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Effect of Reaction Temperature and Heat Treatment Time on Electrical and Mechanical Performance of TiB_2 Particles and TiB Whiskers Reinforced Copper Matrix Composites

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Abstract: In order to achieve a reasonable balance between the high electrical conductivity and high tensile strength of TiB_2 particles (TiB_{2p}) and TiB whiskers (TiB_w) reinforced copper matrix composites prepared by in situ reaction casting, the effects of reaction temperature and heat treatment time on the electrical conductivity and tensile strength of composites were studied. The results show that the electrical conductivity increased while the tensile strength decreased with the increase in reaction temperature from 1300 °C to 1500 °C. With the increase in heat treatment time, the electrical conductivity increased, while the tensile strength of the composites increased first and then decreased. The electrical conductivity and tensile strength of composites are related to the degree of in situ reaction at liquid or solid state, and the reasons for the improved performance are also discussed. Finally, two optimized preparation processes are proposed by cooperative controlling the reaction temperature and heat treatment time, the comprehensive properties of (TiB_{2p}+TiB_w)/Cu composites are 79.6% IACS/603 MPa and 83.7% IACS/602 MPa, respectively.

Keywords: hybrid reinforced copper matrix composites; reaction temperature; heat treatment time; high strength and high conductivity

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1. Introduction

Copper matrix composites reinforced by hybrid particles (TiB_2, WC, Al_2O_3 and ZrB_2, etc.) and whiskers (TiB, SiC and CNTs, etc.) with high conductivity and high strength may become potential application materials that can be used in high-speed train contact wires, high performance lead frames and high voltage switchgear contact [1]. Compared with particles and whiskers with different components, such as Al_2O_3 (or WC) particles and SiC (or TiB) whiskers, the TiB_2 particles (TiB_{2p}) and TiB whiskers (TiB_w) are easier to obtain through in situ reaction at the same time, and their lower resistance and higher hardness are worthier of focus [2]. At present, a variety of in situ methods, such as powder metallurgy [3], spray deposition [4] and reaction casting [2], were used to prepare TiB_2/Cu composites, among which the casting method has become a research hotspot due to its low cost, short process flow and high efficiency [5]. However, current research is more concerned about how to optimize the size, distribution and morphology of the reinforcements to improve the strength [6–8], but the factors affecting the electrical conductivity should also be considered and the relevant reports are lacking. Research has shown that the solid solution of elements in Cu has a great influence on conductivity, among many other factors [9]. According to the equilibrium phase diagrams of Cu-Ti and Cu-B, the limit solid solubility of Ti and B in the Cu matrix are 6.2 wt.% and 0.05 wt.%, respectively [10,11]. Thus, a small amount of Ti in Cu will cause a serious decrease in the conductivity [12–14], while the doping of B has less damage to the conductivity of Cu when compared with Ti [15]. Based on the above considerations, it is necessary in principle to achieve a sufficient reaction of Ti and B, which

may significantly improve the electrical conductivity of the composite. In combination with the advantages of in situ reactions, the reaction parameters and the post-processing parameters may be the key factors affecting the simultaneous improvement of electrical conductivity and tensile strength of the composites.

For composites prepared by in situ reaction casting, Kumar et al. [16] studied the effects of reaction temperature and holding time during the reaction on the properties of TiB_2/Al composites. It was found that the hardness of TiB_2/Al composites is higher and more TiB_2 particles are formed at 800 °C for 30 min compared with the lower temperature for a shorter time. Lawrence et al. [17] studied the effect of the holding time on TiB_2/Al6061 composites at the same reaction temperature. The results showed that a longer holding time is beneficial to the formation of TiB_2 particles and that contributes to the strength of the composites. In addition, Sobhani et al. [18] compared the effect of heat treatment time on the conductivity and strength of TiB_2/Cu composites formed through casting. The conductivity and tensile strength are 65% IACS and 580 MPa when the heat treatment time increased to 10 h, increased by 32.1% and 6.8%, respectively, which is attributed to the formation of secondary TiB_2 particles. The above studies on TiB_2/Al or Cu composites have shown that adjusting the reaction parameters (reaction temperature, reaction time) or heat treatment parameters can achieve more sufficient reaction of Ti and B, resulting in the improvement of composite properties. Therefore, it is possible to obtain the composites with better comprehensive properties by studying the preparation parameters.

