Microstructure evolution of Ti_5Si_3 in Cu-Ti-Si alloys

*Qing Liu^{1,3}, Xiao-cui Zhang², Qiang Wang¹, Wen-zhi Miao^{1,3}, Chun-yan Li^{1,3}, Hai-min Ding^{1,3}

1. School of Energy, Power and Mechanical Engineering, North China Electric Power University, Baoding 071003, China

2. State Grid Shandong Electric Power Maintenance Company, Jinan 250021, China

3. Hebei Key Laboratory of Electric Machinery Health Maintenance & Failure Prevention, North China Electric Power University, Baoding 071003, China

Abstract: The Cu-Ti-Si alloys containing in-situ formed Ti_5Si_3 are prepared. In order to clarify the Ti_5Si_3 formation processes and its microstructure characteristics, the as-cast and deeply etched Cu-Ti-Si alloys with different compositions and cooling rates were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). It is found that the eutectic Ti_5Si_3 phases in Cu-Ti-Si alloys are rod-like with hexagonal cross section which tend to intertwine with each other to form a firm skeleton like a bird nest structure which can make the alloys keep their original shape even after etching off the Cu matrix. In addition, there is Cu in the center of many Ti_5Si_3 rods, resulting in a core-shell structure. With the increase of the cooling rate, Ti_5Si_3 distributes more uniformly, and the diameter of Ti_5Si_3 significantly decreases, with a minimum size of less than 100 nm, while the aspect ratio of Ti_5Si_3 increases.

Key words: microstructures; Cu alloys; Ti_5Si_3 ; intermetallic compounds

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Copper is widely used due to its high electrical and thermal conductivity, excellent ductility and low cost. However, poor mechanical strength limits its application^[1-3]. One way to improve its mechanical properties is in-situ formation of intermetallic compounds with high melting point, high hardness and modulus by adding alloying elements^[4, 5]. For example, Cu-Mn-Si alloys which are reinforced by Mn_5Si_3 have been widely used in mechanical friction parts such as synchronizer rings, self-lubricating bearings and high-speed hydraulic rotors^[6-9]. Another intermetallic compound, Ti_5Si_3 , which has similar crystal structure and properties to Mn_5Si_3 ^[10], has been used either as a structural material itself^[11-13] or the reinforcement phase in Ti alloys for high temperature applications^[14-19] due to its high melting temperature, low density, excellent oxidation resistance, corrosion and creep resistance. However, few researchers have paid attention to the application of Ti_5Si_3 in Cu alloys.

In this work, Cu-Ti-Si alloys containing in-situ formed Ti_5Si_3 are prepared. The influences of Ti and Si contents

as well as the cooling rate on the microstructures of Ti_5Si_3 are systematically studied. It is considered that the results in this work are meaningful for developing Cu alloys with Ti_5Si_3 intermetallic compound.

1 Experimental procedure

Cu-Ti-Si alloys with nominal compositions of Cu-1.43Ti-0.5Si, Cu-2.86Ti-1Si and Cu-5.72Ti-2Si (wt.%) were prepared. Firstly, the electrolytic pure copper was melted in a quartz crucible inside the SPG-20B high frequency induction heating furnace. Then, Ti and Si were added into the Cu melts and held for about 1 min. Finally, the melts were poured into molds to obtain Cu-Ti-Si alloys. The cooling rate was controlled by using the graphite, steel and copper molds with different sizes ($\Phi 18$ mm and $\Phi 10$ mm).

The as-cast samples were mechanically grounded and polished by standard routines, and then characterized via a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscope (TEM). Fracture surfaces of the samples were also examined by SEM. In addition, in order to further identify the structure and morphology of Ti_5Si_3 , the samples were deeply etched using a solution of 10% H_2SO_4 , 30% H_2O_2 and 60% water (vol.%), and Ti_5Si_3 was extracted from the

*Qing Liu

Female, born in 1986, Ph.D, Lecturer. She has been working in the field of carbon materials and their composites. Her academic research has led to the publication of 18 papers in journals and three invention patents of China.

