In situ reaction mechanism of Cu–Ti–CuO system in pure copper melts

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Abstract

In situ reaction was carried out using Cu–Ti–CuO as reaction system and pure copper melt as reaction medium. When the melt temperature is close to the melting point of pure copper, the sample was obtained by casting near the melting point. The effects of reaction parameters, such as the molar ratio of reactants and melt preheating temperature, on the in situ reaction mechanism, as well as the effects of the size, shape and distribution of the reaction products on the near melting point casting structure of the matrix copper were studied, so as to prepare Cu–TiO2 composites with good electrical and mechanical properties. The results show that Cu–Ti–CuO reaction system can produce rutile titanium dioxide particles smaller than 2 μm of pure copper melt, without TiXCuY intermetallic compound, with the molar ratio of Ti to CuO of 1:2, the content of diluent of 50%, the forming pressure of 10 MPa, and the preheating temperature of pure copper melt of 1250 °C. The morphology of TiO2 particles is nearly spherical and dispersed in the copper matrix. The reasons for the formation of TiO2 particles in Cu–Ti–CuO reaction system were analyzed from the perspectives of thermodynamics, kinetics and Redox reaction. When the mass fraction of TiO2 is 3%, the solidification structure of the sample is more uniform than that of pure copper, the grains are refined, and the average grain size is 103.29 μm.

1. Introduction

The application fields of high-strength and high-conductivity copper-based composite materials, such as resistance welding electrodes, integrated circuit lead frames, and railway contact wires [1–5], require higher and higher performance of the materials. Therefore, how to further improve the strength of copper while maintaining high conductivity has always been the focus of research [6, 7]. At present, particle-reinforced copper-based composite materials can be divided into external composite materials and endogenous composite materials according to the introduction of reinforcing phase particles [8–10], of which the latter reacts in situ in the copper melt to generate reinforcing phase particles through chemical reaction. As the reinforcing phase is generated in situ in the matrix, the interface between the reinforcing phase and the matrix is clean, with good wettability and strong binding force [11–15]; and the chemical reaction will release a certain amount of energy, making the reinforcing phase uniformly dispersed in the matrix [16]. Ceramic particles are characterized by high Young’s modulus, high hardness and excellent high-temperature performance [17, 18], and thus are suitable for use as the reinforcing phase of high-strength and high-conductivity copper-based composites [19].

In this paper, Cu–Ti–CuO is used as the reaction system to produce in situ particles in pure copper melt. When the melt temperature is close to the copper melting point, the sample containing in situ particles is obtained by casting. The reaction mechanism of Cu–Ti–CuO system in copper melt, the morphology, size and distribution of the reaction product in the copper matrix as well as the influence of the morphology, size, quantity and distribution of the reaction product on the microstructure of the pure copper matrix are studied.
2. Experimental procedure and method

From the perspective of thermodynamics, the possible reactions of Cu–Ti–CuO as a reaction system were analyzed. The DSC curve of the Cu–Ti–CuO system was tested using differential scanning calorimetry. The possible reactions were analyzed according to the position of the exothermic peak in the heating process. Assuming that the reaction occurred under adiabatic conditions, with the reaction rate if 100% and without heat loss, whether the adiabatic temperature of the reaction system in the pure copper melt met the self-propagating reaction conditions was determined [20].

In the experiment, pure copper ingot (purity 99.95%) served as the matrix (reaction medium), and Ti powder (300 mesh, purity 99.99%), CuO powder (300 meshes, purity 99.9%), and Cu powder (200 meshes, purity 99.9%) as a reaction system. The appearance of the reactant is shown in figure 1. As can be seen from the figure, Ti powder is lamellar, CuO powder is quasi-spherical, and Cu powder is a mixture of spherical and near-spherical.

The sample preparation process is shown in figure 2. Ti, CuO, and Cu powder was weighed according to a certain proportion ($n_{Ti}:n_{CuO}:n_{Cu} = 1:2:3.25$), and was then uniformly mixed by grinding for 1 h. The appearance and morphology of the mixed powder are shown in figure 1 (d). The raw materials were uniformly distributed, and the mixed powder was compressed into a cylindrical prefabricated block ($\Phi 15$ mm × 2 mm) with a powder tableting machine under the molding pressure of 10 MPa, for the pressure holding time of 5 min. The pure copper ingot was melted in an intermediate frequency induction melting furnace. When the temperature was increased to 1250 °C, the preform was compressed into the pure copper melt so as to react in

![Figure 1. The appearance of the reactants: (a) Ti; (b) CuO; (c) Cu; (d) Cu–CuO–Ti Mixed powder.](image)

![Figure 2. The preparation process of sample.](image)
The main oxides of titanium include TiO$_2$, TiO, Ti$_2$O$_3$ and Ti$_3$O$_5$ according to the inorganic thermodynamics.

