

Effects of Milling Time on the Properties of In-Situ Binary Niobium-Titanium-Carbide Reinforced Cu Based Composite

Ảnh hưởng của thời gian nghiền đến tính chất của compozit nền đồng cốt hạt in-situ liên cacbit titan niobium

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Abstract

Mechanical alloying was used to synthesize in-situ copper based composite reinforced by binary niobium-titanium-carbide from Cu, Nb, Ti and graphite powder mixture. The nominal composition was corresponded to Cu-30 vol.% (Nb,Ti)C. XRD patterns showed that (Nb, Ti)C was not formed in the as-milled powder after 5 hours of milling but was precipitated with a subsequent sintering at 900°C. Milling time has showed a great influence on both mechanical and physical properties of the sintered composite pellets. Increasing milling time leads to an increase of the microhardness of the composite due to a higher degree of deformation that enhanced hardening. On the other hand, the electrical conductivity decreases considerably when the milling time increases. This phenomenon could be attributed to the increase of density of grain boundaries, which acts as a centre of electron scattering, with milling time.

Keywords: Cu, (Nb, Ti)C, Mechanical alloying, Sintering.

Tóm tắt

Phương pháp hợp kim hóa cơ học được sử dụng để tổng hợp vật liệu compozit nền đồng cốt hạt cacbit hợp kim (Nb, Ti)C tự sinh từ hỗn hợp bột của các nguyên tố thành phần bao gồm Cu, Nb, Ti và graphit. Phổ nhiễu xạ tia Ronghen của hỗn hợp bột với thành phần tương ứng với 30% thể tích (Nb,Ti)C cho thấy pha cacbit chưa được tạo thành sau 5h nghiền nhưng xuất hiện sau khi thiêu kết ở 900°C trong môi trường khí argon. Thời gian nghiền ảnh hưởng mạnh đến cả tính chất cơ học và tính chất vật lý của vật liệu compozit. Kéo dài thời gian nghiền làm tăng độ cứng của vật liệu compozit do sự tăng mật độ khuyết tật trong mạng tinh thể của vật liệu. Mặt khác, tăng thời gian nghiền làm giảm độ dẫn điện của vật liệu do sự tăng của mật độ biên giới hạt tinh thể, qua đó làm tán xạ sự chuyển động của các điện tử trong vật liệu.

Từ khóa: Đồng, Cacbit hợp kim (Nb, Ti)C, Nghiền năng lượng cao, Hợp kim hóa cơ học, Thiêu kết.

1. Introduction

In an in-situ reinforced metal matrix composites, the reinforcements are formed within the metal matrix during the fabrication of the composite by some chemical reactions [1]. The in-situ reinforced MMCs have more advantages over conventional ex-situ composites such as thermodynamic stability of the reinforcing phases, finer reinforcing particle size with clean particle-matrix interfaces and good mechanical properties [1-3]. In-situ copper-based composite reinforced by carbide dispersed particles has now emerged as a promising candidate for high performance electrical materials for such applications as sliding electrical contacts. Particle reinforced copper matrix composites present high-specific strength and good wear resistance while maintaining its high electrical conductivity [4,7].

In our previous work [8], copper based reinforced in-situ binary niobium-titanium-carbide (Nb,Ti)C composite powders have been successfully synthesized by mechanical alloying. We investigated the influence of the milling time on the formation of the in-situ carbide in the copper matrix. The obtained results showed that the maximum volume fraction of the carbide was reached after 20 hours of milling. The as-milled powder exhibited a good dispersion of (Nb, Ti)C particles within copper matrix with an excellent interfacial bonding. The in-situ carbide (Nb,Ti)C particle size ranged from 20 to 80 nm.

However, milling time influences not only the formation of the in-situ carbides in the copper matrix but also the properties of the bulk in-situ composite. In the present work, the in-situ copper nanocomposite reinforced with 30 vol.% (Nb,Ti)C was synthesized by mechanical alloying. The milling time was varied to investigate the microstructure and the morphology evolution of the formed binary niobium-titanium carbide of the bulk composite after sintering.