E-mail: 52452061@ncepu.edu.cn

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alloys. The etched samples were investigated by SEM and XRD. The XRD analysis was performed on a Rigaku D/Max 2500 V diffractometer with Cu-K α radiation operated at 40 kV, 250 mA ($20^\circ \leq 2\theta \leq 90^\circ$).

2 Results and discussion

Figure 1 shows the SEM results of the three Cu-Ti-Si alloys prepared by pouring the melt into the graphite molds with a diameter of 10 mm. In Fig. 1(a), a gray phase with an obvious directional distribution can be observed. According to the alloy composition, the gray phase should be a Ti-Si intermetallic compound.

It is known that Ti and Si can form various intermetallics such as TiSi, TiSi₂, Ti₃Si, Ti₅Si₄, Ti₅Si₃, etc.^[14]. In order to accurately determine the Ti-Si intermetallic type, the Cu matrix was absolutely etched off from the as-cast sample and then the extracted powder was analyzed by XRD. The result is given in Fig. 2(a). It can be found that there are no other intermetallics except Ti₅Si₃.

The microstructure of the as-cast Cu-2.86Ti-1Si sample is shown in Fig. 1(c). It is obvious that more Ti-Si phases are present, and according to the XRD result given in Fig. 2(b), the Ti-Si phase is also Ti₅Si₃. However, compared with the Ti₅Si₃ in Cu-1.43Ti-0.5Si alloy, the Ti₅Si₃ in Cu-2.86Ti-1Si is not directional but more uniformly distributed. The EDS mapping

Fig. 1: Microstructures of different samples by graphite molds with a diameter of 10 mm before (a, c and e) and after (b, d and f) deep etching: (a, b) Cu-1.43Ti-0.5Si; (c, d) Cu-2.86Ti-1Si; (e, f) Cu-5.72Ti-2Si

Fig. 2: XRD patterns of extracted powders from different as-cast samples: (a) Cu-1.43Ti-0.5Si; (b) Cu-2.86Ti-1Si; (c) Cu-5.72Ti-2Si

analysis shown in Figs. 3(b)–(d) further confirms the uniform distribution of Ti_5Si_3 in Cu-2.86Ti-1Si.

In addition, it is also noticed that many Ti_5Si_3 rods are not formed by a single phase, there is another phase in the center, as shown in Fig. 4(a). The TEM analysis and corresponding EDS point analysis shown in Figs. 4(b), (c) prove that the phase in the Ti_5Si_3 center is Cu. It is also found from Figs. 4(a), (b) that the Ti_5Si_3 is rod-like with hexagonal cross section, which is similar to the Mn_5Si_3 in Cu-Mn-Si alloys^[7].

The microstructure shown in Fig. 1(e) demonstrates that with an increase in contents of Ti and Si, the Ti-Si phase aggregates into particles with a larger size, but the XRD result in Fig. 2(c) proves that the Ti-Si phase in Cu-5.72Ti-2Si is still Ti_5Si_3 . In addition, two kinds of morphologies of Ti_5Si_3 formed in Cu-5.72Ti-2Si: one is rod-like, which is similar to that in Cu-2.86Ti-1Si, while the other one is block-like with a larger size.

Fig. 3: EDS mapping of as-cast Cu-2.86Ti-1Si: (a) SEM image; (b-d) mapping micrographs for Cu, Ti and Si elements

According to Ti-Si phase diagram^[20, 21] and the microstructure characteristics of the alloys mentioned above, it can be deduced that Ti_5Si_3 in the Cu-1.43Ti-0.5Si and Cu-2.86Ti-1Si alloys are formed by the eutectic reaction. While in the Cu-5.72Ti-2Si alloys, besides eutectic Ti_5Si_3 , some primary Ti_5Si_3 phases are also formed.

