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Research status and development trend of preparation technology of ceramic particle dispersion strengthened copper-matrix composites

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Abstract: Copper is equipped with excellent electrical and thermal properties. However, its poor mechanical properties and poor high-temperature stability prevent its extensive used in structural materials. Therefore, establishing an effective strengthening method that enables copper to increase its strength and high-temperature tolerance can promote wide-ranging copper applications. An effective method is the addition of ceramic particles as a reinforcement phase to improve the mechanical properties of copper. The preparation processes of several ceramic particles reinforced copper-based composites are discussed in this paper, including three powder metallurgy processes as mechanical alloying, internal oxidation, and wet chemistry, as well as friction stir processing, reactive spray deposition, and liquidus in situ reaction. The effects of each process on the

mechanical properties of copper-matrix composites are introduced.

Key words: Copper; Ceramic particles; Dispersion strengthening; Mechanical properties

1 Introduction

Given that copper and its alloys are equipped with excellent electrical and thermal properties, they are extensively used in electrical equipment such as electrical contact materials, integrated circuit lead frames, and resistance welding electrodes [1, 2]. However, the strength and hardness of these copper alloys are often lower at room temperature. The lack of hardness also leads to higher wear rates of copper alloys, which limits their many applications in structural materials. Moreover, with increased temperature, the strength of copper and its alloys are greatly reduced, which prevents the application of copper alloys on first-wall material diverters [3]. The copper-matrix composites (hereinafter called CMCs) are usually prepared by the addition of fine dispersed ceramic particles to the copper matrix. The dispersion strengthening mechanism is another important strengthening mechanism compared with the main solid solution strengthening mechanism in copper alloys. Researchers have conducted many studies on the preparation and properties of CMCs based on this idea. Unlike alloy elements that are solid-dissolved in copper, there is a clear interface between the ceramic particles and the copper matrix, so it is called the second phase. The main strengthening phases of ceramic particles are currently Y_2O_3 [3], Al_2O_3 [4], ZrO_2 [5], SiC [6], TiB_2 [7], and AlN [8]. Abd-Elwahed et al. [1] doped zirconia in copper so that the hardness was threefold higher than that of the pure copper. Fu et al. [9] added the rare earth element Ce to Cu- Al_2O_3 to solve the agglomeration problem of nano-alumina particles in the copper matrix and improve the yield strength and conductivity of Cu- Al_2O_3 .

The potential excellent properties of the CMCs arouse great interest from scholars at home and abroad. They have developed a series of relatively complete preparation processes. Currently, the preparation processes of CMCs materials primarily include: (1) Mechanical alloying (MA) [10], (2) internal oxidation [11], (3) wet chemistry [12], (4) friction stirring processing (FSP) [13], (5) reactive spray

deposition [14], and (6) liquidus in situ reaction [15]. This paper summarizes the achievements made by the predecessors on the above several preparation processes and analyzes the influence of each process on the properties of copper and their advantages and disadvantages.

2. Preparation process

2.1 Powder metallurgy technique

Different from traditional powder metallurgy, the following several milling processes are introduced in this paper to improve the dispersion of the second-phase particles in the copper matrix: Mechanical alloying, internal oxidation and wet chemical methods, together with different sintering processes, guarantee the production of more dense and uniform copper-matrix composites.

2.1.1 Mechanical alloying (MA)

Mechanical alloying is a complex physical and chemical process, which mixes powders into high-energy ball mills or ball mills for continuous deformation, cold welding, and crushing, and finally obtains the atomic alloying [16,17]. The process prepared by the MA process is of a uniform and fine microstructure and a dispersed strengthening phase. The mechanical properties are often better than those of similar materials prepared by the traditional process [18]. In addition, the traditional process refers to the simple mixing of powders through a powder mixer, and there is no atomic-level mixing between different powders.

To investigate the effect of atmosphere (He/5%H₂) on the powder morphology and microstructure, Aghamiri et al. [19] successfully prepared Cu-0.42wt% Y₂O₃ composites by mixing copper powder with yttrium oxide powder and adding 1% stearic acid to mechanically mill in a protective(He/5%H₂) atmosphere. After ball milling for 48 h, the grain size could be refined to 28 nm, and the dislocation density and hardness could reach the saturation levels of $1.7 \times 10^{15} \text{ m}^{-2}$ and 226 HV_{0.1}, respectively. After the powder was treated by spark plasma sintering (SPS) and hot-rolled annealed at 900 °C for 60 min, the average grain size could reach 1.14 μm [Fig. 1(a)], and the crystals are of a weak texture in the {110} direction [Fig. 1(b)]. Transmission electron microscopy (TEM) images revealed that fine Y₂O₃ particles

were uniformly distributed on the copper matrix. The interface between the two phases showed a semicoherent relationship. The average size of the oxide particles and the spacing between the particles was 10.8 and 152 nm, respectively (Fig. 2). Yield strength and elongation reached 272 MPa and 12%, respectively. Huang et al. [20, 26] conducted a series of studies on the preparation and properties of Cu-10vol% Y_2O_3 by a new multistep ball milling method. The step of this new method was to mix copper powder with yttrium oxide powder, performed the two-step ball milling and two-step reduction, and followed by SPS (Fig. 3). For the two-step reduction, the 1st milled powders was isothermally reduced at 120 °C in CO atmosphere for 100 min in a tubular electrical furnace, and the 2nd milled powders was then isothermally annealed at 400 °C in H_2 atmosphere for 30 min. Fig. 4 shows that CuO is completely reduced, and yttrium oxide is evenly distributed on the copper matrix. The particle size of the powder is nanoscale. Comparing the properties of the sintered block sample with the cast copper (Table 1): The microhardness of the sample reached 209.6 HV, which is threefold that of the cast copper as 71.1. The substantial increase in microhardness may be due to the copper grain size reaching the nanometer level and the effect of fine grain strengthening, on the other hand, the dispersion distribution of yttrium oxide also hinders the movement of dislocations, thereby increasing the strength. In addition, the conductivity of Cu-10vol% Y_2O_3 was dropped to 53.8% International Annealed Copper Standards (hereinafter called IACS).

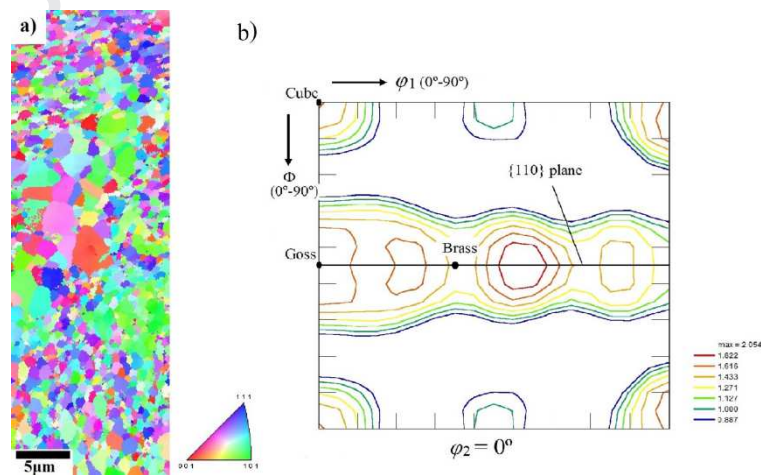


Fig. 1. EBSD results of MA ODS copper hot roll-annealed at 900/60 min including a) IPF map, b) ODF map [19].