### 3.1. Thermodynamic analysis

The main oxides of titanium include TiO$_2$, TiO, Ti$_2$O$_3$ and Ti$_3$O$_5$ according to the inorganic thermodynamics data manual. Therefore, it can be inferred that the reaction expressed in equations (1)–(8) in table 1 may occur in the Cu–Ti–CuO system. Ti and CuO were used as the reactants and copper powder as diluent in the Cu–Ti–CuO system, aiming to reduce the violent degree of the thermal explosion reaction and prevent the reaction from being too violent and splashing. According to the Gibbs free energy formula [21] (9), the relationship between free energy and temperature in the reaction equations (1)–(8) was calculated.

$$
\Delta G = \Delta H - T \Delta S
$$

where $\Delta G$ is the Gibbs free energy (kJ mol$^{-1}$); $\Delta H$ is the enthalpy change (J mol$^{-1}$); $\Delta S$ is the entropy change (J mol$^{-1}$K$^{-1}$).

The thermodynamic data was obtained according to the practical inorganic thermodynamic data manual, as listed in table 1. The relationship curve between temperature (T) and Gibbs free energy ($\Delta G$) was drawn, as shown in figure 3. As can be seen from figure 3, $\Delta G < 0$ of equations (1)–(4), and with the increase of the 

![Figure 3. The Gibbs free energy varies with temperature.](image)

**Table 1.** The values of Gibbs free energy ($\Delta G$) as a function of temperature are required [21].

| Reaction equation | $\Delta G^0$ (kJ mol$^{-1}$) |
|-------------------|-----------------------------|
| Ti + 2CuO $\rightarrow$ TiO$_2$ + 2Cu | $\Delta G_1$ = $-633.039$–$0.737$ T |
| Ti + CuO $\rightarrow$ TiO + Cu | $\Delta G_1$ = $-363.737$–$10.933$ T |
| 2Ti + 3CuO $\rightarrow$ Ti$_2$O$_3$ + 3Cu | $\Delta G_1$ = $-1053.280$ + $10.924$ T |
| 3Ti + 5CuO $\rightarrow$ Ti$_3$O$_5$ + 5Cu | $\Delta G_1$ = $-1679.876$ + $9.895$ T |
| 2Ti + Cu $\rightarrow$ Ti$_2$Cu | $\Delta G_1$ = $-36.393$ + $14.06$ T |
| Ti + Cu $\rightarrow$ TiCu | $\Delta G_1$ = $-22.412$ + $6.54$ T |
| 3Ti + 4Cu $\rightarrow$ Ti$_3$Cu$_4$ | $\Delta G_1$ = $-68.238$ + $15.95$ T |
| Ti + 4Cu $\rightarrow$ TiCu$_4$ | $\Delta G_1$ = $-30.035$ + $11.70$ T |

The pure copper melt. When the temperature decreased to 1100 °C, the metal liquid was rapidly poured into the cylindrical mold ($\Phi$100 mm x 150 mm) and cooled to obtain the sample.

Phase analysis of the reaction product: since the mass fraction of the reaction product contained in the sample was less than 5%, a part of the sample was weighed and put in a 68% nitric acid solution, and then soaked for 12 h to corrode the copper matrix. It was found to be insoluble in the solution. The solid powder of nitric acid was cleaned with deionized water and dried to obtain a powder insoluble in nitric acid solution. The acid-etched powder was analyzed by x-ray diffraction analyzer, the size and morphology of the reaction product in the acid-etched powder and the distribution of the reaction product in the sample were observed by field emission scanning electron microscope (SEM, FEI QUANTA 650 FEG), and the microstructure of the sample was observed by an optical microscope (OM).

### 3. Results and discussion

**3.1. Thermodynamic analysis**

The main oxides of titanium include TiO$_2$, TiO, Ti$_2$O$_3$ and Ti$_3$O$_5$ according to the inorganic thermodynamics data manual. Therefore, it can be inferred that the reaction expressed in equations (1)–(8) in table 1 may occur in the Cu–Ti–CuO system. Ti and CuO were used as the reactants and copper powder as diluent in the Cu–Ti–CuO system, aiming to reduce the violent degree of the thermal explosion reaction and prevent the reaction from being too violent and splashing. According to the Gibbs free energy formula [21] (9), the relationship between free energy and temperature in the reaction equations (1)–(8) was calculated.

