Influence of Sintering Temperature on the Properties of in-Situ Carbide-Reinforced Hybrid Copper-Based Composite

Ảnh hưởng của nhiệt độ thiêu kết đến tính chất của vật liệu compozit nền đồng cốt hạt in-situ liên cácbit titan niobium

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Abstract

The aim of this research is to investigate the influence of the sintering temperature on the properties of the in-situ carbide (Nb,Ti)C in a copper matrix synthesized via mechanical alloying and powder metallurgy from elemental powders of Cu, Nb, Ti and graphite. The mixture of starting powders with compositions corresponding to Cu-15vol.% (Nb, Ti)C was mechanical alloyed using a planetary ball mill for 20 hours. The as-milled powders then were uniaxial cold pressed at compaction pressure of 800 MPa and sintered in a vacuum sintering furnace for 1 hour at different temperatures from 700 to 1000°C. The obtained results revealed that sintering temperature was an important factor to produce a bulk in-situ Cu-(Nb, Ti)C composite. Higher sintering temperature led to an increase in density and electrical conductivity of the bulk composite with a decrease in microhardness as a result of higher rate of recrystallization and the elimination of dislocation at higher sintering temperature.

Keywords: Cu, (Nb, Ti)C, mechanical alloying, sintering temperature.

Tóm tắt

Bài báo trình bày nghiên cứu ảnh hưởng của nhiệt độ thiêu kết đến tính chất của vật liệu khối compozit nền đồng cốt hạt cacbit hợp kim (Nb, Ti)C tự sinh được tổng hợp bằng phương pháp hợp kim hóa cơ học và luyện kim bột từ bột của các nguyên tố thành phần bao gồm Cu, Nb, Ti và graphit. Hỗn hợp bột được trộn với tỷ lệ tương đương với 15% về thể tích của cacbit (Nb, Ti)C và hợp kim hóa bằng máy nghiền hành tinh trong 20 giờ. Bột nghiền sau đó được ép nguội một chiều với áp lực ép 800 Mpa và thiêu kết trong lò chân không trong 1 giờ ở nhiệt độ trong khoảng từ 700 đến 1000°C. Kết quả nhận được cho thấy nhiệt độ thiêu kết là một thông số quan trọng để chế tạo vật liệu khối compozit Cu-(Nb, Ti)C. Nhiệt độ thiêu kết tăng thúc đẩy quá trình kết tinh lại và loại bỏ các khuyết tật mạng tinh thể dẫn đến làm tăng tỷ trọng và độ dẫn điện trong khi làm giảm độ cứng của vật liệu.

Từ khóa: đồng, cacbit hợp kim (Nb, Ti)C, hợp kim hóa cơ học, nhiệt độ thiêu kết.

1. Introduction

In the last few years, the synthesis of in-situ copper nanostructured composite reinforced by ceramic particles using mechanical alloying has been successfully achieved [1-6]. Such solid state powder processing is normally performed in a high-energy ball-mill, enabling it to synthesize homogeneously dispersed composite particles. Ceramic particles that have NaCl-type crystalline structure, such as niobium carbide (NbC) and titanium carbide (TiC), have thermal stability, extremely high melting point and high hardness [7-9] and therefore can potentially be used as reinforcing phases in metal matrix composite. Marques et al. [6] have produced in-situ nanostructured copper composite with 10 and 20%vol. of NbC at room temperature by mechanical alloying.

The conventional route for fabricating the bulk in-situ Cu-(Nb,Ti)C composite includes synthesis of the in-situ composite powder from elemental powders via mechanical alloying, compaction by uniaxial cold pressing and sintering. In addition to mechanical alloying parameters, powder consolidation steps also have significant influence in determining the final properties of the in-situ copper matrix composite prepared by powder metallurgy. Sintering temperature is believed to be one of the most crucial parameters for developing a process to produce a bulk in-situ Cu-(Nb,Ti)C composite with a good combination of strength and electrical conductivity. Increasing the sintering temperature greatly increased the rate and magnitude of any changes occurring during sintering [10]. It remarkably influenced the densification of the green compacts and thus

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influenced the final properties of the powder metallurgical products.

