Mechanical alloying and sintering of nanostructured TiO₂ reinforced copper composite and its characterization

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Article info
Article history:
Received 1 November 2013
Accepted 15 January 2014
Available online 25 January 2014

Keywords:
Mechanical alloying
Cu–TiO₂ composite
Electrical conductivity

Abstract
Mechanical alloying is a suitable method for producing copper based composites. Cu–TiO₂ composite was fabricated using high energy ball milling and conventional consolidation. Ball milling was performed at different milling durations (0–24 h) to investigate the effects of the milling time on the formation and properties of produced nanostructured Cu–TiO₂ composites. The amount of the TiO₂ in the final composition of the composite assumed to be 0, 1, 3, 5 and 7 wt%. The milled composite powders were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy to investigate the effects of the milling time on the formation of the composite and its properties. Also hardness, density and electrical conductivity of the sintered specimen were measured. High energy ball milling causes a high density of defects in the powders. Thus the Cu crystallite size decreases, generally to less than 50 nm. The maximum hardness value (105 HV) of the sintered compacts belongs to Cu–5 wt%TiO₂ which has been milled for 12 h.

1. Introduction

Copper based materials are widely used where high electrical and thermal conductivity are required. Rotating source neutron targets, combustion chamber liners, the electrode of resistance welding and high voltage switches are the applications of interest. These applications require special properties, e.g., high electrical conductivity and excellent mechanical properties at elevated temperatures [1–3]. The combination of high electrical conductivity and high hardness is particularly suitable for welding electrodes and sliding contacts. Oxide Dispersion Strengthening (ODS) is a suitable method to improve the mechanical properties of the copper matrix composites [4]. Due to high interfacial energy between the molten metal and oxide particles melting and casting techniques are not used to fabricate such composites; therefore these composites should be produced by the powder metallurgy methods. The main step of these methods is the production of composite powder, followed by consolidation to get a bulk material [5].

The suitable methods for preparing copper based composites are mechanical alloying (MA) and internal oxidation [1,6]. Nanoparticulated composites reinforcing and grain refinement achieved by MA process are very common techniques for producing the copper-based composites with high mechanical properties. Therefore, dispersion hardening and grain refinement strengthening mechanisms result in the improvement of mechanical properties of these composites [7].

Copper based ODS composites could be reinforced by different fine oxide particles such as Al₂O₃ and TiO₂ due to their chemical and thermal stability [8]. Cu–Al₂O₃ composites have been investigated by many researchers [1–4], but the Cu–TiO₂ composite has not well studied yet. Warrier and Rohatgi [9] showed that TiO₂ dispersions can improve the mechanical properties of copper. El-Eskandarany [10] investigated the possibility of the mechanical solid state reduction (MSSR) of Cu₂O to metallic Cu using Ti powder as reducing agent and showed that the final product of the MSSR process is a mixture of nanocrystalline Cu and TiO₂ powder. Akarapu [11] showed that wear resistance of Cu–TiO₂ composite coating after a certain amount of sliding is better than Cu–Al₂O₃ composite coating.

In this paper, the fabrication of the copper matrix composite strengthened by nanosized TiO₂ using MA method is expatiated. The effect of the milling time and the amount of TiO₂ content on the structure and properties of the composites were also investigated.

2. Experimental details

Powders of copper (Cu; 99.7% purity; average particle size 120 μm), copper (II) oxide (Cu₂O 99.5% purity; average particle size
120 µm) and titanium (Ti; 99.97; average particle size 70 µm) were used as raw materials for MA. Milling was carried out in a planetary ball mill using a hardened steel cup and stainless steel balls with diameters of 10 mm. The speed of the milling was 250 rpm and a Ball-to-powder weight ratio (BPR) was 20:1. The vial was purged with argon before the MA process to prevent the oxidation of the powder during the milling. According to the stoichiometric reaction (1), Cu–Ti and Cu₂O mixed powder were milled together at various times (0, 1, 6, 12 and 24 h) to indicate the effect of the milling time on the microstructure and synthesis process. The amount of the required CuO for the reaction was calculated using the following equation [12]:

\[
\text{xCu} + 2\text{Cu}_2\text{O} + \text{Ti} \rightarrow \text{TiO}_2 + (4 + x)\text{Cu}
\]

(1)

The amount of the formed TiO₂ in the final composition of the composite was assumed to be 0, 1, 3, 5 and 7 wt%. The produced powder were cold pressed with a pressure of 650 MPa and sintered under argon atmosphere at 900 °C for 1 h. The milled powders and sintered composites were subjected to X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) with EDS spectra and transmission electron microscopy (TEM). The sintered composites densities were determined according to Archimedes' method (ASTM: B962-13). The hardness and electrical conductivity of sintered composites were measured using the Vickers hardness method and four-point probe techniques, respectively.

