TECHNICAL NOTE

BEHAVIOR OF CU-CR POWDER MIXTURES DURING MECHANICAL ALLOYING

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Abstract In the present work, the behavior of Cu-Cr powder mixtures during mechanical alloying has been studied. The powder mixtures with 1, 3 and 6 weight percents of Cr in Cu were treated. They were milled in a ball mill with two different speeds of 250 and 500 rpm using equal numbers of 1 and 2 centimeters balls. The weight ratio of balls to powders was 10 to 1 under argon atmosphere. Ethanol was used as the process control agent and milling times were 4, 12, 48 and 96 hours. After every hour of milling, a half–an–hour stop was applied to avoid temperature rise. The milled powder mixture was evaluated by a scanning electron microscope equipped with energy dispersive spectroscopy and an optical microscope equipped with image analyzer. Results have shown profound effects of milling conditions (the change in time, speed, etc.) on the behavior of milled powders.

Keywords Mechanical Alloying, Cu-Cr Powder, Particle Size

چکیده رفتار مخلوط پودرهای Cu-Cr در حین آلیاژسازی مکانیکی بررسی شد. برای این منظور سه ترکیب ١، ٣ و ٦ درصد وزنی کرم تحت دو سرعت ٢٥٠ و ٥٠٠ دور در دقیقه بدون استفاده و با استفاده از اتانول و مخلوط مساوی از گلوله‌های ١و ٢ سانتی‌متری و نسبت وزنی گلوله به پودر ١٠:١ تحت اتمسفر آرگون آسیاب شدند. زمان‌های آسیاب ٤، ١٢، ٤٨ و ٩٦ ساعت انتخاب گردید. به‌منظور سرد شدن محفظه بعد از هر ساعت آسیاب نیم‌ساعت استراحت منظورشد. نتایج با میکروسکوپ الکترونی روبشی مجهز به‌دستگاه طیف‌نگار تفکیک انرژی و میکروسکوپ نوری مجهز به image analyzer مورد بررسی قرار گرفت. نتایج حاکی از رفتارهای متفاوت ذرات پودری با تغییر دور، زمان و... است.

1. INTRODUCTION

Alloys such as Cu-Cr exhibiting high mechanical strength together with high electrical and thermal conductivity at elevated temperatures are in increasing demand. Their desired behaviors have led to be used in making filaments, solar cells, welding electrodes and water-cooled molds in the continuous casting process [1-3]. The above-mentioned alloying element has very little solubility in copper under equilibrium condition. However under non-equilibrium condition it is possible to increase its solubility and therefore alter the behaviors and properties of the alloy to desired conditions. The solid processing of materials by mechanical alloying and/or milling has become of widespread interest due to its capabilities to produce equilibrium and nonequiblibrium phases [4].

During milling, powder particles undergo high-energy impacts by balls [5]. The high-energy impacts result in cold working, increasing dislocation density in particles, which in turn give rise to repetitive cold working, flattening and fracturing of them [6]. During the above processes, the surfaces come into contact in atomic scale.

From the point of view of mechanical alloying, powders are classified into three main groups of: ductile-ductile, ductile-brittle and brittle-brittle systems [6]. In addition, some other parameters such as milling velocity, temperature, process control agent are effective in the behaviors and properties of the final powder mixture.

Since mechanical alloying is desirable when cold welding and fracturing processes move into steady state [7], in present work, the behavior of Cu-Cr powder mixture, which is a ductile-ductile system, during milling, has been studied.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

