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Preparation and Study by Electron Microscopy of the Development of Texture with Temperature of a Porous Exhydroxide Nickel Oxide

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A series of NiO samples has been prepared from $Ni(OH)_2$, at low temperature, in air flow. The starting hydroxide is obtained from a "turbostratic hydroxide" in the form of thin platelets suitable for electron microscopy and selected area diffraction studies. The reaction of dehydroxylation is pseudomorphic and topotactic with $(00.1)Ni(OH)_2//(111)NiO$ and $(1\bar{1}.0)Ni(OH)_2//(1\bar{1}0)NiO$. At the beginning of the reaction it is clearly shown that germination occurs at numerous points on the sides of the platelets so that a continuous interface is immediately formed. Each particle of the resulting oxide is finely porous and may be considered as a mosaic monocrystal formed by a great number of small (5–7 nm) and slightly misoriented crystallites. The pores are disposed in a rather regular array. The further development of the texture of NiO with temperature proceeds in two steps. The first step occurs between 200 and 600°C: it may be considered as a "textural ordering" with pore and crystallite growth and retention of the hexagonal habit. During the second step beyond 600°C, the platelets are broken up, then there is an intergranular sintering and a nonporous material is obtained.

The first step can be used for obtaining a series of NiO samples the main properties of which are continuously variable, though they present the same habit. The variation of some of these properties is studied: textural properties, adsorbed species and deviation from stoichiometric composition.

I. INTRODUCTION

The physicochemical and catalytic properties of finely divided nickel oxide have been repeatedly investigated by different authors. Nevertheless, the interpretation of these properties is made complicated owing to the fact that the divided nickel oxide has numerous characteristics which are closely interrelated: deviation from stoichiometric composition (*1*), magnetic properties (*2–4*), electrical properties (*5*) and state of division.

Generally, the physicochemical and catalytic properties are very dependent on the oxide history and it becomes difficult to draw significant comparisons between the experimental results due to the wide range of sample preparation methods and further treatments of the initial oxides.

Accordingly, it is essential that a sufficiently extensive range of samples from the same starting material and presenting a continuous variation of their main characteristics, should be prepared in order to facilitate the comparison of the experimental results and the correlation of the different properties.

On the other hand, the best possible knowledge of the texture of nickel oxide particles should help the study of the other properties. Some authors have approached this question by means of indirect methods such as surface and porosity measurements (*6–7*), analysis of X-ray diffraction line profiles and small angle scattering data (*8*). However, few direct studies by electron microscopy and diffraction (*9*) have given rise to detailed observations, probably due to the lack of samples suitable for this technique.

We have been able to obtain a nickel hydroxide which gave by dehydration a nickel oxide the characteristics (habit and texture) of which allow an easier study by electron microscopy and diffraction than in previous work. Moreover, by varying the thermal conditions of dehydration, we obtained a range of samples which showed a continuous evolution of a number of properties.

II. EXPERIMENTAL METHODS

1. Preparation and Characterization of $Ni(OH)_2$

The hydroxide is prepared in two steps.

First, an ammonia solution is added to a nickel nitrate solution at room temperature. The precipitate is then washed and collected by centrifugation several times. It may be considered as a hydrated nickel hydroxide. This hydroxide is formed by layers similar to those found in well crystallized $Ni(OH)_2$ but these layers are randomly oriented and they are separated by intercalar water molecules which join them. We called this hydroxide: "turbostratic hydroxide" (*10*).

In a second step, an aqueous suspension of this turbostratic hydroxide is treated hydrothermally at 200°C. The end product is then a well crystallized nickel hydroxide.

The hydroxide thus obtained is a powder, the particles of which are seen by electron microscopy as nonporous, hexagonal thin platelets (Fig. 1a). The selected area electron diffraction (SAED) pattern of an isolated grain corresponds to a single crystal lying on the (00.1) plane (Fig. 1b). The diameter of the particles in this plane is several hundred nanometers; their mean thickness in the direction [00.1], determined by metal shadowing, is 30 nm. The crystallite size inferred from X-ray diffraction (see Sect. 4) is 30 nm in the direction [00.1] and about 50 nm in the direction [11.0], parallel to the base plane of the platelets. Therefore, the hydroxide particles may be considered as mosaic single crystals.

