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Contamination during the high-energy milling of atomized copper powder and its effects on spark plasma sintering

G. Cipolloni *, M. Pellizzari, A. Molinari, M. Hebda, M. Zadra

Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123 Trento, Italy

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ABSTRACT

Mechanical milling is a suitable technique to enhance various properties of copper by the severe plastic deformation involved during the process. Contamination from milling media is one of the major problems of mechanical alloying. In this study, the behaviour of copper powder during mechanical milling was investigated in order to minimize iron and chromium contaminations. Hence, three different parameters have been studied to highlight the high influence of ball milling parameters on the final products. The parameters included the type of process control agent (none, toluene or stearic acid), the ball-to-powder weight ratio (33:1 or 10:1) and finally, a change in the milling cycle (interrupted or continuous) in an interactive procedure according to the experimental results. As a result, the best morphology and contamination level combination was observed in powder milled with stearic acid; it was 10:1 for the ball to powder ratio when using a continuous milling cycle. Once the best milling conditions were determined, the resulting samples were exposed to spark plasma sintering (SPS). The sintering parameters were selected based on a previous thermal gravimetrical measurement of the milled powders to avoid residual porosity. The final density of all of the samples is very good, 99%, confirming an effective densification process and sintering activated by severely strain-hardened and nanostructured particles.

1. Introduction

Mechanical alloying is a solid-state powder processing technique involving repeated welding, fracturing and re-welding of powder particles in a high-energy ball mill [1]. In recent years, ball milling has attracted considerable interest due to the wide range of materials exhibiting good properties that can be fabricated using this process, especially in the production of metal matrix composites [2–5]. A major issue with this process is the contaminations that arise from the milling medium and the atmosphere [6–8]. Copper contaminations could negatively affect the electrical and thermal conductivity by acting as a barrier to the electrical and thermal flow [6–9]. Even if milling in a highly pure inert atmosphere or a vacuum avoids contaminations from the atmosphere [1], contaminations resulting from the milling medium are unavoidable. Contamination depends on the nature of the raw materials [10–12] and the milling conditions. Here, the importance of optimizing the milling parameters are discussed [13].

It was found that metallic powder can easily form a thin coating on the surface of grinding balls and the inner walls of the containers, especially in the case of ductile powders [14]. This coating may decrease contamination by preventing the milling medium from making contact with the milled powders [15]. Creating a ductile coating on the milling medium surface prior to the addition of the hard particles could be a good solution in the production of metal matrix composites. Process parameters such as the use of a process control agent, the ball-to-powder weight (charge) ratio and the milling time play an important role in the nature and kinetics of the formation of the protective layer [1].

The use of a process control agent (PCA) overcomes the contamination of the final powder caused by the repeated collision that the powders sustain against the grinding bodies [6]. Moreover, in the absence of a process control agent, there is a predominance of welding events over the fractures, which resulted in the production of hollow spherical particles up to millimetres in diameter [9,16]. Therefore, it is also important to inhibit welding events to produce a fine powder, and it is generally necessary to use a specific process control agent or to cool the vial by an interrupted milling cycle [1]. The choice of a PCA depends on the nature of the powder being milled and the purity of the final products [17–19].

Another important variable in the milling process is the ball-to-powder mass ratio (BPR). At a high BPR, the number of collisions per unit time increases; consequently, more energy is transferred to the powder particles. Mechanical alloying occurs faster [20,21], but at the same time, the abrasion of the milling medium increases at a high BPR. Moreover, a high BPR decreases the milling time while increasing the internal temperature, which may promote unwanted reactions [22]. An interrupted cycle is, therefore, preferable in order to cool the vial, even if it increases the milling time.

Mechanical alloying refines the structure of the powders, leading to ultrafine and nanosized grain size. Such features are required to be maintained during sintering to obtain materials with high mechanical

* Corresponding author. Tel.: +39 0461282402.
E-mail address: g.cipolloni@unitn.it (G. Cipolloni).

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resistance. Spark plasma sintering (SPS) is perhaps the most suitable technology for this purpose. The simultaneous application of pressure and pulsed continuous current, the fast heating rate and the short sintering time make SPS an excellent technology by which highly dense, bulk, ultrafine and nanostructured materials can be obtained [23–28].

The objective of this study was to systematically investigate how milling conditions affect contamination in the milled powder. Moreover, the decomposition of PCA has been analysed to determine the parameter of the SPS cycle to minimize the residual porosity. Meanwhile, the morphology of the milled powders, the microstructure, the density and the hardness of the sintered products were also investigated.