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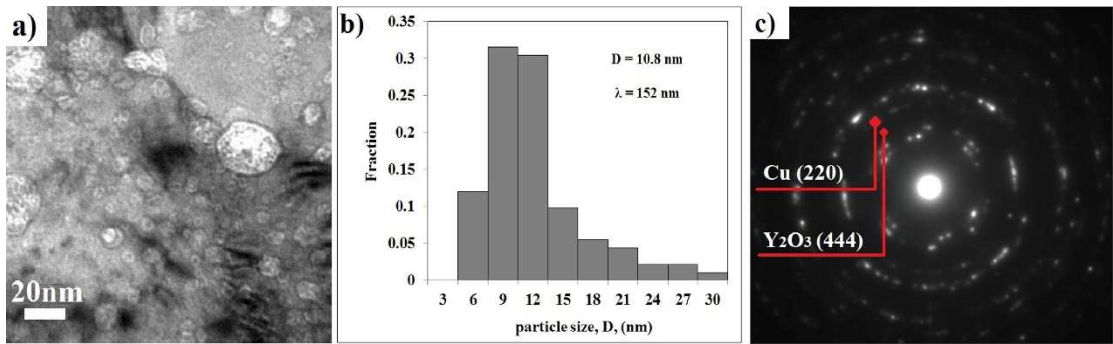


Fig. 2. TEM micrograph showing distribution of oxide particles in consolidate ODS copper alloy, b) size distribution diagram of oxide particles, c) ring diffraction pattern taken from copper matrix and oxide particles [19].

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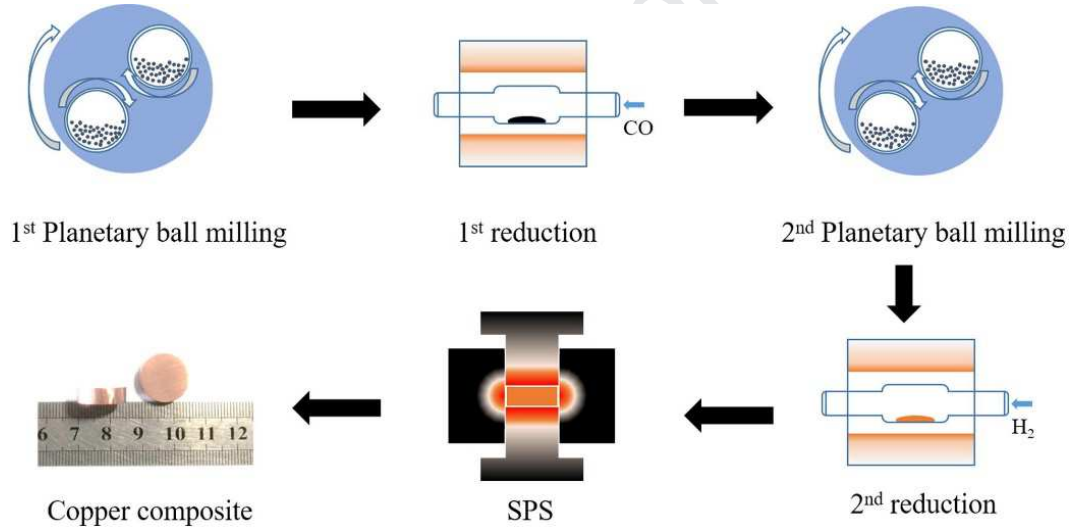


Fig. 3. Schematic illustration of Multi-step ball milling and reduction for the fabrication of Cu-10vol% Y_2O_3 [20].

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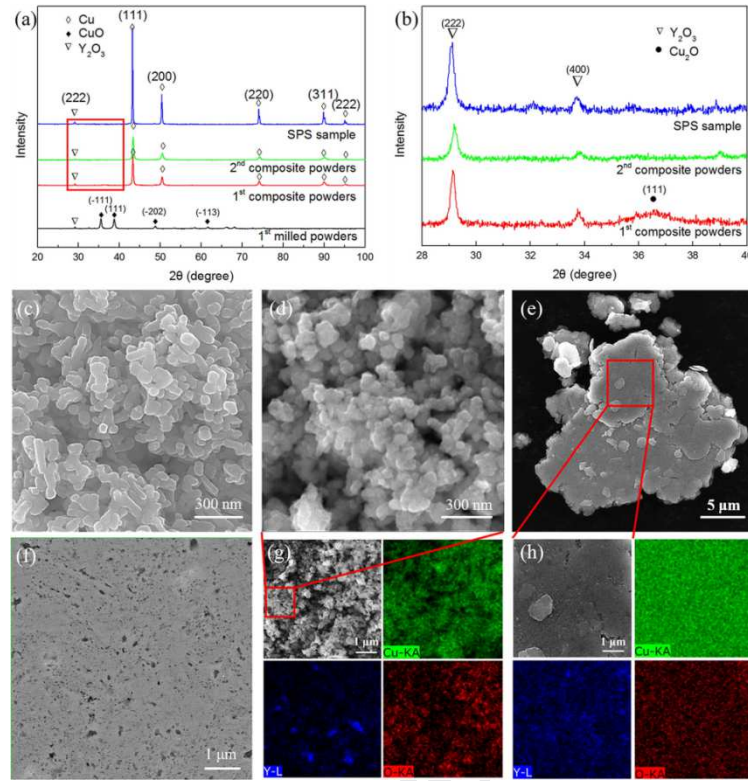


Fig. 4. (a) XRD patterns of composites samples after different steps, (b) XRD patterns corresponding to the red square frame area in (a); SEM images of composite samples after different steps, (c) 1st milled powders, (d) 1st composite powders, (e) 2nd composite powders, (f) SPS sample; Elemental maps of (g) 1st composite powders, and (h) 2nd composite powders [20].

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Table 1 Mechanical and electrical properties of as-cast copper and consolidated Cu-10vol%Y₂O₃ composite via MSBMRP [20].

	HV _{0.1}	R _{pc0.2} (MPa)	R _{mc} (MPa)	ε (%)	EC (%IACS)
As-cast Cu	71.1±3.4	89	/	>50	99.6
Cu-Y ₂ O ₃	209.6±9.7	655	932	33.4	53.8

(Table 1 of Ref. [20], Copyright © Elsevier B. V.)

Qin et al. [6] prepared Cu–SiC composites by MA and sintering, and studied the effect of SiC particle size on the friction properties of copper composites. When the size of the SiC particle was less than 2 μm, the worn surface of the material appeared as a small and narrow groove, and when the size was greater than 2 μm, the worn surface showed large flaking. Therefore, the former was abrasive wear, and the latter was three-body wear. The wear rate of the sample was not greatly affected by the SiC

particle size under low load. However, the wear rate increased with the increase of SiC size under higher load. To study effects of Y+CuO amount on the microstructure and mechanical properties of the Cu-Y₂O₃ powders and bulks, Huang et al. [21] prepared in situ finer dispersed yttria dispersion-reinforced copper composite by MA and hot isostatic sintering. The preparation idea was to mix copper powder with yttrium powder by ball milling first, then added CuO powder for second ball milling, and finally performed hot isostatic sintering. Because yttrium has a much more affinity to oxygen than copper, yttrium will react with copper oxide to transfer oxygen to yttrium under the energy provided by the ball grinding process, and finally yttrium oxide is produced. The content of yttrium oxide was controlled by the content of Y + CuO. With the increase of Y + CuO amount, the relative density could be increased to nearly 100%, whereas the grain size of copper was reduced. The microhardness could be increased to 275 HV. Chandrasekhar et al. [22] prepared Cu-1vol% Al₂O₃ alloy by MA and hot extrusion sintering. Its grain size was 146 nm, and the microhardness increased to 164 HV_{1.0}. Bagheri et al. [23] obtained Cu-TiC composites with different contents by mixing Cu powder with Ti powder and performing the ball mill for 60 h and then adding graphite for secondary ball-milling and sintering. With increased TiC content, the relative density and electrical conductivity of Cu-TiC composite materials decreased, whereas the hardness and wear resistance of the materials increased.