The aim of the present work is to study the sintering behaviour, microstructure and properties of the bulk in-situ Cu-(Nb,Ti)C composite. The hybrid in-situ Cu-(Nb,Ti)C composite was synthesized by mechanical alloying and consolidated using powder metallurgy techniques of cold pressing and sintering. The sintering temperature were varied in order to investigate the changes in properties, such as density, microhardness and electrical conductivity, of the sintered in-situ Cu-(Nb,Ti)C composites with a correlation with phase and microstructure evolution.

2. Experimental procedure

The starting powders used were pure elemental Cu, Nb, Ti and C powders with mixture composition corresponding to Cu-15vol.%(Nb-Ti)C. The copper powder was of 99.8% purity with an average particle size of 32.93 µm; the niobium powder was of 99.9% purity with an average particle size of 4.74 µm; the titanium powder was of 98% purity with a particle size of 30.15 µm; and the graphite powder was 99.99% pure with an average particle size of 4.08 µm. The mixture of powders was milled using a Fritsch Pulverisette 6 planetary ball mill in an argon with a rotation speed of 400 rpm. The ball-to-powder ratio was 10:1 with 10mm-diameter stainless steel balls. After 20 hours of milling, the as-milled powders were extracted for further characterization by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The as-milled powders were compacted in a cylindrical steel mould and then the compacted composites were sintered by vacuum sintering. To study the effects of sintering temperature the sintering temperature was varied from 700 to 1000ºC with a fixed compaction pressure of 800MPa. The density of the sintered in-situ Cu-(Nb,Ti)C composite was determined based on Archimedes principle using a Satorious electronic analytical balance and reported as relative density. Micro-hardness and electrical conductivity of the composite were measured using a Shimadzu Vickers micro-hardness tester at a load of 100 g and a four-point probe Changmin Tech CMT-SR2000N, respectively.

3. Results and discussion

X-ray diffraction patterns of the sintered Cu-(Nb,Ti)C composite at 20-hour-as-milled powder in the range of 700-1000ºC are shown in Figure 1. These XRD patterns indicated the presence of (Nb-Ti)C peaks after sintering and no evidence of any other phase was found. As can be seen, the diffraction peaks of (Nb-Ti)C are more intense and well-defined with the increase in sintering temperature indicating the increase in fractional volume of the formed carbides in the copper matrix.

Figure 2 presents a SEM image in backscattered mode of the sintered pellet surface from 20h-as milled powder. EDX analysis indicates that the fine white spot consists of a high weight fraction of Nb, Ti and C, which suggests that these white spots in the SEM image were (Nb,Ti)C particles.

