

The influence of oxygen and nitrogen contamination on the densification behavior of cryomilled copper powders during spark plasma sintering

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Abstract It has been found difficult to fully densify some mechanically milled pure metal powders by spark plasma sintering (SPS). In this study, the densification behavior of cryomilled, nanostructured (NS) Cu powders during SPS was related to changes to the chemistry of the powders. The results showed that the presence of very small amounts of O and N in the powders, which were introduced during cryomilling and handling, significantly influenced the densification response. Moreover, reduction/removal of O/N via thermal annealing of the powders before SPS led to complete densification of the powders during subsequent SPS. The mechanisms responsible for this behavior were ascertained: O and N existed in the cryomilled powders in the form of thermally unstable compounds, and the subsequent thermal decomposition of these compounds during SPS generated the gaseous species, leading to porosity formation and incomplete densification; annealing of the powders before SPS removed the gases which resulted from thermal decomposition, thereby facilitating complete consolidation during subsequent SPS.

Introduction

A “two-step” approach, in which nanocrystalline (nc) powders are first prepared and then consolidated via various techniques, is widely used to produce bulk

nanostructured (NS) metals [1–3]. Mechanical milling, especially cryomilling (milling in a cryogenic liquid such as liquid nitrogen), represents an approach that can be used to generate a large quantity of nc metallic powders in a single batch [4, 5]. However, a drawback associated with mechanical milling is that contamination is unavoidable from the milling media, atmosphere, and process control agents (PCAs) [6]. Spark plasma sintering (SPS), which involves rapid heating of powders by pulsed DC current with the simultaneous application of external pressure, is an efficient consolidation technique which enables densification of nc powders at significantly lower temperatures within much shorter time [7–9]. The decided advantages of SPS over conventional sintering methods including hot-pressing mainly derive from the application of electric field/current, which provides high heating rate and enhances mass transport by increasing point defect concentration, reducing activation energy for migration of defects, or enhancing mobility of the defects [10, 11]. Published articles on SPS include experimental studies of process variables, and theoretical model analyses of densification mechanisms during SPS [12–16].

Inspection of the scientific literature reveals that nc metallic powders of various compositions have been successfully produced by mechanical milling or cryomilling, followed by consolidation via SPS [17–25]. However, changes to the chemistry of the powders during milling, and particularly during SPS, are seldom discussed, and moreover, the final relative density of SPS-consolidated bulk material is often calculated and reported on the basis of the theoretical density of the pure metal or alloy with a nominal composition (i.e., ignoring the chemistry changes that are induced by the milling environment and during SPS). This lack of attention to the chemistry raises two important questions. First, is there a change during SPS to

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the chemistry of the milled powders with impurities introduced during milling? Second, what is the influence of this chemistry change on the densification response during SPS?

Despite of the successful densification of various milled metallic powders via SPS, it has been found that it is difficult to fully densify cryomilled powders of some pure metals such as Al, Ni, and Cu. In related studies, a high temperature of 873 K, which represents 93.5% of Al's melting point, was used to fully densify mechanically milled Al powders by SPS [23]. In this study, the authors demonstrate that failure to attain complete densification of cryomilled Cu powders during SPS is not related to the selection of densification parameters (e.g., pressure, temperature, heating rate, holding time, etc.), but instead it is related to changes in the chemistry of the powders. The adsorption of N₂ and O₂ at powders surfaces and subsequent formation of thermally unstable compounds during milling and handling, and the subsequent thermal decomposition of these compounds during SPS generating gaseous species, led to porosity formation, and consequently, incomplete densification. Complete densification of the cryomilled Cu powders was achieved, only after careful thermal degassing before SPS. The associated mechanisms responsible for this behavior are described and discussed.