Zhou et al. [24] incorporated different mass fractions of Ti into Cu-Y₂O₃. They found that the addition of Ti was beneficial to improve the thermal stability of Cu-Y₂O₃. When Ti content was higher than 0.4%, hardness basically remained unchanged with the increase of annealing temperature (Fig. 5). Moreover, Zhang et al. [25] added a trace rare earth element La to Cu-Al₂O₃. The addition of La enabled the distribution of alumina particles in the copper matrix to be more uniform. A semicoherent relationship was observed between the two (Fig. 6), thereby reducing the interfacial energy. The improvement in microstructure increased the yield strength of Cu-Al₂O₃ with increased La from 126 MPa to 236 MPa, and the elongation from 11.4% to 14.8%, whereas the resistance decreased from $2.01 \times 10^{-8} \Omega/\text{m}$ to

$1.86 \times 10^{-8} \Omega/\text{m}$. Therefore, the addition of trace alloy elements is an important measure to improve the mechanical properties of copper composites.

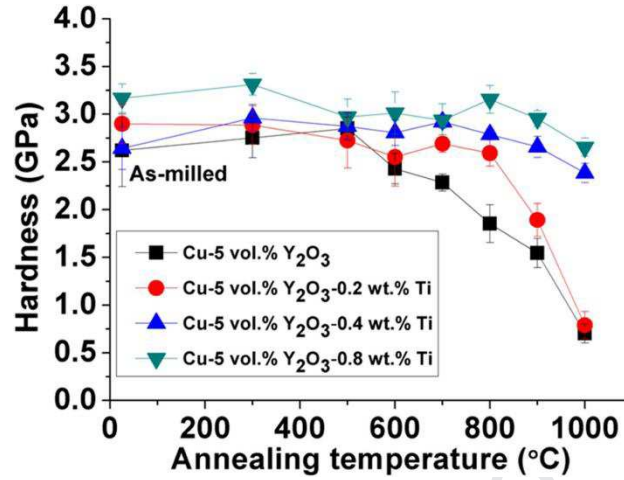


Fig. 5. Hardness values of the as-milled Cu-5vol% Y₂O₃-(0,0.2,0.4 and 0.8) wt% Ti composite powder particles as a function of annealing temperature[24].

(Figure 6 of Ref. [24], Copyright © Elsevier B. V.)

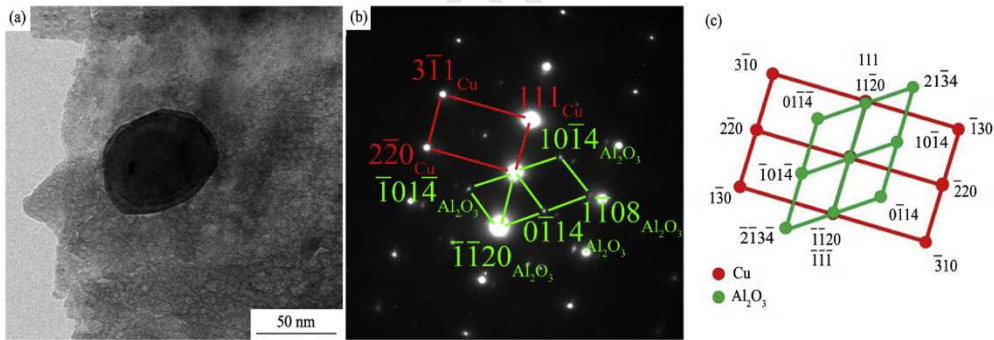


Fig. 6. (a) Bright field images of Al₂O₃ particle in Cu-Al₂O₃-La; (b) SADP of (a); (c) A diagram of the orientation relationship between Cu and Al₂O₃ particles [25].

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Compared with the commercial GlipCop Cu-Al₂O₃ alloys, the hardness of the samples obtained by MA are almost above 200HV, while the hardness of Glipcop Cu-1.1wt%Al₂O₃ is only 152HV, which indicates that MA can greatly improve mechanical properties of samples (The data of the GlidCop alloys come from Hoganas AB, Sweden[54]). In addition, Y₂O₃ ceramic particles are usually used as the reinforcement phase when mechanical alloying is used to prepare ODS copper. Only Al₂O₃ ceramic particles are slightly used to improve the mechanical properties of copper. This protocol is performed because taking the phenomenon that the oxide is

coarsened in the copper matrix into consideration is necessary when the oxide-enhancing phase is selected [23]. Generally, the higher enthalpy of oxide leads to a more stable oxide in the copper matrix and less likely occurrence of coarsening. Yttrium oxide is of higher thermal stability and lower dispersibility because the enthalpy of forming Y_2O_3 (1905 kJ/mol) is higher than that of Al_2O_3 (1667 kJ/mol) [24]. Moreover, researchers also tried adding microalloying elements Ti and La to ODS copper to improve the mechanical properties of copper composites. Notably, although ODS copper has higher hardness than pure copper, its electrical conductivity is reduced to varying degrees. This disadvantage requires further research to be solved.

2.1.2 Internal Oxidation

The internal oxidation method is performed to selectively oxidize the solid solution alloy in an atmosphere with a certain oxygen partial pressure so that the solute elements form oxides and are evenly distributed in the matrix [27]. The internal oxidation method is a relatively advanced process for preparing electrical contact materials. This method is extensively used due to its simple process, low cost, and excellent contact performance [31].

Yan et al. [28] prepared Cu- Al_2O_3 composites by internal oxidation method, and studied three different consolidation methods on the microstructure and properties of the Cu- Al_2O_3 alloys. The specific experimental process was to prepare first Cu-Al powder by water mist method, and then added a certain amount of Cu_2O powder. Excess oxidant was removed by hydrogen reduction after selective oxidation. Fig. 7 shows that the shape of the powder before the internal oxidation is irregular and the particle sizes of the powder are in a wide range. After internal oxidation, the small particle powder disappeared and could be considered to be incorporated into the larger particles. This phenomenon increased the particle size of the powder, which could be confirmed from the particle size data in Table 2. Finally, they respectively sintered the powder after three consolidation methods: high-velocity compaction (HVC), hot pressing (HP), and hot extrusion (HE). Among them, the biggest characteristic of HVC is that the pressing speed is fast, the hammer head speed of the press can reach

up to 30m / s, and the powder is densified by high energy impact in a very short time. The advantage of this method is that it can produce high-density, high-performance and low-cost parts. The relative density of the samples sintered by the three methods reached a high level, in which the lowest relative density of HVC was 98.4%, and the highest relative density of HE reached 100%. The microhardness and compressive strength of HVC were the highest, reaching 132HV and 443 MPa, respectively. The performance of HP sample was always observed between the two processes. Different sintering methods can be used to obtain different performance advantages for the same powder. Therefore, selecting the appropriate sintering process based on the required properties of the sample is important.

Table 2 Particle size distribution before and after internal oxidation [28].

Powder type	D_{10}	D_{50}	D_{90}
Cu-Al powder	5.11	12.29	22.35
Cu-Al ₂ O ₃ powder	8.63	22.02	40.14

Note: D_{10} , D_{50} , and D_{90} represent the particle diameters at 10%, 50% and 90% points on an accumulation curve of a particle size distribution when the total weight is 100%.