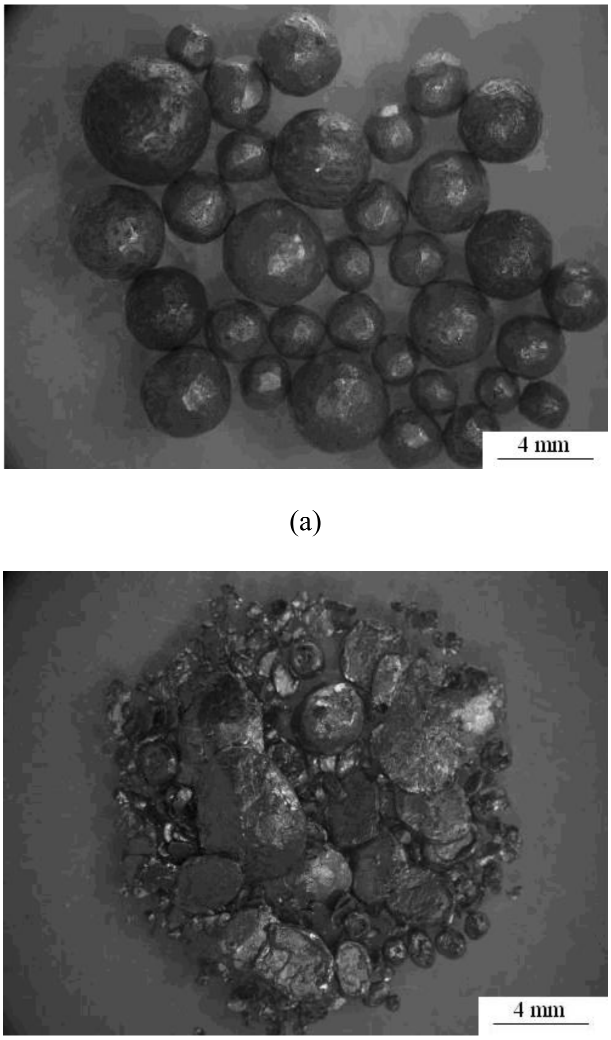
Elemental powders of Cu (99.97% under 63 microns) and Cr (99.98% under 150 microns) were precisely weighed to obtain the mixtures containing 1, 3 and 6 weight percent Cr in Cu. Therefore, 21.858 grams of powder mixtures were milled in a ball mill (Pulverisette 6, a single-station mill) containing equal number of 1 and 2 cm diameter steel balls . The steel vial of the ball mill had 250 ml capacity. Different ball sizes improve random collisions during milling operation [8], and minimize the surface layers on the ball [9] and also provide maximum impact energy [10].

The milling times were chosen as 4, 12, 48 and 96 hours. To avoid temperature rise after every hour of milling, half an hour stop was applied. The ball to powder weight ratio was 10 to 1, and two milling velocities of 250 and 500 rpm were conducted with and without ethanol as process control agent (PCA). The container atmosphere was controlled by argon gas.

The morphologies and size distributions of mechanically alloyed powder mixtures under different conditions were investigated using an SEM in a Cam Scan MV2300 equipped with EDS and an Olympus optical microscope equipped with image analyzer.

3. RESULTS

Figures 1a and b illustrate the Cu-1wt % Cr milled powder mixtures under 500 and 250 rpm without PCA. As seen in Figure 1a, at 500 rpm, the powder mixtures have been converted into solid balls of 0.5 centimeter and no evidence of any fracturing process is observed. At 250 rpm, (Figure 1b) relatively big particles have been produced as the result of the milling operation, but many particles have been fractured.

