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The kinetics of grain growth in near-micrometre grain size copper produced by spark plasma sintering

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Abstract. Samples of copper with a grain size in the near-micrometre regime and in a nearly fully recrystallized condition have been prepared by a spark plasma sintering (SPS) process. The thermal stability of these samples in the temperature range from 950 to 1050 °C has been investigated by an analysis of the kinetics of grain growth, based on microstructural measurements using electron backscatter diffraction. In the temperature range from 950 to 1000 °C the activation energy for grain growth is approx. 300 kJ mol⁻¹, corresponding to a value one and a half times the activation energy for self-diffusion in pure copper. In the temperature range from 1000 to 1050 °C the activation energy for grain growth is found to decrease, although annealing in this temperature range additionally results in non-uniform grain growth. For preparation of samples with a desired uniform grain size at present the best method appears to be via control of the temperature during the SPS process.

1. Introduction

It has been reported that metal materials with a microstructural scale in the near-micrometre regime have interesting mechanical properties, such as the presence of a yield point phenomena [1], annealing hardening and deformation softening [2], and enhanced mechanical strength [3]. The traditional route for the preparation of bulk samples with a near- or sub-micrometre scale involves severe plastic deformation followed by an annealing treatment. A complication in the analysis of the mechanical properties of such samples though is the presence in the microstructure of low angle deformation boundaries, and of a strong deformation texture. An alternative approach is the use of a spark plasma sintering (SPS) process [4,5] where it has been found that samples with a nearly fully recrystallized structure and almost random texture can be prepared.

For aluminium, grain size control of samples prepared by SPS can be achieved by selecting the initial powder size, as the native alumina film results in a dispersion of fine oxides around each original powder particle, thereby strongly pinning grain growth [4]. In copper such an approach is not possible, and instead it has been shown that grain size control in the near-micrometre regime can be achieved by the use of a fine initial powder size combined with sintering at different temperatures [6]. As an alternative to this annealing of as-sintered samples can also be considered as a method to achieve a desired grain size. It is known, however, that nanocrystalline materials may exhibit a remarkable resistance to grain growth [7] and hence investigation of the grain growth kinetics of SPS is therefore of interest for the control of grain size in near-micrometre grain size samples prepared using the SPS process.



2. Experimental

Based on previous work [6] the samples used in this investigation were prepared using a sintering temperature of 800 °C for a duration of 180 s, using an applied load of 50MPa. All samples were prepared using a SPS-1050 machine (Sumitomo Heavy Industries Ltd., Japan), starting with spherical copper powder (99.5% purity) with an initial particle size of approx. 0.5 μm . The density of each sample was measured using the Archimedes method. In each case the final density was typically above 98%. For the annealing treatments each sample was first sealed in a vacuum tube and evacuated to a pressure of 10^{-5} Pa. Annealing was carried out at either 950, 1000 or 1050 °C for different annealing durations in an air furnace (up to 14400 s), followed by cooling to room temperature in the furnace.

