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Effect of sintering temperature on microstructure and properties of nano-WC particle reinforced copper matrix composites prepared by hot-pressing sintering

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Abstract

A novel nano-WC/Cu-based composite with nanometer WC dispersed in the copper matrix was successfully prepared by vacuum hot-pressing sintering. The effects of different hot-pressing sintering temperatures on the microstructure, conductivity, strength, and hardness of the composite were investigated. As a result, with the increase of temperature, the distribution of nano-WC particles in the matrix is more even, and the relative density can reach about 100% when sintering temperature increase to 1075 °C. The electrical conductivity of the composites sharply increases from 62.5 to 90% IACS when sintering temperature increase from 950 °C to 1100 °C. Furthermore, as the sintering temperature rises from 950 °C to 1100 °C, the ultimate tensile strength gradually increases from 123 to 425 Mpa, and the hardness increases from 127.5 to 150 HV. In addition, the composite also displayed excellent resistance to high temperature softening at 800 °C.

1. Introduction

The Cu-based composites not only have good electrical conductivity and thermal properties but also exhibit high mechanical strength and wear resistance [1, 2]. Recently, a great deal of research has been carried out on dispersion strengthened (DS) copper matrix composites [3–7]. Moreover, the DS copper alloys are usually fabricated via internal oxidation [8] and mechanical alloying (MA) [9, 10]. For instance, the alumina DS copper alloys prepared by internal oxidation have been extensively used as electrode materials in the welding process because of their high thermal and electric conductivity, and reasonable mechanical strength and thermal stability [11–16]. Whereas, it has been reported that the alumina dispersions are unevenly distributed in copper matrix during the fabrication process [17, 18] which results in relatively low strength and conductivity. The MA method has advantages of simple equipment and simple process compared with the internal oxidation. Moreover, the WC DS copper alloys fabricated by MA combine favorable properties, such as high hardness, good conductivity, and high operating temperature. They have wide application prospects in integrated circuit lead frames, resistance welding electrodes, contact materials, commutators, etc [19–21]. However, WC as a refractory metal compound does not dissolve in the copper matrix [22, 23], which means that the compactness and uniformity of the composite prepared by conventional methods are not particularly good.

The hot-pressing sintering is an effective low-temperature forming method, and its sintering temperature is 100 °C–150 °C lower than atmospheric sintering. Compared to traditional casting, during the process of hot-pressing sintering, vacuumizing can not only prevent the material from being oxidized in the sintering process, but also promote the elimination of gases produced in the sintering process and the densification process [24]. For example, JIA et al [25] prepared Ti-22Al-25Nb composite with excellent properties through vacuum hot-pressing sintering, and investigated the effect of the sintering temperatures on compactness of gas atomized pre-alloyed powders. LIU et al [26] manufactured FeCoCrNiMnTi0.1C0.1 composites by using MA and hot-pressing sintering, which greatly improved the mechanical properties of the composite. The tribological characteristics of powder metallurgy processed Cu-WC/SiC metal matrix composites have been investigated by
SATISHKUMAR et al [27], and the results have shown clearly that reliable reinforcement for the development of copper matrix composites. PAN et al [28] systematically analyzed the thermal stability (i.e. phase stability and anti-oxidation) of Cu–40 wt% Zn up to high temperatures and confirmed the beneficial role of WC nanoparticles in the enhanced thermal stability of Cu–40 wt%/WC nanocomposites. However, none of these studies mentioned above can improve the mechanical properties and conductivity of copper matrix composites at the same time, and the copper matrix composites cannot be used at high temperatures. In addition, these methods have the disadvantage of complicated process and high cost. Ordinarily, the mechanical properties and conductivity of copper matrix composite are always trade off. It is difficult to take into account of the conductivity, strength, and high-temperature performance of the existing copper alloys at the same time, which cannot meet the requirements of the rapid development of aerospace, aviation, microelectronics, and other technologies [29]. Thereby, it has an extraordinary significance to prepare copper matrix composite with excellent mechanical properties, satisfied conductivity, and suitable for high-temperature environments utilizing hot-pressing sintering.