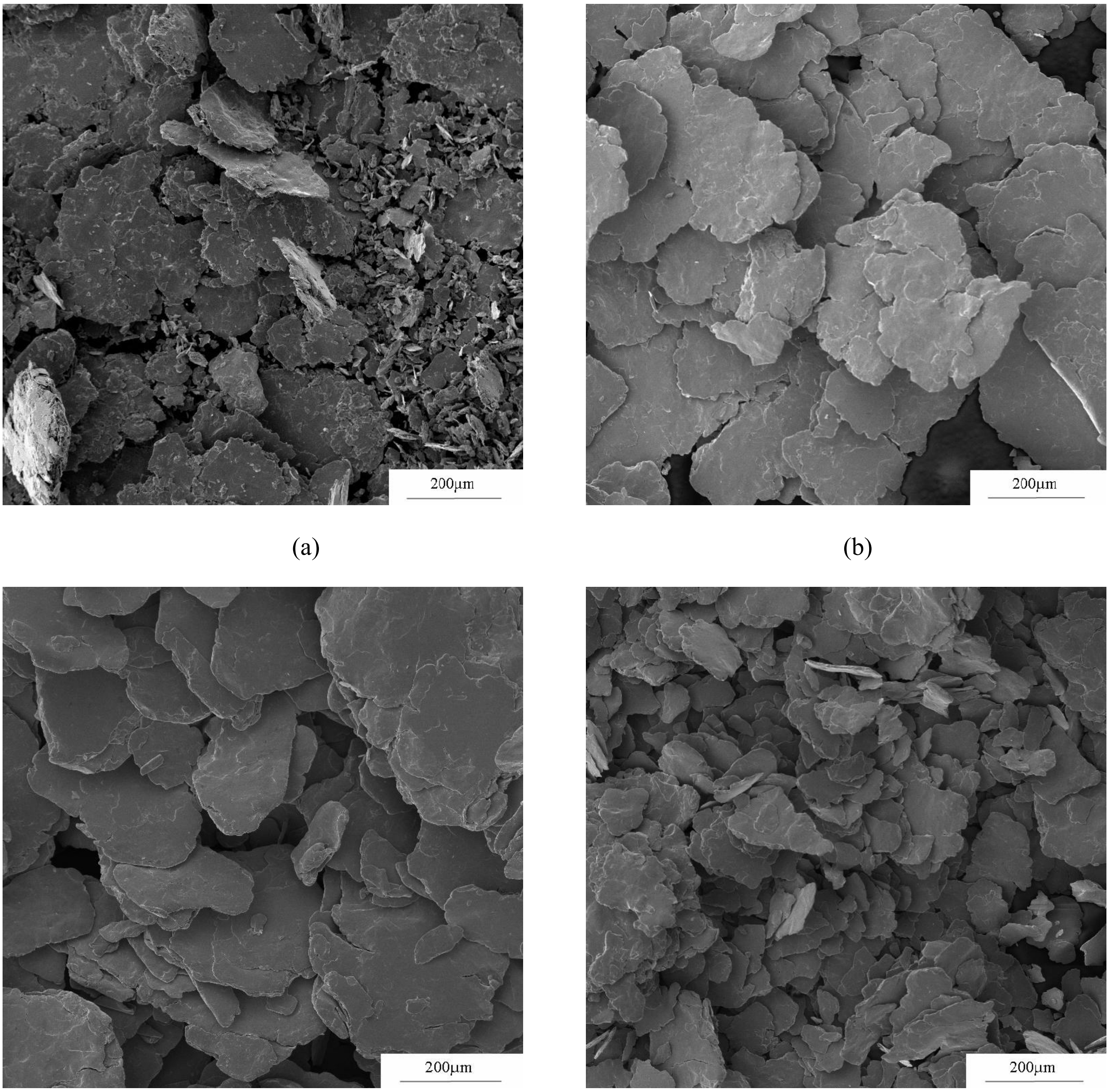


(a)

(b)

Figure 1. Powder particles of Cu–1wt % Cr after 4 hours milling, (a) 500 rpm and (b) 250 rpm.

Figures 2a-d show the morphologies of the powder particles of Cu-1wt % Cr at 250 rpm with 1cc ethanol as PCA. As can be seen, the powders are (considerably) smaller in size compared to those in Figure 1b, which shows the effect of PCA that prevents the agglomeration of powder particles. During milling operation, at the beginning particles become larger, but at longer times the particles become plate-like in shape and smaller in size. The quantitative measurements of