One often can see Bragg extinction contours as on Fig. 1a. This feature implies that the platelets are often slightly bent and corroborates a rather good crystalline perfection.

One can say from ir spectra (Fig. 2a) that this nickel hydroxide retains a small amount of adsorbed water: band of weak intensity at 1630 cm^{-1} (bending vibration of H_2O molecules), shoulder near 3500 cm^{-1} (stretching vibration from hydrogen bonded OH species). The large and multiple band near 1380 cm^{-1} may be assigned to adsorbed nitrate and carbonate ions (*11–12*).

2. Preparation of the Oxide

The powdered hydroxide is heated in air flow with rising temperature (5°C/hr). The sample is then maintained at the final temperature, varying from 200 to 1000°C, for about 30 hr.

3. Electron Microscopy and Diffraction

The observations were made by electron transmission with a Sopelem 100 kV microscope. The specimen holder grid was covered with a thin vacuum-deposited carbon film. The sample was suspended in water to which were added several drops of a surface active foaming agent. The suspension was then agitated and the grid was

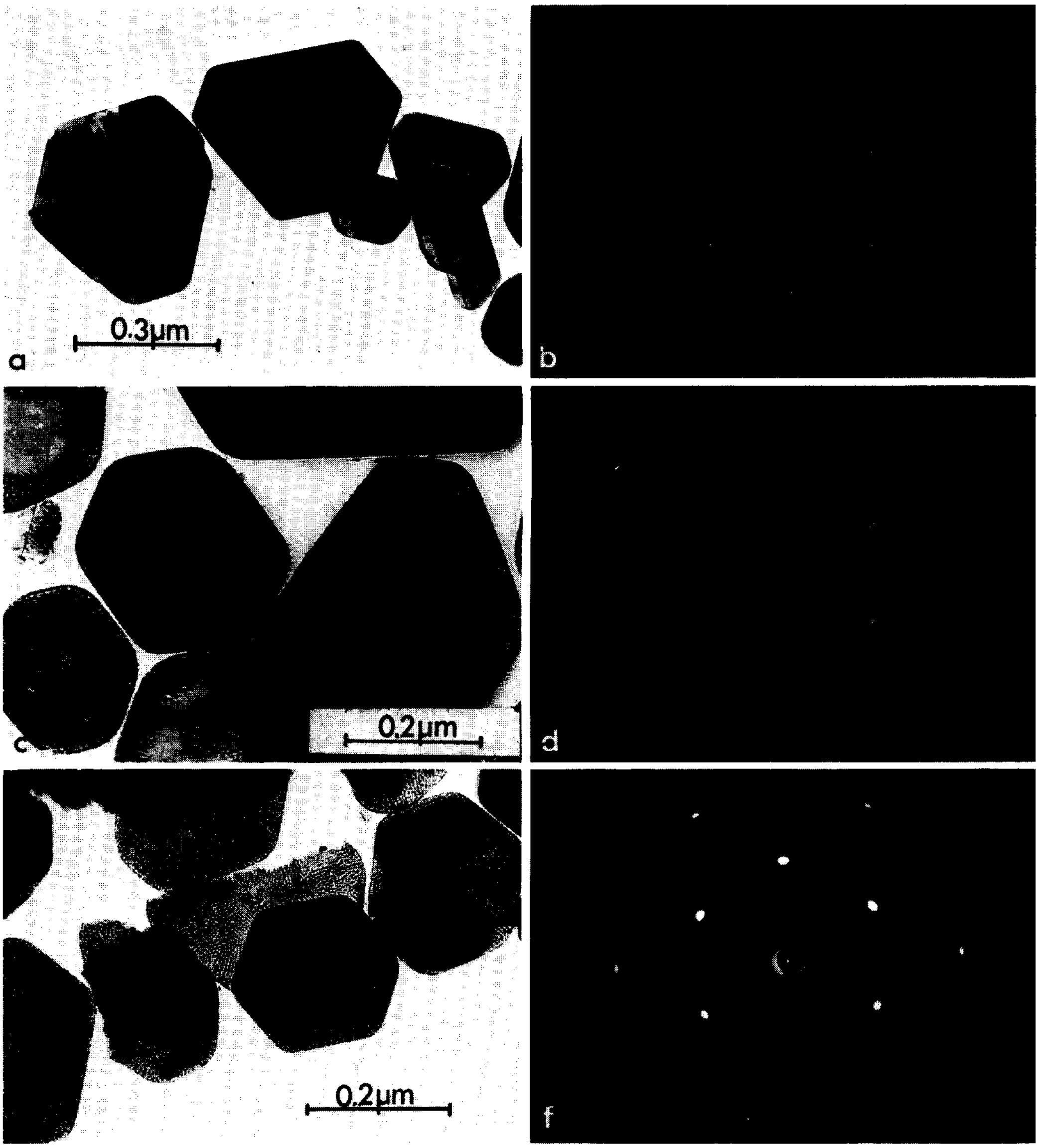

FIG. 1a. Starting material: $Ni(OH)_2$ prepared by hydrothermal treatment from an aqueous suspension of turbostratic nickel hydroxide. (b) Selected area electron diffraction (SAED) of a $Ni(OH)_2$ single particle lying on the (00.1) plane. (c) Set of $Ni(OH)_2$ particles during dehydroxylation at 200°C in an air flow. (d) SAED of a single particle. One can see the topotactic relation between $Ni(OH)_2$ and NiO. (e) Set of particles of finely divided nickel oxide. (f) SAED of a single particle of NiO.

