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Dislocation density in carbonyl nickel during sintering

A. TASKINEN
Institution of Process Metallurgy, Helsinki University of Technology, SF-02150 Espoo 15, Finland

Three different size fractions of carbonyl nickel powder were sintered for 2 h at temperatures of 300 to 940° C. In addition to linear shrinkage measurements, the internal structures of the specimens were examined with X-ray line broadening and in some cases with TEM. The shrinkage of the different fractions was compared with the calculated dislocation densities. The results show that dislocations which originate from the production process are rearranged during the presintering process and are annihilated in a normal coarse powder at the very beginning of the sintering process. Only when the sintering particles are of micron-size or less, do dislocations remain during the sintering process, making it possible for them to contribute to the material transport. The mechanisms by which dislocations can do this are discussed in this paper.

1. Introduction

The importance of dislocations in sintering has been discussed in several papers during the last 30 years. There are two distinct opinions: (1) dislocations do not contribute to sintering in any way in the absence of an applied pressure [1–5] and, (2) dislocations can contribute to material transport [6–14]. Lenel and co-workers have indicated that the effects depend on the particle size of the powder; i.e. if the particles are of micron-size, the plastic deformation by dislocation motion is of importance up to relatively large values of x/a (x is the radius of the neck and a is the radius of the particle). Those who support the role of dislocations assume the sintering process to be analogous to secondary creep, while those who feel dislocations are not important have attempted to prove that the available stress is insufficient to nucleate new dislocations.

It may be important to note here that two expressions have been confused in the literature concerning sintering: the controlling mechanism and the dominating mechanism. In the case of successive reactions, the process with the lowest reaction rate controls the overall rate of the reaction. This pattern is common in heterogeneous reaction kinetics, where the slowest unit process is frequently called the controlling mechanism. In the case of parallel reactions, however, the process with the highest reaction rate is the dominating one. Solid state sintering belongs typically to this group. For example, if dislocation motion is assumed to be the dominating mechanism, the contribution of dislocations to material transport would be the most important one, which means that single crystals could sinter only slightly.

Transmission electron microscopy (TEM) experiments have shown that particle rotation and twinning of two or three small metal powder particles can occur during annealing [15–19]. However, TEM experiments have not established the role of dislocations in sintering. A weakness of these experiments is the fact that the phenomena taking place during annealing in a small number of particles are not necessarily the same as those in a pressed compact. On the other hand, X-ray line broadening can reveal the internal structure of a pressed compact. Also, because carbonyl nickel powder has a high density of lattice defects originating from the production process, it is a most suitable material for experiments where the behaviour of dislocations during sintering is to be followed. Therefore, in this study the change in the linear shrinkage and in the density of dis-

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locations in carbonyl nickel powder with different surface areas has been examined.

2. Experimental details

2.1. Materials

The material used was Mond carbonyl nickel powder type 123 which was fractioned into three parts with different particle sizes. BET-surface areas of the fractions were 0.73, 1.62 and 2.53 m^{-2} g^{-1} and Fisher particle sizes were 8.8, 3.6 and 1.3 μm, respectively. Scanning electron micrographs showed that the surfaces of the coarse particles were deformed during fractioning and the particles formed agglomerates about 30 μm in size.

2.2. Methods

Cylindrical specimens (diameter 11.3 mm, height 9 mm) were pressed using a pressure of 88 MPa. Sintering time was 2 h and the atmosphere was flowing, dry hydrogen. Temperatures were between 300 and 940° C.

The linear shrinkage of diameters was measured with a micrometer and the internal structures with an X-ray line broadening method using the line profiles of the reflections (1 1 1) and (2 2 2), which were scanned in steps of 0.01° using Ni-filtered CuK_α radiation.

The correction for the $\alpha_1\alpha_2$-doublet was made according to Rachinger [20]. The finest fraction sintered for 2 h at 700° C was used as the reference, because its integral breadths were the narrowest observed. The relative density of this reference standard was 96% theoretical density. According to Halder and Wagner [22] the crystallite size and the internal strain were calculated from the equation [21]

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \frac{16\epsilon^2 \sin^2\theta}{\beta \lambda \cos\theta} \qquad (1)$$

where β is the corrected line breadth, λ the wavelength used, θ the Bragg angle, D the crystallite size and ϵ the internal strain.