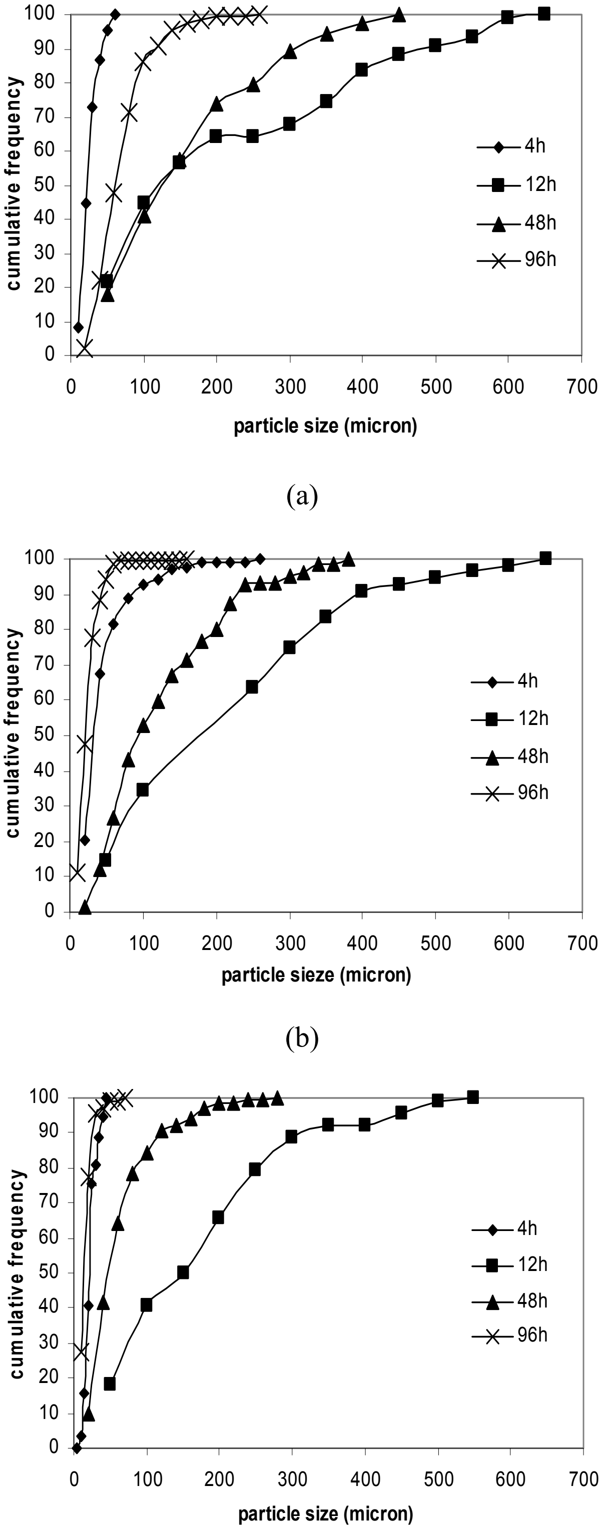
(a) (b)

(c) (d)

Figure 2. Morphologies of Cu–1Wt % Cr powder particles, 250 rpm and 1 % ethanol as PCA, (a) 4, (b) 12, (c) 48 and (d) 96 hours.

particle size are depicted in Figures 3a-c. These diagrams show coarsening of particles at the beginning of milling operation and refining them at longer times.

Figure 4 shows the SEM micrographs of three different powder mixtures, which have been processed under the same condition. As these micrographs show, with increasing Cr-content, the MAed powder mixtures have smaller average particle size. Figure 5 illustrates the quantitative measurements of the same samples on their particle sizes.