plunged into the foam in order to collect some particles.

4. X-Ray Diffraction

The X-ray diffraction patterns were obtained by means of a CGR diffractometer with a counter scanning speed of 0.05° θ $\min^{-1}$ and cobalt $K\alpha_1$ radiation ($\lambda\alpha_1 = 0.17889$ nm). The crystallite sizes of the oxide samples were inferred from the peak breadth at half maximum intensity of the 111 and 200 lines using Scherrer's formula and after correcting these breadths for instrumental broad-

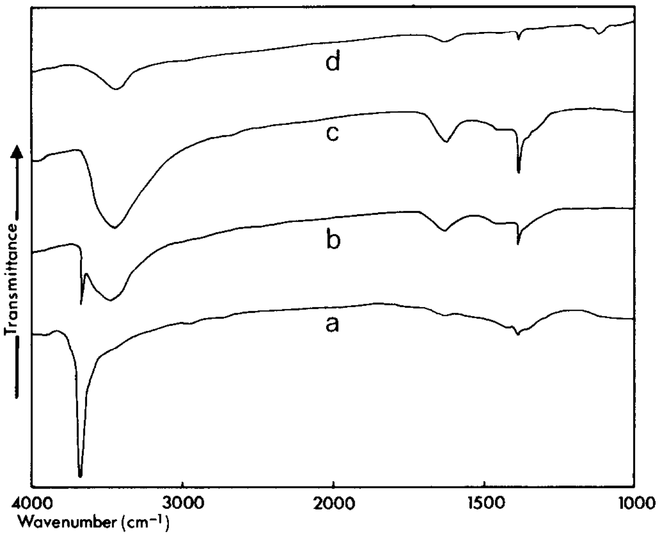

FIG. 2. Infrared spectra: (a) unreacted $Ni(OH)_2$; (b) $Ni(OH)_2$ partly dehydroxylated; (c) finely divided NiO; (d) NiO after textural ordering.

ening. A study which is presently being conducted clearly shows that we are not in the limiting case of a pure particle size effect and that microstrains also contribute to the line broadening. The separation of these two effects will provide us a more significant value of the effective crystallite size.

5. Infrared Spectra

The ir absorption spectra were obtained with a Perkin-Elmer 457 spectrophotometer from NiO samples mixed and pelleted with KBr.

III. RESULTS AND DISCUSSION

1. Transformation $Ni(OH)_2 \rightarrow NiO$ (*13*)

The complete dehydration of $Ni(OH)_2$ is only possible above 200°C.