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The thermodynamic data was obtained according to the practical inorganic thermodynamic data manual, as listed in table 1. The relationship curve between temperature (T) and Gibbs free energy ($\Delta G$) was drawn, as shown in figure 3. As can be seen from figure 3, $\Delta G < 0$ of equations (1)–(4), and with the increase of the
temperature, the Gibbs free energy of reactions (3) and (4) decreases; equations (1), (2) The Gibbs free energy is reduced; Therefore, from a thermodynamic point of view, reactions (1)–(4) can occur spontaneously, and reactions (5)–(8) may occur to form Ti₃Cu₅ intermetallic when the temperature is less than 1200K. Differential scanning calorimetry (DSC) was used to test the evenly mixed Cu powder, Ti powder and CuO powder. The obtained DSC curve was used to verify the thermodynamic calculation results, as shown in figure 4. The exothermic peak in the DSC curve between 600 °C and 800 °C indicates that one or more of reactions (1)–(4) occurred in the powder mixture. The endothermic peak appeared at 1085 °C at which copper melted in the powder mixture. Cu and Ti reacted between 800 °C and 900 °C to form Ti₃Cu₅ intermetallic compound [22], but there was no exothermic peak and endothermic peak in the DSC curve between 800 °C and 900 °C, indicating that no Ti₃Cu₅ intermetallic compound was generated in this reaction system. Combined with thermodynamic calculation results and DSC curves, it is proved that Cu–Ti–CuO can be used as a reaction system.

Since Cu–Ti–CuO system reacted in pure copper melt at 1250 °C, the adiabatic temperature of Ti+2CuO → TiO₂ + 2Cu was calculated according to equation (10) [21].

$$\sum n_i(H^\circ_T - H^\circ_{298})_{Product} = \sum n_i(H^\circ_T - H^\circ_{298})_{Reactant} - \Delta H^\circ_{298}$$

where n is the balancing coefficient in the equation; is the enthalpy of the substance at T; is standard molar enthalpy of formation; the adiabatic temperature of the system calculated by equation (10) was 3850 K (> 1800 K), indicating that the heat released by the reaction system itself was sufficient to maintain the reaction itself and meet the conditions for the occurrence of self-propagating reaction [21].
3.2. In situ reaction products and their mechanism analysis

XRD results of acid etched powder are shown in figure 5. The figure shows that the main component of the acid etched powder is rutile TiO$_2$, thus belonging to the Tetragonal system. The reaction of

![Figure 6](image1.png)

Figure 6. Microstructures of the extract powder from prepared Cu–TiO$_2$ samples. (a) SEM micrographs of the extract powder; (b) EDS patterns of Point 1 shown in figure 6(a).

![Figure 7](image2.png)

Figure 7. Microstructure and energy spectrum analysis of Cu–2TiO$_2$ sample; (a) Microstructures of Cu–2TiO$_2$ sample; (b) a magnified view of area A in figure 7(a); (c) a magnified view of area B in figure 7(b); (d) Ti; (e) Cu; (f) O.
Ti\(_2\)CuO \rightarrow TiO\(_2\) + 2Cu mainly occurred in Cu–Ti–CuO system in pure copper melt. The Gibbs free energy of the equations Ti+2CuO \rightarrow TiO\(_2\) + 2Cu and Ti+CuO \rightarrow TiO + Cu decreased with the increase of temperature, indicating that high-temperature condition was favorable to the occurrence of the two reactions. From the perspective of dynamics, after the addition of preform blocks into pure copper melt, Ti element in the reactants reacted with O element in CuO, forming an atomic aggregate of Ti and O through diffusion in the early stage of reaction. The formation of TiO\(_2\) requires one titanium atom and two oxygen atoms. Compared with the formation of Ti\(_2\)O\(_3\) and Ti\(_3\)O\(_5\), the formation of TiO\(_2\) particles requires less energy and fewer atoms, and thus is easier. Therefore, TiO\(_2\) particles are preferentially generated. Moreover, Ti and CuO have a REDOX reaction, and Ti is oxidized by CuO as a reducing agent. The main oxides of titanium include TiO\(_2\), TiO, Ti\(_2\)O\(_3\) and Ti\(_3\)O\(_5\). Among them, the titanium element in TiO\(_2\) has the highest valence, so the REDOX reaction under the same conditions will give priority to the generation of high-priced TiO\(_2\).

The microscopic morphology of acid etched powder was observed by SEM, as shown in figure 6. Figure 6(b) is the energy spectrum analysis of point 1 in figure 6(a). It can be seen from figure 6 that the etched powder was nearly spherical with a particle size of less than 2 \(\mu\)m. The amount of diluent content in the prefabricated blocks has a direct impact on the reaction process and reaction products. If the diluent is too small, the contact surface area between the reactants is large, the reaction is more violent, and the reaction products are easy to agglomerate. Excessive and insufficient contact between the reactants is likely to cause the reaction to fail. The experimental results indicate that the reaction effect was the optimal when the mass of diluent Cu powder accounted for 50% of the mass of the entire prefabricated block. The energy spectrum results in figure 6(b) indicate that the main elements in the acid etched powder were Ti and O, and that the atomic ratio of Ti to O was close to 1:2. Combined with XRD results, TiO\(_2\) particles were generated in situ in pure copper melt using Cu–Ti–CuO as reaction system and pure copper melt as reaction medium.