Our previous research on (TiB_{2p}+TiB_w)/Cu composites shows that the addition of rare earths (La, Ce and Y) is beneficial to the improvement of tensile strength [19], and the composite with La has a better comprehensive performance (73.1% IACS/606 MPa), but further improvement in electrical conductivity is needed. The current work extends the previous study in terms of analysing the effects of reaction temperature and heat treatment time on the microstructures and properties of the (TiB_{2p}+TiB_w)/Cu composites with La to further improve the comprehensive properties. Finally, the process parameters were optimized based on the above research. This work paves an avenue for the performance optimization of in situ metal matrix composites via reaction control and heat treatment.

2. Materials and Methods

The pure Cu (99.9% purity), Ti (99.9% purity), B (99.9% purity) and Cu-10 wt.% La were used as raw materials. According to composition design, 3 wt.% (TiB_{2p}+TiB_w)/Cu composites with 0.04 wt.% La were prepared by a special in situ casting device, which was described in detail in our previous work [20]; for clearness, the composites are uniformly written as (TiB_{2p}+TiB_w)/Cu throughout the text. Firstly, the Cu-B and Cu-Ti master alloys were prepared by vacuum induction melting furnace under a protective argon atmosphere. Then, two master alloys were both heated to 1300 °C, 1400 °C and 1500 °C (in situ reaction temperature), respectively, mixed the two melts in the "Z"-shaped runner at the same time for in situ reaction, and solidified quickly in the copper mould to form hybrid reinforced composites. The as-cast composites were heat-treated at 900 °C for 180 min, then hot-rolled at 900 °C with a 30% reduction in thickness, and finally rolled at room temperature with a total of 90% reduction in thickness. In addition, the as-cast composites prepared at 1500 °C were kept at 900 °C for 120 min, 150 min and 180 min (heat treatment time), respectively, and then subjected to the same hot rolling and cold rolling deformation as above.

The microstructures of the composites were characterized by scanning electron microscope (SEM, Phenom Pure+, Netherlands). The samples to be observed for SEM were electrolytic corroded with 70% H_3PO_4 and 30% C_2H_5OH corrosive solution after polishing. In order to quantify the size of reinforcements, the equivalent diameter of the reinforcements is obtained through image processing, which is based on the reinforcements contour; the contour area is equivalent to the circular area and achieves an equivalent diameter [6]. Furthermore, at least 10 different SEM images of each composite were used for reinforcement size statistics, totalling more than 1000 particles. The phases and microstructures were characterized using the transmission electron microscope (TEM, FEI TECNAI G2 F20,

FEI Company, Hillsboro, OR, USA). Preliminary thinning of the samples was carried out by mechanical grinding and electrochemical double spray methods and an ion thinner (Gatan691, Gatan Inc., Pleasanton, CA, USA) was used for final thinning. The electrical conductivity of deformed composites was measured by an eddy-current instrument (Sigma 2008B, Shanghai, China) with temperature calibration and expressed in International Annealed Copper Standard (% IACS); at least 20 measurements were taken on a 20 mm × 200 mm sample and averaged. The strength of the composites was tested on the tensile testing machine (AG-IC 100KN, Shimadzu, Kyoto, Japan) at a tensile rate of 0.5 mm/min. Three tensile tests were carried out for each composite and averaged. The dimensions of the tensile specimens with a fillet radius of 10 mm are shown in Figure 1. In addition, in order to analyse the mixing effect of molten Cu-B and Cu-Ti master alloys at different temperatures, the viscosity changes of Cu-1.2 wt.% B and Cu-2.8 wt.% Ti melts at 1200 °C–1450 °C were measured on the high temperature rotary vibration type viscosity measuring instrument (OSVM, SAP, Tokyo, Japan).

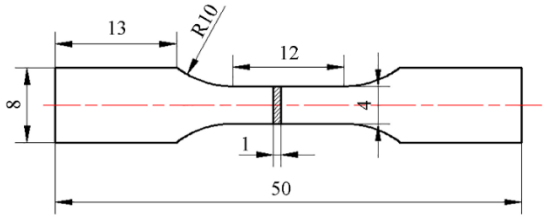


Figure 1. The dimensions of the specimens for tensile testing.