In this study, we use nano-WC as the second-phase reinforcement particle to prepare DS Cu-based composite through the combination of the MA and vacuum hot-pressing sintering for the first time. It greatly simplifies the complex process and reduces the cost. Moreover, the composite shows good mechanical properties, high conductivity, and excellent resistance to high temperature softening at the same time. The effects of different sintering temperatures on the microstructure, conductivity, strength, and hardness of the composite were studied in particular. Furthermore, the mechanism of reinforcement was also analyzed.

2. Experiment method

2.1. Materials preparation

The raw materials used in this work were industrial electroplated copper powder (99.99% purity, average particle size of 30 μm) and self-prepared nano-WC powder (99.99% purity, average particle size of 70 nm). Ammonium metatungstate and water-soluble organic carbon source were used as raw materials, and spray drying was carried out after full dissolution of raw materials in water. Then, nano-WC powder with an average particle size of 70 nm was prepared by continuous carbon–hydrogen coreduction–carbonization in a tube furnace and followed by ball milling.

Firstly, certain amounts of pure Cu powder (270 g), pure nano-WC powder (30 g), and an appropriate amount of anhydrous ethanol were blended in a planetary ball-milling machine (QXAM-20-CM) for 24 h with a rotation speed of 120 rpm. The ball to powder weight ratio was 5:1. Before ball-milling, the bowl was filled with high-purity argon to prevent oxidation. Secondly, the mixed brown slurry was dried at 110 °C and finely ground for further use. Then, the powder was annealed in a vacuum furnace (TL1200-1200-1) to avoid oxidation. Finally, the powder mixture was consolidated into a cylindrical block sample by vacuum hot-pressing furnace (BR-22RY) in vacuum of less than 10⁻² Torr. The detailed sintering parameters as following: constant pressing pressure of 50MPa, a heating rate of 10 °C·min⁻¹, the sintering temperature of 950 °C, 1000 °C, 1025 °C, 1050 °C, 1075 °C, and 1100 °C for 60 min, respectively.

2.2. Structure and performance characterization

Metallographic specimens were cut from the center region of each composite sample by electric spark machining, and then ground, polished following standard procedures, and etched with 10 wt% FeCl₃ and HCl aqueous solution to reveal microstructure. The specimens of TEM were firstly mechanically ground to 50 μm and then thinned further by the Precision Ion Polishing System (PIPS). The microstructure observation was conducted by scanning electron microscope (SEM, FEI Quanta 200 F) and transmission electron microscopy (TEM, FEI Talos F200X). The relative density of each sample was determined according to Archimedes’ principle 30.

The diameters of cylindrical block sample by vacuum hot-pressing are 80 mm. Tensile specimens were machined from the center region of the samples, and their dimensions are shown in figure 1. The tensile tests were conducted with an electromechanical universal testing machine (E45.105) at a crosshead speed of 0.5 mm min⁻¹. The average of five tests was taken as the actual tensile properties. Some typical fracture surfaces from the tensile tests were carefully observed and analyzed by the SEM.

Besides, to analyze the softening resistance at high temperature, the specimens were annealed at 200 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C for 1 h, respectively. And then their hardness was measured using Vickers hardness tester (HVST-1000SZ) under an applied load of 200 g for 15 s. The Eddy Current Conductometer (7501A) was used to test the electrical conductivity of the specimens. The average of five tests was taken as the actual properties of hardness and conductivity.
3. Results and discussion

3.1. Microstructure observation

Figures 2(a)–(b) show the morphology of the raw materials of copper and nano-WC powders, respectively. The average sizes of dendritic electroplated copper particles and spherical nano-WC particles are 30 μm and 70 nm, respectively. Figure 2(c) shows the morphology of composite powder ball-milled for 24 h. It can be seen that the size of the copper particles decreased significantly while the surface became smoother after 24 h of ball-milling as shown in figure 2(c). Likewise, the WC is uniformly dispersed on each copper particles without agglomeration. In fact, the two mixed powders collided intensely in the process of ball-milling, and the copper particles repeatedly occur ‘deformation-welding-crushing’. Nevertheless, the WC has the properties of high strength and hardness to embed into the copper matrix and distribute homogeneously on the surface of copper particles. Therefore, it can be concluded that the ball-milling method can achieve an excellent mixing result.