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2. Experimental procedure

The starting powders were pure elemental Cu (99.8%), Nb (99.9%), Ti (99.9%) and graphite (99.99%), purchased from Sigma Aldrich, with mixture composition corresponding to Cu-30vol.% (Nb,Ti)C. The mixture of powders was milled using a Fritsch "Pulverisette 6" planetary ball milling in argon atmosphere with a rotation speed of 400 rpm. The ball-to-powder ratio used was 10:1 with 10mm-diameter stainless steel balls. After 5, 10, 20, and 30 hours of milling, the as-milled powders were extracted. The as-milled powders were uniaxially compacted in a cylindrical steel mould at 800 MPa and then sintered in vacuum at 900°C for 1 hour. The density of the sintered in-situ (Nb,Ti)C-Cu composite was determined based on Archimedes principle using a Satorious electronic analytical balance. 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

According to our previous work [8], the as-milled powder showed the diffraction peaks of the starting elemental Nb and Ti powders after 5 hours of milling. From 10 hours to 30 hours of milling the peaks of Nb and Ti powders are no longer existed while almost all of the (Nb, Ti)C major reflections (111), (200) and (220) are detected.

Figure 1 shows the XRD patterns of the in-situ sintered composites. The peaks of (Nb, Ti)C in the XRD patterns of sintered samples of 5-hour as-milled powder (Fig. 1a) are clearly visible. (Nb, Ti)C were not formed in the as-milled powder after 5 hours of milling but was precipitated with a subsequent sintering at 900°C. According to [9], the reaction temperatures for the formation of the carbide from the elements Ti, Nb and carbon is higher than 1300°C. The precipitation of (Nb, Ti)C in this present work occurred at a much lower temperature with the enhanced diffusivity of atoms due to the MA process. The refinement of the grain size during MA increased the number of grain boundaries. The numerous interfaces provided a high density of short-circuiting diffusion paths [10].

In the case of others composites (Fig. 1b-d), the diffraction peaks from the sintered in-situ composite, compared to those of the as-milled powders, are more intense and well-defined than the peaks of as-milled powder. This phenomenon indicates that heat treatment recovered considerable internal strains and made the crystallite size increase remarkably.

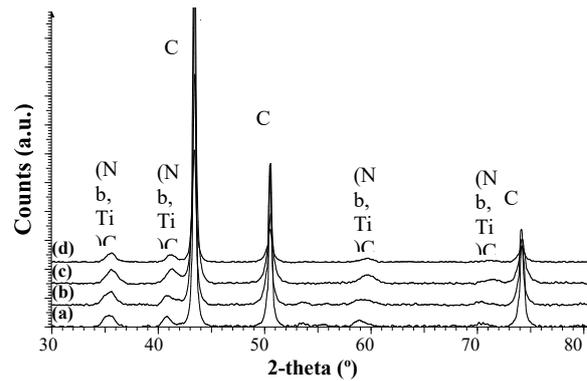


Fig. 1. XRD patterns of sintered samples at 900°C/1h from the powders of different milling times: (a) 5, (b) 10, (c) 20 and (d) 30 hours

Copper crystallite size was determined by the Williamsons-Hall method from their corresponding XRD patterns acquired on the sintered samples of different milling times. The variations in the average crystallite size of Cu (D_{Cu}) in both as-milled powders and sintered pellets for different milling times are presented in Figure 2. The crystallite size decreases rapidly, from 41 nm of starting copper powder at the initial state of MA to 22 nm after 5 hours of milling. The average crystallite size of Cu drops slightly from 10 to 20 hours of milling time, and after 20 hours of milling the crystallite size of Cu decreases to 17 nm. No change of D_{Cu} value occurs after 20 hours of milling, indicating that steady-state is attained at 20 hours of milling.