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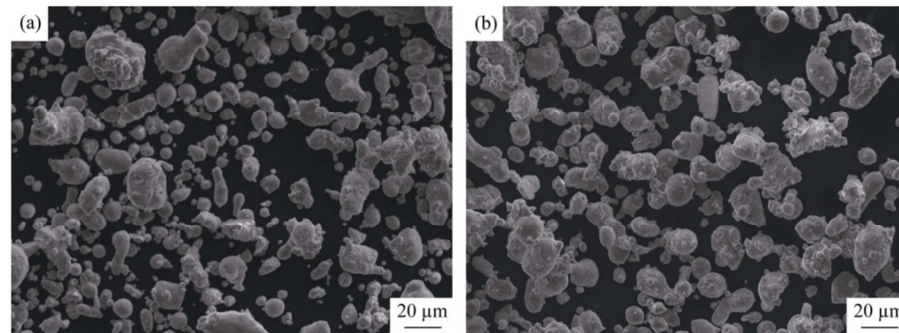


Fig. 7. SEM images of powders before and after internal oxidation: (a) Cu-Al powder; (b) Cu-Al₂O₃ powder [28].

(Figure 1 of Ref. [28], Copyright © Springer Nature.)

Li et al. [29] prepared Cu-4.5vol% Al₂O₃ composites through a novel process. The specific experimental procedure was to add first Cu-50wt% Al (Cu50Al) powder into the hydrochloric acid solution to remove excess Al, which was called dealloying. The reacted product was filtered and dried, which was called Cu50Al-DA powder.

Subsequently, the de-alloyed powder was divided into two batches R1 and R2, which were respectively treated under different heat treatment processes, as shown in Fig. 8. The two powders were named as R1-PCE700 and R2-PCE700 after sintering and extrusion. The elemental composition of the powder after dealloying is shown in Table 3 below. The Al element content is greatly reduced, and the impurities Fe and Si also decrease to varying degrees. The introduction of oxygen is due to the rapid surface oxidation and introduction of Cu_2O during dealloying. The bulk samples R1-PCE700 and R2-PCE700 had average grain sizes of 508 and 566 nm, tensile strength of 387 and 522 MPa, and conductivity of 95% and 90% IACS, respectively. The main reason why the tensile strength of R2-PCE700 sample is higher than that of R1-PCE700 sample is that the number of intergranular Al_2O_3 particles of R2 is more than that of R1, making the Orowan strengthening of R2 is higher than R1. The copper-matrix composites obtained by this method can improve the strength while maintaining the electrical conductivity at a high level.

Table 3 Main elements contents of the Cu50Al and Cu50Al-DA powders [29].

Powder	Al	Fe	Si	O
Cu50Al	50	0.20	0.06	/
Cu50Al-DA	0.84	0.006	0.045	1.51

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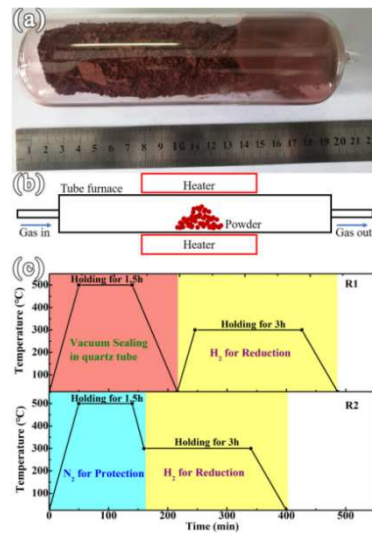


Fig. 8. Image of quartz tube with powder in it, (b) schematic drawing of a tube furnace with powder in it; (c) schematic temperature-time plots for R1 and R2 heat treatment routes respectively [29].

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Zhang et al. [30] prepared Cu-2.75vol% Al_2O_3 composites through internal oxidation and cold isostatic pressing, and the feature of Al_2O_3 dispersoids and the strengthening mechanism were analyzed. The micromorphology of the sintered bulk sample is shown in Fig. 9. The copper matrix grains and alumina particles are of a certain crystallographic orientation relationship, such as $(20\bar{2})_{\text{Cu}}//(\bar{2}\bar{6}0)_{\gamma\text{-Al}_2\text{O}_3}$ and $[111]_{\text{Cu}}//[001]_{\gamma\text{-Al}_2\text{O}_3}$. A coherent relationship is observed between the copper matrix and $\gamma\text{-Al}_2\text{O}_3$ particles. The tensile strength of the sample reached 570 MPa, yield strength of 533 MPa, and conductivity of 85%. Hardness reached 86 HRB (168HV), and grain size was refined to 0.5 μm . The electrical conductivity of the material was not greatly reduced, as the coherent relationship between copper and alumina enabled the resistance of electrons to directional movement to be much smaller. Zhang et al. [31] prepared the $\text{Al}_2\text{O}_3\text{-Cu}/(25)\text{W}(5)\text{Cr}$ and $\text{Al}_2\text{O}_3\text{-Cu}/(35)\text{W}(5)\text{Cr}$ electrical contact material through internal oxidation and vacuum hot pressing sintering. The relative density, conductivity, and Brinell hardness of the former were 97.25%, 67.28% IACS, and 102.31 HBW (108HV), whereas the latter were 97.62%, 62.2% IACS, and 126.78 HBW (132HV), respectively. Xu et al. [32] prepared the Cu- Al_2O_3 composite powder through internal oxidation. A layer of carbon nanotubes was deposited on the surface of the powder by chemical vapor deposition. Fig. 10 shows a scanning electron microscopy (SEM) image of a CNTs/Cu- Al_2O_3 nanometer composite powder. The figure shows that the carbon nanotubes were evenly distributed on the surface of the particles without agglomeration. Because Al_2O_3 particles and carbon nanotubes all have the strengthening effect on copper matrix, the composite strengthening effect of the two is stronger than the single strengthening effect, thereby obtaining better mechanical properties.

Internal oxidation is usually used to prepare Al_2O_3 dispersion-strengthened copper composites. Compared with MA, although internal oxidation method has no advantage in mechanical properties, its conductivity is maintained at a high level (mostly above 80%IACS) due to the low electron scattering of alumina. This enables the internal oxidation process products to be widely used in electrical equipment. The

Cu-Al₂O₃ composite material prepared by the internal oxidation method can ensure the high mechanical properties and good electrical conductivity compared with the Cu-Y₂O₃ composite material prepared by the mechanical alloying method.

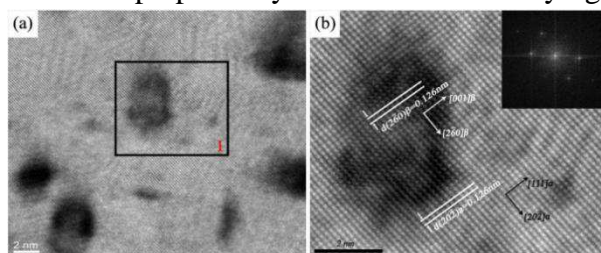


Fig. 9. (a) HRTEM image of alumina dispersed in the IRS-ADSC composite and (b) Fourier filtered image of region I in the image (a) [30].

(Figure 5 of Ref. [30], Copyright © Elsevier Ltd.)

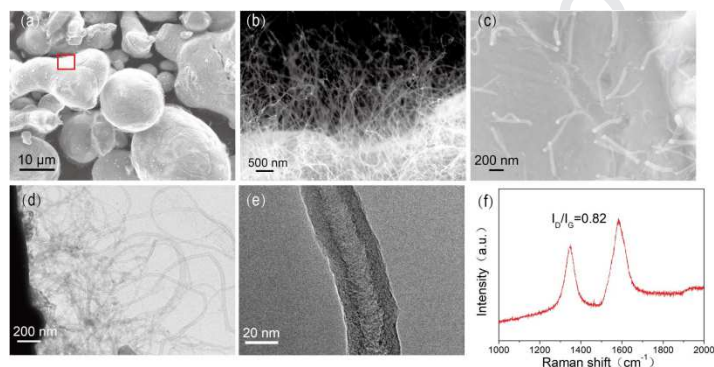


Fig. 10. SEM images (a, b, c) of the as-received CNTs/Cu-Al₂O₃ composite powders, TEM images (d, e) and Raman spectra (f) of as-received CNTs [32].