Figure 3 shows the microstructures of the composites at different sintering temperatures. It is clear that the microstructures are composed of nano-WC particles (the grey white particles) and solidified structures (Cu-based, the gray matrix). Because of lower sintered temperature, the nano-WC particles contact with the matrix at discontinuous points and are only extruded and formed under the action of external load, which makes the...
interfacial bonding do not firm enough. But the distribution of the nano-WC particles is still quite dispersive. Figures 3(a) and (f) show the morphology of composite sintered at 950 °C and 1075 °C before etching, respectively. It is clear that the lumps distributed on the surface are CuCl2 crystal (marked by the arrows in figure 3(b)) that did not been cleaned up and remains on the surface of the copper particles after corrosion due to the numbers of pores distributed on matrix surface (as shown in figure 3(a)). With the increase of sintering temperature, the strength of copper matrix is gradually decreased, which makes deformation easier and contributes to fill the pores, accompanied by the uniform distribution of the nano-WC particles (compare figures 3(a) and (f)). In addition, the filling of pores by the liquid phase due to partial melting or the flow deformation of Cu matrix are the principal mechanism for increasing the compactness of the microstructure, which makes it easier to receive a dense matrix surrounding with WC. Therefore, it can be expected that the higher hot-pressing sintering temperatures can improve the densification level of the composite.

3.2. XRD and TEM analysis
A series of WC-Cu-based specimens with 10 wt.% WC were prepared at different hot-pressing sintering temperatures, which were analyzed by XRD. The XRD determination results show that the composite is composed of WC and Cu phase without other impurities or oxides as shown in figure 4. The result suggests that the final specimens are pure WC-Cu composites.

The morphology and elemental analysis of the fabricated nano-WC/Cu-based composite are shown in figure 5. It is clear that the white round particles are nano-WC particles, without the phenomenon of growth and agglomeration. The elemental distribution mapping of Cu, C, and W illustrated in figure 5 indicates homogenous distribution of the nano-WC in the composite. Moreover, due to the relatively low carbon content, it is not shown clearly on the graph. However, based on the size and distribution of W in the energy spectrum and the result of XRD pattern, it can be determined that the final composite is WC-Cu. The results showed the nano-WC particles are homogenous distributed in the matrix, and the higher hot-pressing sintering temperatures can improve the densification level of the composite.

3.3. Physical properties
The specific values of both experimental density and theoretical density were used to quantitatively evaluate the compactness of synthesized composites. It can be concluded that these composites keep a compact structure which is consistent with the analytical results of SEM microtopography. The variation of the relative density and electrical conductivity with different sintering temperatures could be more clearly seen in figure 6. The results show that the sintering temperature significantly affects the density and electrical conductivity properties of the composites. The relative density gradually increases as the sintering temperature rises, whose value can reach about 100% when sintering temperature increase to 1075 °C. The density remains basically invariable when the temperature increases further. But, when the temperature exceeds the melting point of copper (1083 °C), it is likely that a large amount of liquid phase will be generated during the hot-pressing sintering process, resulting in the liquid being squeezed out and damaging the equipment. Furthermore, as the sintering temperature increases, the pore number of the composites decreases contributing to the increase of electron transfer path.
Ultimately, the electrical conductivity of the composites sharply increases from 62.5 to 90% IACS when sintering temperature increases from 950 °C to 1100 °C.

### 3.4. Mechanical properties

Figure 7 shows the variation of the tensile properties of the composites with various hot-pressing sintering temperatures. The ultimate tensile strength gradually increases as the sintering temperature rises from 950 °C to 1100 °C, and attains a value of 425 MPa at 1100 °C. Furthermore, as the temperature increases, the hardness value increases gradually from 127.5 to 150 HV. The hardness remains basically invariable when the...
temperature further increases from 1050 °C, which is in good agreement with the variation of the relative density.