Nowadays in almost all the crystallite size calculations the Fourier method derived by Warren and Averbach [23] is used. The ratios in the results of the integral and the Fourier methods have been formulated by Buchanan *et al.* [24].

$$D_I = 2\,D_F \qquad (2)$$

$$\epsilon_I = 1.25\,\epsilon_F \qquad (3)$$

In order to give comparable results, the mean dis-

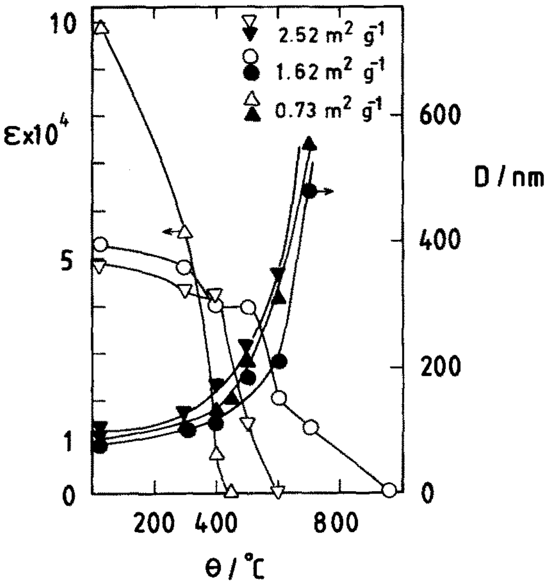

Figure 1 Crystallite size and internal strain of the sintered compacts calculated by integral breadth method.

location density was calculated for each treatment using D_F and ϵ_F. According to Williamson and Smallman [25] the mean dislocation density, $\bar{\rho}$, is

$$\bar{\rho} = \left(\frac{3n}{D_F^2} \cdot \frac{16.1\epsilon_F^2}{\mathbf{b}^2}\right)^{1/2} \qquad (4)$$

where **b** is the Burgers vector and n is the number of dislocations per unit of crystallite surface. When the dislocations are randomly distributed as assumed in this case, the value for n is 1.

Normal cold cell etching techniques gave the best results in preparing samples for TEM. Several experiments were performed to obtain thin samples

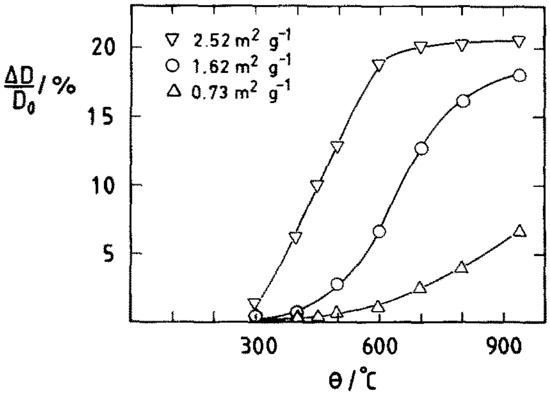

Figure 2 Linear shrinkage of the compacts in 2 h sintering.