3. Results and Discussion

3.1. Effect of Reaction Temperature on Microstructures and Properties of Composites

3.1.1. Microstructures of As-Cast Composites

Figure 2 shows the microstructures of the as-cast (TiB_{2p}+TiB_w)/Cu composites at different reaction temperatures.

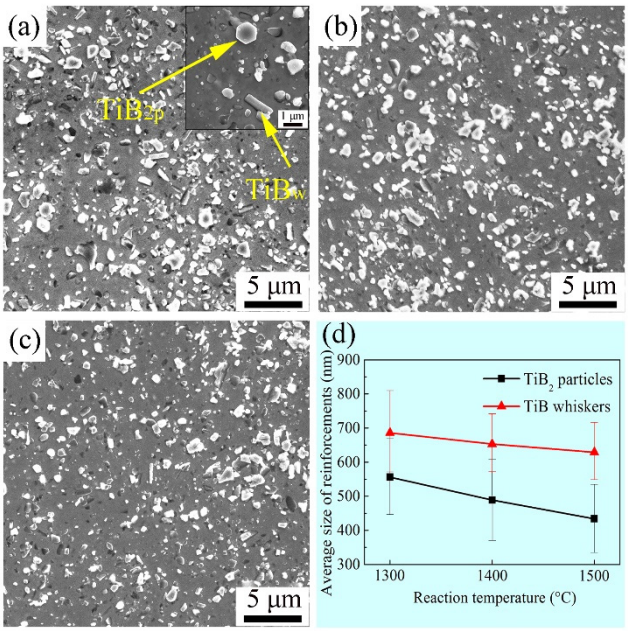


Figure 2. The microstructures and average size of reinforcements in as-cast (TiB_{2p}+TiB_w)/Cu composites at different reaction temperatures. (**a**) 1300 °C, (**b**) 1400 °C, (**c**) 1500 °C, (**d**) the average size of reinforcements versus reaction temperature.

The morphology of TiB_2 particles is mainly irregular or nearly spherical, while the morphology of TiB whiskers is mainly short rod, which is consistent with our previous research [19]. The TiB_{2p} and TiB_w are uniformly distributed in the composites, especially at 1500 °C. The average sizes of the reinforcements (TiB_{2p} and TiB_w) were also obtained through image processing [6], as shown in Figure 2d. It is found that the size of TiB_2 particles and TiB whiskers are refined with the increase in reaction temperature, which is related to the higher temperature that is beneficial to promote the nucleation of the reinforcements [2].

Figure 3 shows the TEM images of as-cast (TiB_{2p}+TiB_w)/Cu composites prepared at 1300 °C. It is found that two kinds of reinforcements with different morphologies are identified as TiB_{2p} and TiB_w. Moreover, unreacted B is found to exist in an amorphous form, as shown in Figure 3d. No other compound phase related to Ti is found and the remaining Ti may be dissolved into the Cu matrix, since the limit solid solubility of Ti in the Cu matrix (6.2 wt.%) is relatively higher.

