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# Powder Technology

# Spark plasma sintering behaviour of copper powders having different particle sizes and oxygen contents

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## ARTICLE INFO

## ABSTRACT

Two different copper powders with different initial oxygen contents (H = high, L = low) were milled and spark plasma sintered to obtain nanosized bulk copper. The characteristics of the milled powders were analysed together with their behaviour in sintering. Spark plasma sintering was carried out at 950 °C for 1 min, applying a pressure of 30 MPa at 700 °C. The consistent difference observed between the two powders is related to the much lower particle size of powder H and its consequent higher surface oxidation. It was observed that even if the finer particle size should lead to a faster and better densification, the much higher oxide amount predominates, slowing down the sinterability of the powder. Moreover, during the sintering process, a higher electrical resistance was measured for powder H due to its higher surface (particle–particle contact area) and oxide content. The degassing process occurring on sintering, caused by the decomposition of the stearic acid used as a process control agent in ball milling, is also markedly influenced by the powder particle size, showing an anticipated decomposition in sample H due to the higher reactivity of this powder.

## 1. Introduction

Spark plasma sintering (SPS) is a powder consolidation process based on the simultaneous application of a low-voltage, high-energy pulse current and uniaxial pressure [1,2]. The importance of this sintering method has been demonstrated by the large number of papers published during the past decade. SPS is used to sinter metallic powders, as well as ceramics, intermetallics and composites [3–6]. One of the main benefits of this technology is its localized heat input and short sintering time, which reduces the grain growth linked to high temperatures. Therefore, SPS is one of the most suitable sintering processes for materials that are very sensitive to temperature like nanostructured powders, being able to consolidate the compact to near full density with limited grain growth.

Different parameters influence the sintering behaviour of a powder; two of the most important are the particle size and the oxygen content. Regarding the particle size, it is well known that the thermodynamic driving force for sintering is proportional to the specific surface area of the powder. Particle size also influences the number and the extension of the contact areas and, in turn, the local pressure and the electrical resistance, which are of great importance in SPS due to its peculiar heating mechanism [7,8].

The second parameter is the powder oxygen content, which refers to the amount of oxides present on the powder particle surface. In sintering, the presence of oxides on the particle surface is detrimental because it slows down all of the mechanisms of mass transport responsible for neck formation. On the other hand, if the metallic powder is milled before sintering, the presence of oxides on the particles is beneficial because they exert a cutting action, promoting the fragmentation of the powder [9].

In the present paper, two different Cu powders with different initial oxygen levels were milled for 100 h to obtain a nanometric grain size and then consolidated in SPS to retain their nanosized structure. Many researchers have focused their attention on the spark plasma sintering behaviour of ultra-fine and nanosized copper [10–16], paying attention mainly to the evolution of the grain size and the microstructural characteristics during sintering. Less attention has been dedicated to the study of the influence of the powder oxygen content on the milling and sintering processes. Because commercially pure copper powders contain a certain amount of oxygen and a drawback associated with mechanical milling is the further unavoidable oxygen contamination by the milling media, atmosphere and process control agent (PCA), it is of great importance to evaluate the effect of the oxygen content on the behaviour of this powder.

## 2. Materials and experimental procedure

Two different Cu powder grades with different initial oxygen contents (powders H = high oxygen amount = 0.5 wt.% and L = low oxygen amount = 0.1 wt.%) were milled for 100 h and sintered in SPS to obtain nanostructured copper compacts.

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The two powders have a similar particle size and morphology, as shown in Fig. 1. The particle size, apparent density and oxygen content are summarized in Table 1.

Milling was carried out in a Fritsch Pulverisette 5 planetary ball mill (Idar-Oberstein, Germany) with a vial and balls of hardened steel at a rotation speed of 400 rpm and a ball to powder ratio (BPR) of 10. 0.5 wt.% of stearic acid was used as a PCA (process control agent). To avoid oxidation, the vial was set under vacuum before milling.

The milled powders were examined under light optical microscopy (LOM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) and through X-ray diffraction. For the microstructural analysis, a conventional grinding and polishing procedure was used.

The grain size and lattice strain of the milled powder and sintered discs were determined through X-ray diffraction (XRD) with a Cu Kα (λ = 0.154056 nm) source and an image plate detector over the 2θ range from 30° to 120° in reflection geometry. The experimental spectra were elaborated using materials analysis using diffraction (MAUD).

The dislocation density was calculated through the formula [17]

$$\rho^{1/2} = \frac{2\sqrt{3}\varepsilon^{1/2}}{Db} \tag{1}$$

where ε = microstrain, D = mean grain size and b = Burgers vector.

