EFFECT OF COMBINATION ON PROPERTIES OF CU-AG NANOCOMPOSITES SYNTHESIZED BY HEAT TREATMENT

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Abstract Ag-Cu solid solutions prepared via ball milling process were subsequently milled for 30 h and investigated by X-ray diffraction technique for Cu-20%Ag, Cu-3.64%Ag and Cu-80%Ag. It was noted that the solid solubility level increased by increasing initial solute content in composition. Results showed peak positions of silver and copper changed with milling time. By heating up to 700 K, the nanocrystalline supersaturated solid solution Cu (Ag) alloy was decomposed to nanophase composite of Ag and Cu. XRD pattern showed that the grain size of Ag and Cu phases increased obviously after heating but grain size was in nanometer range. Then, ultimate compressive strength and electrical conductivity of samples were determined that Cu-20%Ag-Cu had the highest ultimate compressive strength and also the highest electrical conductivity.

Keywords Mechanical alloying, Nanocomposites, Copper, Silver, Strength, Electrical conductivity

چکیده مخلوط های جامد Ag-Cu که توسط فرایند آسیاب گلوله ای تهیه شده بودند به مدت 30 ساعت آسیاب شده و از تکنیک XRD برای بررسی مخلوط Cu- 20% Ag ، CU- 3.64 Ag و Cu- 80% Ag استفاده گردید. قابل توجه است که میزان حلالیت جامد با افزایش میزان حل شونده در مخلوط افزایش یافت. نتایج نشان داد که موقعیت پیک های نقره و مس با زمان آسیاب تغییر یافت. با گرما دهی تا 700K مخلوط جامد فوق اشباع نانو کریستالین Cu (Ag) به نانو کاموزیت Ag و Cu تجزیه شد. نتایج XRD نشان داد که اندازه ذرات Ag و Cu بعد از حرارت دهی افزایش یافت. اما اندازه ذرات در محدوده نانو بود. سپس حد نهایی تراکم پذیری و هدایت الکتریکی نمونه ها تعیین شدند که Cu-20% Ag بالاترین قدرت تراکم پذیری و بیشترین مقدار هدایت الکتریکی را داشت.

1. INTRODUCTION

Mechanical alloying process has become a widely used technique to form powder materials and to synthesize a large rang of non-equilibrium phases, from amorphous materials to nano-crystalline phases, to extended solid solutions [1-3]. Solid solubility extensions have been achieved in many alloy systems by non-equilibrium processing methods such as RSP (Rapid Solidification Processing) and vapor deposition. Similarly, mechanically alloyed powders exhibit extension of equilibrium solid solubility limits. In addition to synthesizing stable (equilibrium) solid solutions, it has also been possible to synthesize metastable (non-equilibrium) supersaturated solid solutions by mechanical alloying starting from blended elemental powders in several binary and higher order systems [3-6]. The amorphization is observed in the alloy system whose heat of mixing is negative and is interpreted as the metastable melting from the mixture of elemental powders which are energetically in a higher state. However, metastable or non-equilibrium crystalline phase formation has scarcely been examined in the alloy systems whose heat of mixing is positive [7-13].As clearly demonstrated by Klassen and coworker [14], low temperature milling results in the stabilization of solid solution, whereas elevated temperature milling results in the coexistence of two terminal solid solutions. This temperature effect is best explained by considering such alloys during milling as driven systems, while thermal diffusion tends to promote phase separation because of the positive heat of mixing, this dynamic competes with an atomic mixing forced by the sustained plastic deformation of material [15-20]. Nano composites are of great interest due to their novel structure, properties, and applications compared to their equivalent counterparts.

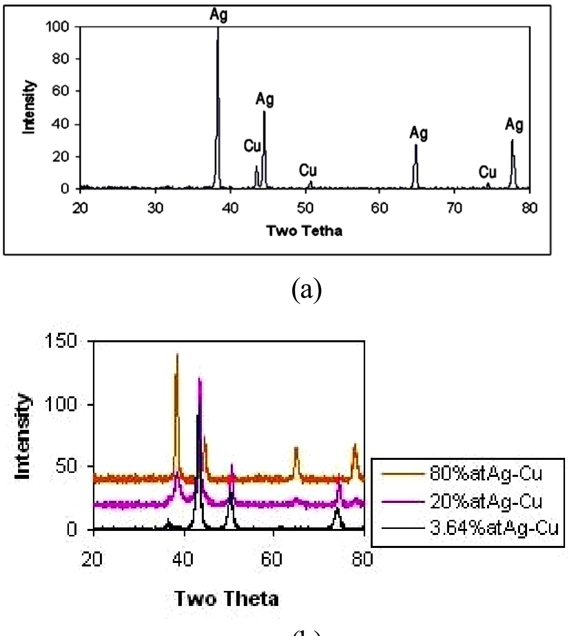
In the present research, formation of silver and copper nanocomposites in Ag-Cu system via mechanical alloying process was investigated.