(Figure 2 of Ref. [32], Copyright © Elsevier B. V.)

Although nanosized alumina particles can be dispersed and distributed on the copper matrix by internal oxidation, alumina particles pose a strong pinning effect on the copper grain boundaries, inhibiting the growth of copper grains to obtain better mechanics performance. However, the implementation of internal oxidation method often needs strict experimental conditions. For example, the oxidation usually lasts for tens of hours, and the partial pressure of oxygen needs to be strictly controlled, which greatly limits the engineering application of the internal oxidation method. The Cu-Al₂O₃ composite material prepared by the external oxidation method is weak at coarse alumina particles, which greatly reduces the mechanical properties of the copper composite material. Lu et al. [33] made up for this drawback through a combination of external oxidation and severe plastic deformation (SPD). The experimental idea was

to oxidize first the Cu–Al alloy powder in the atmosphere, which was then reduced with hydrogen. The powders were hot extruded and then subjected to equal channel angular extrusion (ECAP) and high-pressure torsion (HPT). The experimental results showed that SPD could refine Cu grains to 50–300 nm, and Al_2O_3 particles could also be broken into smaller particles. Such improvements in microstructure enhanced the mechanical properties. The microhardness of Cu-0.5wt% Al_2O_3 increased from 105.0 HV to 136.2 HV after ECAP treatment and to 189.8 HV after HPT treatment.

2.1.3 Wet chemical method

Wet chemical method is also called as chemical coprecipitation method in a narrow sense and refers to a method of preparing powders from liquid phase in a broad sense. Many studies are currently focused on the wet chemical method for preparing metal matrix composites (MMCs). For example, Li et al. [34] prepared W- La_2O_3 by wet chemical method, and Zhao et al. [35] prepared W-Ni/ Yb_2O_3 by this method. Such second-phase particles significantly improved the mechanical properties of W and improved the brittleness of tungsten.

Fathy et al. [36–38] prepared the Cu- ZrO_2 composite material by the chemical reactions of raw material $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and $\text{NH}_4(\text{OH})$. The obtained powder was pressed at room temperature under 700 MPa, and then sintered under the hydrogen atmosphere at 950 °C for 2 h. And they studied effect of ZrO_2 nanoparticle contents on the morphology, structure analysis and microstructure. Fig. 11 is a FE-SEM image of composite powder with different zirconia content. We can see that the particle size of the composite powder decreases with increased zirconia content. The microhardness of the sintered bulk sample increased with increased zirconia content; when the mass fraction was 9%, the microhardness reached 130 HV and the thermal conductivity of decreased from 370.8 W/mK to 101.3 W/mK (Fig. 12). Elmahdy et al. [40] prepared homogeneously Cu- ZrO_2 composites by wet chemical method, and investigated the effect of ZrO_2 on the microstructure and properties of Cu- ZrO_2 . The ZrO_2 crystal grain size could reach 30–50 nm. The microhardness and compressive strength reached the highest at 146.5 HV and 474.5 MPa, respectively, when the mass fraction of zirconia was 10%. However,

the density decreased by 7.2%, and then conductivity decreased to 53.8%. The wear resistance of copper was also greatly improved by the presence of the hard and brittle phase ceramic particles of zirconia. Consequently, the wear rate of the sample was lower than that of pure copper.

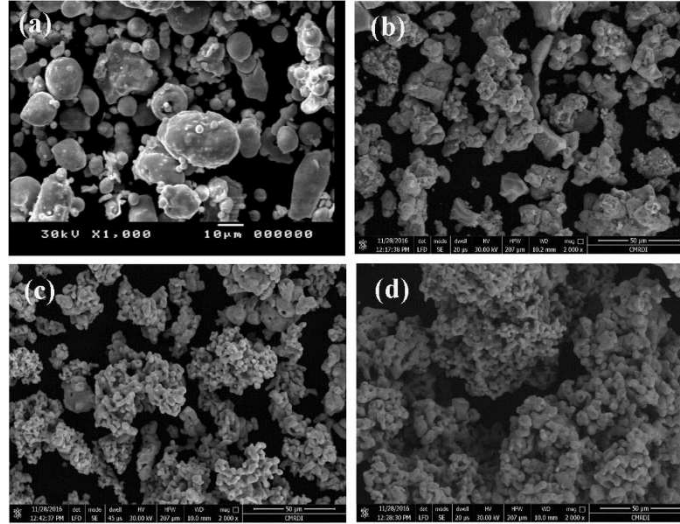


Fig. 11. FE-SEM micrograph of the nanocomposite powder; (a) Cu, (b) Cu-3wt%ZrO₂; (c) Cu-6wt%ZrO₂; (d) Cu-9wt%ZrO₂ [36].

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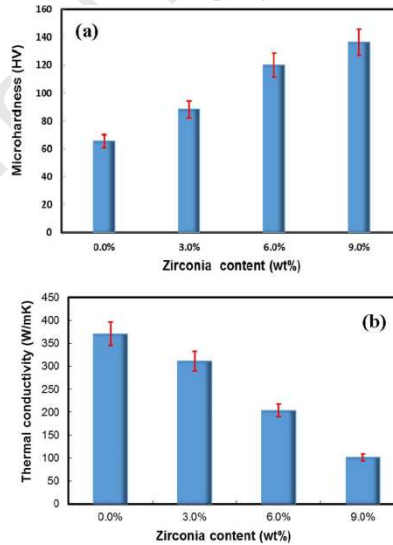


Fig. 12. (a) Microhardness and (b) Thermal conductivity of the Cu-ZrO₂ nanocomposite [36].

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Liu et al. [39] dissolved copper and aluminum sulfate in distilled water into a mixed solution, adding a quantitative solution of aluminum hydroxide and hydrazine hydrate to keep the PH above 10. Then the precipitation was filtered, washed and dried to obtain Al(OH)₃/Cu powder, and finally the Cu-Al₂O₃ samples were pressed

and sintered. The dispersibility in copper matrix of the alumina was the optimum at 12% mass fraction, and the Vickers hardness reached the highest at 108 HV. Sorkhe et al. [40] prepared Cu-TiO₂ composite material by spray drying a mixed solution of Cu (NO)₂ and Ti (NO₃)₄ at 220 ° C to obtain nitrate powder, which was then desalted and oxidized immediately to obtain a mixture of CuO and TiO₂ and finally subjected to hydrogen reduction. During hydrogen reduction, CuO is reduced by hydrogen, and TiO remains the same. In terms of mechanical properties, when the mass fraction of TiO₂ reached 2.5%, the samples achieved an optimal balance between high hardness and high conductivity: 115HB (120HV) and 78% IACS, respectively.

The advantage of the wet chemical method is that the ceramic particles can be uniformly dispersed in the metal matrix, so that the performance of each part of the material is consistent. Compared with mechanical alloying in which ceramic particles are directly added to the copper matrix and mixed, the ceramic particles are in situ generated on the copper matrix in wet chemical method, which makes the interface between the copper matrix and the strengthened phase particles more closely. Given that the bonding between ceramic particles and copper matrix is stronger, it serves as a suitable method for preparing CMCs.

2.2 Other processes

Although many techniques for preparing CMCs through powder metallurgy are available, many shortcomings that cannot be ignored exist [43]. For example, (1) the bonding between the matrix and the oxide particles is usually poor, which also leads to the generation of many pores and a decrease in density. (2) The uneven distribution of the second-phase particles may lead to differences in the performance of various parts of the material. (3) The size of the workpiece prepared by powder metallurgy is limited. Therefore, many other non-powder metallurgical processes have been derived. Three processes are introduced in this paper, such as Friction stir processing, reactive spray deposition, and in situ reaction at liquidus temperature.