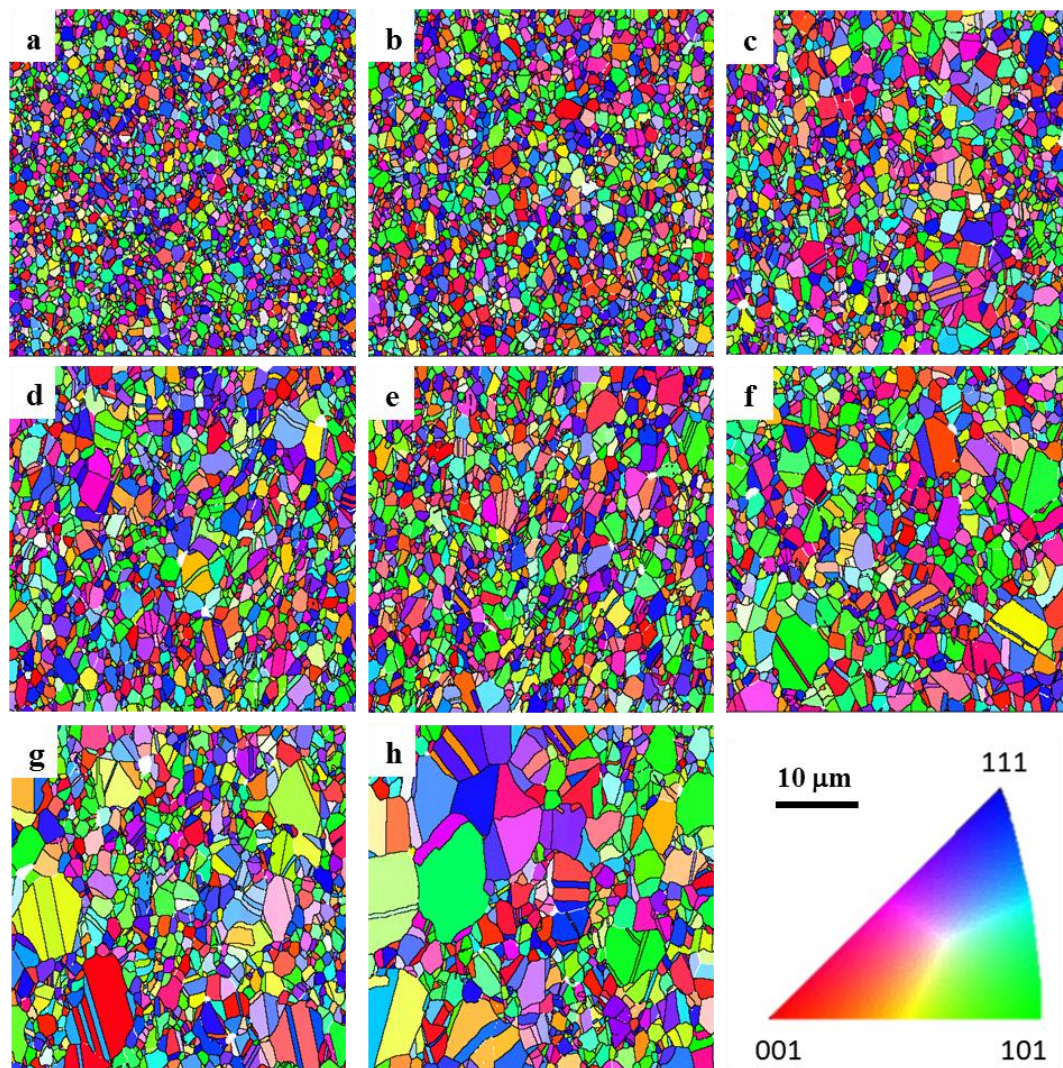


Figure 1. EBSD images of copper SPS samples processed under different annealing conditions: a) as-sintered sample, (b) 950 °C for 14400 s; (c) 1000 °C for 3600 s; (d) 1000 °C for 14400 s; (e) 1050 °C for 1800 s; (f) 1050 °C for 3600 s; (g) 1050 °C for 7200 s; (h) 1050 °C for 14400 s. In each case the colouring corresponds to the crystal direction parallel to the applied load during the SPS preparation of the samples.

For metallographic examination the annealed samples were first sectioned in a mid-plane, and then ground on SiC paper to 1000 grit. This was followed by a polishing treatment using argon gas in a

cross-sectional polisher machine (JEOL IB-09020 CP, Japan). The microstructure and texture of the sintered samples were studied in the scanning electron microscope (SEM) and using electron backscatter diffraction (EBSD). All investigations were carried out in a plane containing the SPS-loading direction. For each annealing condition (combination of time and temperature) between five and seven EBSD maps were collected. The average grain size of each case D , was measured from the EBSD data using a line intercept method, taking a grain boundary misorientation angle definition of 15° . Note that in this study twin boundaries were excluded from the calculations of the grain size (i.e. were not counted as grain boundaries).

3. Results and discussion

A summary of the evolution of the microstructure in samples annealed under different conditions is given in figure 1. It is seen that the grain size increases as expected with annealing time and temperature. In all case the samples have a nearly random texture. The average grain size, D_0 , for the as-sintered SPS sample (figure 1a) is approx. $0.7 \mu\text{m}$. Only a small amount of grain growth is seen in the sample annealed at 950°C for 14400 s (figure 1b). Annealing at a temperature of 1000°C results in increased grain growth, with a clear increase in grain size seen after 3600 s annealing at this temperature (figure 1c). Annealing at a temperature of 1050°C for 14400 s results in the development of a non-uniform grain size (figure 1h), with evidence of this already seen after 7200 s annealing at this temperature (figure 1f).

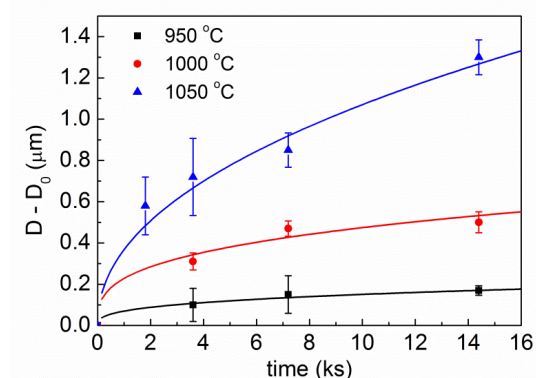


Figure 2. Evolution of the average grain size as a function of different annealing time at temperatures of 950, 1000, and 1050°C .