2. Materials and method

A water atomized copper powder (99.55%) was used. Mechanical milling was conducted in a Fritsch Pulverisette 6 planetary mono mill at 400 rpm in a vacuum (0.13 mbar). A 0.5 wt.% PCA of either toluene or stearic acid was added. Vials and spheres in 100Cr6 (63 HRC) with diameters of 10 mm were used to obtain ball-to-powder ratios of 33:1 and 10:1 (in mass). Two different milling strategies were investigated: interrupted operation at 2 min on and 9 min off for an effective total milling time of 20 (time I) and 200 min (time II); continuous cycles for the same effective time period. In Table 1, all of the different milling conditions are reported. The powder morphology was characterized by quantitative image analysis of the metallurgical cross sections of the particles. To obtain statistical support, at least 10 optical micrographs for each sample were considered. Two distinct parameters were analysed, namely, the particle cross sectional area and the aspect ratio, i.e., the ratio between the maximum and minimum length of each particle. The first parameter is representative of the particle size, while the second is representative of the particle morphology. The iron and chromium contamination of the powder was measured by an inductively coupled plasma mass spectrometry (ICP), while oxygen and carbon content were measured by combustion analysis (LECO). The same analyses were carried out on the sintered samples. Thermo-gravimetrical analyses of the milled powders were carried out in an argon atmosphere at a temperature of up to 1060 °C and with a heating rate of 20 °C/min; these analyses were combined with quadrupole mass spectrometry STA409CD (Netzsch). The powders were sintered in a DR.SINTER® SPS1050 (Sumitomo Coal & Mining, now SPS Syntex, Inc.) apparatus with graphite punches and dies. All samples had cylindrical geometry with a height of 5 mm and a diameter of 20 mm. SPS was performed at a nominal temperature (measured with a thermocouple inserted into a blind hole in the die wall) of 950 °C, with a uniaxial pressure of 30 MPa applied at 700 °C. The heating rate was 100 °C/min up to 900 °C and 50 °C/min up to the sintering temperature. The maximum temperature and pressure were held for 1 and 3 min, respectively, before allowing the furnace to cool to room temperature. The density of the SPS-processed pellets was measured according to Archimedes' principle, considering the theoretical densities of pure Cu as 8.96 g/cm^3. Vickers micro-hardness of sintered samples was measured using a Vickers Paar MHT-4 micro-indenter by applying a load of 0.5 N at a rate of 0.05 N/s and with a dwell time of 10 s. Scanning electron microscopy (SEM) was performed with a Philips XL30 apparatus for the observation of the powder and of the fracture surface of the sintered specimens. The metallographic cross section of the sintered samples was obtained by precision micro-cutting with a diamond blade. Standard metallographic preparation was also accomplished, including grinding with SiC papers up to 4000 grit, final polishing with 3-μm and 1-μm diamond pastes, and chemical etching with 120 mL of distilled water, 30 mL of hydrochloric acid and 10 g of iron chloride [29]. The microstructure was also evaluated using an optical microscope.

Table 1
Different milling parameters.

Step	Sample	PCA	BPR	Effective time	Cycle
1	b-I	–	33	20	Interrupted
	b-II	–	33	200	Interrupted
	c-I	Toluene	33	20	Interrupted
	c-II	Toluene	33	200	Interrupted
	d-I	Stearic acid	33	20	Interrupted
	d-II	Stearic acid	33	200	Interrupted
2	e-I	Stearic acid	10	20	Interrupted
	e-II	Stearic acid	10	200	Interrupted
3	f-I	Stearic acid	10	20	Continuous
	f-II	Stearic acid	10	200	Continuous

3. Results and discussion

3.1. Powder characterization

Fig. 1 shows a SEM micrograph of the atomized Cu powder and a metallographic cross-section obtained using the optical microscope. Copper is characterized by the irregular morphology typical of the water atomization process and by particle sizes smaller than 75 μm. Fig. 2 shows the SEM micrographs of the milled powder. The particle size increases after mechanical milling because copper is very ductile; this favours the predominance of welding events over fracturing actions. The particle size increases with milling time, and the morphology changes towards a flake shape, especially without any PCA use. The benefit of using a PCA is evident because it impedes the clean metal-to-metal contact necessary for cold welding and leads to the dispersion of aggregates. In turn, milling efficiency is improved, especially in the case of toluene (Fig. 2). Additionally, the image analysis results confirm the effectiveness of PCA in reducing the particle size (Fig. 3). When using toluene after 200 min, the particles are smaller (Fig. 2cI–II),

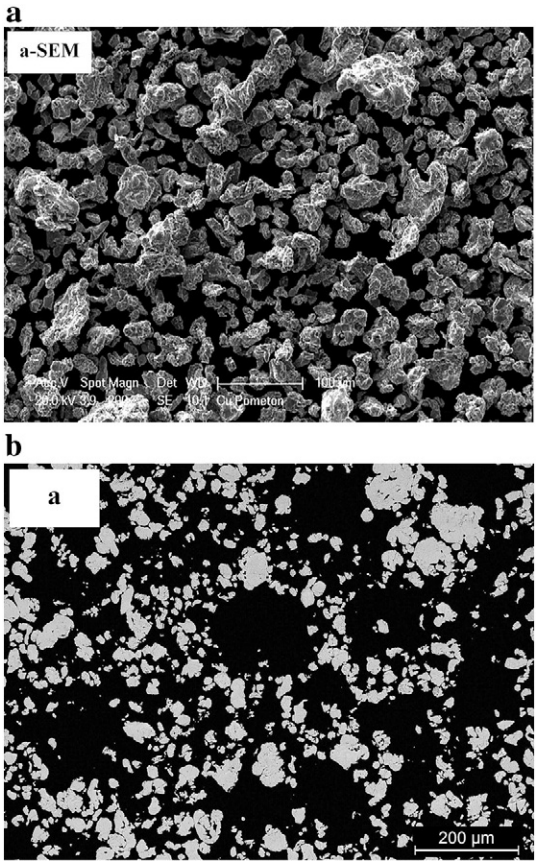

Fig. 1. SEM micrograph and metallographic cross section of atomized copper powder.