2.2.1 Friction stir processing (FSP)

FSP originates from a welding technique: Friction stir welding [43]. By locally modifying and controlling the microstructure of the surface layer of metal materials,

the mechanical properties of materials are improved. The FSP process leads to large plastic deformation of the surface of the material and the component mix, so that the grains of the processed material is significantly refined and uniformized [44]. Many aluminum and magnesium matrix composite material may be prepared by FSP method [45].

Avettand-Fènoël et al. [43] prepared Cu–Y₂O₃ surface composite material by FSP, whose main principle is shown in Fig. 13(a) below. Two parallel V-shaped grooves were opened on the copper substrate, a certain amount of Y₂O₃ powder was added, and a layer of thin copper plate was pressed on the copper substrate (to prevent the powder from being lost during the stirring process). Friction stir processing was performed with a tool made of tool steel and its shape is shown in Fig. 13(b) below. The experimental results showed that the Cu matrix grain size decreased with increased number of indenter cycles in that the Cu grain size was refined from 17 μm to 8 μm. This is because when the passes amount increasing, the yttrium oxide clusters break up, become finer and more uniformly distributed on the surface of the copper matrix, thus refining the grain size of the copper matrix.

Thankachan et al. [46] prepared Cu + (25% AlN + 75% BN) surface composites with different volume fractions by FSP. Fig. 14 below is a surface SEM image of composites with different volume fractions (In the figure, the hybrid reinforcement refers to the mixing of two nitrides (25%AlN+75%BN), the meaning of which is of the same as that in Fig. 15). The ceramic particles are evenly distributed on the copper surface matrix, which is due to the severe plastic deformation and sufficient material flow of the copper matrix surface during the FSP process. Moreover, in terms of mechanical properties, increased volume fraction of ceramic particles resulted in increased Vickers hardness, tensile strength, and yield strength to varying degrees and in decreased wear rates and ductility. Moreover, Cu- (5 vol%, 10 vol%, and 15 vol%) AlN were also prepared in this method [46, 47]. Fig. 15 shows the changes in their microhardness. The following can be observed: (1) The microhardness value in the friction stir center is significantly higher than that in the unprocessed area, which results from the combined effect of grain refinement due to recrystallization that

occurs during FSP, and the dispersion strengthening of the second-phase particles. (2) The microhardness in the central region also increases with increased volume fraction of AlN. Moreover, the ductility of the sample is decreased from 12.15% of 5vol% AlN to 8.33% of 15vol% AlN. This phenomenon can be verified from the SEM image of the fracture morphology of the sample (Fig. 16). With increased amount of AlN particles, the fractured flat surface increases and the sample becomes brittle.

Dinaharan et al. [48] studied the effects of different kinds of ceramic particles (SiC, Al₂O₃, B₄C, and TiC) on the microstructure and mechanical properties of copper surface composites. Experimental results showed that Cu/B₄C indicated the highest hardness and wear resistance. Based on a large number of experiments, Sathiskumar et al. [49] studied the effects of experimental parameters such as tool rotation speed, traverse speed, groove width, and type of ceramic particle on the microstructure and mechanical properties of surface composites and established empirical formula (Eqs. (1) and (2)). Results showed that the higher tool rotation speed (from 800 rpm to 1200 rpm) led to a more uniform distribution of ceramic particles, whereas the microhardness was significantly reduced. This result is because the ceramic particles (B₄C) are still agglomerates when the rotation speed is low, failing to sufficiently enter the copper matrix, thereby resulting in higher hardness. With increased rotation speed, the hardness of the ceramic particles decreases after the ceramic particles are completely dispersed. Moreover, a lower traverse speed and a smaller groove width improve the mechanical properties of the sample.

$$\text{Microhardness (HV)} = 152.702 - 8.750N + 8.583S + 15.917W - 4.333C + 6.114N^2 + 3.864S^2 - 7.136C^2 \quad (1)$$

$$\text{Wear rate } (\times 10^{-5} \text{ mm}^3/\text{m}) = 210.511 + 11.417N - 12.083S - 22.583W - 5.167C - 5.178N^2 - 3.803S^2 + 6.072C^2 \quad (2)$$

where N is the rotation speed; S is the traverse speed; W is the groove width; C is the type of ceramic particles[49].

As can be seen from the above summary, many factors can affect the surface properties of the material, such as the type and content of ceramics, and the speed of the indenter, the speed of movement, and the size of the V-shaped groove. Different

from the aforementioned powder metallurgy methods, the most important feature of FSP is that it only changes the composition, microstructure and mechanical properties on the surface of the copper-based material, while the interior of the copper matrix remains unchanged. So the existing literature shows that the FSP is primarily used to prepare copper matrix surface composites.

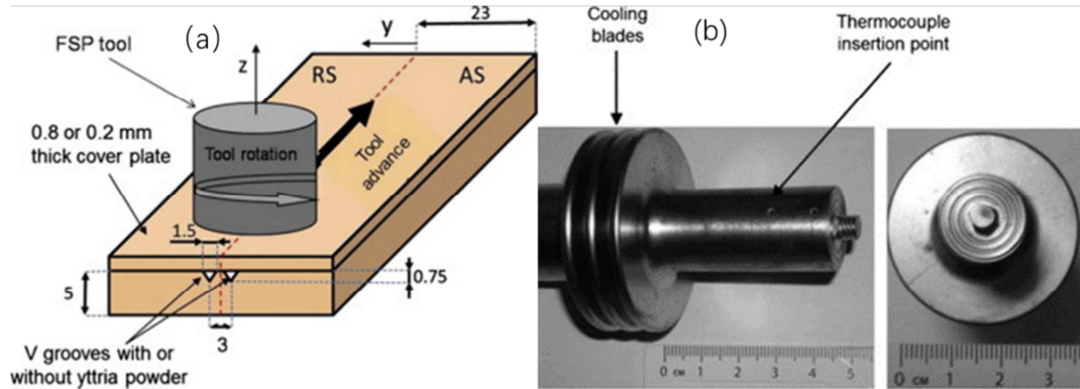


Fig. 13. (a) Schematic diagrams of the machined plates (RS=retreating side, AS=advancing side), (b) Features of the tool shoulder and probe and position of the thermocouple [43].

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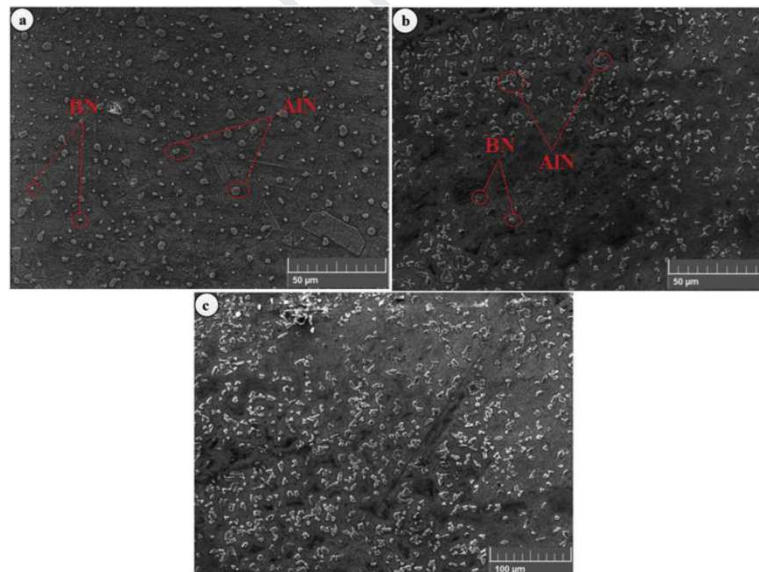


Fig. 14. SEM micrographs of (a) Cu + 5% hybrid reinforcement (b) Cu + 10% hybrid Reinforcement (c) Cu + 15% hybrid reinforcement [46].