Experimental

Commercially pure (purity 99.9% on metal basis) coarse-grained Cu powders purchased from Alfa Aesar (Ward Hill, Massachusetts) with particle sizes of 44–149 μm were cryomilled for 8 h in liquid nitrogen with a stainless-steel-ball to powder ratio of 30:1, without PCA. Cryomilled and unmilled Cu powders were consolidated using a SPS-515S apparatus (SPS Syntex Inc., Kanagawa, Japan) at different sintering temperatures (the accuracy of temperature measurement was 0.1 °C) for 5 min with a heating rate of 100 °C/min, using a graphite die of 20 mm in diameter. The initial pressure applied was 12.5 or 100 MPa and the holding pressure at sintering temperatures was always 100 MPa (the accuracy of load was 0.3 MPa). Note that 12.5 MPa (4 kN) is the lowest load which can be applied in the continuous displacement mode for our SPS equipment. The vacuum pressures, with an accuracy of 0.001 Pa, as a function of temperature were recorded by the components attached to the SPS apparatus. In some other experiments, cryomilled Cu powders were heat treated in a vacuum furnace at 550 or 750 °C for 20 min with a heating rate of 20 °C/min, and then consolidated by SPS at 550 or 750 °C using an initial pressure of 12.5 MPa. The relative density of the SPS'ed bulk samples was determined in distilled water by the Archimedes method, which has an error not

higher than 0.2%. Impurity contents (primarily O and N) in unmilled, as-cryomilled and heat-treated cryomilled Cu powders, and SPS'ed bulk samples were analyzed in a commercial laboratory (Luvak Inc., Boylston, MA) using the method of inert gas fusion and following the ASTM E 1019-08 standard. Transmission electron microscopy (TEM) was used to characterize the microstructures of as-cryomilled, 550 °C heat-treated cryomilled Cu powders and SPS'ed bulk samples. The procedures for preparing TEM specimens are described as follows. For powders, epoxy was used to glue powders together into a bulk sample, and thin foils were obtained by grinding the bulk sample. In the case of SPS'ed bulk samples, thin foils were sectioned from the samples. The TEM specimens were obtained by mechanically grinding and dimpling the thin foils to a thickness of ~10 μm, and further thinning to electron transparency using a Gatan PIPS 691 ion milling system. TEM observations were carried out on a Philips CM12 microscope operating at 120 kV. A thermogravimetric analysis (TGA)–mass spectrometry (MS) coupling technique which consisted of a Netzsch TG 209F1 thermogravimetric analyzer with a sensitivity of 0.1 μg and a QMS 403 mass spectrometer with a resolution of ion current measurement of 0.01 pA was used to study the possible decomposition of impurities in the cryomilled Cu powders during heating. The sample was placed in an alumina crucible and heated at a rate of 10 °C/min from room temperature to 850 °C in an argon flow with ultra high purity (99.999%) with a flow rate of 20 mL/min.

Results and discussion

It was found that it was difficult to densify cryomilled Cu powders, as indicated by the density results of SPS'ed bulk samples shown in Fig. 1 (note that for these sets of SPS experiments, the initial pressure applied was 12.5 MPa). With increasing sintering temperature, the density increased slowly and reached only 94.5% at 750 °C (~80% of Cu's melting point), which was surprisingly low. Interestingly, SPS at 750 °C of unmilled Cu powders using exactly the same parameters resulted in a final density of 99%. From statistical TEM analysis, the cryomilled Cu powders have an average grain size of 45 nm [26]. In principle, densification should be enhanced by the presence of the nanostructure, given that diffusion pathways at the grain boundaries are increased and the driving force for densification is enhanced. However, the authors observed that densification of the cryomilled Cu powders is even more difficult than that of the unmilled coarse-grained Cu powders, indicating that there may be some special structural/compositional characteristics associated with the cryomilled Cu powders.

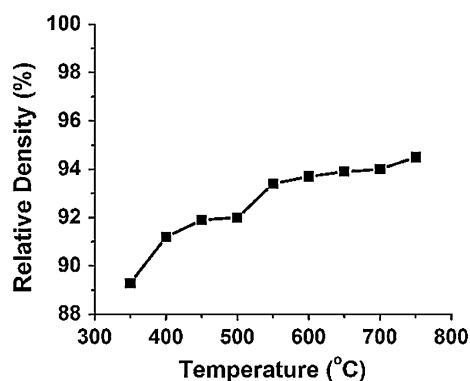


Fig. 1 Density of SPS'ed cryomilled Cu at different sintering temperatures

The vacuum pressure change during SPS as a function of temperature is rarely reported. However, it was recorded in this study, and the results are shown in Fig. 2 for SPS of cryomilled Cu powders at 750 °C with an initial pressure of 12.5 MPa applied which resulted in a final density of 94.5%. It can be seen that there was significant vacuum pressure change during SPS. Interestingly, there are two sharp peaks in the vacuum pressure curve at ~ 550 and ~ 705 °C, respectively, indicating release of gaseous species, which may have an influence on the SPS process.