3. Results and discussion

3.1. Microstructure and phase analysis

XRD patterns of the initial powder mixture and milled powders with different milling times are shown in Fig. 1. The XRD spectra show that during the milling process of Cu–Ti–Cu₂O powder mixture, Ti reduces Cu₂O to copper and forms TiO₂ in situ after 1 h; but the formation of TiO₂ completes after 6 h of milling. By increasing the milling time, the crystallite size decreases, thus the diffraction lines were broadened. Further milling after 6 h just affected the crystallite size and did not influence on the phase formation. According to Eq. (1), phase formation occurred in situ which is affected by repeated welding and fracturing of particles. MA influences on the kinetics of the reduction process. This is because the repeated welding and fracturing of powder particles increases the area of the contact between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact repeatedly; this allows the reaction to proceed without the necessity for diffusion through the product layer. As a result, reactions that normally require high temperatures and long times will occur at lower temperatures and short times during MA. Crystallite size and internal strain were determined by the Williamson–Hall method [13]:

\[
B \cdot \cos \theta = \frac{0.89\lambda}{D} + 2\eta \sin \theta
\]

(2)

where \(B\) is line broadening, \(\theta\) is the corresponding Bragg's angle, \(\lambda\) is the used X-ray wavelength, \(D\) is the crystallites size and \(\eta\) is the internal strain. Measurements of Cu crystallite size and internal strain as a function of milling time are shown in Fig. 2. Prolonged milling time indicate a high density of defects into the powders, and reduces the crystallite size of Cu, generally to less than 50 nm. A progress in line broadening with milling time is the result of a severe lattice distortion and crystallite size refinement [14]. It has been suggested, for pure metals, that the ultimate grain size achievable by ball milling is determined by the minimum grain size that can sustain a dislocation pileup within a grain and by the rate of recovery during ball milling. The addition of a second phase to a pure metal increases the strength and hardness of the material, resulting in a smaller final grain size after milling [15]. The most intensive grain refinement occurs in the early stages of the milling when the grain size abruptly decreases from about 470 to 105 nm, whereas at the milling time between 6 and 12 h, the grain size refinement has a lower rate and after 12 h of milling the crystallite size remains practically constant, i.e. approximately 40 nm. This finding is a direct result of nanostructured copper-based composite that was produced in this work. Fig. 2, also illustrates a rapid increase of internal strain during 12 h of milling. The internal strain becomes less evident at longer milling times. This result is in agreement with the hypothesis that the deformation of powder particles occurs during the early stages of the milling and increasing in location density saturated when milling has been prolonged. During milling the morphology and microstructure of the powder particles changes as a result of repeated deformation, fracturing and welding [16]. The changes of particle morphology of Cu-5 wt%TiO₂ composite during the milling is illustrated in Fig. 3. Fig. 3(a)–(d) shows composite powder microstructure after 1, 6, 12 and 24 h of milling, respectively. The particle size increases during the milling time up to 6 h. The agglomeration of particles increases up to 6 h, because the particle size decreases and consequently the surface of these particles increases due to predominance of welding. After 12 h of milling, the particles size decreases since the fracturing predominates (Fig. 3(d)), also the particles are quite uniform in size and are almost equiaxed in shape. Therefore it could be concluded that a balance between fracturing and welding process has been reached. As the ball milling is prolonged, the ability of the particles to accept further plastic deformation was diminished; therefore, fracturing becomes a significant process, which leads to a decrease in particle size until a balance time was reached between cold welding and fracturing. After 24 h of milling, the particles appear to be more uniform than the powder milled below 24 h, but the powder particle shape is not equiaxed and angular (Fig. 3(f)). Moreover these particles are rather flattened because of strong plastic deformation, whereas the higher magnification of Fig. 3(c) (which is related to the powder milled for 12 h and shown in Fig. 3(c)) shows a relatively rounded particle agglomerates with ultrafine particles ranging...
from 0.1 to 2 μm. Overall, the changes in particle morphology observed in this work by the SEM are very similar to the general trends observed in other mechanical alloying processes [16,17].