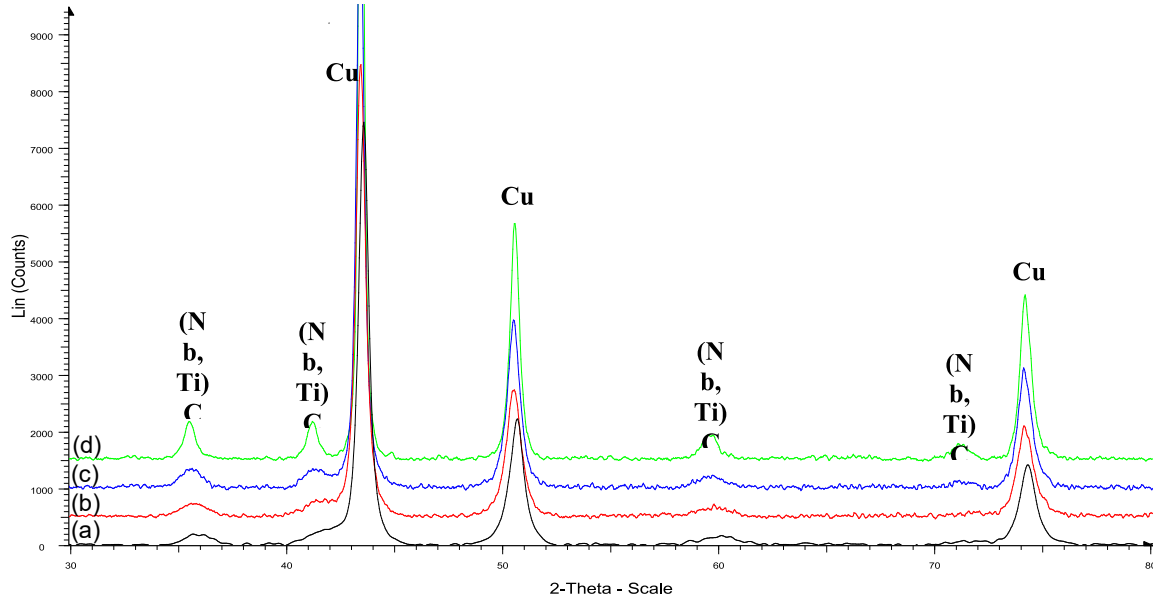

Fig. 1. XRD patterns of the Cu-15%vol.(Nb,Ti)C bulk composite of 20-hour-as-milled powder sintered at (a) 700, (b) 800, (c) 900 and (d) 1000ºC

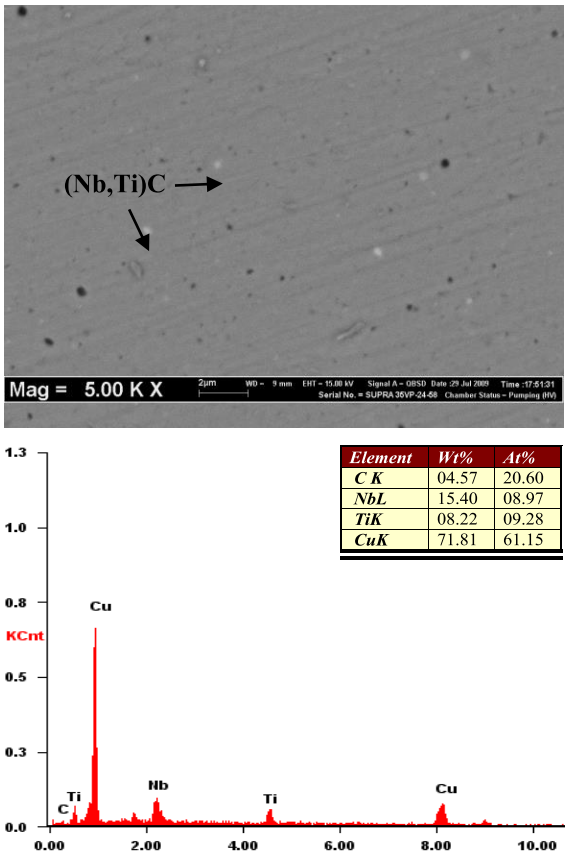

Fig. 2. SEM micrographs of sintered in-situ Cu-15%vol.(Nb,Ti)C composite powder after 20hours of milling and EDX pattern corresponding to "(Nb,Ti)C" area. Sintering temperature is 900°C.