The initial pressure applied during SPS was found to have a significant influence on the final density of the consolidated bulk sample. When an initial pressure of 100 MPa was applied, the final density of 750 °C SPS'ed cryomilled Cu was 91.0%, contrasted by 94.5% achieved for it when an initial pressure of 12.5 MPa was used. Notably, when an initial pressure of 100 MPa was applied, there was almost no vacuum pressure change during SPS, contrasted by the significant change in vacuum pressure shown above when adopting an initial pressure of 12.5 MPa. The sintering curves (displacement versus temperature) of the SPS when an initial pressure of 100 and

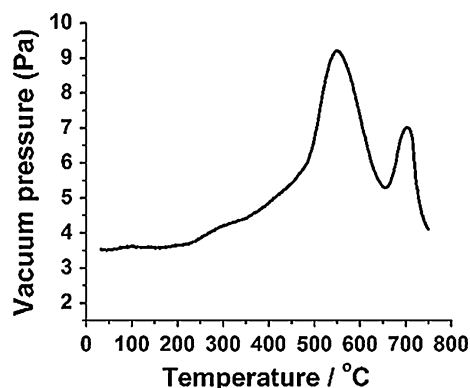


Fig. 2 Vacuum pressure as a function of temperature during SPS of cryomilled Cu powders with an initial pressure of 12.5 MPa (only temperature ramping stage is plotted)

12.5 MPa was applied are shown in Fig. 3. From the displacement–temperature curves, it can be seen that when an initial pressure of 100 MPa was applied, the densification of powders was fast during the earlier stage of the sintering, as indicated by the large slope of the curve between ~ 50 and ~ 400 °C. The displacement reached a plateau at ~ 515 °C, and decreased after the plateau. The lower-temperature densification can be explained by the contribution of high pressure to increasing the driving force for sintering, which leads to a decrease in the sintering temperature [10]. The decrease of displacement after the plateau was primarily attributed to gas generation. It is noted that densification took place at temperatures lower than the gas-generation temperatures of the powders. Consequently, almost all gases generated during SPS were trapped in the powder compact. The trapped gases contributed to more porosity in the final consolidated bulk and accordingly significant reduction in the density. By contrast, when an initial pressure of 12.5 MPa was used, significant densification did not take place until a sintering pressure of 100 MPa was applied at the sintering temperature (750 °C). Therefore, gases generated from the powders can be released, which contributed to a higher density. These results are in agreement with some reports in the literature [27–29] that lower initial pressure used for SPS led to higher density of consolidated bulk Cu. However, in those reports, in which vacuum pressure change during SPS was not monitored, the underlying mechanism was not elucidated. In addition, for Fig. 3, it should be noted that the initial pressure was applied at room temperature and there was a displacement right after the pressure application, but this displacement was zeroed before the temperature ramp-up and further displacements after heating were recorded and plotted in Fig. 3. In the case of the initial pressure of 100 MPa, the initial displacement zeroed out was much larger than that for the initial pressure of 12.5 MPa. This fact explains why in Fig. 3, the peak displacement for the former is much smaller than that for the latter.