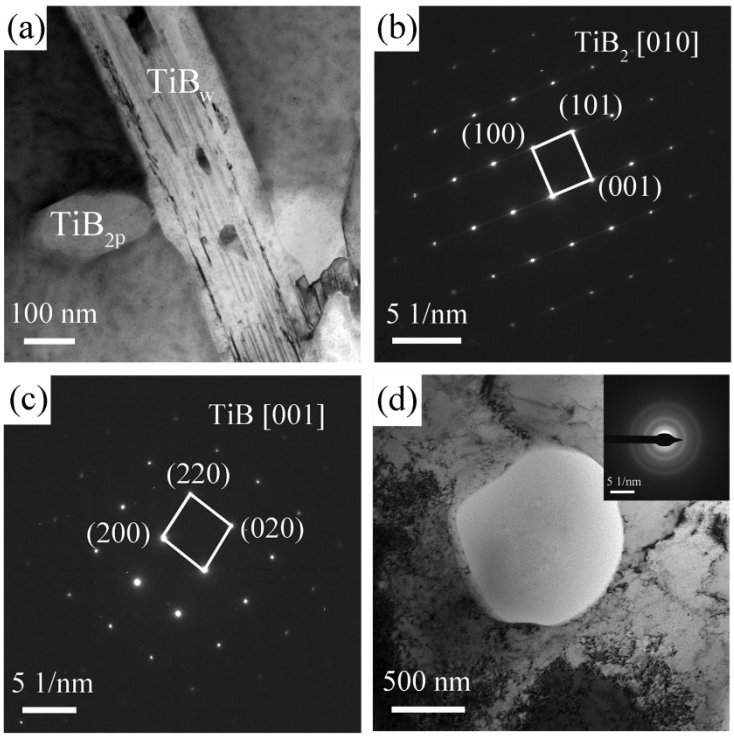


Figure 3. The TEM images of as-cast (TiB_{2p}+TiB_w)/Cu composites prepared at 1300 °C. (**a**) Bright field of TiB_{2p} and TiB_w, (**b**) The diffraction pattern of TiB_{2p}, (**c**) The diffraction pattern of TiB_w, (**d**) Unreacted B exists in amorphous form.

3.1.2. Properties of Composites

Figure 4 shows the tensile stress–strain curves of deformed (TiB_{2p}+TiB_w)/Cu composites at different reaction temperatures, and the measured electrical conductivity and tensile strength are gathered in Table 1. The conductivity of the composites increased significantly with the increase in reaction temperature, the conductivity increased from 73.1% IACS to 89.5% IACS when the reaction temperature increased from 1300 °C to 1500 °C, increased by 22.4%. Meanwhile, the tensile strength decreased from 606 MPa to 525 MPa and decreased by 13.4%. It can be concluded that the influence of the reaction temperature on the electrical conductivity and tensile strength is contradictory under the same post-treatment process, i.e., an increase in conductivity will sacrifice tensile strength.

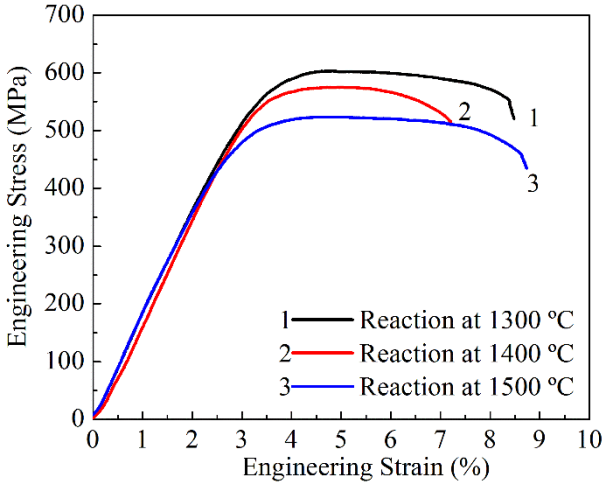


Figure 4. Stress–strain curves of deformed (TiB_{2p}+TiB_w)/Cu composites at different reaction temperatures.

Table 1. The properties of (TiB_{2p}+TiB_w)/Cu composites at different reaction temperatures.

Reaction Temperature (°C)	Electrical Conductivity (% IACS)	Tensile Strength (MPa)
1300	73.1 ± 2.1	606 ± 3.1
1400	78.5 ± 1.8	574 ± 2.2
1500	89.5 ± 1.1	525 ± 1.4

The electrical resistivity of copper alloys or copper matrix composites can be expressed as follows [21]:

$$\rho = \rho_{pho} + \rho_{def} + \rho_{int} + \rho_{imp} \quad (1)$$

where ρ_{pho} is the contribution of phonon scattering to resistivity, which is only related to temperature and can be ignored at room temperature, ρ_{def} is the resistivity caused by defects such as dislocations, vacancies and grain boundaries, ρ_{int} is the influence of interface scattering on resistivity, and ρ_{imp} is the influence of impurities on resistivity. Many studies [22,23] have shown that ρ_{imp} has a more obvious impact on electrical conductivity, especially when the solute atoms are dissolved into the matrix. For (TiB_{2p}+TiB_w)/Cu composites prepared by reaction casting in this study, ρ_{imp} is mainly determined by residual solutes and reinforcements, which are closely related to the degree of in situ reaction. For this purpose, the viscosity of two specific composition master alloys varies with the temperature and was measured as shown in Figure 5. It is found that the viscosity values of molten Cu-B and Cu-Ti master alloys both decrease with the increase in temperature. The decrease in the viscosity for the two melts is beneficial to their rapid and uniform mixing in the "Z"-shaped runner [24,25], resulting in a rapid thermal diffusion and adequate in situ reaction of Ti and B. Otherwise, there may be residual solute due to the insufficient reaction, as shown in Figure 3d. Therefore, for (TiB_{2p}+TiB_w)/Cu composites, the reaction may be more sufficient at 1500 °C than that at 1300 °C before rapid solidification in the copper mould, i.e., the residual amount of Ti at 1500 °C is lower than that at 1300 °C and more fine particles are generated (as shown in Figure 2d), but for ρ_{imp}, the damage of the reinforcements to the conductivity is much less than that of the residual solutes [9], which finally leads to an increase in conductivity. Our previous work [13] about the relationship between Ti content and conductivity also confirmed this; the results show that the conductivity can reach more than 80% IACS, but only if the Ti content is less than 0.1 wt.%. Meanwhile, the effect of residual solute enhancement (solution strengthening) is weakened due to the content of residual solute elements (especially Ti) in the matrix, which

is reduced by adequate in situ reaction. This results in a decrease in the tensile strength of composites at 1500 °C.

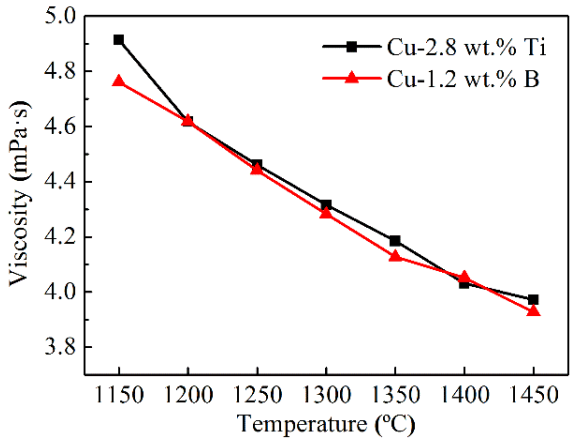


Figure 5. Viscosity–temperature curves of the molten Cu-B and Cu-Ti master alloys.

3.2. Effect of Heat Treatment Time on Microstructures and Properties of Composites

3.2.1. Microstructures of Composites

In addition to controlling the degree of in situ reaction at liquid state by reaction temperature, as discussed in Section 3.2, the study carried out by Sobhani et al. [18] shows that heat treatment is also an effective method to optimize the properties of TiB_2/Cu composites, i.e., the residual Ti and B in Cu matrix may further react at solid state during heat treatment with a high temperature. Based on the above considerations, the effect of heat treatment time at 900 °C on the microstructures and properties of (TiB_{2p}+TiB_w)/Cu composites prepared at 1500 °C were studied. Figure 6 shows the microstructures of the (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time (120 min, 150 min and 180 min). It is found that the morphologies and the average size of reinforcements formed by in situ reaction at liquid state have no obvious change with the increase in heat treatment time, which may be due to the size of the reinforcements generated by an in situ reaction at solid state, which is relatively small and makes it difficult to obtain quantitative data statistics through image processing.

3.2.2. Properties of Composites

Figure 7 shows the tensile stress–strain curves of deformed (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time at 900 °C; the measured electrical conductivity and tensile strength are gathered in Table 2. The conductivity of the composites increased from 64.8% IACS to 89.5% IACS with the increase in heat treatment time from 120 min to 180 min, increasing by 38.1%. The increases in conductivity may be ascribed to the consumption of residual solute that does not fully react. With the increase in heat treatment time, fine particles were found in the TEM characterization of the heat-treated composites, as shown in Supplementary Figure S1; the remaining solute in the Cu matrix may form reinforcements through thermal diffusion reaction [18]. It is worth noting that the increase in conductivity was not significant when the time increased from 120 min to 150 min, but the conductivity rapidly increased to 89.5% IACS with 180 min. According to the diffusion behaviour of B and Ti in the Cu matrix reported by Rexer et al., with the diffusion activation energy (Q) of Ti and B at 800 °C and 900 °C [26], it was found that Q_{Ti} (209.3 KJ/mol) is greater than Q_B (156.9 KJ/mol), i.e., the diffusion of Ti requires a higher activation energy, resulting in a longer diffusion period for in situ reaction at solid state. Therefore, the results show that the thermal diffusion reaction of the residual solutes in the matrix may require an incubation period; the solute atoms may still remain in the matrix if the heat treatment time is not enough. The research carried out by Sobhani et al. [12] and Jelena et al. [27]