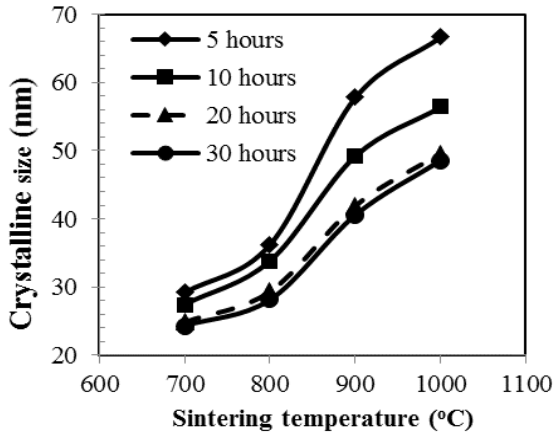

Fig. 3. Evolution of crystallite size of copper matrix of different milling time with sintering temperature

Figure 3 shows the effect of sintering temperature on the variation in crystallite size of the composite sintered in the temperature range of 700-1000°C for 1 hour. Copper crystallite size was determined by the Scherrer method based on the XRD patterns of the sintered composites with different milling times and sintering temperature. It can be seen that the crystallite size of copper grew slowly and steadily below 800°C. Above 800°C, the crystallite growth accelerates dramatically. The rapid grain growth during this stage of sintering must be controlled to minimize grain coarsening. The crystallite growth with increasing sintering temperature can be understood by the coarsening effect. The driving force of sintering is the reduction of the total interfacial energy. Hence the reduction in total interfacial energy occurs via densification and grain growth.

The evolution of morphology of sintered Cu-(Nb,Ti)C is demonstrated in Figure 4, which shows the cross sectional surface of the sintered composites obtained by sintering at 700, 800, 900 and 1000°C. The samples sintered at lower temperatures (700 and 800°C) consist of fine particles with high fraction of large sized pores, indicating that the densification of powder particles is partial at lower sintering temperatures. In contrast, the microstructures of the samples sintered at higher temperatures (900 and 1000°C) show dense packing with no clearly defined particle boundaries and low fraction of small sized pores which are responsible for the high density.

Figure 5 shows the density of the Cu-(Nb,Ti)C composite with different milling time as a function of sintering temperature, ranging from 700°C to 1000°C. It is clear that the density of the composite increases linearly with increasing sintering temperature at all milling times. The density of the bulk Cu-(Nb,Ti)C composite after 20 hours of milling increases from 6.57 g/cm^3 (corresponding to 86.8% TD) after sintering at 700°C to 7.04 g/cm^3 (93.0% TD) after sintering at 1000°C.

An increase in temperature causes more densification and produces less porous bulk composite. According to Ravinder [11], the number of pores was reduced at a higher temperature as a result of the individual grains coming closer to each other and the effective area of grain contact increased.

The increase of density of Cu-(Nb,Ti)C composite with higher sintering temperatures can also be explained by Equation 1, which shows the dependence of diffusion to sintering temperature [12].

$$D = D_o \exp\left(\frac{Q}{RT}\right) \qquad (1)$$

where D is the diffusion coefficient, Do is constant, Q is the activation energy, R is Boltzman's constant and T is the sintering temperature. According to Equation 1, at higher sintering temperatures, higher diffusion rates are achieved resulting in a denser structure [13].

