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Abstract

In this paper, the possibility of production of Cu-NiO nano-composite powder using mechanochemical reaction was studied. Cu-NiO nano-composite powder was produced by high energy ball milling of CuO and Ni powder mixture. Structural and morphological evolutions were characterized by X-ray diffraction and scanning electron microscopy. Particular attention has been paid to the reaction mechanism. The reaction was initiated after about 1.5h and with continuing of milling up to 5h, NiO was formed completely in the nanocrystalline Cu matrix. It was found that, the crystallite size of Cu in the final product were 92nm. Formation of Cu$_2$O and Cu(Ni) solid solution, as intermediate phases, have been observed during the reaction. Furthermore, ultrafine Cu-NiO composite powder had relatively agglomerated structure.

Keywords: Nano-composite; Ball milling; Mechanochemical; Mechanism.

1. Introduction

Copper matrix composites have a vast industrial application because of their unique properties like high thermal and electrical conductivity and good wear resistance. They can be produced by dispersing hard particles like oxides, carbides or nitrides into the copper matrix either by liquid or solid state techniques, Tjong and Lau (2000), Ping Liu et al. (2006), Sheibani et al. (2009). Mechanochemical processing is a novel technique for preparation of nano-sized materials. In this method, powder particles are subjected to severe mechanical deformation during collisions with
balls and vial and are repeatedly deformed, cold welded, and fractured, so that solid-state reactions in powder blends can be generate, Jiang et al.(1998). The mechanochemical reduction of copper oxide with different reductants has been already investigated, Schaffer and McCormick (1991), Schaffer and McCormick (1990), Sheibani et al. (2007). When this process is combined with mechanical milling, nanostructured composites with uniform distribution of reinforcement particles are synthesized. Dispersing fine reinforcement and nanostructured matrix are beneficial to the mechanical properties of the composite. Relatively few studies have been directed towards synthesis of Cu-NiO nano-composite by mechanical milling, Schaffer and McCormick (1990). Hence, further development requires better understanding of the process. In the present work, formation of Cu-NiO nano-composite powder by mechanochemical reaction between CuO and Ni powders according to reaction 1, Suryanarayana (2001), was described. Particular attention has been paid to the mechanism of this process via structural and morphological variation during mechanical milling.

\[ \text{CuO} + \text{Ni} \rightarrow \text{Cu} + \text{NiO}, \quad \Delta H^\circ = -77.8 \text{kJ/mol} \]  

1. Experimental Procedure

A mixture of 10gr pure CuO powder (99%, 5-40μm) and Ni powder (99%, <1μm) were used as the starting ingredients. The quantity of each reactant was determined regarding the stoichiometry of reaction 1. The powder samples were milled in a high energy PM2400 planetary ball mill using hardened steel vial and balls with the rotation speed of 300rpm, under argon atmosphere. The ball-to-powder ratio was 25:1. X-ray diffraction (XRD) (Philips PW 3040/60) with a radiation of Cu Kα was used for phase identification. The line broadening due to the instrument was calculated from Warren's method, Cullity and Stock (2001). The mean crystallite size was calculated using Williamson-Hall plot, Williamson and Hall (1953). The lattice parameters were calculated from XRD data, Correia et al. (1997). Morphological analysis of the product was investigated by a field emission scanning electron microscope (FESEM) (Hitachi S4160) equipped with an Energy Dispersive Spectrometer (EDS) (Samx).

2. Results and Discussion

3.1. XRD results

Figure 1 represents the progress of reaction during different milling times through XRD patterns. All the peaks tend to broaden as the milling time increases and their intensities decrease. This could be explained by mechanical deformation introduced into the powder and therefore, particle and crystallite refinement occurs and the lattice strain increases, Suryanarayana (2001). Also, it can be found that almost all CuO peaks disappeared after milling for 1h which is probably due to the CuO amorphization, Suryanarayana (2001). The Cu and NiO peaks appeared with increased milling time up to 1.5h and the reaction completed gradually after 5h. The mean crystallite size of copper produced after 5h of milling measured from XRD data was about 92nm. It should be noted that, the appearance of Cu2O phase after 1.5h of milling is an indication of intermediate phase formation. On the other hand, the adiabatic temperature that is a measure of the local heat generated by the reaction is used to characterize the mechanism of reactions. It requires that the adiabatic temperature be at least 1800 K for a reaction to become combustive, Schaffer and McCormick (1991). The adiabatic temperature calculated from thermodynamic data for reaction 1 was 1288 K that results a gradual transformation which is consistent with low enthalpy of the reaction and gradual changes in XRD peaks, Schaffer and McCormick (1991).
For further details on the structural evolution during milling, the lattice parameter changes of copper were calculated from shifts in peak positions in XRD patterns. Fig. 2 shows the lattice parameter changes of Cu during milling. The lattice parameter first decreases with increased milling time, reaching a minimum value of 0.35961 nm after 3 hours of milling, and increases by further milling. The decrease of lattice parameter is probably attributed to Cu(Ni) solid solution formation. As nickel’s atomic radius (1.2459 nm) is smaller than that of copper (1.2780 nm), the solid solution formation causes a decrease in lattice parameter, Lubarda (2003). Similar observation has also been reported previously during mechanical alloying in a Cu-Ni system, Ban et al. (2011). However, the increase of the Cu lattice parameter after 3h of milling may be related to the NiO phase formation by further reaction. In fact, when this phase forms, Ni solute atoms are driven out of the solid solution. It can be concluded that the Cu$_2$O and Cu(Ni) solid solution appear as intermediate phases during the milling process, suggesting that the reaction progresses gradually.
3.2. SEM analysis

Figure 3 represents the particles morphology of the sample at different milling times. The FESEM image of the initial powder mixture is shown in Fig. 3a. The dark areas with flat surfaces are CuO particles and the bright small particles with relatively irregular shapes are Ni. The particles morphology after 0.5h of milling is shown in Fig. 3b. Heterogeneous mixtures of relatively coarse particles can be seen in this image. It clearly indicates an agglomerated structure and it is not possible to distinguish amongst different materials. The particles morphology after 5h of milling can be seen in Fig. 3c. It is clear that towards the end of the milling process, the nano-composite particles became finer and a considerable reduction in the mean particle size to nanometer scale can be observed. Based on the surface morphology, ultrafine particles tend to be formed by individual agglomerated nano-particles.

Fig. 3. FESEM images of milled powder mixture for (a) 0, (b) 0.5 and (c) 5h.
4. Conclusion

Formation of Cu-NiO nano-composite powder was possible by mechanochemical reaction between CuO and Ni powder using high energy ball milling. Detailed investigations were conducted on the reaction mechanism. The reaction completed gradually after 5 hours and the crystallite size of copper was reached to 92nm. It may be concluded that, the Cu2O and Cu(Ni) solid solution appear as intermediate phases during the milling process. Also, FESEM results showed that the ultrafine Cu-NiO nano-composite powder after 5 hours of milling had relatively agglomerated structure.

Acknowledgements

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References