Samples taken out during the course of the reaction were observed by electron microscopy (Fig. 1c). The nonporous hydroxide is clearly distinguished from the oxide which is finely porous. The formation of a continuous interface homothetic with the platelet edges could thus be observed from the beginning of the reaction. SAED of a single platelet which had partly reacted shows that the oxide pattern still corresponds to a single crystal pattern. The oxide is in a definite and reproducible orientation relative to the hydroxide:

$$(00.1)Ni(OH)_2//(111)NiO \text{ and } (1\bar{1}.0)Ni(OH)_2//(1\bar{1}0)NiO.$$

One can also see in Fig. 1d that the reflections corresponding to $Ni(OH)_2$ are very sharp spots and that the reflections corresponding to NiO are broad arcs. We shall return to this point in the following section.

As the reaction proceeds, the dehydration interface moves from the outside to the center of each particle. Simultaneously, one can see in ir spectra (Fig. 2b) the decrease of the narrow band of the stretching vibration of the structural hydroxyl groups and the increase of the amount of adsorbed water.

2. Study of the Most Finely Divided Oxide of the Series

The end product of dehydration no longer shows X-ray diffraction lines of $Ni(OH)_2$; very broad lines corresponding to NiO can be seen. The crystallite size inferred from these lines is about 5 nm for a dehydration temperature of 200°C or 8.5 nm at 250°C.

The particles of this oxide retain the habit of the starting hydroxide (Fig. 1e). On a SAED pattern obtained on a single particle (Fig. 1f) one can see, as we have already noticed, that the spots are broad and appear as small arcs. The particle can nevertheless be considered as a single crystal lying on the plane (111). These features and the fact that the crystallite size (crystallite = domain which coherently diffracts X-rays) is clearly much smaller than the size of the particles indicate that the texture of the oxide consists of a great number of tiny crystallites which are slightly misoriented. Such a single crystal may be called a mosaic single crystal (*15*).

Extra spots of weak intensity which are not expected in the (111)* plane of the reciprocal lattice of NiO, can be seen on the pattern of Fig. 1f. These spots appear in positions corresponding to the spots of the first order Laue zone. These extra spots may be explained by the misorientation of the diffracting planes from one crystallite to another. Nevertheless, this interpretation may be insufficient to explain the occurrence of extra spots near the center of the pattern.

Moreover, each particle contains a great number of small pores (about several nanometers) which have a very homogeneous size. These pores often show a particular orientation with one another, thus one can see pore lines. These pore lines sometimes show the symmetry of the 3-fold axis [111] of the oxide.

In order to give a more complete picture of these oxides, we measured the ratio (Ni^{3+}/Ni_{tot}) and it was therefore possible to know the deviation from stoichiometric composition of the oxide $Ni_{(1-x)}O$. The amount of Ni^{3+} was measured in an inert atmosphere by iodometric titration after the sample was dissolved in a hydrochloric acid solution. The total amount of nickel was determined by a complexometric method and by atomic absorption. For the most finely divided oxide $Ni^{3+}/Ni_{tot} = 6 \times 10^{-2}$.

From ir spectra (Fig. 2c) it can be said that finely divided oxide still retains a great amount of adsorbed water molecules (band at 1630 cm^{-1}, broad band in the 3500 cm^{-1} region). This last band may be mainly assigned to the stretching vibration of adsorbed water molecules hydrogen bonded with one another. Nevertheless superficial, hydrogen bonded hydroxyl groups may also make a contribution to this broad band as shown in previous work (*14*) on CoO prepared by the same way. This statement is probably still valid for NiO due to the great similarity between the ir spectra of these two oxides.

On the other hand finely divided NiO still retains nitrate and carbonate ions initially adsorbed on the starting hydroxide.

3. Development of the Texture of the Oxide with Temperature

a. Textural Development from 200 to 600°C

The evolution of the texture, as followed by electron microscopy, is shown in Fig. 3a–d. In this temperature range the grains of oxide still retain the habit of the parent hydroxide. The size of the pores clearly increases with temperature. Above 500°C, there only remain a few pores which now present a hexagonal form with their edges parallel to the edges of the platelet (Fig. 3d).

The size of the crystallites increases monotonically, from 5 nm for the most divided oxide to 35 nm for an oxide prepared at 550°C.