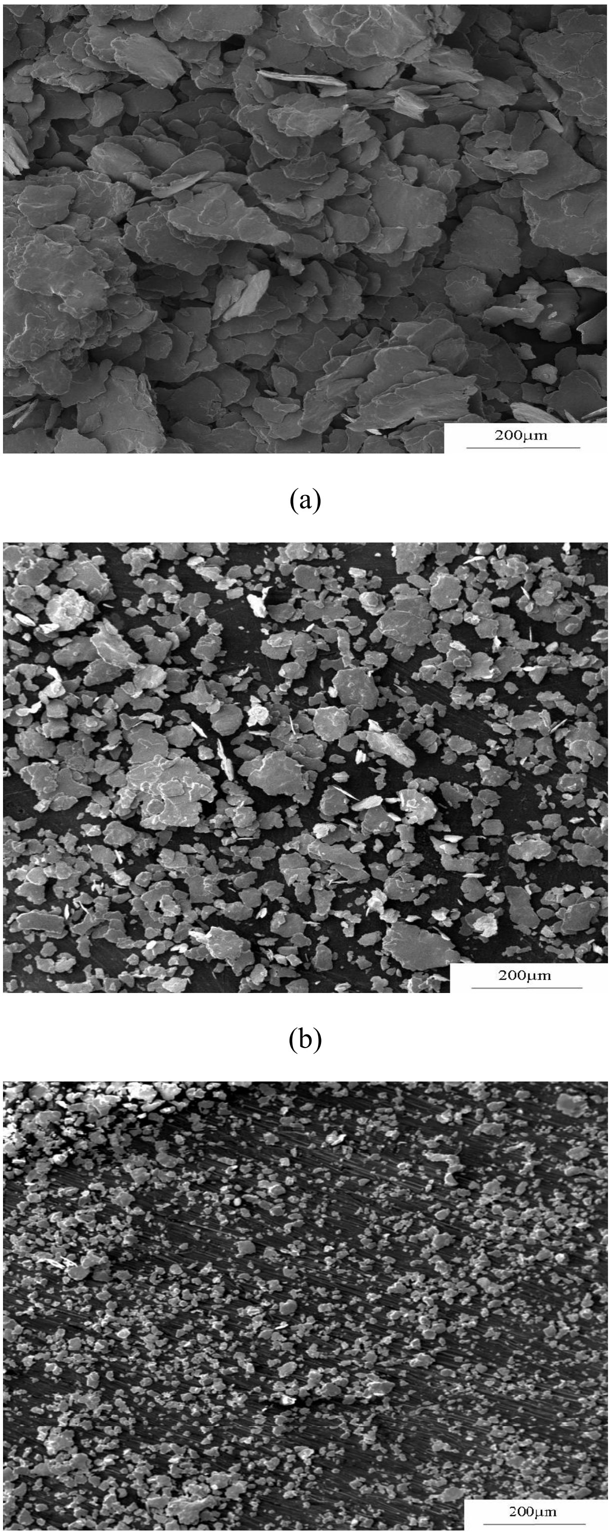


(a)

(b)

(c)

Figure 3. Cumulative frequencies of particle size distributions as functions of milling time and Cr–content, (a) 1 wt % Cr, (b) 3 wt % Cr and (c) 6 wt %Cr.



(a)

(b)

(c)

Figure 4. The effect of Cr–content on the morphologies of produced powder particles after 96 hours milling, (a) 1 wt % Cr, (b) 3 wt % Cr and (c) 6 wt % Cr.