3.5. Fractography observation

Figure 8 shows the fractography of the specimens sintered at different temperatures. When the hot-pressing sintering temperature is 950 °C, the fracture surface exhibits numerous pores formed during sintering process (figure 8(a)). The cross-sectional graph of the fracture surface indicates that most copper particles are dispersed and do not form grain boundaries, which represents particle interfacial debonding. During the tensile tests, the pre-existing pores preferentially act as crack initiation and extension source (marked by arrows in figure 8(b)). As is well known, the composite can fracture at lower than expected stress levels if there are some regions where extreme concentrations of stress exist. Because of a number of pores distributed on the surface of the composite sintered at 950 °C, they reduce the bearing capacity per unit area and generates a concentration of stress during the tensile test, leading to a reduction in the strength of the composite. Figures 8(c)–(f) show the fracture mechanisms of the specimens are mainly ductile model with many fine dimples, and where WC is uniformly dispersed. As the temperature increases, it can be seen that the dimples and density increase while the distribution of WC is more uniform, which is in good agreement with the analysis results of previous SEM images. Consequently, it can make the interface of composite have a better combination to prevent interfacial debonding resulting in excellent performance. In fact, the tensile properties of composites are determined by the strength of the reinforcement/matrix interface, which is crucial for effective reinforcements. The strengthening mechanisms of nano-WC/Cu-based composites are due to the Orowan strengthening.
mechanism \[32, 33\], thermal discrepancy \[34\], and load transfer \[35\] which contribute to the strengthening of composites. The Orowan strengthening mechanism is caused by the resistance of closely nano-WC particles against the movement of dislocations. In addition, the difference of the thermal expansion coefficient between WC and Cu results in dislocation accumulation at the interface of composites. Finally, when the composite is subjected to load, the soft matrix deforms plastically and then the strained matrix transfers the load to the reinforcing particles through interfacial shear stress, which increases the tensile strength of the composite.

3.6. The properties of resistance to high temperature softening

The softening temperature of dispersion-strengthened copper matrix composites mainly depends on the recovery degree of composites at high temperatures and the thermal stability of enhanced particles. Figure 9 shows the Vickers hardness variation curve of the composite sintered at 1075 °C after annealing at different annealing temperatures for 1h. It is clear that the hardness of composite decreases slowly with the increase of annealing temperature. The initial hardness value of the composite is 150 HV at room temperature. As the annealing temperature rose to 800 °C, the hardness value of the composite still remain at 120.1 HV, which is

![Figure 8. SEM fracture morphology of nano-WC/Cu at different hot pressing sintering temperatures. (a) 950 °C, (b) 1000 °C, (c) 1025 °C, (d) 1050 °C, (e) 1075 °C, and (f) 1100 °C.](image)

![Figure 9. Variations of the hardness with different annealing temperatures.](image)
much higher than that of pure copper. This is due to the thermal stability of nano-WC particles and the pinning effect of dislocation and grain boundary preventing recovery, which can be proved from the microstructure in figure 8. It is concluded that the composite has excellent resistance to high temperature softening.

4. Conclusions

(1) With the increase of sintering temperature, the strength of copper matrix is gradually decreased, which makes deformation easier and contributes to fill the pores. When the hot-pressing sintered at 1075 °C under a pressure of 50 MPa, the composites with nano-WC uniformly distributed on the copper matrix were prepared, and its relative density could reach 100%. The density remains basically invariable when the temperature increases further.

(2) The filling of pores by the liquid phase due to partial melting or the flow deformation of Cu matrix are the principal mechanism for increasing the compactness of the microstructure, which makes it easier to receive a dense matrix surrounding with WC. The microstructure analysis results confirm that the nano-WC particles are homogenous distributed in the matrix, and the higher hot-pressing sintering temperatures can improve the densification level of the composite.