We called these textural modifications of the grains without change of their habit a "textural ordering." The transport of matter observed during this phenomenon probably occurs by means of a surface dif-

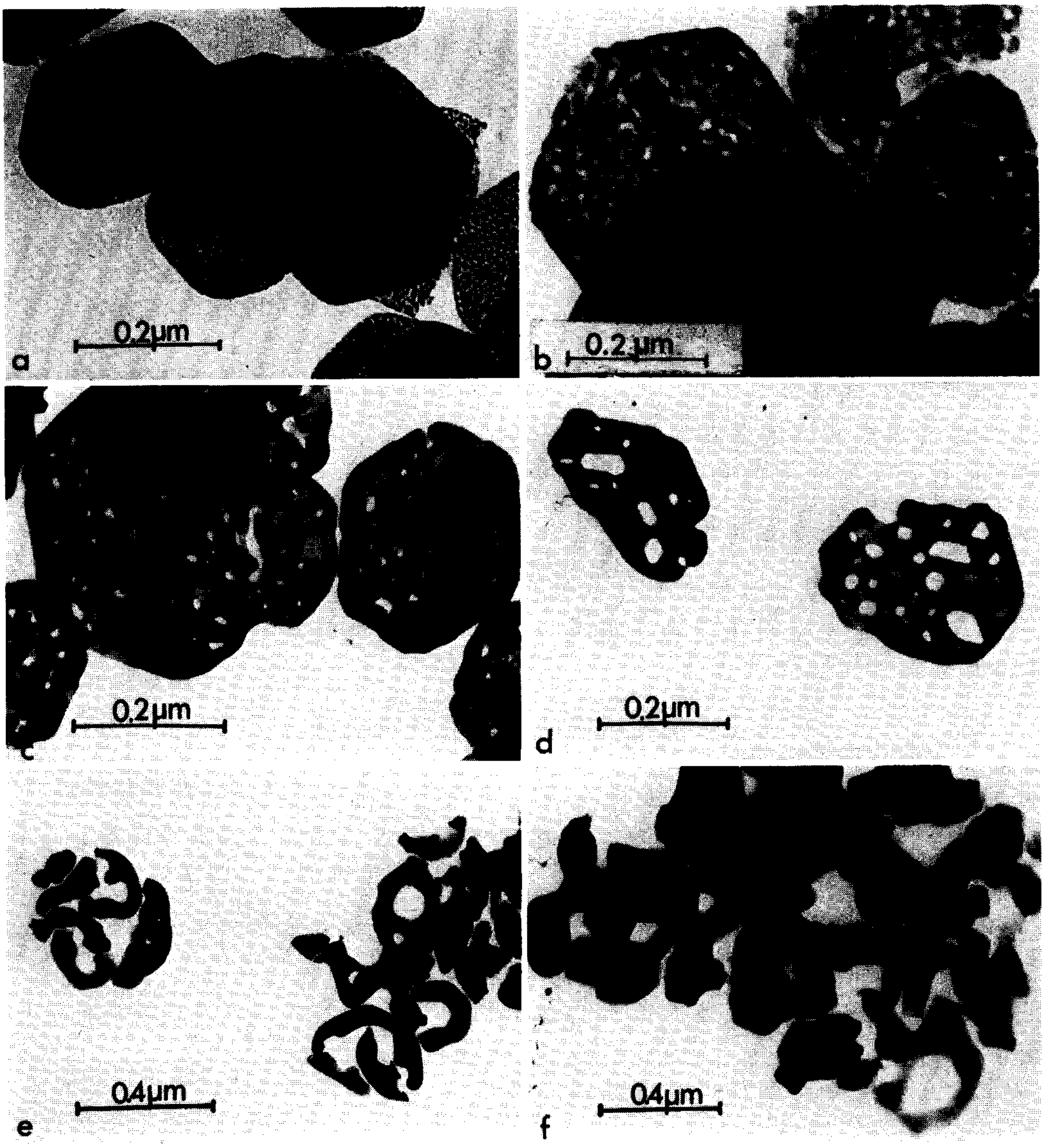

FIG. 3. Texture evolution of NiO platelets with calcination temperature: (a) 285°C, (b) 400°C, (c) 520°C, (d) 550°C (textural ordering); (e) 780°C, (f) 975°C (intergranular sintering).

fusion process in which adsorbed water molecules play a prominent part.

The amount of adsorbed water and of adsorbed nitrate and carbonate ions decreases with increasing calcination temperature (Fig. 2d).