also show that the TiB_2 particles can be formed again when the heat treatment time for the Cu-Ti-B block, prepared by casting or laser melting, is sufficiently long.

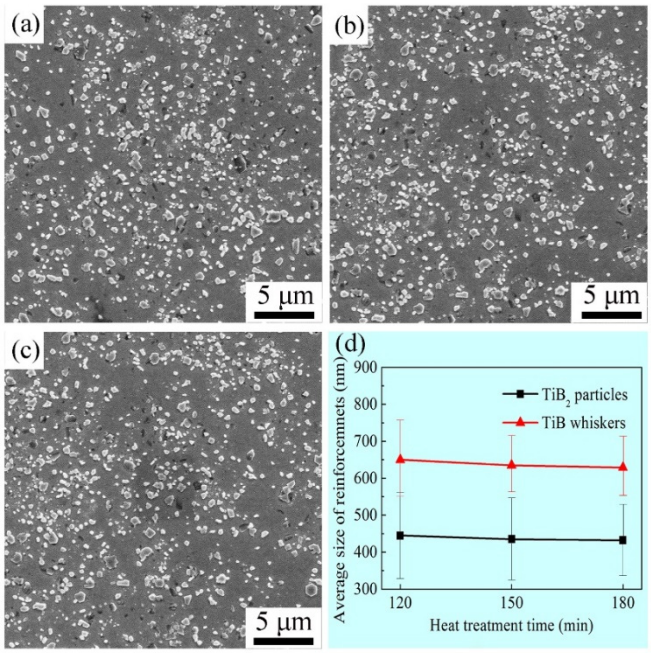


Figure 6. The microstructures and average size of reinforcements in (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time. (**a**) 120 min, (**b**) 150 min, (**c**) 180 min, (**d**) the average size of reinforcements versus heat treatment time.

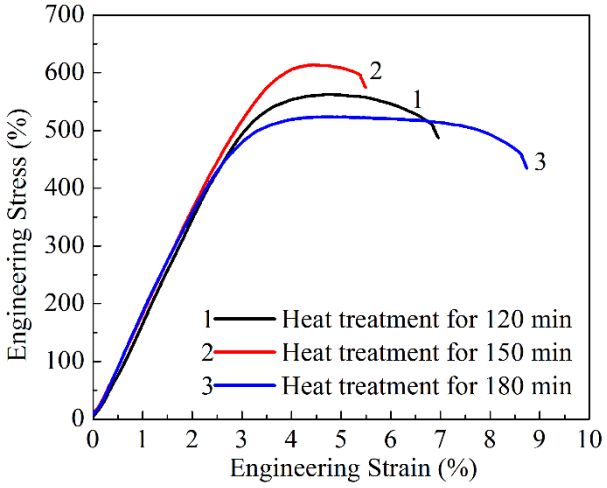


Figure 7. Stress–strain curves of deformed (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time.

Table 2. Properties of (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time at 900 °C.