The evolution of the average grain size under different conditions of annealing time and temperature from 950 to 1050°C is shown in figure 2. Also shown in the figure are error bars corresponding to the standard deviation in the grain size measurements. It can be clearly seen that the grain size increases with annealing time and temperature. The graph confirms the visual observation that at 950°C grain growth occurs very slowly, with the average grain size increasing by less than $0.2 \mu\text{m}$ after 14400 s annealing. At an annealing temperature of 1050°C grain growth occurs more rapidly, with the average size increasing by more than $0.5 \mu\text{m}$ during the first 1800 s of annealing.

In order to determine the grain growth kinetics the data have been fitted at each temperature to the equation for classical grain growth kinetics [7-10] where the average grain size and annealing time are related by the equation:

$$D - D_0 = Kt^{1/n}, \quad (1)$$

where D is the mean grain size, D_0 is the initial grain size, K is a temperature dependent constant, t is the annealing time and n is the grain growth coefficient representing the grain growth behaviour (typically with values of between 2 and 4 for the annealing of metals).

The results are shown as the solid lines in figure 2. Values of n representing the grain growth kinetics at temperatures 950, 1000 and 1050°C are found from the fitting to be 3.0, 3.1 and 2.2, respectively. Theoretically a grain growth exponent of $n = 2$ represents a classical uniform grain

growth process driven by grain boundary curvature. In the present case the value of $n = 2$ at 1050 °C corresponds however to a process where non-uniform coarsening takes place.

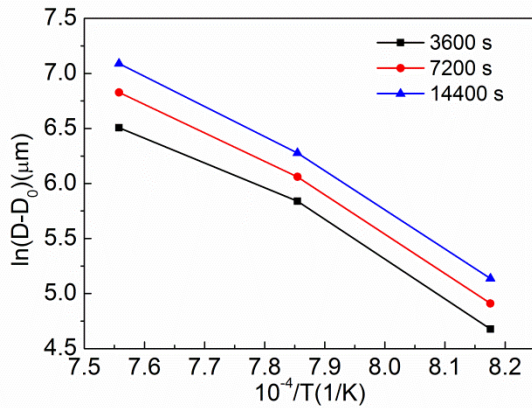


Figure 3. Plot of $\ln(D-D_0)$ versus $1/T$ for the Cu SPS samples annealed at durations of 3600, 7200, and 14400 s at 950, 1000, and 1050 °C.

For a constant value of n the activation energy, Q , for the grain growth process can be calculated using the standard assumption that K can be expressed in Arrhenius form according to [11,12]

$$K = K_0 \exp(-Q/RT), \quad (2)$$

where Q is the activation energy, T is the temperature in Kelvin, K_0 is the pre-exponential value, which we assumed here to be constant over the temperature range investigated, and R is the gas constant. Accordingly the value of Q can be calculated from a plot of $\ln(D - D_0)$ versus $1/T$ at fixed annealing durations, where the slope of the plot is $-Q/R$. The data for the present experiment are plotted in figure 3. Not surprisingly, given the change in n between 1000 and 1050 °C, the points do not lie on a straight line. Accordingly the activation energy has been calculated separately for the ranges of 950 to 1000 °C and 1000 to 1050 °C (values given in table 1). The value of approx. 300 kJ mol⁻¹ for the range 950 to 1000 °C can be regarded as a reasonable estimate, as the grain growth exponent, n , is approximately constant in this range, whereas the lower value of 200 kJ mol⁻¹ for the range 1000 to 1050 °C should be regarded as an upper bound, given the increase in n over this range.

Table 1. Activation energies for grain growth during annealing of SPS samples calculated from figure 3.

Annealing time	Activation energy (kJ mol ⁻¹)	
	950 – 1000 °C	1000 – 1050 °C
3600 s	301	187
7200 s	298	215
14400 s	295	228

The activation energy can also be calculated by determining the annealing time required to achieve the same increase in grain size (i.e., for fixed values of $D - D_0$), in which case the effect of the change in the grain growth exponent, n , at the highest temperature can be explicitly taken into account. For a fixed change in grain size we can write

$$\exp(-Q/RT_2)t_2^{1/n_2} = \exp(-Q/RT_1)t_1^{1/n_1}, \quad (3)$$

from which the activation energy in the range T_1 to T_2 can be calculated as

$$Q_{T_1-T_2} = R \left[\frac{\ln t_1}{n_1} - \frac{\ln t_2}{n_2} \right] \left/ \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \right. . \quad (4)$$

Results for this second method are presented in table 2, where is seen that the activation energy decreases from approx. 300 kJ mol⁻¹ to approx. 140 kJ mol⁻¹ as the annealing temperature is increased

from 1000 to 1050 °C. It should be remembered, however, that the latter is still only an apparent activation energy, as the value of n changes at some unknown temperature in the range 1000 to 1050 °C. It is nevertheless instructive to compare these values with those for grain boundary and self-diffusion in high purity copper, which are approx. 120 and 200 kJ mol⁻¹, respectively [13]. The activation energy for grain growth in the lower temperature range is much higher than either of these values, with the activation energy between these value in the higher temperature range. In either case an activation energy near that for grain boundary diffusion would be expected for a normal grain growth process in a pure metal.