2. EXPERIMENTAL PROCEDURE

Cu (Merck Art No.102703) and Ag (Aldrich Art No.32707-7) powders were used as starting materials. Initial grain size of Cu was “fine powder GR particle size < 63 μm” and Ag was “flake, <10μm”.The powder mixture of Cu-20% Ag, Cu-3.64% Ag and Cu-80%Ag were hermetically sealed in stainless steel vials together with hardened steel balls and milled in a planetary ball mill. The weight ratio of powder to ball (PBR) was kept 1:15 for all experiments. Handling of powders and milling process were performed under protection of commercial gas at different times. The vial was rotated at 300 rpm. The mechanically alloyed powders were heated at 700 K for 1 hour under protection of commercial gas and characterized by X-ray diffraction method using CuKα radiation. Average grain sizes of Cu and Ag phases were estimated by peak broadening from X-ray diffraction patterns using Wiliamson Hall method [17]. The ultimate compressive strength and electrical conductivity were determined. For determination of ultimate compressive strength, samples were prepared in cylindrical shape with 5mm diameter and 7mm height and electrical conductivity was determined by two probes method.

3. RESULT AND DISCUSION

Ball milling of pure silver and copper powders, caused the broadening of the X-ray diffraction peaks and the intensity of certain peaks (such as intensity of 111 unit?) became smaller by increasing milling time. However, the peak positions of silver and copper hardly changed with milling time. The usual decrease of the intensity of diffraction peaks and their broadening consequent to the formation of nanometer-sized coherent diffraction domains and the accumulation of lattice defects were initially observed. Local mutual dissolution processes induced successively the formation of a new face-centered cubic (fcc) phase with the intensity of (111) peak intermediate between the Ag and Cu (111) reflections, as shown in Figure1. Diffraction peaks of Cu shifted toward lower angles, indicating an increase of lattice constant due to dissolving of Ag into Cu, owing that the atomic radius of Ag (0.144nm) is larger than that of Cu (0.128nm). In contrast, diffraction peak of Ag shifted toward upper angles, indicating a decrease of lattice constant due to dissolving of Cu in Ag. Table 1 shows that the grain size is about nanometer for each of them after heating.

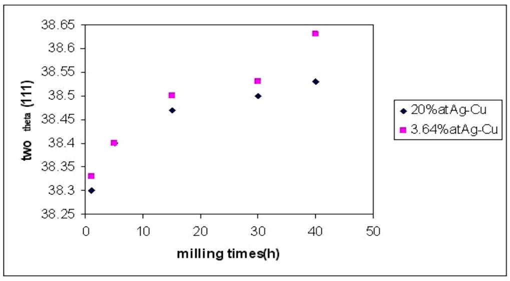


(a)

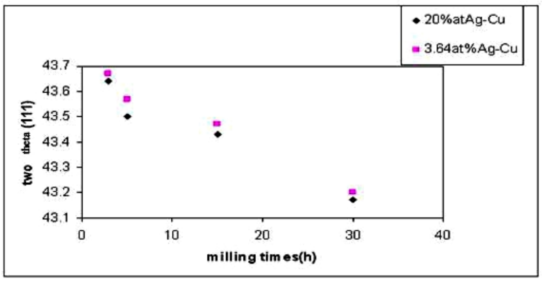
(b)

Figure 1. X-ray diffraction pattern of (a) as received Ag and Cu powders (b) Cu-20 at.%Ag and Cu-3.64atm% Ag and Cu-80%atAg at milling times 30 h.

Figure 2 reveals changes of 2θ with milling time for (111) of silver and copper.