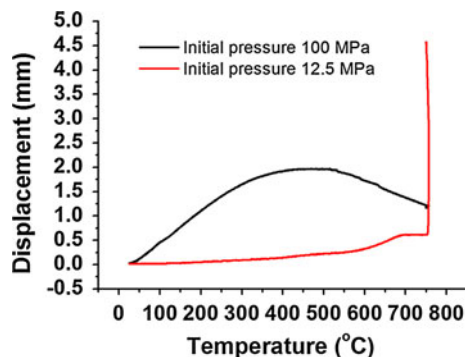


Fig. 3 Displacement as a function of temperature during SPS of cryomilled Cu powders with different initial pressures of 12.5 and 100 MPa (both temperature ramping and holding stages are plotted)

In view of the results of this study showing gas generation during SPS, which may influence the densification response, the authors studied the degassing response of the cryomilled Cu powders before SPS processing to see if it has any influence on the subsequent SPS densification. The results showed that SPS at 750 °C (initial pressure 12.5 MPa) of cryomilled Cu powders which were heat treated at 750 °C before SPS resulted in no vacuum pressure change during SPS and a final density of 98.6%, which represents a dramatic improvement over the density of 94.5% achieved by SPS of as-cryomilled Cu powders using exactly the same parameters. The absence of a vacuum pressure change during SPS indicated that gases which would be generated during SPS had been removed during thermal annealing in vacuum, which resulted in nearly full density of SPS'ed bulk sample. Notably, when using a sintering temperature of 550 °C for SPS of 750 °C-annealed cryomilled Cu powders, the final density was 98.5%. In addition, when the cryomilled Cu powders were heat treated at 550 °C followed by sintering at 550 °C by SPS, the final density was 94.4%. Therefore, only when the annealing temperature exceeded the higher peak temperature for gas generation, which was ~ 705 °C (see Fig. 2), was complete densification of the annealed cryomilled Cu powders achieved.

Gas generation from the powders during heating indicates chemistry change of the powders. In order to confirm the presence of chemistry change during heating and its influence on SPS densification, chemical analyses were conducted on unmilled, as-cryomilled and heat-treated cryomilled Cu powders as well as on SPS'ed bulk samples. O, N, C, Fe, Al, and Cr were analyzed for the as-cryomilled Cu powders, and their contents in weight percent were 0.512, 0.26, 0.027, 0.064, <0.0005, and 0.0094%, respectively. Other powders and bulk samples were analyzed for O and N contents, and the results are summarized in Table 1. The unmilled powders (Sample #1) and as-cryomilled powders (Sample #2) had similar O contents, but there was 0.26% N in the cryomilled powders whereas the N content in the unmilled powders was negligible. In the SPS'ed unmilled Cu (Sample #3) which achieved 99.0%

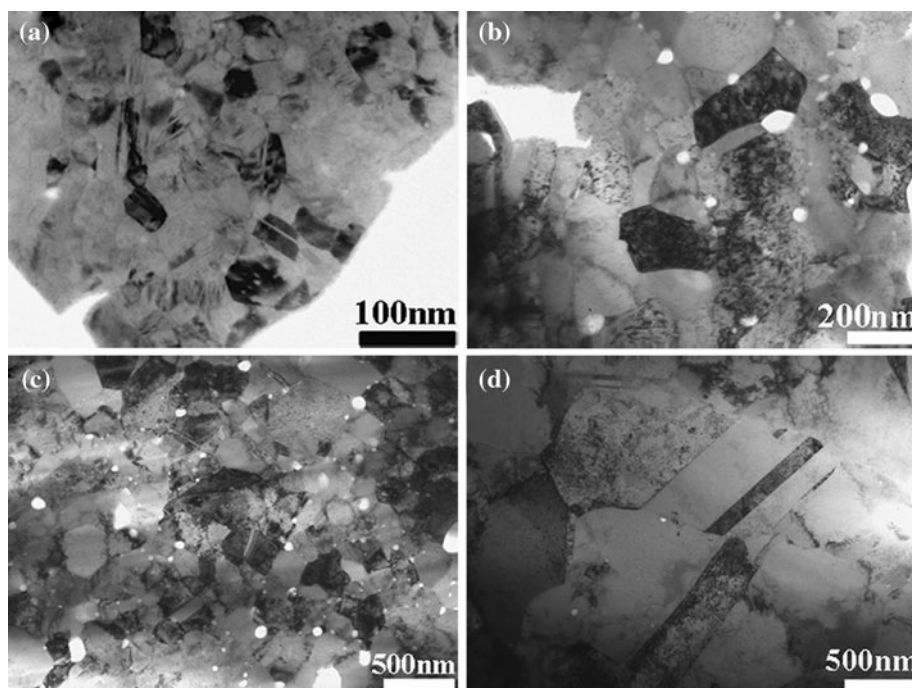
density, the O content was reduced by 50% relative to the initial powder (Sample #1). Notably, in the SPS'ed cryomilled Cu with 12.5 MPa initial pressure applied during SPS and final density of 94.5% (Sample #4), both O and N contents decreased by nearly a half relative to the initial powder (Sample #2); while in the SPS'ed cryomilled Cu with initial pressure of 100 MPa and final density of 91.0% (Sample #5), both O and N contents almost remained unchanged. This difference supports our previous argument that when a high initial pressure was used during SPS, gases were all trapped in the powder compact and resulted in significant reduction in the final density. Interestingly, after the cryomilled powders were annealed at 750 °C (Sample #6), the O content was reduced by about 50%, while the N was almost removed. Subsequent SPS processing (Sample #7) of the cryomilled powders which were annealed at 750 °C barely changed the O content, suggesting that the O was stabilized, possibly as some type of oxide phase, after annealing in vacuum. The nearly full density achieved for the SPS'ed annealed cryomilled Cu (Sample #7) indicates that annealing under vacuum of the cryomilled powders effectively removes gaseous species which result from decomposition of thermally unstable species, thereby facilitates complete consolidation during subsequent SPS. In contrast, although when a low initial pressure is applied during SPS of the as-cryomilled powders (Sample #4), the vacuum and temperature conditions present during SPS did promote removal of some of the gases from the powders; as supported by the chemical analysis results, this was not sufficient for complete densification because part of the gases were still entrapped in the powder compact.