Table 2. Different annealing times to achieve the same increase in grain size and correspondingly calculated activation energies.

$D-D_0$ (μm)	Time to achieve fixed increase in grain size (s)			Activation energy (kJ mol ⁻¹)	
	950 °C	1000 °C	1050 °C	950-1000 °C	1000-1050 °C
0.5	-	11818	1970	-	134
0.4	-	5909	1212	-	135
0.3	-	2424	606	-	144
0.17	14384	485	-	288	-
0.1	2909	75	-	306	-

The high value of the activation energy at 950 and 1000 °C, together with calculated values for the grain growth exponent and the microstructural observations of non-uniform coarsening at 1050 °C suggest the possibility of either an unknown impurity or micro-porosity in the SPS samples [14], resulting in either pinning or drag of the grain boundaries below a certain temperature. Preliminary microstructural examination in a field-emission gun SEM has not revealed the presence of fine oxides or pores, though it is possible such features, if present, can only be seen using higher resolution imaging.

It should be pointed out that non-uniform coarsening seen at 1050 °C implies that some grains do indeed grow at a faster rate at this temperature, with a correspondingly lower activation energy for grain growth. This again suggests some pinning or solute breakaway transition, as non-uniform grain growth in pure metals is usually texture-related i.e., the rapid growth of an isolated with a very different orientation inside a strong texture [15]. The SPS samples, however, have a nearly random texture so such an explanation is unlikely to account for the onset of the non-uniform coarsening.

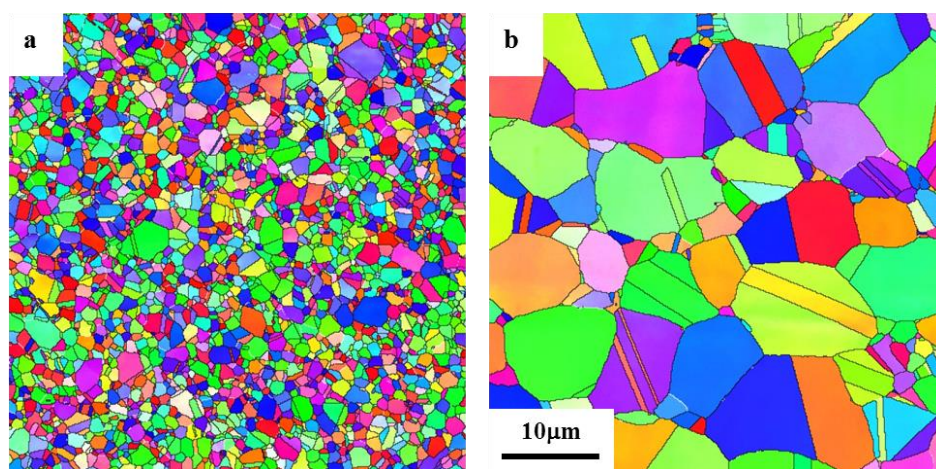


Fig. 4. EBSD images of Cu SPS samples prepared at different sintering temperatures: (a) 900 °C; (b) 1000 °C. In each case a sintering time of 180 s and an applied sintering load of 50 MPa were used.

The microstructure of samples sintered at 800 °C and then annealed can also be compared with those directly sintered at a higher temperature. Figure 4 shows the microstructure of samples prepared by SPS at temperatures of 900 and 1000 °C using a sintering time of 180 s and an applied pressure of 50 MPa. It is clearly seen that increasing the sintering temperature from 900 and 1000 °C results in a large change in grain size even with the short sintering duration of 180 s. Moreover the grains in the sample sintered at 1000 °C for 180 s have a similar size to those in the sample sintered at 800 °C and then annealed at 1050 °C for 14400 s, but with a more uniform size distribution. It will be interesting in future work to explore whether this is related to the effect of the sintering pressure on recrystallization during the early stages of sintering or whether the sintering pressure also affects the grain growth kinetics.

4. Summary and conclusions

Copper samples with a grain size in the near-micrometre regime and in a nearly fully recrystallized condition have been prepared by use of the SPS process, and the kinetics of grain growth in these samples has been studied. A high activation energy of approx. 300 kJmol⁻¹ (one and a half times larger than the activation energy for self-diffusion in copper) is found for grain growth in the temperature range from 950 to 1000 °C, confirming the relatively high thermal stability of the SPS samples. In the temperature range from 1000 to 1050 °C the activation energy for grain growth decreases and annealing in this temperature range results in non-uniform grain growth. For preparation of samples with a desired uniform grain size at present the best method appears to be via control of the temperature during the SPS process.

Acknowledgements

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