Fig. 4 shows the changes of Cu–5 wt% TiO₂ composite density vs. milling time. The sintered density mostly depending on the green density; the more the green density will result in higher sintered density. According to Fig. 7, the milled powders were found to have higher green and sintered densities in comparison with the unmilled powder mixture because of the morphology and particle size distribution; but the density of the unmilled powder has a higher increase after sintering against the milled powder since larger particles in size need lower diffusion bonding energy. With the increase in milling time up to 12 h, cold welding and fracturing occurs during the milling process, which usually changes the powder particles morphology and shapes. At steady state, the particles become equiaxial but agglomerated, altering powder morphology and affecting the strength of the green compact [16]. Moreover, a large number of particle contacts are more likely to be conducted by very fine particles rather than by coarse particles [18]. High green density is normally obtained when the particles of a smaller size have are by extending milling time [19]. Therefore by increasing the milling time, the green density increases due to the decrease of the particle size. TiO₂ particles formed during the milling did not have a noticeable effect on the green density. The TiO₂ particles embed uniformly in the ductile copper matrix by increasing the milling time and as a result it resists against the arrangement of particles in the powder mixture during the compaction and sintering. Work hardening has a little influence on the green density since the plastic deformation still dominates the consolidation mechanism [20]. After 24 h of milling, the powder particles have an angular and irregular shape which decreases both green and sintered densities.
Fig. 5 illustrates optical micrographs of composite powders. Fig. 5(a) shows microstructure of the Cu–5 wt% TiO$_2$ composite sintered at 900 °C for 1 h. It is obvious that the milled powder particles have a lamellar structure (typically marked with arrows) which is typically for high energy milled powders. Also it is clear that some internal porosities were remained after sintering process which could reduce density, electrical conductivity and hardness of the sintered composites. Fig. 5(b) shows composite agglomerated particle which have a laminated by a lot of thin layers produced during repetitive welding and fracturing of milling process. MA causes severe plastic deformation of the entrapped powders due to ball-to-ball and ball-to-wall collisions, significantly enhancing the generation of dislocation. Powder fracturing during milling introduces defects into the powder and generates new clean surfaces that are beneficial for atomic diffusion. The TiO$_2$ particles dispersed in the copper matrix could affect diffusion flow during sintering because the presence of oxide particles at the copper–copper interface hinders to a greater extent material transport [21]. It is known that the sintering process is useful in promoting inter particle diffusion. In this case, the Cu particles built a network because they are ductile particles that exert a heavy influence on the densification of the composite. However, breaking up the agglomerates of MA powder is difficult during cold compaction as that process generally leaves residual porosity and voids (which could be seen in Fig. 5(a)) after sintering process.

Fig. 6 shows a high magnification SEM micrograph and the corresponding EDS analysis of the Cu–5 wt% TiO$_2$ composite sintered at 900 °C for 1 h. According to the quantitative results, the oxygen content is a bit more than the estimated value. The entered oxygen during the milling or sintering processes would be the reason of this addendum.

Fig. 7 shows SEM micrograph and corresponding MAP analysis which are performed to determine the distribution of the elements in the structure. The results of the surface scanning show a homogeneous distribution of the elements in the structure. Considering this figure, it can be seen that copper covers almost the entire surface and the surface scanning of titanium and oxygen show that these two elements are less present in the structure of the sample and the surfaces they occupy are inter-lapping, which corresponds to the existence of dispersed TiO$_2$ in the structure; except for small regions marked by arrows, where there was no lapping of titanium and oxygen, whereas titanium was beside copper. This leads to the assumption of the presence of Cu–Ti interstitial solid solution. Elemental titanium solved in the copper lattice at early stages of the milling may be remained, but because of the small amount, XRD does not confirm the presence of Cu–Ti phase.

TEM observation was performed to determine the copper matrix crystal size and TiO$_2$ particles dimensions. The bright-field image (BFI) and corresponding dark field image (DFI) of the milled composite powder after 12 h are shown in Fig. 8. Obviously, the powder particles consist of fine grains with an average diameter of 30 nm (typical grains were marked with white circles in Fig. 8(a)). It is a mixture of Cu (agglomerate dark grains) and TiO$_2$ (light and fine grains) as shown in Fig. 8(b). DFI indicates a bimodal size distribution of TiO$_2$ particles with an average size of about 5–10 nm for smaller crystals (Fig. 8(b), point A) and about 15–24 nm for the larger ones (Fig. 8(b), point B). Finer reinforcement particles are better for strengthening of the composite because they act as a suitable dislocations movement barrier and can be dispersed at grain boundaries uniformly. According to Fig. 2, the most intensive grain refinement occurs in the early stage (up to about 6 h) of the milling. In the milling time between 5 and 20 h, the grain size of the powders remained practically constant (between 25 and 55 nm). Therefore TiO$_2$ particles formed at the initial stages of the milling are larger than the particles formed later. Moreover at initial times of the milling, powder mixture was
not uniformly mixed. Also, the raw material's particle size could affect the morphology, size, and microstructure of the composite powder formed during the milling.

Fig. 9 shows TEM image and corresponding EDS analysis of the Cu–5 wt%TiO$_2$ powder mixture milled for 12 h. Nanometric TiO$_2$ particles mostly located at the grain boundaries can be seen (region A). Region B and corresponding EDS analysis show the presence of copper and oxygen. This area should be representing the unprocessed copper oxide or copper with oxygen contamination during the milling process or handling. Region C shows pure copper region.