Figures 1(b), (d) and (f) show the microstructures of Ti_5Si_3 extracted from the samples. It can be more obviously seen that the eutectic Ti_5Si_3 phase actually grows into a rod shape, and then gathers to bundles with obvious directionality in Cu-1.43Ti-0.5Si. In Cu-2.86Ti-1Si, the rod-like eutectic Ti_5Si_3 is

interlaced and overlapped on the Cu matrix to form a structure like the bird nest, as shown in Fig. 1(d), and the particle size and aspect ratio of Ti_5Si_3 phase are in a narrower distribution range. It is also noticed from Fig. 5(a) that the Cu-2.86Ti-1Si samples still maintain the original shape after etching. This result further demonstrates that the intertwined Ti_5Si_3 prevents the sample from collapsing after etching away the Cu matrix. In addition, in Cu-5.72Ti-2Si, besides the rod-like Ti_5Si_3 , some primary Ti_5Si_3 phases grow into a large sheet-like structure, as shown in Fig. 1(f).

Fig. 4: TEM images of Ti_5Si_3 in Cu-2.86Ti-1Si: (a) hexagonal cross section; (b) longitudinal section; (c) EDS analysis result of Point P1 shown in Fig. 4b

Fig. 5: Cu-2.86Ti-1Si (a) and Cu-2.86Ti-1Si (S) (b) samples before and after deep etching, and microstructures of as-cast (c) and deeply etched (d) Cu-2.86Ti-1Si

The Cu-2.86Ti-1Si alloy was then used to investigate the influence of cooling rate on the size, morphology and distribution of Ti_5Si_3 . The Cu-2.86Ti-1Si melt was poured into the graphite mold with a diameter of 18 mm in order to decrease the cooling rate, and the obtained sample was designated as Cu-2.86Ti-1Si(S). As shown in Fig. 5(b), Cu-2.86Ti-1Si(S) also maintained its the original shape after etching, which indicates that the Ti_5Si_3 is overlapped each other. This can be confirmed by the microstructure shown in Fig. 5(d). The results shown in Figs. 5(c) and (d) also indicate that the microstructures of Cu-2.86Ti-1Si have been modified by changing the cooling rate. Comparing Fig. 5(d) with Fig. 1(d), the aspect ratio of rod-like Ti_5Si_3 is decreased due to the lower cooling rate. Additionally, it can be found that some Ti_5Si_3 are hollow rods with hexagonal prisms after etching out the Cu matrix, which further confirms that Ti_5Si_3 is a core-shell structure with Cu core. In addition, it is also can be seen from Fig. 5(d) that there are many Ti_5Si_3 which are rod-like but without Cu core.

As mentioned above, Ti_5Si_3 has a hexagonal structure. The arrangement of Ti and Si atoms along $[0001]$ and $[11\bar{2}0]$

directions is shown in Fig. 6. According to the Hartman-Perdok theory^[22], like the growth of Mn_5Si_3 reported by Li et al.^[7], the growth direction of Ti_5Si_3 crystal is mainly determined by the periodic chain of Ti-Si covalent bond due to the lower binding energy of Si-Si or Ti-Ti. As a result, the growth rate along $\langle 11\bar{2}0 \rangle$ direction on $\{0001\}$ face is higher than other directions due to the complete periodic bond chain of Ti-Si. Moreover, the crystal growth rate along $\langle 0001 \rangle$ direction should be higher than that along $\langle 11\bar{2}0 \rangle$ direction, because the binding energy of Ti-Si bond chain is greater in $\langle 0001 \rangle$ direction due to the atomic arrangements with shorter distance. Therefore, Ti_5Si_3 will grow into a rod-like hexagonal prism. The reason for the formation of core-shell prisms with Cu cores is that the diffusion of Ti and Si to the inner region of crystal during the growth will become difficult due to the long diffusion distance. As a result, the growth rate of the outside region along the prism $\langle 0001 \rangle$ direction is much faster than that of the inner region and then the hollow will be formed in the center of Ti_5Si_3 . Consequently, Cu melts will incorporate into the hollow to make Ti_5Si_3 transform into core-shell structure with Cu core.