(3) The strengthening mechanisms of nano-WC/Cu-based composites are due to the Orowan strengthening mechanism, thermal discrepancy, and load transfer which contribute to the strengthening of composites. Consequently, the composite sintered at 1075 °C not only shows excellent tensile strength (420 MPa) and high hardness (150 HV) but also high electrical conductivity (90% IACS).

(4) Due to the thermal stability of nano-WC particles and the pinning effect of dislocation and grain boundary preventing recovery. The composite has excellent resistance to high temperature softening. Therefore, it can play an important role in aerospace, microelectronics, and other fields.

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References

[1] Qiu T X, Pan S Y and Fan C 2020 Effect of Ni-coated MoS2 on microstructure and tribological properties of (Cu-10Sn)-based composites Trans. Nonferrous Met. Soc. China 30 2080–490
[2] Zhou S F, Lei J B and Xiong Z 2016 Effect of Fe content on microstructure and mechanical properties of Cu-Fe-based composite coatings by laser induction hybrid rapid cladding Trans. Nonferrous Met. Soc. China 26 3195–204
[3] Qin Y Q, Tian Y and Peng Y Q 2020 Research status and development trend of preparation technology of ceramic particle dispersion strengthened copper-matrix composites J. Alloy. Compd. 848 156475
[4] Fu Y B, Pan Q F and Cao Z Q 2019 Strength and electrical conductivity behavior of nanoparticles reaction on new alumina dispersion-strengthened copper alloy J. Alloy. Compd. 798 616–21
[5] Lu T X, Chen C G and Li P 2021 Enhanced mechanical and electrical properties of in situ synthesized nano-tungsten dispersion-strengthened copper alloy Mater. Sci. Eng. A 799 140161
[6] Groza J 1992 Heat-resistant dispersion-strengthened copper alloys J. Mater. Eng. Perform. 1 113–21
[7] Li M and Zinkle S J 2012 Physical and mechanical properties of copper and copper alloys compr. Nucl. Mater. 4 667–90
[8] Rajkovic V, Bozic D and Iovanovic M T 2007 Properties of copper matrix reinforced with various size and amount of Al2O3 particles J. Mater. Process. Technol. 200 106–14
[9] Jena P K, Brocchi E A and Motta M S 2001 In-situ formation of Cu-Al2O3 nano-scale composites by chemical routes and studies on their microstructures Mater. Sci. Eng. A 313 180–6
[10] Travizkly N A 1998 Microstructure and mechanical properties of alumina/copper composites fabricated by different infiltration techniques Mater. Lett. 36 114–7
[11] Lee D W and Kim B K 2004 Nanostructured Cu-Al2O3 composite was produced by the thermochemical process for electrode application Mater. Lett. 58 378
[12] Fathy A and El-Kady O 2013 Thermal expansion and thermal conductivity characteristics of Cu-Al2O3 nanocomposites Mater. Des. 46 355
[13] Shi Z Y and Wang D Q 2000 Surface dispersion hardening Cu matrix alloy Appl. Surf. Sci. 167 107–12
[14] Zhou G H and Ding H Y 2013 Wear performance of alumina-reinforced copper-matrix composites prepared by powder metallurgy J. Eng. Tribol. 227 1011–7
[15] Tian B H, Liu P, Song K X, Li Y, Liu Y, Ren F Z and Su J H 2006 Microstructure and properties at elevated temperature of nano-Al₂O₃ particles dispersion-strengthened copper base composite Mater. Sci. Eng. A 435–436 705–10
[16] Jamaati R and Toroghinejad M R 2010 Application of ARB process for manufacturing high-strength, finely dispersed, and highly uniform Cu/Al₂O₃ composite Mater. Sci. Eng. A 527 7430–5