Heat Treatment Time (min)	Electrical Conductivity (%IACS)	Tensile Strength (MPa)
120	64.8 ± 3.1	567 ± 2.5
150	66.5 ± 2.2	618 ± 8.1
180	89.5 ± 1.1	525 ± 1.4

Meanwhile, the tensile strength of the composites increased first and then decreased with the increase in heat treatment time, which may be due to the trade-off among the

reinforcements formed at solid state, Cu matrix grains and residual solutes. As for the increase in tensile strength, it may be dominated by the Orowan strengthening contributed by small reinforcements produced by in situ reaction at solid state [2]. Regarding the decrease in the tensile strength, it can be explained by considering the following two aspects. On the one hand, recrystallization coarsening may occur for the Cu matrix grains with the increase in heat treatment time; Supplementary Figure S2 shows that the matrix grains with heat treatment for 180 min are larger than with heat treatment for 120 min with the same post-treatment, and the refinement strengthening effect of the matrix grains decreases. On the other hand, the content of residual solute elements (especially Ti) in the matrix is reduced by thermal diffusion reaction under the action of long-time heat treatment, and the strengthening effect (such as solution strengthening of Ti) caused by the residual solutes is weakened.

3.3. Optimization of Electrical Conductivity and Tensile Strength

According to the analyses of Section 3.1 (Table 1) and Section 3.2 (Table 2), increasing the reaction temperature or prolonging the heat treatment time are all beneficial to improving the electrical conductivity of (TiB_{2p}+TiB_w)/Cu composites, but they will sacrifice the tensile strength at the same time. Therefore, in order to achieve a reasonable balance between electrical conductivity ($\geq$ 80% IACS) and tensile strength ($\geq$ 600 MPa), it is necessary to cooperatively control the reaction temperature and heat treatment time. Based on the above analysis, two optimized preparation processes were proposed after multi experiments screening. Preparation process I: the composite was prepared at 1300 °C, and the subsequent heat treatment time was extended to 200 min. Preparation process II: the composite was prepared at 1500 °C, and the subsequent heat treatment time was reduced to 170 min. Figure 8 shows the stress–strain curves of the corresponding processes and the fracture morphology. The measured properties of deformed (TiB_{2p}+TiB_w)/Cu composites with different optimized preparation processes are listed in Table 3.

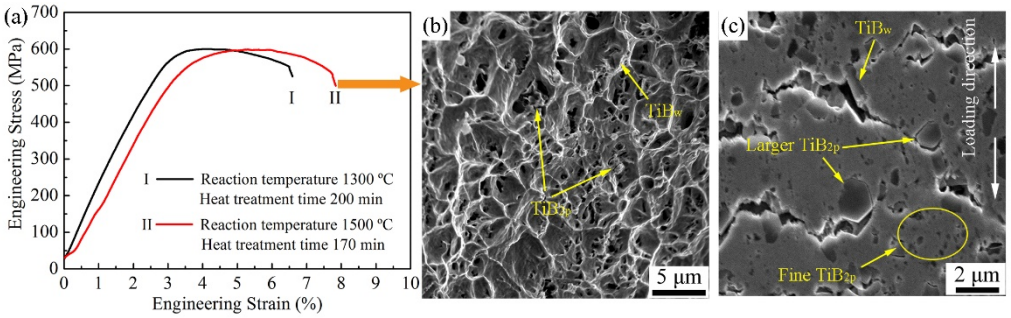


Figure 8. (**a**) Stress–strain curves of (TiB_{2p}+TiB_w)/Cu composites with optimized preparation process, (**b**) the fracture morphology, (**c**) fracture morphology on the side of the tensile specimen.

Table 3. Properties of (TiB_{2p}+TiB_w)/Cu composites with different optimized preparation processes.

Preparation Process	Electrical Conductivity (%IACS)	Tensile Strength (MPa)
I	79.6 ± 1.6	603 ± 3.8
II	83.7 ± 1.3	602 ± 2.1

For preparation process I, when the composite prepared at 1300 °C with the heat treatment time increased from 180 min to 200 min, the electrical conductivity of the composite is increased from 73.1% IACS to 79.6% IACS, increasing by 8.9%, while the tensile strength of the composite is decreased from 606 MPa to 603 MPa, only decreasing by 0.5%. For preparation process II, when the composite prepared at 1500 °C with the heat treatment time decreased from 180 min to 170 min, the electrical conductivity of the com-

posite decreased from 89.5% IACS to 83.7% IACS, decreasing by 6.5%, while the tensile strength of the composite is increased from 525 MPa to 602 MPa, increasing by 14.7%. In addition, many dimples, tearing ridges and debonded reinforcements were found in the fracture morphology of deformed composites, as shown in Figure 8b, which are typical characteristics of plastic fracture. Figure 8c shows the fracture morphology on the side of the tensile specimen. It was found that the cracks are easily generated from the interface of the reinforcements (especially the large size), and propagate along the interface of the reinforcements, and finally the reinforcements are debonded or pulled out. However, the probability of crack initiation and propagation is reduced around small reinforcements, since the stress concentration is lower around the small reinforcements [19,28,29], which delays crack initiation and propagation.