(Figure 5 of Ref. [46], Copyright © Elsevier Ltd.)

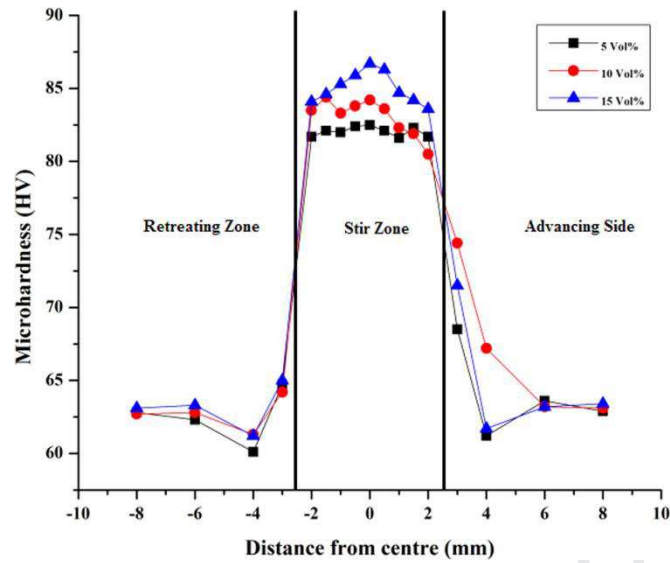


Fig. 15. Microhardness mapping results [47].
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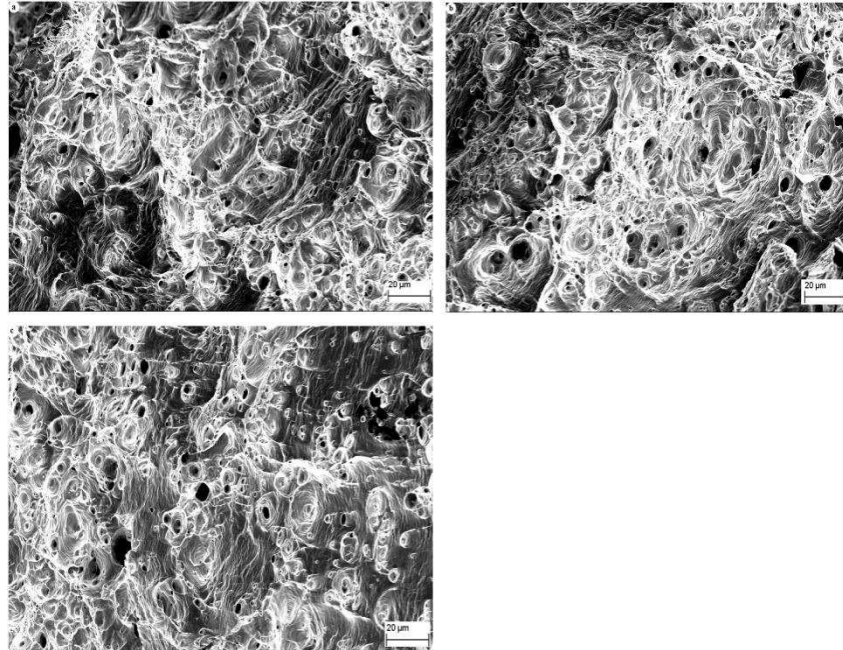


Fig. 16. SEM micrographs of fractured surface of (a) Cu + 5% hybrid reinforcement (b) Cu + 10% hybrid reinforcement (c) Cu + 15% hybrid reinforcement [47].

(Figure 8 of Ref. [47], Copyright © Elsevier Ltd.)

2.2.2 Reactive spray deposition

This method combines spray deposition and in situ reaction. The main principle is shown in Fig. 17. First, the copper–aluminum alloy is sprayed out with a nozzle after it is melted to form mist droplets. Moreover, a mixed gas of $N_2 + O_2$ is introduced. Utilizing the characteristics of higher affinity between aluminum and

oxygen than that with copper, aluminum is first oxidized, thereby forming an Al_2O_3 oxide layer on the surface of the droplet. Such droplets are finally solidified and deposited on the matrix. Moreover, the content of Al_2O_3 is controlled by controlling the oxygen content in the mixed gas.

Han et al. [50] prepared a $\text{Cu}/\text{Al}_2\text{O}_3$ composite through reactive spray deposition and SPS, and investigated the microstructure and properties of bulk materials under the influence of different oxygen partial pressure in spray gas. The oxygen concentration gradient set in the experiment was 0–8 vol%. Alumina particles were not formed in the powder when the oxygen content was less than 2 vol%. This result may be due to the facts that the probability of contact between oxygen and aluminum is low when the oxygen content is too low and the duration of the solidification and deposition phase of the droplets is extremely short. Therefore, oxygen did not react with aluminum. When the oxygen content was higher than 3 vol%, alumina was formed at the copper grain boundaries, shaping as slender filaments or circles. And the mechanical properties of the sintered samples were also tested. Results show that the tensile strength, yield strength, or hardness of the material increases with increased oxygen content when the oxygen content is >2 vol%. The reason is that the increase in alumina content in turn increases the dispersion-strengthening effect. Wang et al. [51] prepared $\text{Cu}-\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ composites by adding Y and La to Cu–Al alloy by reactive spray deposition. After the sample was stored at 980°C for 2.5 h, the density is about 8.69 g/cm^3 , the conductivity is 95.21% IACS, and the hardness is 92 HV. After cold working, the electrical conductivity and elongation decrease, whereas the hardness and tensile strength increase. The maximum tensile strength is about 550 MPa at 70% cold working, and the maximum hardness is about 190 HV at 80% cold working.

Common processes such as internal oxidation, mechanical alloying and wet chemical processes for the preparation of CMCs are faced with such problems as high production cost and insufficient mass production. In addition, different metal matrix composites require different processes. Reactive spray deposition is a novel process to get ceramic particles dispersion strengthened alloys by a single process, and can get

high mechanical properties. However, one of the biggest problems is that the strengthening phase particles are mainly distributed in grain boundary of copper, but not uniformly distributed in copper matrix, which makes the strengthening effect of ceramic particles not reach the best. Therefore, how to solve this problem to further improve the performance of CMCs is the research direction of researchers.

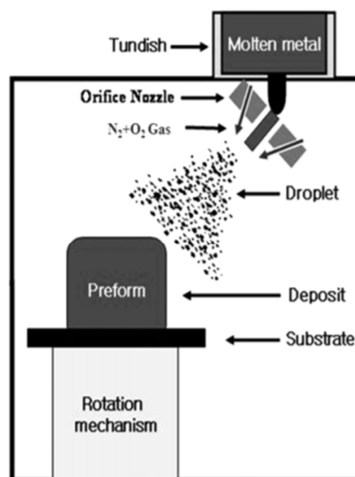


Fig. 17. A schematic diagram of the spray in-situ synthesis casting process [50].

(Figure 1 of Ref. [50], Copyright © The Korea Institute of Metals and Materials and Springer Science Business Media Dordrecht.)

2.2.3 In situ reaction at liquidus temperature

Principle of in situ reaction at liquidus temperature is shown in Fig. 18: The copper alloy is first heated above the liquidus temperature to a molten status. Nitrogen that contains a certain oxygen partial pressure is introduced, and oxygen reacts with alloying element to form oxide particles. On the one hand, the content of alloying element around the oxide particles decreases and tends to zero, so the melting point of the liquid around the oxide is already higher than the actual temperature. On the other hand, the oxide particles can also act as nucleating agents. As a result, the liquid around the oxide begins to solidify isothermally, eventually forming an equiaxed crystal structure with oxide particles as the core.