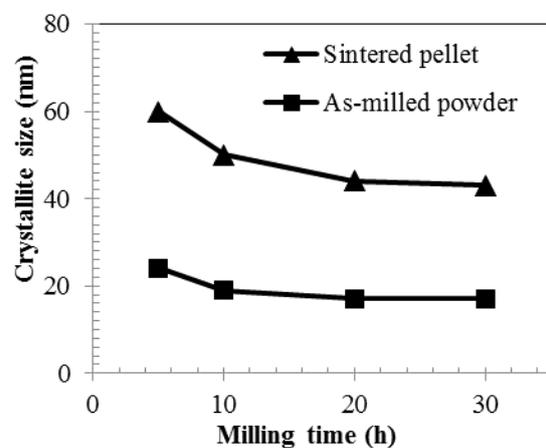


Fig. 2. Copper crystallite size measured from XRD pattern for as-milled powders and sintered composite with different milling times

At this stage, a balance was achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average composite particle size [10]. Compared to the crystallites of Cu in as-milled powders, the crystallites of Cu in sintered pellets are

larger and follow a similar increasing trend. It is due to the heat-treatment results in recrystallization and crystallite growth.

In contrast to crystallite size, the internal strain of Cu is increased with increasing milling time as shown in Figure 3. At the beginning of milling the internal strain in the Cu lattice structure increases rapidly due to the dissolution of carbon in the copper matrix. After 20 hours of milling, the lattice strain of copper increases slightly, possibly because during the MA powder particles are subjected to high-energy collisions, causing a heavy plastic deformation that is associated with a high density of defects, such as dislocations and stacking faults [11], which is the main contributor to the increase in lattice strain. The internal strain for Cu in the sintered in-situ composite is lower than that in the as-milled powder, probably because the stored energy in the as-milled powder particle is released because of a recovery or relaxation process within the boundaries during the sintering process.

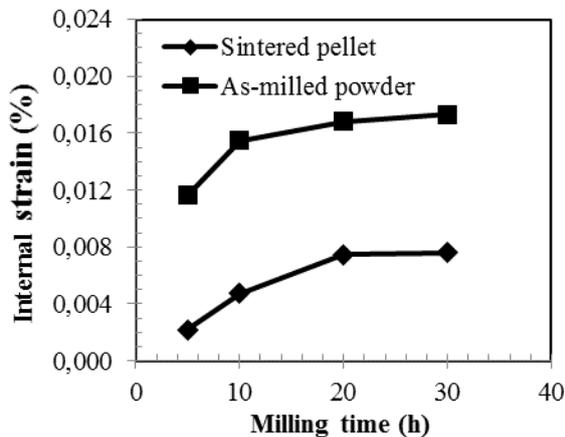


Fig. 3. Internal strain of Cu measured from XRD pattern for as-milled powders and sintered composite with different milling times

The change in density of the bulk Cu-(Nb,Ti)C composite as a function of milling time is shown in Figure 4. As can be seen, the density of the sintered Cu-(Nb,Ti)C composite is significantly influenced by duration of MA. Sintered density increases with prolonged milling time, i.e. from 6.45 g/cm³ [corresponding to 85.10% of theoretical density (TD)] after 5 hours of milling to 6.87 g/cm³ (corresponding to 90.72% of TD) after 30 hours. A possible explanation for the increase in density is that a variety of crystal defects such as dislocations, vacancies, and stacking faults as well as the number of grain boundaries increases when extending the milling time, and the presence of this defect structure enhances the diffusivity of atoms during sintering

[10]. The low density of sintered composite after the initial milling time may be also due to the low-uniform distributions and the larger size of Nb and Ti particles in 5-hour-as-milled powder.

Furthermore, the refined microstructural features decrease the diffusion distances [10]. The mechanisms can easily be understood, the finer particle size results in a higher surface energy for a compact, thus a higher driving force for grain growth (growth of crystallites) and densification to reduce the system's Gibbs energy [12]. Furthermore, the higher amount of contact points between the particles activated the transport of matter leading to a high number of necks between particles, motivating the diffusion and evaporation–condensation of the matter on surfaces with consequent bulk densification [13].