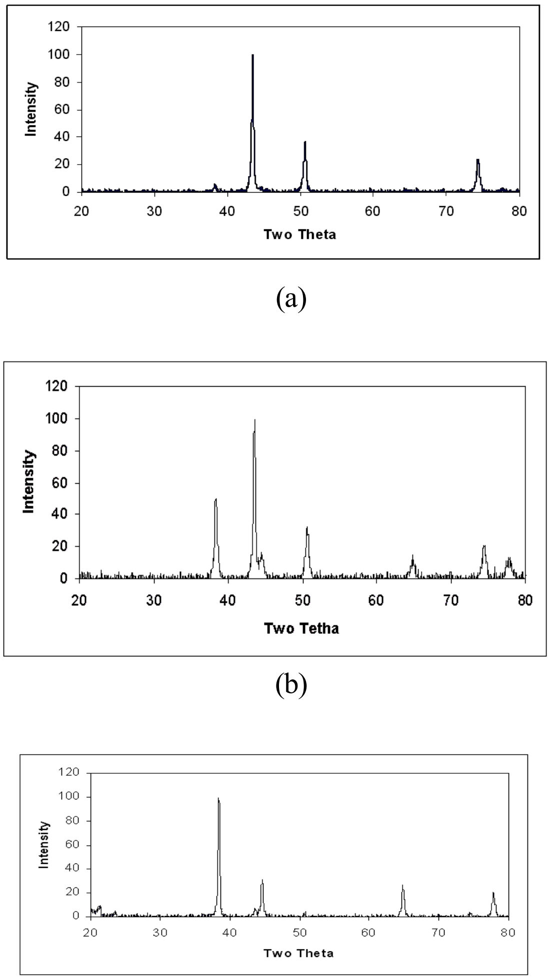


(a)



(b)

Figure 2. Changes of 2θ with milling time for (111) (a) Ag (b) Cu



(a)

(b)

(c)

Figure 3. X-ray diffraction of powder heated at 700K after 30 h of milling (a) 3.64%atAg-Cu (b) 20%atAg-Cu (c) 80%atAg-Cu.

Figure 3 reveals that the diffraction peaks of Cu significantly shift toward higher angles, indicating that Ag solutes dissolved in Cu begin to precipitate by heating up to 700 K. The diffraction peaks of Ag phase appear in the X-ray diffraction and the positions of Cu peaks almost coincide with those of un-milled Cu powders, which mean that Ag atoms dissolved in Cu almost completely precipitated. The diffraction peaks of both Cu and Ag phases become narrow upon further heating, as shown in Figure 3, which indicates an apparent grain growth of both Cu and Ag phases.

TABLE 1. Grain size of silver and copper [nm]

Time	Composition	d_{Ag}	d_{cu}
After 30h milling	3.64%Ag-Cu	18	8.35
After 30h milling	20%Ag-Cu	16	5.68
After 30h milling	80%Ag-Cu	41.6	23.57
After 1h heating	3.64%Ag-Cu	46.2	58.72
After 1h heating	20%Ag-Cu	37.46	48.5
After 1h heating	80%Ag-Cu	56.8	55.36

TABLE 2. Electrical conductivity and ultimate compressive strength of nanocomposite

Composition	Ultimate compressive strength (Mpa)	Electrical conductivity $(\Omega.Cm)^{-1}$
3.64%Ag-Cu	173.39	81000
20%Ag-Cu	191.45	106666
80%Ag-Cu	168.52	110852

Table 2 shows the conductivity and ultimate compressive strength of nanocomposite. Cu-20%Ag shows the highest level of ultimate compressive strength and conductivity.