The microstructures of powders and SPS'ed bulk samples were studied by TEM. Figure 4a–d shows TEM images of as-cryomilled powders, 550 °C-annealed powders, 600 °C SPS'ed cryomilled Cu, and 550 °C SPS'ed 750 °C-annealed cryomilled Cu. It is evident that the as-cryomilled powders have equiaxed grains of ~ 45 nm in size, with very few nanopores present between grains. Note that the average size of powder particles is ~ 50 μ m because of significant cold welding during cryomilling

Table 1 Chemical analysis results of O, and N contents in various powders and SPS'ed bulk samples

No.	Sample identification	O (wt%)	N (wt%)
1	Unmilled Cu powders	0.45	0.004
2	Cryomilled Cu powders	0.512	0.26
3	750 °C SPS'ed unmilled Cu, initial pressure 12.5 MPa, 99.0%	0.225	0.002
4	750 °C SPS'ed cryomilled Cu, initial pressure 12.5 MPa, 94.5%	0.281	0.14
5	750 °C SPS'ed cryomilled Cu, initial pressure 100 MPa, 91.0%	0.485	0.25
6	750 °C-annealed cryomilled Cu powders	0.247	0.025
7	750 °C SPS'ed 750 °C-annealed cryomilled Cu, initial pressure 12.5 MPa, 98.6%	0.227	0.022

Fig. 4 TEM images of **a** as-cryomilled Cu powders, **b** 550 °C-annealed Cu powders, **c** 600 °C SPS'ed cryomilled Cu, **d** 550 °C SPS'ed 750 °C-annealed cryomilled Cu



[24]. In contrast, after heat treatment at 550 °C, a high concentration of pores is evident, primarily at grain boundaries, and the grain size grows to ~ 200 nm. The presence of pores can be rationalized on the basis of gas release at ~ 550 °C during annealing (see Fig. 2). Similarly, a number of pores can be seen in the 600 °C SPS'ed cryomilled Cu sample whose density is 93.7% (see Fig. 1), with an average grain size of ~ 300 nm. In contrast, pores are barely evident in the sample obtained via SPS at 550 °C of 750 °C-annealed cryomilled Cu powders, indicating nearly full density, which is consistent with the density value (98.5%). Because gases were released at ~ 550 and ~ 705 °C, it can be anticipated that large quantity of pores were generated in the 750 °C-annealed cryomilled powders. However, these pores were successfully eliminated during SPS. The large grain size (1–2 μm) of this sample is primarily attributed to the high temperature annealing at 750 °C.