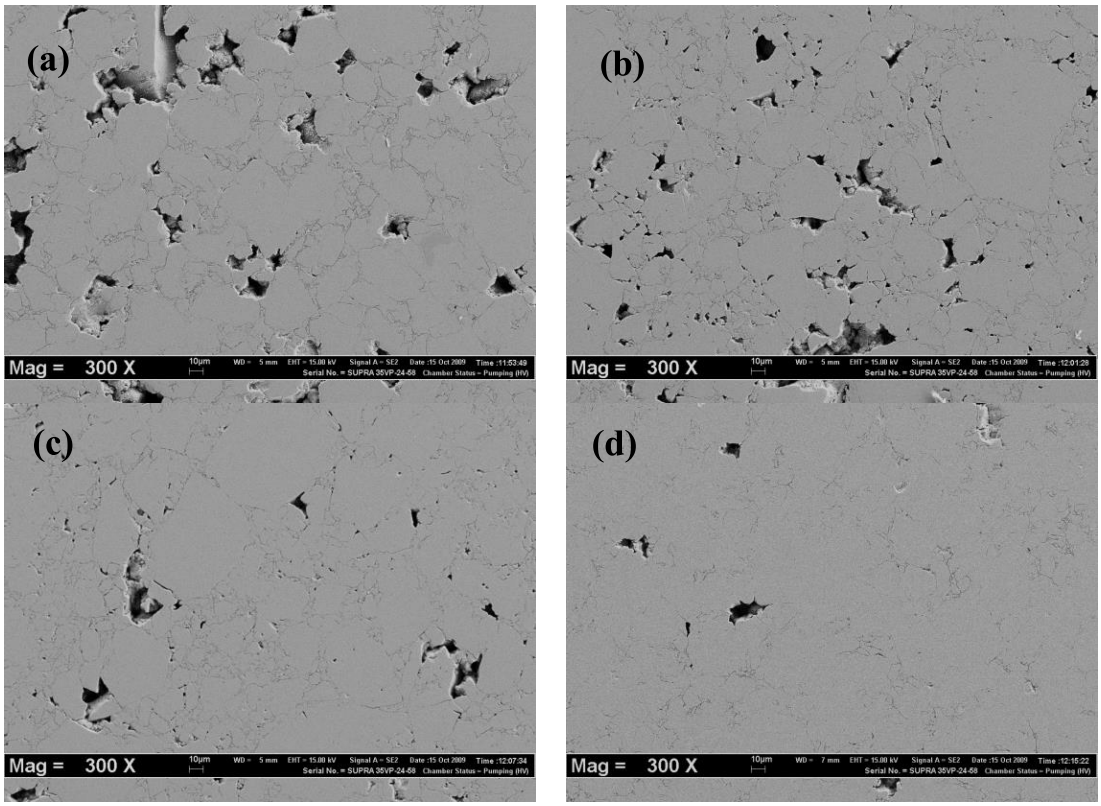

Fig. 4. Evolution of microstructure of the Cu-(Nb,Ti)C bulk composite of 20-hour-as-milled powder with different sintering temperatures, (a) 700ºC, (b) 800ºC, (c) 900ºC and (d) 1000ºC

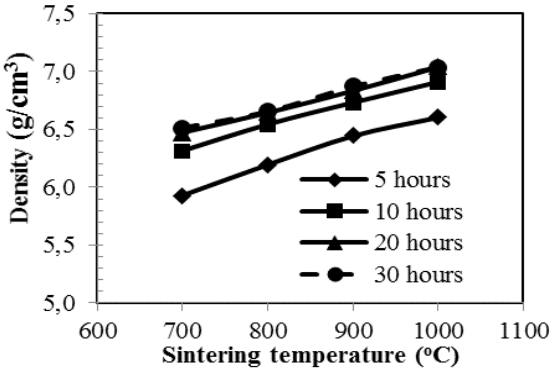

Fig. 5. Effect of sintering temperature on the density of Cu-(Nb,Ti)C composite with different milling time

The effect of sintering temperature on the microhardness of Cu-(Nb,Ti)C composite with different milling time is shown in Figure 6. The microhardness of the composite increases considerably when the sintering temperature rises in the range 700 to 800ºC and varies little from 800 to 900ºC. The composite achieves a maximum value of microhardness at 900ºC. At higher sintering temperature (above 900ºC), the microhardness of the composite decreases. The porosity of the sample of 5-hour-as-milled powder sintered at 700ºC was too high (about 21%), thus its hardness as well as electrical conductivity measurements could not be performed.

The change of the microhardness of composite with sintering temperature is controlled by three main processes including the precipitation of carbides (in the case of sample of the 5- and 10-hour-as-milled powders), densification, and recrystallization of the copper matrix and growth of the copper grains. These processes take place during sintering and influence the hardness of the composite. In particular, the precipitation of the carbides and densification lead to an increase of the microhardness and, conversely, the recrystallization process and grain growth result in a decrease in microhardness.