### 3.3. Micromorphology of in situ reaction products and distribution in copper matrix

Figure 7 shows the microscopic morphology and surface scan analysis of TiO\(_2\) particles in Cu-2TiO\(_2\) samples. Figure 7(b) is an enlarged view of area A in figure 7(a). From these two images, it can be seen that the TiO\(_2\) particles were not agglomerated and were evenly distributed on the grain boundaries and inside the grains. The
position of the grain boundary and TiO\textsubscript{2} was indicated in the figure. Figure 7(c) is an enlarged view of area B in figure 7(b). According to the surface scan analysis, it is further proved that the dark black particles in figure 7(c) are all TiO\textsubscript{2}. It can be also found from figure 7(c) that the TiO\textsubscript{2} particles were embedded in the copper matrix, with a particle size of about 1.5 \( \mu \text{m} \).

3.4. Influence of in situ reaction products on the solidification structure of pure copper

Figure 8 shows the as-cast structure of Cu-1TiO\textsubscript{2}, Cu-2TiO\textsubscript{2} and Cu-3TiO\textsubscript{2} prepared by in situ reaction near melting point casting under the conditions of the same reaction process parameters, and the as-cast structure of pure Cu matrix cast by near melting point casting as comparison. Figure 8(a) shows the microstructure of pure copper. The morphology of grains in the microstructure of pure copper is different and the grain size is not uniform. There are equiaxed crystals of large size and dendritic crystals of small size. The near melting point casting method was used to prepare the composite material, which increased undercooling degree and nucleation rate, so that the grains could not grow up and formed larger equiaxed grains and smaller dendrites. In figures 8(b)–(d), the mass fraction of TiO\textsubscript{2} is 1 wt%, 2 wt% and 3 wt% respectively. With the increase of the content of reinforcing phase, the grain shape and size of the sample gradually became uniform, and the grain was gradually refined. As can be seen from figure 8(b), grains presented a preferred orientation for growth. The grains grew in a certain direction, and the grains were all large dendritic crystals. According to figure 8(c), the grain shape and size become uniform, and the dendritic size decreases. In figure 8(d), the grain is further refined, the dendritic grain size becomes smaller, and grains grow in a uniform direction. The Nano Measurer software was used to calculate the size of the crystal grains in the corresponding microstructure in figure 8, and the results are shown in figure 9. When the mass of TiO\textsubscript{2} is 3%, the average grain size of the composite material is the smallest, being 103.29 \( \mu \text{m} \). The main reason for grain refinement is that TiO\textsubscript{2} particles with high melting point are generated in the in situ of pure copper melt, which can be used as Heterogeneous nucleation particles during solidification, and the increase of nucleation rate leads to the increase of the number of crystal nuclei per unit area [23–26], thereby increasing the number of grains per unit area and thus refining grains. At the same time, in the process of grain growth, part of TiO\textsubscript{2} particles distributed at grain boundaries hinder the movement of grain boundaries, thus hindering grain growth and achieving grain refinement [27–32]. On the one hand, the critical nucleation radius and critical nucleation work were reduced by increasing undercooling degree, thus the
nucleation rate per unit volume was increased and the grain size was refined by using near melting point casting method. On the other hand, a liquid metal was poured into a mold close to the melting point of pure copper, making it too late for the cooled crystals to melt again. In the solidification process, these chilled crystals were used as nucleation particles to increase the nucleation rate, thus increasing the number of grains and refining grains.

4. Conclusion

With Cu–Ti–CuO as the reaction system, rutile TiO$_2$ particles were generated in situ by thermal explosion reaction in pure copper melt, and TixCu$_y$ Intermetallic compound was not formed. When the molar ratio of Ti to CuO was 1:2, the content of diluent was 50%, and the preheating temperature of copper melt was 1250 °C, TiO$_2$ particles, with a size of less than 2 μm were produced in situ in pure copper melt. These particles were dispersed in the copper matrix. From the perspective of thermodynamics, the Gibbs free energy of Ti+2CuO → TiO$_2$ + 2Cu reaction decreases with the increase of temperature, so the reactions occur spontaneously. In terms of dynamics, the reaction of Ti and CuO to form TiO$_2$ particles requires less energy and fewer atoms. According to the analysis of the characteristics of REDOX reaction, TiO$_2$ has the highest valence among the oxides of Ti, and the high-priced TiO$_2$ is generated first during the reaction. Therefore, the Cu–Ti–CuO system reacts in pure copper melt to produce TiO$_2$ particles.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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