Simultaneous TGA and MS studies were conducted to provide fundamental insight into the phenomena of gas generation during heating of cryomilled Cu powders. TGA analysis can provide quantitative information about weight loss during heating due to the release of gaseous species, and MS is able to qualitatively ascertain the chemical nature of these gaseous species. The TGA–MS results are shown in Fig. 5, in which the sample weight in percent (TG) as well as the currents of various fragment ions are plotted versus temperature. From the TG curve, there are two temperature ranges of weight loss, namely,

~ 300 – 600 °C and ~ 670 – 800 °C. From the dynamic TG (weight loss per minute) curve which is not shown in the figure, the peak weight loss rate is reached at 530 and 720 °C, respectively, for the two temperature ranges of weight loss. For the ion current curves, the numbers indicated besides the curves are the mass number (mass/charge ratio) of ions. Based on the relation of MS mass number–fragment ions–parent molecules [30] and the chemical composition of the cryomilled Cu powders, mass numbers of 14, 28, 16, 32, and 46 correspond to N^+ , N_2^+ , O^+ , O_2^+ , and NO_2^+ , respectively, and these fragment ions originate from the parent molecules of N_2 , N_2 , O_2 , O_2 , and NO_2 , respectively. Therefore, during heating of the cryomilled Cu powders, N_2 , O_2 , and NO_2 are generated and released from the powders.

It can be seen that there is a relatively broad peak at ~ 530 °C in the ion current curves of 16 and 32, which is attributed to release of O_2 . The generation of O_2 at this temperature should be due to decomposition of CuO to Cu_2O . The Cu powders were oxidized in laboratory air at room temperature during handling. The oxidation products of Cu in the air at room temperature include Cu_2O and CuO [31, 32]. CuO is decomposed to Cu_2O at different temperatures under different O_2 pressures, and when the O_2 pressure is $\sim 10^{-2}$ Pa, the decomposition temperature of CuO is ~ 520 °C [33, 34], which is in agreement with the release of O_2 at ~ 530 °C during TGA–MS measurement (the thermogravimetric analyzer can be evacuated down to 10^{-2} Pa).

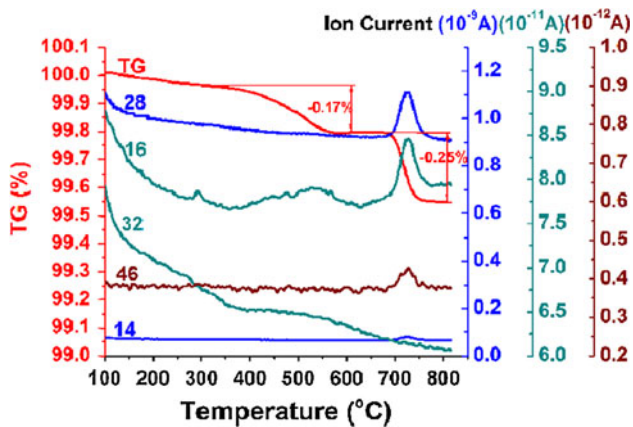


Fig. 5 TGA–MS results of the cryomilled Cu powders. The sample weight in percent (TG) and the currents of fragment ions are plotted versus temperature. On the TG curve, the values of weight losses are labeled for the two temperature ranges of weight loss. On the ion current curves, the numbers indicated beside the curves are the mass/charge ratio of ions. The three vertical axes for ion current from left to right correspond to current curves of 28–14, 32–16, and 46, respectively