Zhuo et al. [52] prepared the Cu-0.9vol% Y_2O_3 by in situ reaction at liquidus temperature, and studied the nucleation and growth process of yttria particles. The TEM figure of the sample shows that Yttrium oxide particles are uniformly distributed inside the copper grains, whereas almost no grain boundaries are observed

(Fig.19). The average particle size of the particles is 5 nm. It's calculated that the misfit parameter δ of the yttrium oxide and the copper matrix was 0.036(<0.05), indicating that the boundary between them is coherent. The mechanical properties of the Cu-Y₂O₃ sample prepared by this method are greatly improved by the coherent relationship. Fig. 20 is a comparison between the tensile curve of the sample and pure copper. This method can enable the tensile strength of the Cu-Y₂O₃ sample to reach 590 MPa, which is threefold that of pure copper. Dang et al. [53] prepared two kinds of copper-matrix composites: Cu-Al₂O₃ and Cu-Al₂O₃-La₂O₃, by such method. The grain size of Cu-Al₂O₃ was refined when only alumina was added. However, alumina particles were distributed at the grain boundary. Although the strength and hardness increase, the conductivity decreases. After adding 0.6wt% La₂O₃, the distance between nano-Al₂O₃ particles and the probability of electron scattering were reduced. So the hardness and conductivity of Cu-Al₂O₃-La₂O₃ material were increased by 8.7% and 7.8% which compared with Cu-Al₂O₃ material.

Compared with the internal oxidation method, although the experimental temperature of in situ reaction at liquids temperature is high, the oxide particles obtained by this method have small size (nanoscale), uniform distribution and high stability, and are not easy to agglomerate. So, the copper-matrix composites prepared by this method are of excellent electrical conductivity and good room temperature strength. However, the research on this process is still incomplete. The in situ formation mechanism of the second-phase particles and the solidification mechanism of the alloy are needed for further research to obtain a composite material with a smaller second-phase particle, a larger dispersion, and a better strengthening effect.

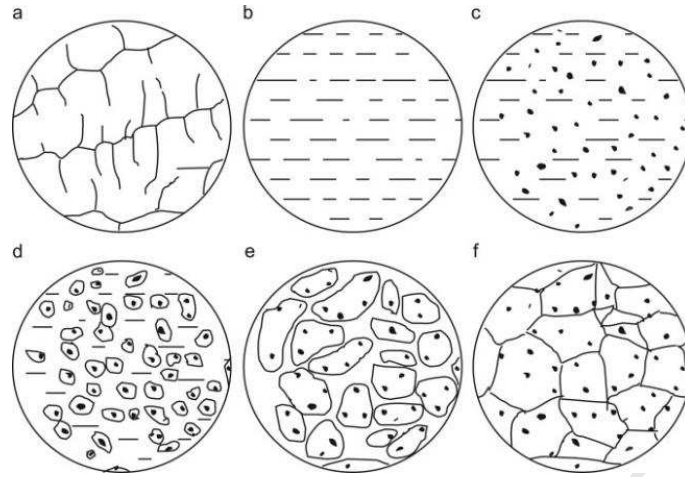


Fig. 18. Schematic diagram of solidification: (a) original microstructure, (b) melts, (c) in situ reaction, (d) nucleation, (e) growth and aggregation, and (f) ultimate microstructure [52].

(Figure 3 of Ref. [52], Copyright © Elsevier B. V.)

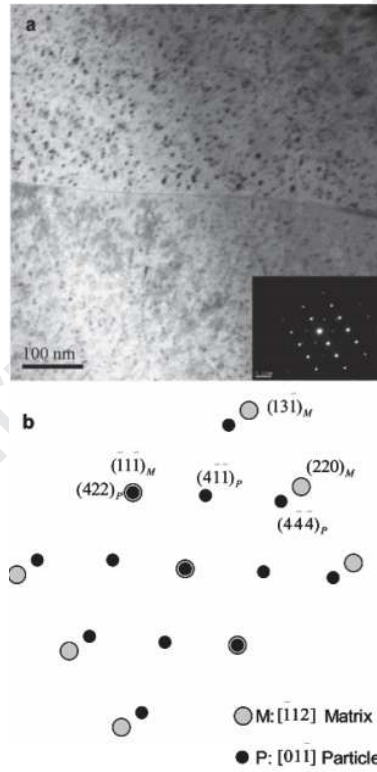


Fig. 19. TEM image of Cu-Y₂O₃ composites (a) inset showing SAD pattern and (b) schematic drawing for SAD pattern [52].

(Figure 4 of Ref. [52], Copyright © Elsevier B. V.)

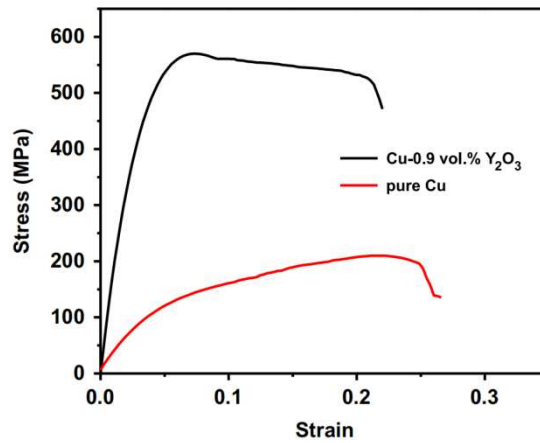


Fig. 20. Tensile stress-strain curves for the Cu-0.9vol% Y₂O₃ composites and pure copper [52].

(Figure 6 of Ref. [52], Copyright © Elsevier B. V.)

3 Conclusions

In summary, the ceramic particles are of great significance for improving the performance of copper. The reinforced phase particles play a pinning role in the copper matrix, preventing the growth of copper grains, and finally achieving the effect of grain refinement. The increase in the number of grain boundaries hinders the movement of dislocations and increases the material strength, consistent with the empirical relationship between strength and grain size in the Hall–Petch formula. The movement of the second-phase particles hindering the dislocation also plays a role in increasing the strength. The hard and brittle ceramic particles increase the hardness of the copper matrix and reduce the wear rate of the material. However, the increase in hardness is often accompanied by a decrease in plastic toughness. The elongation of copper in the literature reviewed in this paper has been reduced. The fracture morphology indicates that the copper composites tend to change from ductile to brittle fracture. Finally, the increase in number of grain boundaries and the presence of second-phase particles hinder the directional movement of electrons in the matrix, which increases resistivity.

In the powder metallurgy process, three kinds of milling methods, including mechanical alloying, internal oxidation method, and wet chemical method, can be used in combination with different sintering processes to prepare different types of ceramic particle-reinforced phase CMCs, which can obtain satisfactory improvements of mechanical properties. The addition of trace alloy elements Ti, La, and so on in

CMCs is of great significance for improving the stability and strength of copper at high temperature. For non-powder metallurgical processes, the FSP is primarily used to improve the mechanical properties of the copper surface. Second-phase particles are generated in situ in copper and can be uniformly distributed in the copper matrix in the reactive spray deposition method. In situ reaction at liquidus temperature overcomes the shortcomings of low solid solubility of yttrium in copper so that finely dispersed yttrium oxide particles are generated in situ.

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> Preparation of copper-matrix composites reinforced by the second phase is reviewed. > Mechanical alloying has the characteristics of simple process and low production cost. > Ti, La, and so on in CMCs is of great significance for improving the stability and strength of copper.> Friction stir process is mainly used to modify copper surface.

Competing financial interests: The authors declare no competing financial interests.

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