The rapid increase in microhardness of the composite in the range of 700-800ºC could be mainly due to the effect of the densification and the formation of carbides in the copper matrix rather than the recrystallization process. In the temperature range between 800 and 900ºC, the effect of densification somewhat compensates for the effect of the recrystallization process leading to a slight increase of microharness. The significant drop in microhardness of the composite with higher sintering temperature (up to 1000ºC) can be attributed to the higher recrystallization process and grain growth of the copper matrix, which according to Hall-Petch theory has led to lower strength and microhardness [14].

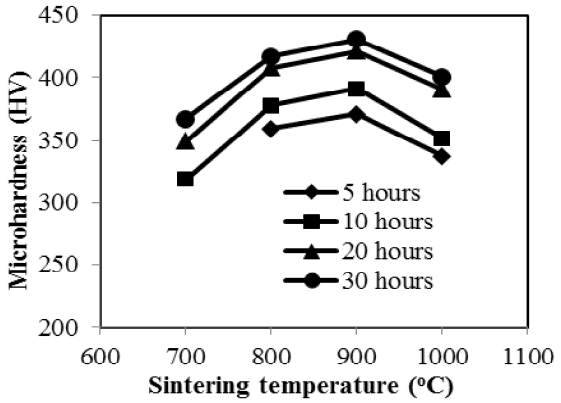

Fig. 6. Effect of sintering temperature on the microhardness of Cu-(Nb,Ti)C composite with different milling times

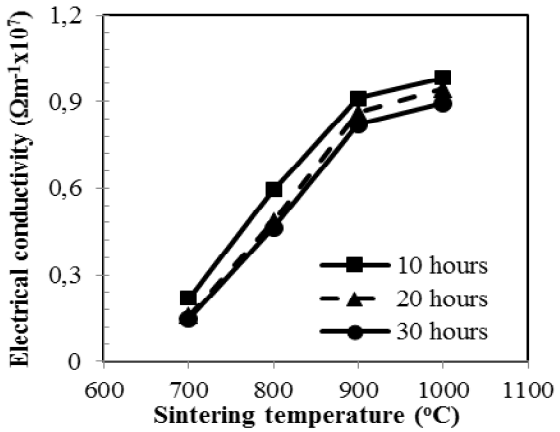

Fig. 7. Effect of sintering temperature on the electrical conductivity of Cu-(Nb,Ti)C composite with different milling times

The temperature dependence of electrical conductivity of Cu-(Nb,Ti)C composites was also investigated. According to the results of density measurements, one could expect the electrical conductivity of the composite to increase with sintering temperature. Figure 7 shows that the electrical conductivity of the composite is progressively increasing with an increase in sintering temperature and achieved a maximum value when sintered at 1000°C. It could be attributed to the increase of densification of the sintered composite which is accelerated by increasing sintering temperature. Another possible reason is due to the higher rate of recrystallization, the elimination of dislocation and the reduction of surface tension at higher sintering temperature. Another important factor influencing the electrical conductivity of such composites is the particle size of the conductive phase [15]. The grain growth of the copper matrix at high sintering temperature also contributes to an increase in the electrical conductivity of the composite.

The microhardness and electrical conductivity results obtained at different sintering temperatures suggest that 900°C is the optimum sintering temperature to produce a Cu-(Nb,Ti)C composite with high microhardness and high electrical conductivity.

4. Conclusion

Sintering temperature was a crucial parameter for developing a process to produce a bulk in-situ Cu-Cu-(Nb,Ti)C composite. Higher sintering temperature leads to an increase in density and electrical conductivity of bulk in-situ Cu-(Nb,Ti)C composite but results in a decrease in microhardness. 900°C is the optimum sintering temperature to produce Cu-(Nb,Ti)C composite with high microhardness and high electrical conductivity, where the microhardness and conductivity were 430.5 HV and 8.77×10^8 $(\Omega m)^{-1}$, respectively.

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