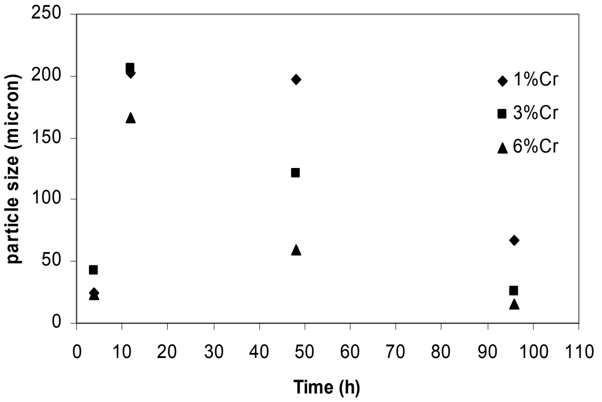


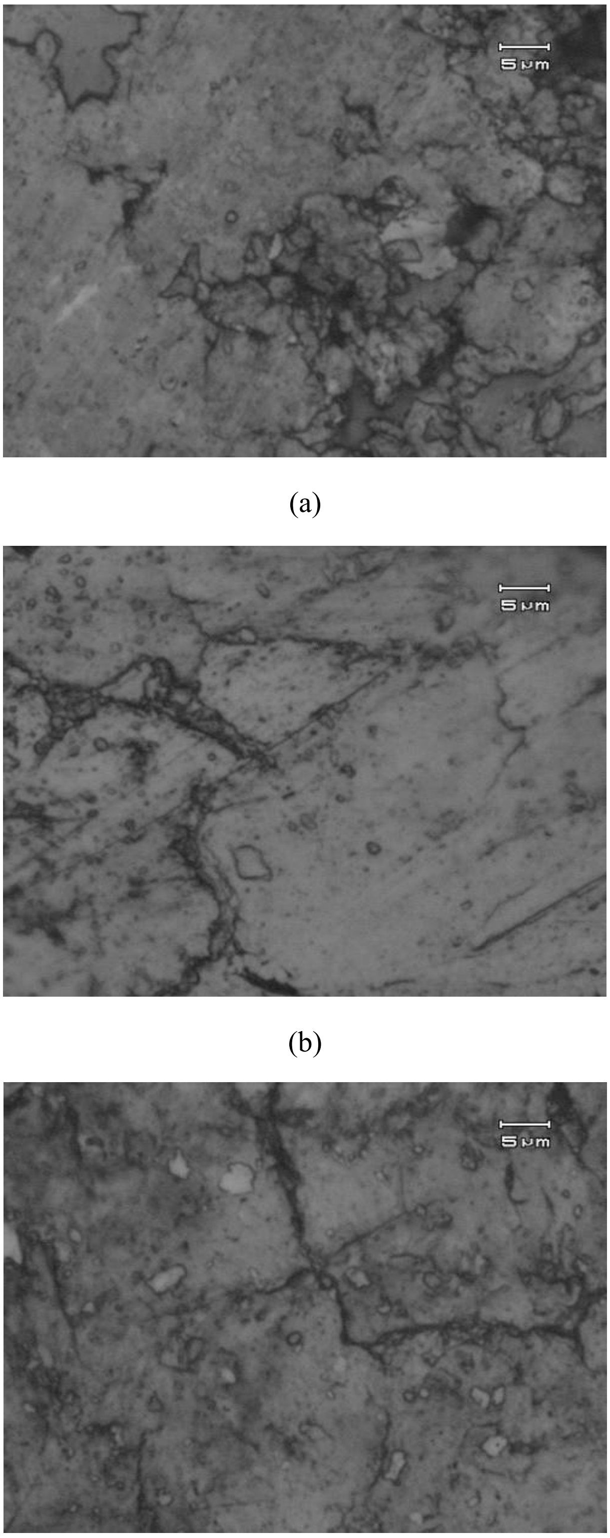
Figure 5. The effect of milling time and Cr–content on the average particle sizes of powder mixtures.

Optical micrographs of Cu-6wt % Cr powder mixtures after different milling times are illustrated in Figure 6. It is evident that chromium particles become finer and more evenly distributed with increasing milling time. Figure 7 shows the micro cracks on deformed particles as well as the presence of chromium particles in the vicinity of the micro cracks. Figure 8 presents the EDS results of the powder mixture of Cu-6wt % Cr which shows Fe contamination on the particles.

4. DISCUSSION

In milling operation at higher velocities, more energy is transferred into powder particles. Therefore, at 500 rpm, the temperature increases substantially which in turn results in the increase of recovery as well as recrystallization processes in deformed particles. Under such conditions, powder particles are cold welded repeatedly without fracturing, giving rise to agglomeration of powder particles as shown in Figure 1a. At lower velocities, with lower temperature, cold working process is more effective and the fracturing process of cold welded particles occurs more frequently. These result in the fractured and relatively smaller agglomerates compared to those produced at higher velocity (Figure 1b).

Adding ethanol as PCA is very effective on the milling operation to decrease particle size as shown in Figure 2a. The process control agent,