The deviation from the stoichiometric composition decreases as well. For instance the ratio Ni^{3+}/Ni_{tot} equals 1.2×10^{-2} and 5.5×10^{-3} at calcination temperatures of 280 and 550°C, respectively.

b. Development of the Oxide Texture Above 600°C

Above 600°C the particle habit of the oxide is broken up into several fragments (Fig. 3e). Then, above about 800°C, these fragments begin to sinter. At 1000°C the particles of the end product can be seen as thick grains without any definite form (Fig. 3f). This intergranular sintering is a step in the development of texture of NiO which is clearly distinct from the first step, i.e., the textural ordering.

Other authors (*8*) have proposed a mechanism of sintering in two steps: the first step is regarded as consisting of a growth of crystallites only along a direction parallel to the (111) plane, and in the second step it is proposed that the particles stick together by their (111) plane. Our observations do not support such a mechanism, but the difference may be explained by the very different textures of the starting hydroxide ["lamellae" very much thinner (3 nm) in this work (*8*)].

CONCLUSION

An improved $Ni(OH)_2$ preparative method has yielded a powdered hydroxide which fits very well the demands of electron microscopy. By means of this hydroxide it has been clearly shown that the dehydration reaction starts on numerous points of platelet edges so that a continuous hydroxide–oxide interface is almost immediately formed. The reaction is pseudomorphic and topotactic. The end product is a black nonstoichiometric oxide; it is finely porous and it may be considered as a mosaic monocrystal formed by a great number of small (5–7 nm) and slightly misoriented crystallites. The pores are disposed in a rather regular array.

The textural modifications observed with increasing calcination temperature occur in two steps. The first step is characterized by the platelet habit remaining and a simultaneous growth of crystallites and pores (textural ordering). The second step consists of a sintering process following the disrupture of the platelets. At the end of this second step, the powdered oxide has the properties of bulk nickel oxide.

The samples taken out at different stages of the textural ordering process are suitable material for the study of the interrelated modifications of the properties of divided NiO, because the particles present a similar habit, whereas the solid phase inside the platelets shows a varying degree of division and order. Some properties are still under investigation, namely, microstrains, lattice parameter and magnetic properties. Comparison of these data with those related here should permit correlation between these properties. It should be interesting to undertake the comparative study of the catalytic activity of these oxide samples.

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REFERENCES

1. Deren, J., and Stoch, J., *J. Catal.* **18,** 249 (1970).
2. Richardson, J. T., and Milligan, W. O., *Phys. Rev.* **102,** 1289 (1956).
3. Cohen, J., Creer, K. M., Pauthenet, R., and Srivastava, K., *J. Phys. Soc. Jap.* **17,** Suppl. B-I, 685 (1962).
4. El Shobaky, G., Gravelle, P. C., Teichner, S. J., and Trambouze, Y., *J. Chim. Phys.* **64,** 310 (1967).
5. Richardson, J. T., *J. Catal.* **6,** 328 (1966).
6. Nicolaon, G. A., and Teichner, S. J., *J. Chim. Phys.* **66,** 1816 (1969).
7. Fahim, R. B., and Abu-Shady, A. I., *J. Catal.* **17,** 10 (1970).
8. Moraweck, B., Renouprez, A. J., and Imelik, B., *J. Chim. Phys.* **70,** 594 (1973).
9. Larkins, F. P., Fensham, P. J., and Sanders, J. V., *Trans. Faraday Soc.* **66,** 1748 (1970).
10. Le Bihan, S., and Figlarz, M., *J. Cryst. Growth,* **13–14,** 458 (1972).
11. Blyholder, G., and Allen, M. C., *J. Phys. Chem.* **70,** 352 (1966).
12. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, London, 1966.
13. Fievet, F., and Figlarz, M. "Cinétique des réactions dans les systèmes hétérogènes." Réunion Int. Soc. Chim. Phys., Dijon, 1974, in press.
14. Vincent, F., Figlarz, M., and Amiel, J., *in* "Reactivity of Solids" (J. W. Mitchell, R. C. De Vries, R. W. Roberts, and P. Cannon, Eds.), p. 181. Wiley, New York, 1969.
15. Figlarz, M, Vincent, F, Lecaille, C., and Amiel, J. *Powder Technol.* **1,** 121 (1967).