Finally, the electrical conductivity and tensile strength obtained through process I and process II are compared with other TiB_y/Cu-X composites prepared by casting with different post-treatment [6,7,14,18,30–35], as shown in Figure 9. It was found that a synergistic regulation of electrical conductivity and tensile strength (80% IACS/600 MPa) are achieved through the optimization of the preparation process in this study. Therefore, the reaction temperature and heat treatment time can be used to control the degree of in situ reaction at liquid or solid state for (TiB_{2p}+TiB_w)/Cu composites, finally achieving synergistic regulation of electrical conductivity and tensile strength, which paves an avenue for the performance optimization of in situ metal matrix composites via reaction control and heat treatment.

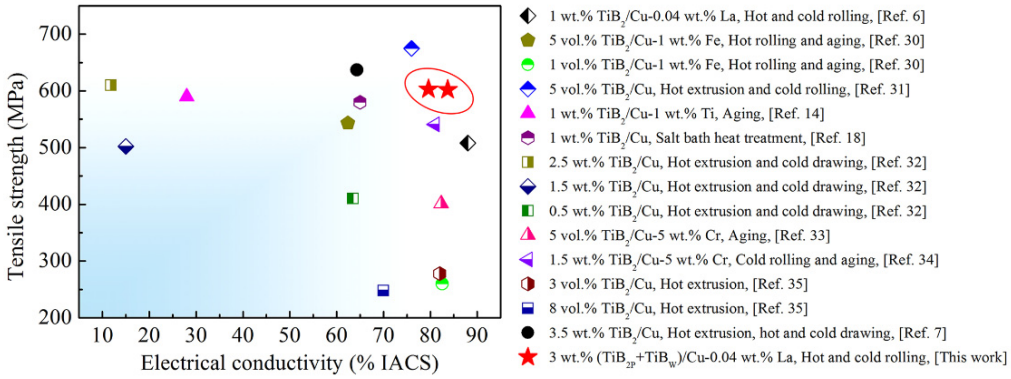


Figure 9. Comparison of electrical conductivity and tensile strength of TiB_y/Cu-X composites prepared by casting with different post-treatment.

4. Conclusions

The effect of in situ reaction temperature and subsequent heat treatment time on the electrical conductivity and tensile strength of (TiB_{2p}+TiB_w)/Cu composites were studied. It was found that a higher reaction temperature and longer heat treatment time are conducive to sufficient in situ reaction at liquid and solid state for the composite, respectively, resulting in an increase in electrical conductivity. The tensile strength of the composites may be related to the trade-off among the reinforcements formed at liquid or solid state—the Cu matrix grains and residual solutes. After preparation process optimization by cooperative controlling the reaction temperature and heat treatment time, the 3 wt.% (TiB_{2p}+TiB_w)/Cu composites with high electrical conductivity and high tensile strength (79.6% IACS/603 MPa and 83.7% IACS/602 MPa) are obtained, which paves an avenue for the performance optimization of in situ metal matrix composites via reaction control and heat treatment.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/met12040592/s1, Figure S1: TEM images of fine particles formed in (TiB_{2p}+TiB_w)/Cu composites heat-treated at 900 °C for 180 min, Figure S2: Bright field and dark field TEM images of deformed (TiB_{2p}+TiB_w)/Cu composites with different heat treatment time.

Author Contributions: Conceptualization, F.C. and X.Z.; methodology, F.C. and Y.J.; validation, F.C., X.Z. and Y.J.; formal analysis, F.C. and Y.J.; investigation, F.C. and X.Z.; data curation, X.Z., P.C. and F.G.; writing—original draft preparation, X.Z.; writing—review and editing, F.C. and Y.J.; supervision, F.C.; project administration, F.C., Y.J. and S.L.; funding acquisition, F.C., Y.J. and S.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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