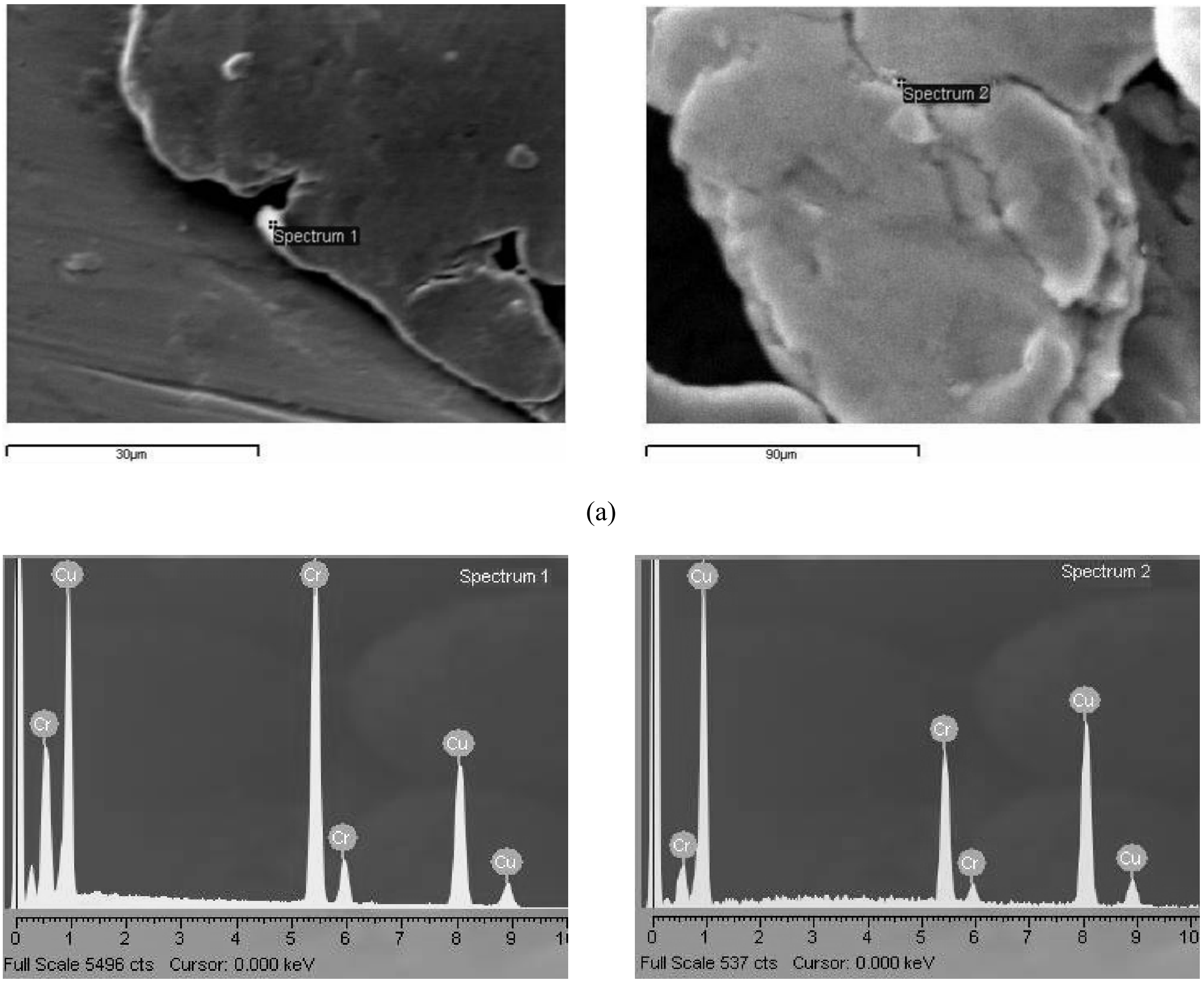


(a)

(b)

(c)

Figure 6. The distribution of Cr-particles after different milling times in Cu-6wt % Cr powder mixtures, (a) 4, (b) 12, and (c) 48 hours.



(a)

(b)

Figure 7. (a) Initiated and propagated micro cracks in the vicinity of Cr-particles and (b) the corresponding EDS analyses for each particle.

being absorbed on the surfaces of the particles, helps to inhibit excessive cold welding and therefore agglomeration of them by lowering surface tension of the particles [7].

Since the energy required for milling operation depends on the plastic deformation of powder particles and the new surface area generated times surface tension, a reduction in surface tension results in finer powder mixture [11]. PCA affects the competing processes of cold welding and fracturing in favor of fracturing process during milling operation. At the beginning, copper particles are more ductile and they are deformed more easily, and therefore, more cold welding occurs resulting in a bigger average particle size. With increasing milling time, cold worked particles tend to break and a decreasing trend in the average particle size is observed, as seen in Figures 2 and 3.