3.2. Properties of sintered Cu–TiO$_2$ nanocomposite

The theoretical densities of the composites have been calculated using the following equation [22], using the full dense values for copper (8.96 g cm$^{-3}$) and titanium dioxide (4.23 g cm$^{-3}$).

\[
\rho_c = \frac{1}{\frac{M\%}{\rho_M} + \frac{R\%}{\rho_R}}
\]

(3)

where $M\%$ and $R\%$ are mass fraction of the matrix and reinforcement, $\rho_M$ and $\rho_R$ are the matrix and reinforcement theoretical densities, respectively. Calculated data reveal a great discrepancy...
between the theoretical and experimental values, TiO₂ particulates have a hindering effect on the densification of the green compacts, since the TiO₂ particles as a ceramic phase resists particle arrangement during the shaping process under uniaxial pressure. Moreover TiO₂ particles have a negative influence on the self-diffusion of Cu atoms during the sintering process of the composite. In the sintering temperature range, which is about 900 °C, the diffusion mobility of the atoms is sufficiently high and a complex diffusion of mass transportation, responsible for the sintering process occurred [23]. Reinforcement particles directly affecting the contacts between the copper matrix particles, contact surface growth, formation of closed pores and grain growth. Therefore with increasing the TiO₂ content, the relative density of the composite decreases monotonously as shown in Fig. 10. It should be expected that both mechanical properties and electrical conductivity might be improved by further density increase, which should be possible to accomplish through plastic working, e.g. hot extrusion.

The hardness values of the sintered samples plotted vs. milling time are shown in Fig. 11. Microhardness of the sintered compacts increases with increasing the milling time, but after 24 h the hardness have slightly increment due to severe plastic deformation of powders, which influences the pressing process and porosity percentage. Moreover contamination during the milling increases with the increase of milling time. Results show that compacts milled for 12 h exhibit significantly higher microhardness (up to 100 HV). The change in microhardness occurs within 6 h of the milling and a prolonged milling results in a negligible change in microhardness. After 6 h of the milling (see Fig. 2), the crystallite size is completely decreased which suggests that small grain size has a very strong effect on hardening of Cu–5 wt%TiO₂ composite. The Orowan mechanism plays a remarkable role on the strengthening of the composites, particularly when the reinforcement size is less than 100 nm [24]. The Orowan mechanism suggests that the presence of non-shearable TiO₂ particles within the matrix causes dislocation loop to be left behind after a dislocation line has passed through TiO₂ particles. It also hinders and/or slows down dislocation motion in copper matrix. The internal strain created during the milling process and TiO₂ nanoparticles distributed in a copper matrix which act as dislocation movements barrier are the other reasons of hardness increase.

The electrical conductivity (% IACS) of the polished sintered compacts were determined using four-point probe technique. In this test, a probe was placed on the specimen and the conductivity was directly read by adjusting a calibrated dial to bring a galvanometer deflection to zero. The error in measurements was 5%. The results of electrical conductivities of the sintered composites as a function of TiO₂ content are presented in Fig. 12. Electrical conductivity decreases with the increase of mass fraction of TiO₂ particles. Low electrical conductivity of the oxide particles is not the only reason of the decrease in electrical conductivity of the composite. Significant contribution of electrical conductivity decrease resulted from the scattering of the conduction electrons [25]. The large number of dislocations produced during the milling process and porosities remained from the pressing and sintering processes are the main reasons of conduction electrons scattering. In addition, the grain boundaries increased by grain refinement causes more barriers against the conductive path. By dispersing TiO₂ particles with an amount higher than 3 wt% in copper matrix, the electrical conductivity wastage is very high, this is due to difficult pressing characteristics of these composite powders which causes more porosities in the sintered specimens.

4. Conclusions

Nanostructured copper based composite strengthened by TiO₂ particles was successfully synthesized by the MA method using
Cu–Ti–Cu₂O powders mixture. The most appropriate milling time of composite powder is about 12 h with a milling speed of 250 rpm and a Ball-to-powder weight ratio of (BPR) 20:1. Maximum hardness (105 HV) of sintered composites belongs to Cu–5 wt%TiO₂ which has been milled for 12 h. Cu crystallite size decreased but internal strain increased with increasing milling time. Increasing the milling time up to 12 h induces more TiO₂ formation and grain refinement, thus improves the hardness of the composite. By dispersing TiO₂ particles below 3 wt% in copper matrix, the electrical conductivity wastage is low, while hardness values are higher than none dispersed copper. Thus it was found that the copper based composite reinforced with about 1–2 wt%TiO₂ particles is a suitable candidate for resistant welding electrodes.

References