[17] Shehata F, Fathy A, Abdelhameed M and Moustafa S F 2009 Preparation and properties of Al₂O₃ nanoparticle reinforced copper matrix composites by in situ processing Mater. Des. 30 2756–62
[18] Chandrasekhar S B, Sarma S S and Ramakrishna M 2014 Microstructure and properties of hot extruded Cu-1wt% Al₂O₃ nano-composites synthesized by various techniques Mater. Sci. Eng. A 591 46–53
[19] Dias M, Pinhão N and Faustino R 2019 New WC-Cu composites for the diverter in fusion reactors J. Nucl. Mater. 521 31–7
[20] Abyzov A M, Kruszewski M J and Ciupinski L 2015 Diamond-tungsten based coating–copper composites with high thermal conductivity produced by pulse plasma sintering Mater. Des. 76 97–109
[21] Yang X H, Liang S H and Wang X H 2010 Effect of WC and CeO₂ on microstructure and properties of W-Cu electrical contact material Int. J. Refract. Met. Hard Mat. 28 305–11
[22] Chen J, Deng X, Gong M F, Liu W and Wu S H 2016 Research into preparation and properties of graded cemented carbides with face center cubic-rich surface layer Appl. Surf. Sci. 386 108–13
[23] Östberg G, Buss K, Christensen M, Norgren S, Andrén H O, Mari D, Wahnström G and Reineck I 2006 Mechanisms of plastic deformation of WC-Co and Ti(C, N)-WC-Co Int. J. Refract. Met. Hard Mat. 24 135–44
[24] Bai Y P, Cheng C, Li J P, Luo J J and Yang Z 2020 Effect of AlN on microstructure, mechanical and thermophysical properties of NiAl/Fc based alloys prepared by vacuum hot-pressing sintering Vacuum 182 109785
[25] Jia J B, Zhang K F and Jiang S S 2014 Microstructure and mechanical properties of Ti-22Al-25Nb alloy fabricated by vacuum hot pressing sintering Mater. Sci. Eng. A 616 93–8
[26] Liu X Q, Cheng H, Li Z J, Wang H, Chang F, Wang W G, Tang Q H and Dai P Q 2019 Microstructure and mechanical properties of FeCoCrNiMnTi0.1Co0.1 high-entropy alloy produced by mechanical alloying and vacuum hot pressing sintering Vacuum 165 297–304
[27] Satishkumar P, Mahesh G, Meenakshi R and Vijayan S N 2020 Tribological characteristics of powder metallurgy processed Cu-WC/ SiC metal matrix composites Mater. Today: Proc. https://doi.org/10.1016/j.matpr.2020.05.449
[28] Pan S H, Yao G C, Sokoluk M, Guan Z Y and Li X C 2019 Enhanced thermal stability in Cu-40 wt% Zn/Al₂O₃ composite Mater. Des. 180 107964
[29] Fu Y B, Pan Q F, Cao Z Q, Li S F and Huo Y Q 2019 Strength and electrical conductivity behavior of nanoparticles reaction on new alumina dispersion-strengthened copper alloy J. Alloy. Compd. 798 616–21
[30] Shi Q, Tse Y Y and Higgins R L 2016 Effects of processing parameters on relative density, microhardness and microstructure of recycled Ti-6Al-4V from machining chips produced by equal channel angular pressing Mater. Sci. Eng. A 651 248–58
[31] Kartikh G M, Ram G D J and Kottada R S 2016 Friction deposition of titanium particle reinforced aluminum matrix composites Mater. Sci. Eng. A 653 71–83
[32] Thilly L, Véronb M, Ludwig O and Lecouturiera F 2001 Deformation mechanism in high strength Cu/Nb nanocomposites Mater. Sci. Eng. A 309 510–3
[33] Zhang Z and Chen D L 2006 Consideration of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites: a model for predicting their yield strength Scr. Mater. 54 1321–6
[34] Tejado E, Dias M, Correia J B, Palacios T, Carvalho P A, Alves E and Pastor J Y 2018 New WC-Cu thermal barriers for fusion applications: high temperature mechanical behaviour J. Nucl. Mater. 498 355–61
[35] Li P B, Chen T J and Qin H 2016 Effects of mold temperature on the microstructure and tensile properties of SiCp/204 Al-based composites fabricated via powder thixoforming Mater. Des. 112 34–45