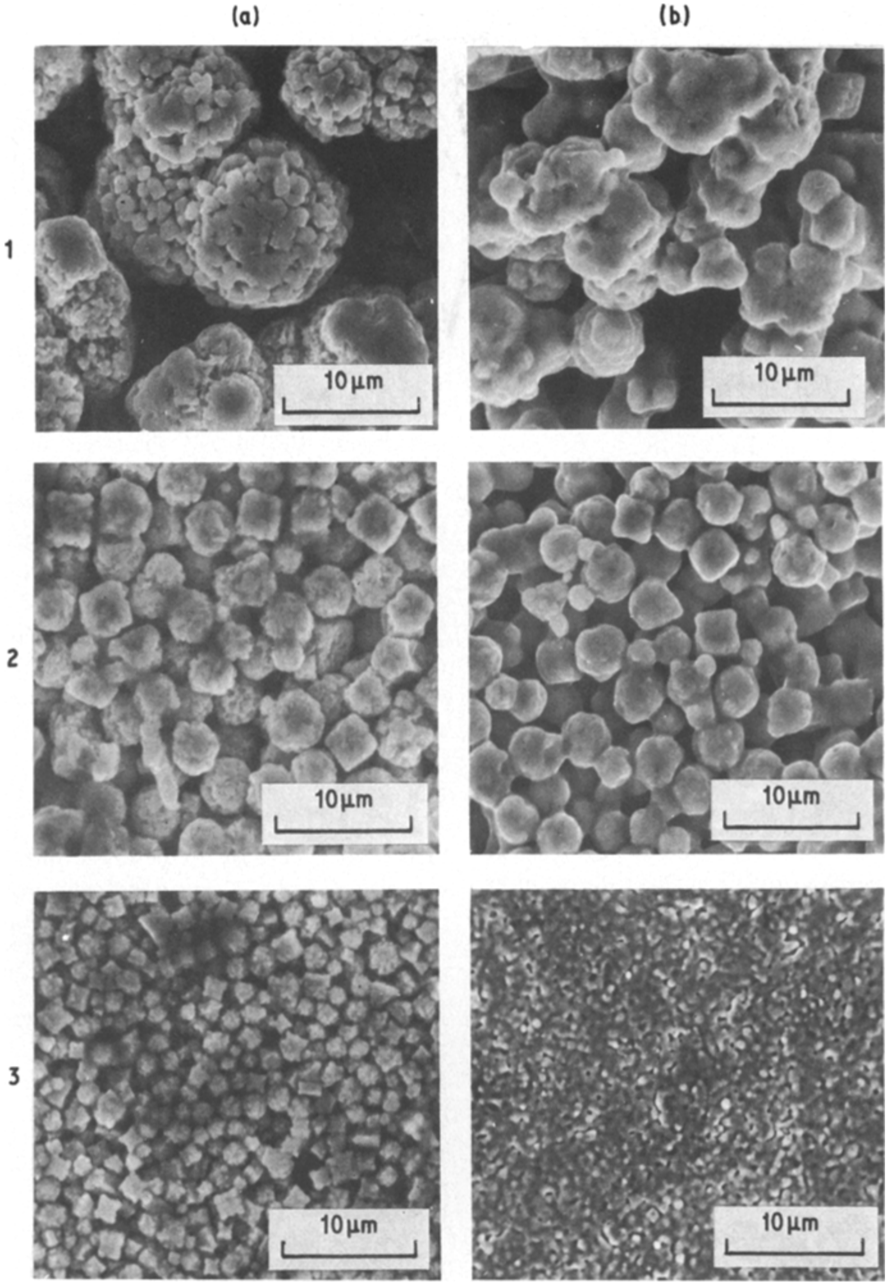

Figure 3 Scanning electron micrographs of the compacts post annealing: (a) sintered at 300° C; (b) sintered at 700° C for 2 h. The specific surface areas (BET) of the initial fractions are 0.73, 1.62 and 2.52 $m^2 g^{-1}$ for the lines 1, 2 and 3, respectively.

from porous material by an ion-bombardment thinning technique, but that technique destroyed the internal structure.

3. Results

Fig. 1 represents the behaviour of crystallite size and internal strain and Fig. 2 the linear shrinkage during sintering. It can be noticed that the crystallite size in all the fractions remains essentially the same up to 600° C.

Scanning electron micrographs in Fig. 3 show clearly the effect of particle size on sintering.

Fig. 4 shows the mean dislocation density versus linear shrinkage. The dislocation density of the

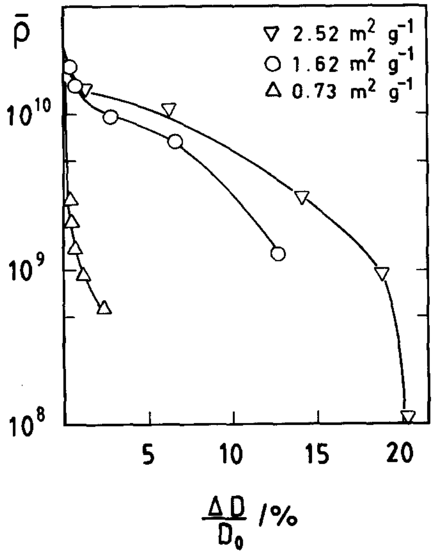

Figure 4 Mean dislocation density versus linear shrinkage of the compacts.

reference, the lowest density in Fig. 4, was determined by TEM.

4. Discussion

The strain in the coarse powder is high because of the agglomerates, and it decreases as soon as the lattice obtains enough thermal energy to recover. The strain in the two finest fractions, which have not been deformed much during preparation, do not decrease during the recovery process. During this stage the crystallite size remains nearly constant and the fractions, except the finest one, sinter only slightly.

The crystallite size begins to increase at a temperature of about $0.5T_\mathrm{m}$ where non-conservative dislocation motion, i.e. climb processes, normally begins to take place. It has been argued by Kolerov [26] that because crystallite growth and sintering occur simultaneously, dislocations do have some role in sintering. However, according to the current results, crystallite growth in a coarse powder takes place without noticeable sintering.

In order to estimate the volume decrease caused by dislocations one has to simplify the process significantly. In the beginning of the densification 1 cm^3 of a pressed compact with a green density of 52% contains $0.52/D^3$ crystallites. It can be assumed that dislocations in the initial stage are randomly distributed, and therefore the total shrinkage can be expressed [13] as

$$\Delta V_{\mathrm{tot}} = \frac{1.04\, b}{D}. \qquad (5)$$

When inserting $b = 0.25$ nm and $D = 50$ nm in Equation 5, a volume decrease due to the dislocations existing in the compact prior to sintering is only 0.5 vol %. This leads to the conclusion that without creation of new dislocations during densification their contribution to the sintering has importance only in the initial stage of the process.

Energetic considerations confirm that the smaller the particle size, the smaller the portion of total energy of a compact that can be attributed to dislocations. It follows that in this case the surface area should play the most important role in sintering. However, Fig. 4 shows that dislocations in a powder having a small surface area vanish before the sintering really begins, while they remain in a powder having a large surface area. Thus, dislocations can contribute to sintering only when the particles are of micron-size.

The most probable mechanism by which dislocations contribute to material transport in sintering is the secondary creep mechanism discussed by Lenel. In addition, it should be noted that grain-boundary ledges may act as dislocation sources [27]. These ledges can easily be formed in the necks because of the rough surfaces of the particles. Finally, dislocations can contribute to material transport by means of pipe diffusion.

5. Conclusions

It is concluded that the material transport in the sintering of normal powder (particle size 50 to 500 μm) is never controlled or dominated by dislocation motion. Only in the case of particles which are of micron-size is it possible for dislocations to contribute to material transport in sintering.

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