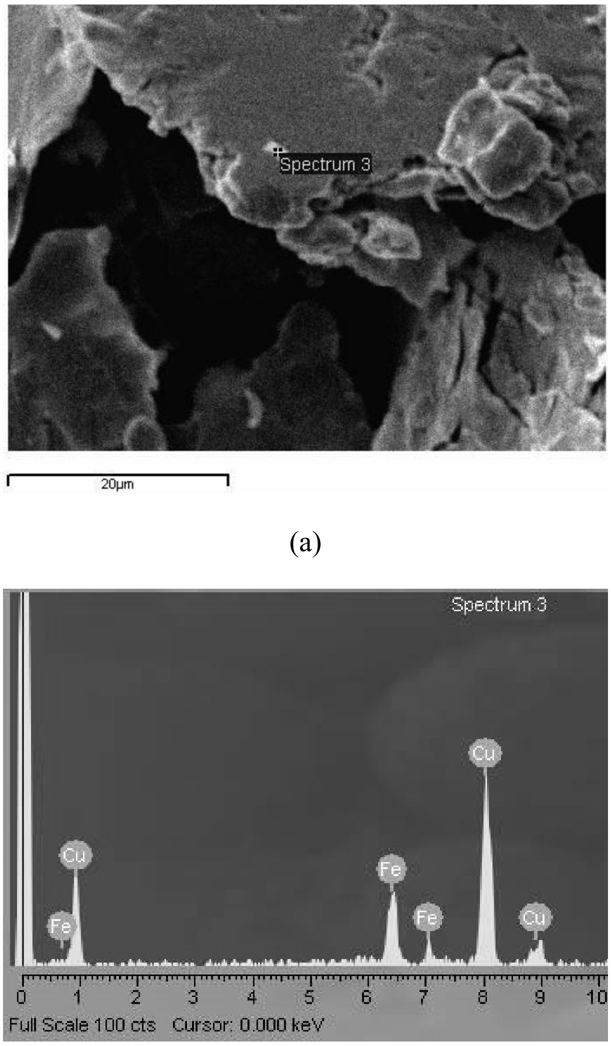
The effect of chromium content in milling operation on the average particle size and morphologies is evident. Higher Cr content has led to finer average particle size under the same milling conditions. Chromium is harder and less ductile than copper [12]. Chromium has BCC crystal system. Therefore, as with other BCC metals, sever cold working may lead to pile-up of edge sessile dislocations and initiation of micro cracks. The micro cracks, in turn, propagate with further cold working and promote fracturing process [13,14]. During milling, Cr particles fracture more frequently than copper particles. Fine Cr–particles are distributed between Cu–powder particles, as shown in Figure 7. The presence of hard and brittle cold worked Cr–particles between and inside of copper particles promotes initiation and propagation of micro cracks, which leads to fracturing of copper particles and refining of average particle size (Figure 7). Presence of chromium particles in the vicinity of the observed micro cracks suggests that the cracks have initiated at the edge of copper particles which contains fine particles of chromium.

During milling, iron content of the powder mixture increases, which indicates that the grinding media contaminate the powder mixtures (Figure 8). Although the iron contamination is not desirable for Cu–Cr powder production, but it may help to refine the average particle size via adhesion iron onto the particle surfaces or maybe it is effective in initiation and propagation of micro cracks.

5. CONCLUSIONS

- In the ductile-ductile system of Cu–Cr, very high velocity of milling leads to agglomeration of powder particles. This should be optimized to get the best results.
- The use of ethanol as PCA is very effective and essential in mechanical alloying of ductile- ductile system of Cu–Cr.
- Chromium with its BCC crystal system promotes initiation and propagation of micro cracks during milling in powder agglomerates of Cu–Cr, leading to fracturing and refining of powder particles. As chromium content increases, the rate of refining increases too.

6. REFERENCES



(a)

(b)

Figure 8. (a) Scanning electron microscopic macrograph showing a steel particle and (b) the corresponding dispersive spectroscopy analyses for the contaminating particle.

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