Notably, there is a sharp peak at ~ 720 °C in the ion current curves of 14, 28, 16, and 46, indicating simultaneous release of N_2 , O_2 , and NO_2 from the powders at this temperature. This peak cannot be attributed to desorption of absorbed gases from the powders, considering the high temperature. The sharp peaks at ~ 720 °C in the ion current curves and the narrow temperature range (~ 670 – 800 °C) for weight loss in the TG curve (with a maximum weight loss rate at ~ 720 °C) indicate thermal decomposition of some chemical compound(s). Cu_3N , if it is present in the powders, decomposes at ~ 300 °C [35, 36]. In addition, Cu_2O is stable and will not decompose to Cu up to a temperature of 1000 °C [33, 34]. Furthermore, decomposition of $Cu(NO_3)_2$, if it is present in the powders, takes place below 300 °C [37]. In the powder diffraction file database of The International Center for Diffraction Data, the only other Cu–N–O ternary compound besides $Cu(NO_3)_2$ is $Cu_8O_8(NO_3)$. However, it is cited from a private communication, and it cannot be verified from the open literature. No other Cu–N–O compounds have been reported in the literature. Therefore, the authors propose that there is an unidentified Cu–O–N ternary compound formed in the cryomilled Cu powders, and this compound decomposes at ~ 720 °C, releasing N_2 , O_2 , and NO_2 simultaneously. The origin of this particular compound is not presently known although one can speculate that its formation may be due to the reaction of N_2 and O_2 with cryomilled Cu powders. Reports available in the literature indicated that Al can react with N_2 and/or O_2 during cryomilling and form AlN, Al_2O_3 , and O-containing AlN [38–40]. Cryomilled Cu powders can be exposed to N_2 and O_2 during both cryomilling and

handling in laboratory air. The reaction may be initiated by adsorption (chemisorption) of O_2 and N_2 on the powder surfaces. The chemisorption of O_2 on Cu surfaces has been well documented [41]. Under ambient conditions, N_2 does not interact with Cu surfaces, due to the strong N–N bond, so the adsorption of N on Cu surfaces has been achieved typically by N-ion bombardment [42, 43]. However, the special structure (e.g., high surface area) and/or energy state (e.g., highly nonequilibrium state) induced by cryomilling may enable adsorption of N_2 on cryomilled Cu powder surfaces. The chemisorption of O and N on the cryomilled Cu powder surfaces is accompanied by the breakage of Cu–Cu surface bonds and creation of new Cu-adsorbate bonds. Thus, a large degree of restructuring occurs, and new ordered structures are created, with the generation of nuclei. The formation of the Cu–N–O ternary compound advances by the growth of the original nuclei. The mechanism described above is proposed based on the processes of chemisorption of O_2 on Cu surfaces and formation of copper oxides [41]. Further studies are underway to confirm the proposed mechanism for the formation of the Cu–N–O ternary compound and ascertain the formula and structure of the compound.

After the 750 °C annealing, the O content in the cryomilled powders is 0.247%. From the TGA–MS analysis described above, after decomposition of CuO and the Cu–O–N compound during heat treatment of the cryomilled Cu powders, O left in the powders is in the form of Cu_2O . Based on these analyses, and considering the existence of Cu_2O , the theoretical density of the SPS'ed 750 °C-annealed cryomilled Cu can be calculated to be 8.84 g/cm³. Therefore, the actual relative density of SPS'ed 750 °C-annealed cryomilled Cu samples should be calculated based on a theoretical density of 8.84 g/cm³ rather than 8.92 g/cm³ (theoretical density of pure Cu). Accordingly, the actual relative density of the sample obtained by SPS at $550/750$ °C of 750 °C-annealed cryomilled Cu powders is calculated as 99.4/99.5%, instead of the nominal value of 98.5/98.6% given before. Therefore, full densification of cryomilled Cu powders was achieved.

Conclusions

In summary, it was difficult to fully densify by SPS as-cryomilled Cu powders which contain O and N as primary impurities, because of the generation of gaseous species from the powders and the subsequent entrapment of part of these gases in the powder compact during SPS. TGA–MS studies confirmed the release of gases during heating of the cryomilled Cu powders: at ~ 530 °C, CuO decomposes into Cu_2O , which generates O_2 ; at ~ 720 °C, decomposition of a probably new Cu–O–N compound

takes place, resulting in release of O₂, N₂, and NO₂. When the cryomilled powders were heat treated at 750 °C under vacuum before SPS, gases generated because of thermal decomposition were removed. Subsequent SPS of the 750 °C-annealed cryomilled powders resulted in full density, if the residual Cu₂O in the material is taken into account. The methodology adopted in this study can be applied to investigate SPS of other mechanically milled metallic powders.

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