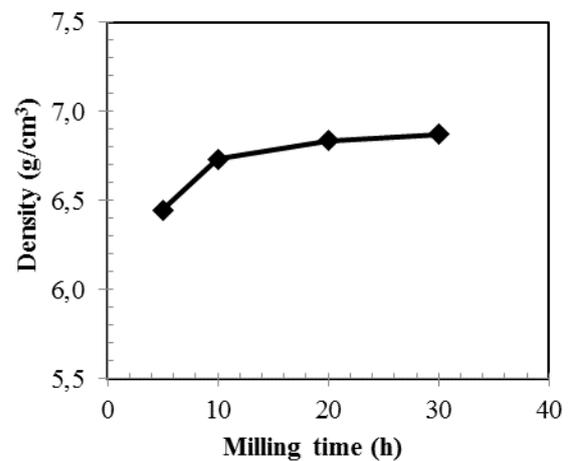


Fig. 4. Variation in sintered density of in-situ Cu-(Nb,Ti)C composites with different milling times

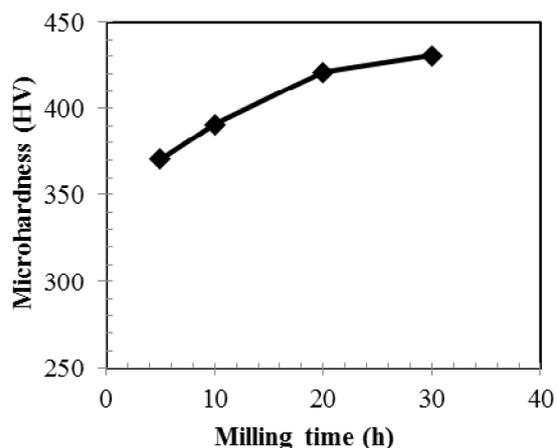


Fig. 5. Variation on microhardness of in-situ Cu-(Nb,Ti)C composites with different milling times

The results of Vickers microhardness measurements performed on polished consolidated

pellet as a function of milling time of the sintered Cu-(Nb,Ti)C composite is shown in Figure 5. The microhardness value increases from 359 HV to 431 HV as the milling time increases from 5 to 30 hours. This is to be expected since during MA the crystallite size was regularly refined to a nanometer level, allowing a higher degree of deformation that produced lattice distortion in the matrix copper. This lattice distortion then created lattice strain and increased the dislocation which enhanced hardening. The ultra-fine particles of (Nb,Ti)C increased the amount of interfacial bonding between the reinforcement and Cu matrix, which also contributed to the composites' enhanced mechanical properties [14].

As shown in Figure 5, the microhardness value rose rapidly between 5 and 10 hours of milling. At this stage, the effect of dislocation is not the main factor in the increased microhardness, instead, the major influence is the formation of the carbide (Nb,Ti)C in the Cu matrix. Furthermore, when the milling time exceeds 20 hours, the Vickers hardness variation is negligible, suggesting that the MA process may have reached steady-state by 20 hours of milling.

The mechanism of strengthening can be explained using Orowan's mechanism. In Orowan's mechanism [15], impenetrable precipitates in the matrix interrupt dislocation migration and thus plastic deformation via interaction with dislocations, which results in an increase in the matrix strength.

The strengthening of the metal matrix by rigid particles is achieved as follows:

$$\tau = \frac{\mu b}{L} \quad (1)$$

where τ is the external stress, μ is the modulus of rigidity of the matrix metal, b is the magnitude of Burgers vector and L is the interparticle distance. It is therefore proposed that the precipitation of in-situ (Nb,Ti)C nanometric particles, which act as a barrier to dislocation motion and are too hard to be cut by dislocations, results in strengthening of the copper matrix. Following Equation 1, when the in-situ carbides particles were refined with milling time, corresponding to a decrease in internal particle distance L , the external stress increases leading to the rise of the microhardness.