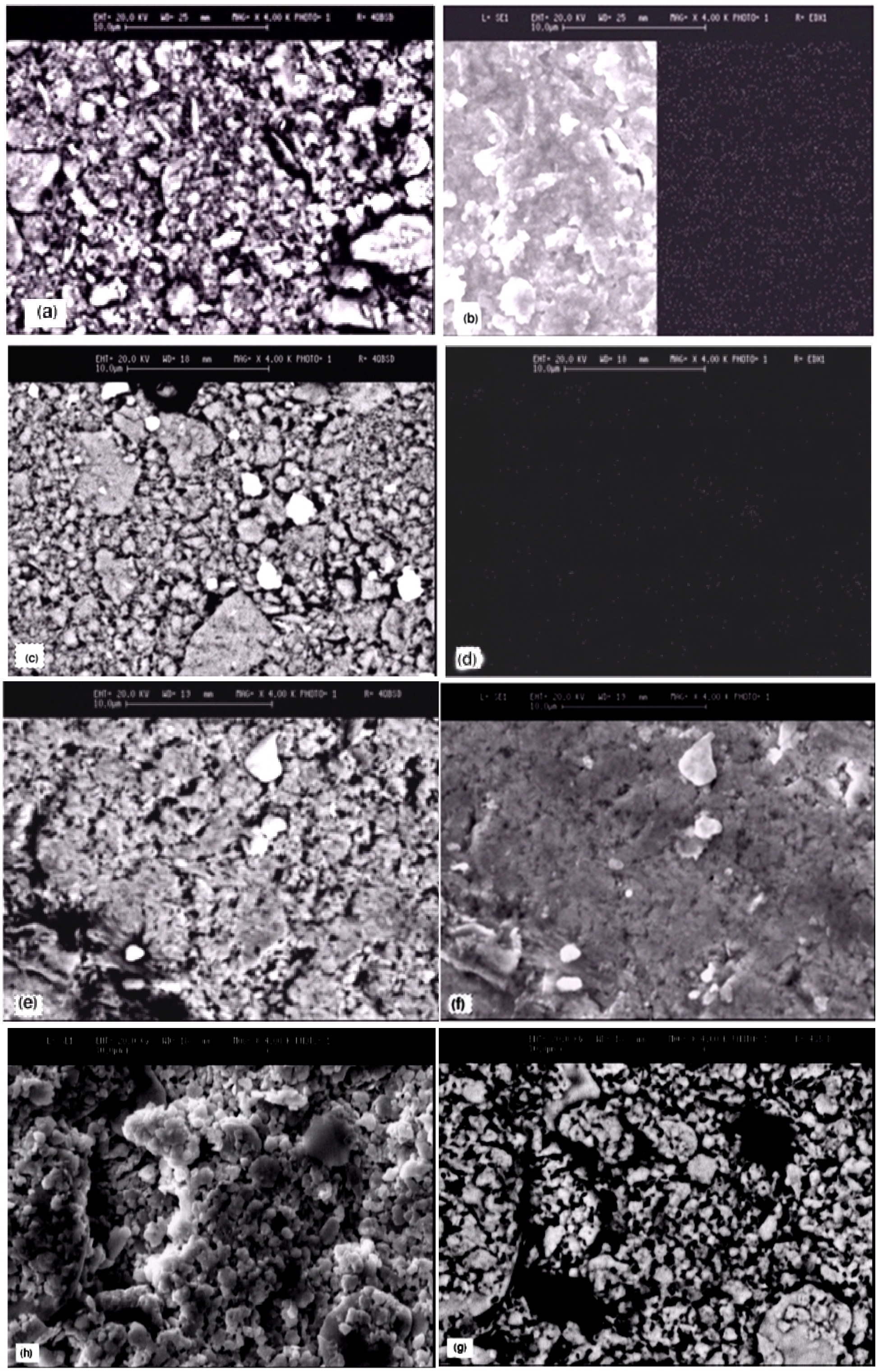


Figure 4. Scanning electron microscopy (SEM) and dot map after heating
After 30 h milling 2o%Ag-Cu (a) BS and (b)SE and Cu dot map
After heating 3.64%Ag-Cu (c) BS and (d) Ag dot map
After heating 20%Ag-Cu (e) BS and (f) SE
After heating 80%Ag-Cu (g) BS and (h) SE

Figure 4 is SEM image that Figure 4a and Figure 4b show the formation of solid solution; Figure 4c and Figure 4d show the formation of nanocomposite for Cu- 3.64%Ag sample; Figure 4e and Figure 4f show the formation of nanocomposite for Cu-20%Ag sample and Figure 4g and Figure 4h show the formation of nanocomposite for Cu-80%Ag sample.

4. CONCLUSIONS

Mechanical alloying process was performed in Ag-Cu system. It has been noted that the solid solubility level increased by increasing the initial solute content in powder mixture that solid solubility levels have generally determined changes in the lattice parameter values calculated from peak shift position in the X-ray diffraction patterns. The diffraction peaks of Cu significantly shifted toward higher angles, indicating that Ag solutes dissolved in Cu begin to precipitate by heating to 700 K and the diffraction peaks of Ag phase appeared in the X-ray diffraction. Nanocomposite Cu-20%Ag-Cu had the highest ultimate compressive strength and electrical conductivity.

5. REFERENCES

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