Thermogravimetric analysis (TGA) of the milled powders was carried out to study their degassing behaviour. TGA was carried out under an argon atmosphere, heating the samples up to 1060 °C at a heating rate of 20 °C/min; these analyses were combined with quadrupole mass spectrometry (QMS) using an STA409CD apparatus (Netzsch) to identify the gases emitted during heating.

The powders were sintered in a DR.SINTER® SPS1050 (Sumitomo Coal & Mining, now SPS Syntex, Inc.) apparatus with graphite punches and dies. The geometry of the samples was a disc 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

**Table 1**
Characteristics of the two initial powders.

|  |  | H | L |
|---|---|---|---|
| Particle size % cumulative | >75 μm | 8.7 | 5 |
|  | >45 μm and <75 μm | 57.6 | 52.8 |
|  | <45 μm | 33.7 | 42.2 |
| Apparent density (g/cm³) |  | 2.32 | 3.23 |
| O₂ |  | 0.5 | 0.1 |

700 °C. The heating rate was 100 °C/min up to 900 °C and 50 °C/min up to the sintering temperature. A holding time of 1 min at the maximum temperature was applied. During the whole SPS sintering cycle, the voltage, current, displacement of the upper punch and temperature were recorded.

The density of the sintered discs was measured by the water displacement method, and the oxygen and nitrogen contents were measured by a LECO TC400 machine.

## 3. Results and discussion

### 3.1. Powders

The milled H and L powders are shown in Fig. 2. A large difference in particle size between the two powders is clearly evident, as also confirmed by the particle size distribution reported in Fig. 3. In the same figure, median values of particle size are reported; they are different by one order of magnitude (7 vs. 78 μm). It is well known that the powder particle morphology and size change with the milling time. The milling process can be indeed divided into two different stages: the flaking stage and the fragmentation stage [9,18]. In the first stage, highly deformed flakes are formed due to collision with the balls. Upon increasing the milling time, the size of the flakes increases through cold welding, as they become thicker and highly strain-hardened so that they can be fragmented during the further collisions (second stage). After 100 h of milling, the fragmentation process of powder H is in an advanced
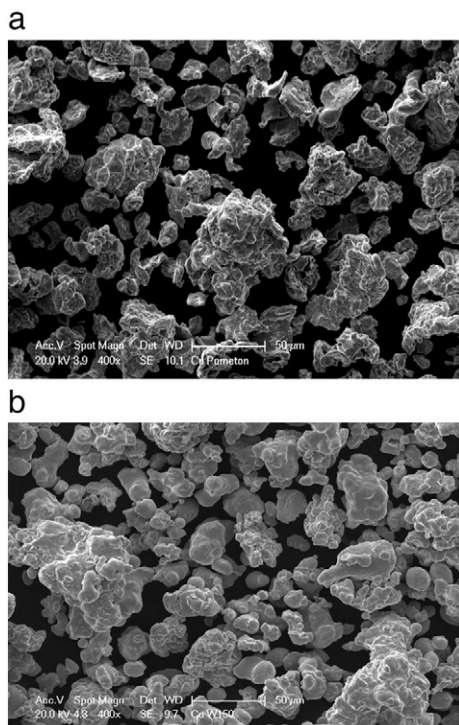


**Fig. 1.** Powders H (a) and L (b) before milling.
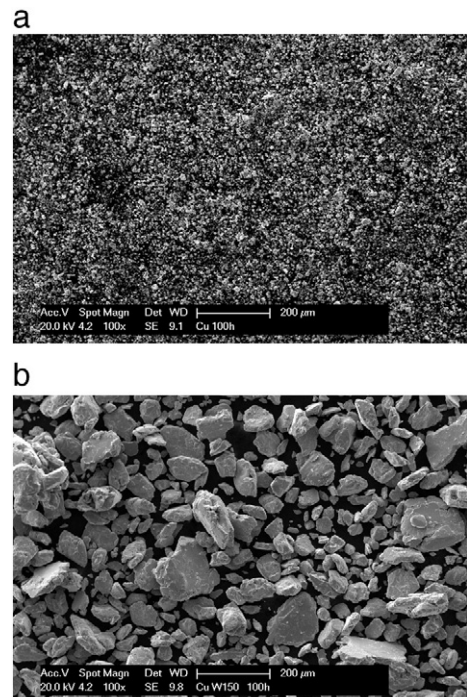


**Fig. 2.** 100 h milled Cu powders: powders H (a) and L (b).