It is well known that the physical properties of metallic materials are influenced by defects such as grain boundaries, solute atoms, dislocations, porosities and second phases. The electrical conductivity of the sintered composites was found to depend on the number of grain boundaries, the

formation of (Nb,Ti)C, and the porosity of the composite. As can be seen in Figure 6, the electrical conductivity increases rapidly from $6.02 \times 10^8 (\Omega m)^{-1}$ after 5 hours of milling to $9.09 \times 10^8 (\Omega m)^{-1}$ after 10 hours of milling. It is due to a considerable reduction in the large degree of porosity that had been found in the 5-hour composite. The electrical conductivity decreases considerably when the porosity increases. The decrease of electrical conductivity with milling time is confirmed by the density results. From 10 to 30 hours of milling the electrical conductivity slightly decreases to $8.17 \times 10^8 (\Omega m)^{-1}$. The possible cause of this slight decrease is the increase of density of grain boundaries, which acts as a centre of electron scattering, with milling time. According to Murty et al. [16], with an increasing amount of grain boundaries, the mean free conductive path decreases, resulting in increased resistivity.

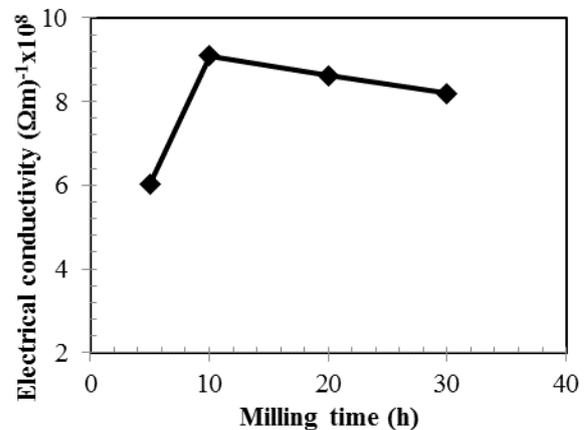


Fig. 6. Variation on electrical conductivity of Cu-(Nb,Ti)C composites with different milling times

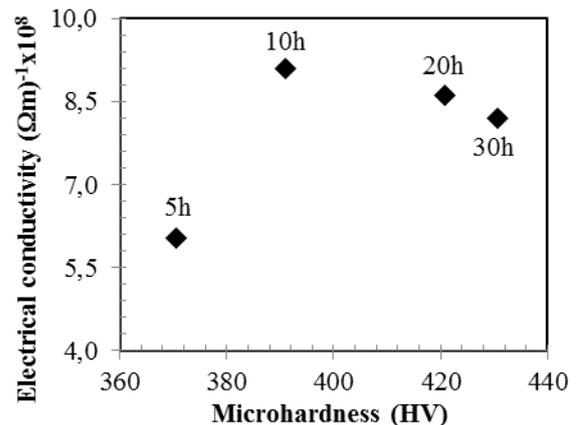


Fig. 7. Microhardness versus electrical conductivity of Cu-(Nb,Ti)C composites at different milling times

A plot of microhardness versus electrical conductivity in Figure 7 indicates that the in-situ Cu-(Nb,Ti)C composite reached a good combination of

microhardness and electrical conductivity after 20 hours of milling, where the microhardness and conductivity are 420 HV and $8.62 \times 10^8 (\Omega\text{m})^{-1}$, respectively. This finding suggests that to produce Cu-(Nb,Ti)C composite with high microhardness and high electrical conductivity, in addition to lower power consumption, the optimum milling duration is 20 hours.

4. Conclusion

The in-situ Cu-(Nb, Ti)C nanocomposite pellets have been successfully synthesized via mechanical alloying and powder metallurgy. Milling time exhibited a great influence on both the mechanical and physical properties of the sintered composite pellets. Increasing milling time leads to an increase of the microhardness of the composite due to a higher degree of deformation that enhanced hardening. On the other hand, the electrical conductivity decreases considerably when the milling time increases. It could be attributed by the increase of density of grain boundaries, which acts as a centre of electron scattering. Our results indicated that the in-situ Cu-(Nb,Ti)C composite reached a good combination of microhardness and electrical conductivity after 20 hours of milling, where the microhardness and conductivity are 420 HV and $8.62 \times 10^8 (\Omega\text{m})^{-1}$, respectively.

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