu matrix in the different composites are tested, and the results are shown in Figure 15b. It can be seen that the change trend of matrix hardness is basically consistent with that of composites. According to the above research, the Cu-6.67Ti-1C forms more TiC and dissolves excessive Ti in the matrix.

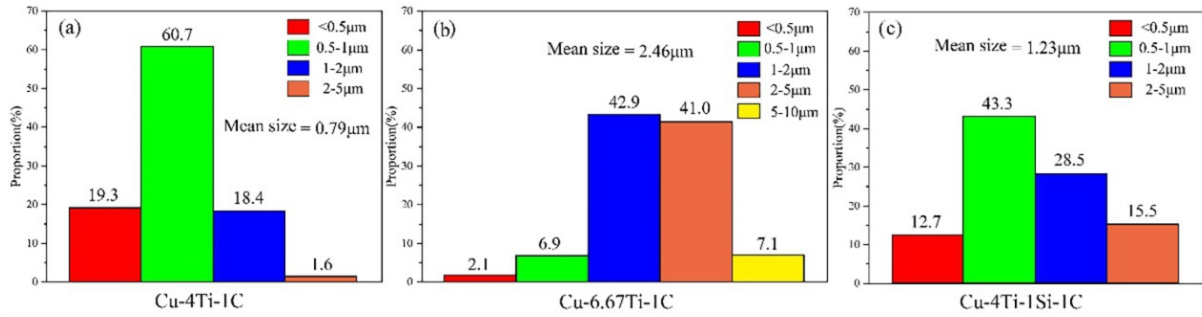


Fig. 14. TiC size distribution statistics (a) Cu-4Ti-1C; (b) Cu-6.67Ti-1C; (c) Cu-4Ti-1C-1Si

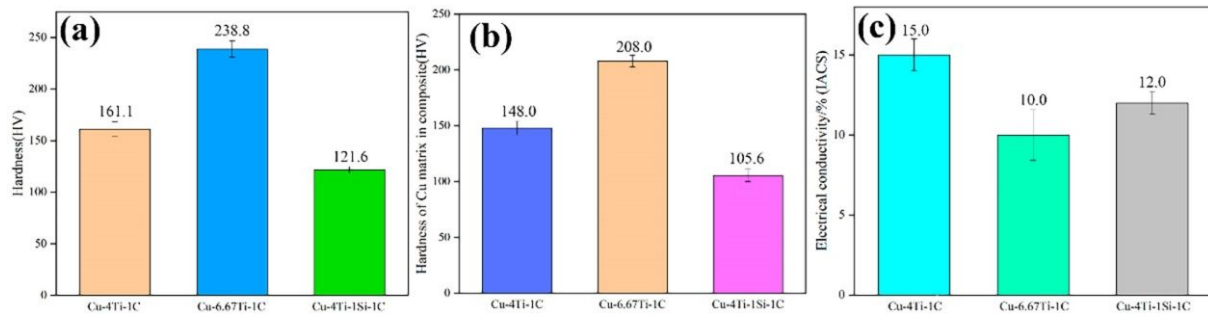


Fig. 15. The properties of the as-cast composites (a) Hardness of the composites; (b) Hardness of Cu matrix; (c) Electrical conductivity

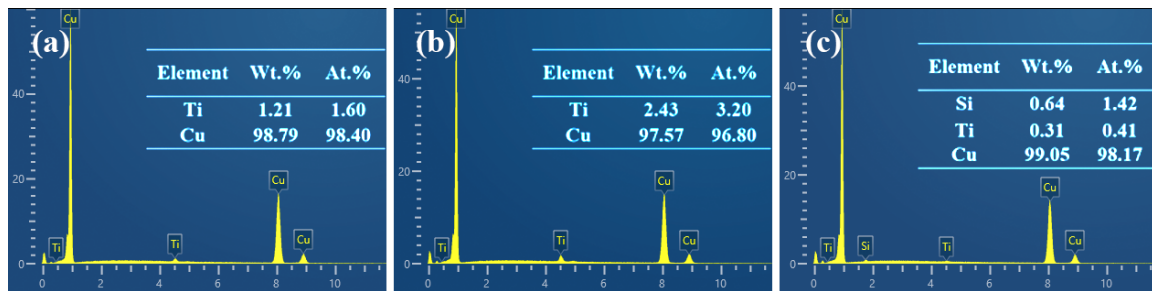


Fig. 16. The EDS point analysis result of Cu matrix in the as-cast composites (a) Cu-4Ti-1C; (b) Cu-6.67Ti-1C; (c) Cu-4Ti-1C-1Si. EDS, energy dispersion spectroscopy

This is the reason why the composite has a higher hardness. This conclusion can be further proved by the EDS point analysis result of Cu matrix, shown in Figure 16. It can be clearly seen that the content of Ti in Cu-6.67Ti-1C is the highest. Also, for Cu-4Ti-1C and Cu-4Ti-1C-1Si composites, since the additive amount of Ti is low, the content of TiC and the dissolved Ti that melts in the Cu are lower after the reaction. This has a great influence on the hardness of composites.

It can be observed from Figure 15c that the conductivity of the Cu-4Ti-1C, Cu-6.67Ti-1C, and Cu-4Ti-1Si-1C composites are 15% IACS, 10% IACS, and 12% IACS, respectively. In our previous work, the conductivity of the Cu-5%TiC composites was observed to be about 41.6% IACS [23]. The low electrical conductivity of the Cu-4Ti-1C that 15% IACS further demonstrates that the reaction between Ti and C in the composites is not sufficient. A certain amount of Ti is residual and dissolved

in the Cu matrix, which will seriously degrade the conductivity. With the increasing of Ti or the presence of Si in the composites, more Ti or Si can also be dissolved in the matrix, which leads to the lower electrical conductivity of the Cu-6.67Ti-1C and Cu-4Ti-1Si-1C composites, as shown in Figure 16.

4. Conclusion

To summarize, in-situ synthesis of TiC in molten Cu based on the reaction of Ti and CNT in the preparation of TiC-reinforced copper matrix composites has been systemically studied in this work. The conclusions are as follows:

1. CNTs can be effectively wetted by Ti-C reaction and successfully introduced into Cu melt to synthesize TiC.
2. The prepared Cu-4Ti-C composite contains many TiC agglomerations, which are caused by the poor wettability of the formed TiC and Cu melt. When the content of Ti increases, the wettability of TiC and Cu melt can be improved, which makes the synthesized TiC agglomeration decrease and the dispersion improve. When Si is added, because Si can react with Ti, the wettability of TiC and Cu can also be improved, but the effect is weak compared with that of increasing the content of Ti.
3. The smallest TiC particles with an average size of 0.79 μm are obtained in Cu-4Ti-C, while the largest ones with an average size of 2.46 μm are formed in Cu-6.67Ti-1C; as for Cu-4Ti-1Si-1C, the size of synthesized TiC is medium, with an average of 1.23 μm .
4. The highest hardness of 238.8 HV could be achieved in the case of Cu-6.67Ti-1C composite, while for Cu-4Ti-1C and Cu-4Ti-1Si-1C, the hardness values obtained are 161.1 HV and 121.6 HV, respectively. The electrical conductivities of all the prepared composites are relatively low, which should be due to the insufficient reaction between Ti and CNTs.

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