Fig. 6: Atom arrangement in Ti_5Si_3 along $[0001]$ (a) and $[11\bar{2}0]$ (b) direction

The shear fractures of the above prepared Cu-2.86Ti-1Si and Cu-2.86Ti-1Si(S) samples were also analyzed and the results are shown in Fig. 7. It can be seen from Figs. 7(a), (b), with a lower cooling rate, the cracks propagate along the interface of Ti_5Si_3 . As a result, many Ti_5Si_3 rods or rod bundles are pulled out along the radial direction. In addition, some Ti_5Si_3 rods are also pulled out along the axial direction. There are also some large dimples. Therefore, the fracture shown in Figs. 7(a), (b) is a quasi-cleavage fracture. There are more dimples in the fracture surface of the Cu-2.86Ti-1Si solidified with a higher cooling rate, as shown in Figs. 7(c), (d), indicating a significant improvement in toughness. Furthermore, it is noticed that most of the Ti_5Si_3 rods are also pulled out along the axial direction in this sample, which should be attributed to the improved distribution and lower directionality of Ti_5Si_3 .

The pullout of Ti_5Si_3 is the main mechanism for breakage of the Cu-2.86Ti-1Si alloys, so, further increasing the aspect ratio and decreasing the diameter of Ti_5Si_3 will be helpful for the property improvement of the alloys, which can be achieved by further increasing the cooling rates. Figure 8 shows the microstructures of the Ti_5Si_3 extracted from the Cu-2.86Ti-1Si alloys prepared using steel and copper moulds, each with a

diameter of 10 mm. As shown in Figs. 8(a), (b), the Ti_5Si_3 with a diameter of about 200 nm and a aspect ratio of greater than 150 is formed in Cu-2.86Ti-1Si alloy poured with a steel mould, while the Ti_5Si_3 nano wires with a diameter less than 100 nm could be obtained in the Cu-2.86Ti-1Si alloy poured with a copper mould, as shown in Figs. 8(c), (d).

3 Conclusions

The microstructures of Ti_5Si_3 in the Cu-Ti-Si alloys with different compositions and cooling rates were investigated. The main conclusions are as follows:

(1) The eutectic Ti_5Si_3 formed in Cu-Ti-Si alloys is rod-like with a hexagonal cross section which tend to intertwine each other to form a bird nest structure. This structure allows the alloys to maintain their original shape even after etching off the Cu matrix.

(2) There is Cu in the center of many Ti_5Si_3 rods, which results in the formation of a core-cell structure.

(3) The size, distribution and aspect ratio of Ti_5Si_3 are significantly changed with the cooling rates. The diameter of Ti_5Si_3 decreases with the increase of the cooling rate, and even

Fig. 7: Fracture microstructures of Cu-2.86Ti-1Si samples solidified in graphite mold with diameters of 18 mm (a, b) and 10 mm (c, d)

Fig. 8: Microstructures of Ti_5Si_3 extracted from different Cu-2.86Ti-1Si alloys poured with steel mold (a, b) and copper mold (c, d) with a diameter of 10 mm

decreases to less than 100 nm. At the same time, the aspect ratio increases and the distribution is more uniform.

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References

- [1] Chen F, Ying J, Wang Y, et al. Effects of graphene content on the microstructure and properties of copper matrix composites. *Carbon*, 2016, 96: 836–842.
- [2] Yao G C, Mei Q S, Li J Y, et al. Cu/C composites with a good combination of hardness and electrical conductivity fabricated from Cu and graphite by accumulative roll-bonding. *Materials & Design*, 2016, 110: 124–129.
- [3] Krishna S C, Jha A K, Pant B, et al. Achieving higher strength in Cu-Ag-Zr alloy by warm/hot rolling. *Rare Metals*, 2017, 36: 263–267.
- [4] Wang W, Li R, Zou C, et al. Effect of direct current pulses on mechanical and electrical properties of aged Cu-Cr-Zr alloys. *Materials & Design*, 2016, 92: 135–142.
- [5] Fu H, Xu S, Li W, et al. Effect of rolling and aging processes on microstructure and properties of Cu-Cr-Zr alloy. *Materials Science Engineering: A*, 2017, 700: 107–115.
- [6] Mindivan H, Çimenoglu H, Kayali ES. Microstructures and wear properties of brass synchroniser rings. *Wear*, 2003, 254: 532–537.
- [7] Li H, Jie J, Liu S, et al. Crystal growth and morphology evolution of D88 (Mn, Fe)₅Si₃ phase and its influence on the mechanical and wear properties of brasses. *Materials Science Engineering: A*, 2017, 704: 45–56.
- [8] Li H, Jie J, Zhang P C, et al. Study on the formation and precipitation mechanism of Mn₅Si₃ phase in the MBA-2 brass alloy. *Metallurgical and Materials Transactions A*, 2016, 47: 2616–2624.
- [9] Sundberg M, Sundberg R, Hogmark S, et al. Metallographic aspects on wear of special brass. *Wear*, 1987, 115: 151–165.
- [10] Zhang L N, Wu J. Ti₅Si₃ and Ti₅Si₃-based alloys: Alloying behavior, microstructure and mechanical property evaluation. *Acta Materialia*, 1998, 46: 3535–3546.
- [11] Shah D M, Berczik D, Anton D L, et al. Appraisal of other silicides as structural materials. *Materials Science Engineering: A*, 1992, 155: 45–57.
- [12] Sandwick T, Rajan K. The oxidation of titanium silicide. *Journal of Electronic Materials*, 1990, 19: 1193–1199.
- [13] Schneibel J H, Rawn C J. Thermal expansion anisotropy of ternary titanium silicides based on Ti₅Si₃. *Acta Materialia*, 2004, 52: 3843–3848.
- [14] Colinet C, Tedenac J C. Structural stability of intermetallic phases in the Si-Ti system. Point defects and chemical potentials in D88-Si₃Ti₅ phase. *Intermetallics*, 2010, 18(8): 1444–1453.
- [15] Schneibel J H, Rawn C J. Thermal expansion anisotropy of ternary titanium silicides based on Ti₅Si₃. *Acta Materialia*, 2004, 52: 3843–3848.
- [16] Li Y, Huang S, Bai P, et al. Effect of Ti/Si ratio on the products of laser igniting self-propagating high-temperature synthesis in Cu-Ti-Si system. *Journal of Alloys Compound*, 2013, 548: 245–248.
- [17] Kang B Y, Ryoo H S, Hwang W, et al. Explosion synthesis of Ti₅Si₃-Cu intermetallic compound. *Materials Science Engineering: A*, 1999, 270: 330–338.
- [18] Wang H Y, Lü S J, Zha M, et al. Influence of Cu addition on the self-propagating high-temperature synthesis of Ti₅Si₃ in Cu-Ti-Si system. *Materials Chemistry and Physics*, 2008, 111(2–3): 463–468.
- [19] Lu J W, Zhao Y Q, Du Y, et al. Microstructure and mechanical properties of a novel titanium alloy with homogeneous (Ti, Hf)₅Si₃ particle-reinforcements. *Journal of Alloys and Compound*, 2019, 778: 115–123.
- [20] Ran H S, Niu J N, Song B B, et al. Microstructure and properties of Ti₅Si₃-based porous intermetallic compounds fabricated via combustion synthesis. *Journal of Alloys and Compound*, 2014, 612: 337–342.
- [21] Awe O E, Odusote Y A, Hussain L A, et al. Temperature dependence of thermodynamic properties of Si-Ti binary liquid alloys. *Thermochimica Acta*, 2011, 519: 1–5.
- [22] Hartman P, Perdok W G. On the relation between structure and morphology of crystals. *Acta Crystallographica*, 1955, 8: 525–529.