

Influence of grinding on the texture, microstructure and chemical reactivity of nickel powders

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The influence of grinding on the morphology, texture and microstructure of nickel powders has been studied. A series of three samples, the as-received one (NiNG) and those comminuted for 3 min (NiG3) and 30 min (NiG30), have been used. SEM observations have shown that cold-welding, leading to a decrease of particle size, takes place during the comminution process. Analysis of the XRD profiles by means of the Willianson and Hall method seems to demonstrate that the broadening of XRD peaks is produced by the microstrains generated during the milling of nickel powders, rather than by the diminution of crystallite size (coherently diffracting domains). On the other hand, it has been reported that the recrystallization temperature of this material by annealing under vacuum protection decreases on increasing the grinding time. Moreover, the mean XRD peak widths of samples annealed at 300 °C decreases according to the following trend: NiG30 < NiG3 < NiNG. This behaviour explains why the catalytic activity of these samples towards the dehydrogenation of formic acid in the vapour phase decreases according to the same trend.

1. Introduction

Considerable research work has been undertaken [1–3] with the aim of demonstrating the relationship between catalytic activity and lattice imperfections of metals induced by mechanical treatment, but discrepant results have been reported. Thus, Anderson [4] concluded after reviewing the topic that there is no evidence supporting the idea that emergent dislocations are active centres of catalysts. This fact would explain the little work carried out in the last years on the topic when compared with the intensive research [5–8] regarding the influence of comminution on both the reactivity and the thermodynamical and kinetic stability of solids.

However, it is noteworthy that in the work reported above, the textural and structural modifications induced by mechanical treatment of the catalysts have been analysed at room temperature. These data have been compared with those concerning the activity of the corresponding materials towards different catalytic reactions which are generally measured at much higher temperatures, in order to get a relationship between both series of results. This procedure implies the assumption that the trend of the lattice defects of the solids as a function of the deformation parameters (grinding time, percentage of cold-rolling, etc.) is independent of the annealing temperature, which is not necessarily true. It would, therefore, be interesting to get information regarding the relationship between textural and structural parameters of solids and their catalytic activity, after submitting the catalysts to

similar thermal treatment to obtain both structural and reactivity data.

2. Experimental procedure

150 g of high-purity nickel powder (designated NiNG) with a particle size smaller than 40 μm were ground for 3 min (NiG3) and 30 min (NiG30), respectively, in a disc oscillating mill. Both the discs and the jar of the mill were made of pure nickel in order to avoid contamination of the samples.

The powder X-ray diffraction spectra of the samples were obtained with a PW 1760 instrument equipped with a scintillation counter using $\text{CuK}\alpha$ radiation and a nickel filter. The scanning rate of the goniometer was 0.125 grad min^{-1} (0.125 deg min^{-1}).

As-received and ground samples were subjected to 1 h annealing treatments at different temperatures under high vacuum protection, in order to prevent oxidation of nickel, before measuring the integral breadth of X-ray profiles. Peak broadening was measured by the integral breadth method after resolution of the $K\alpha_1$ component by Rachinger's method [9].

The crystallite size D and microstrain ϵ of the nickel samples were determined from analysis of the $K\alpha$ component of the (1 1 1) and (2 2 2) peaks by means of the Willianson and Hall method [10].

The SEM micrographs were obtained with a Hitachi electron microscope, model HHS-2R.

A conventional continuous-flow reactor was employed to study the catalytic activity of nickel powders

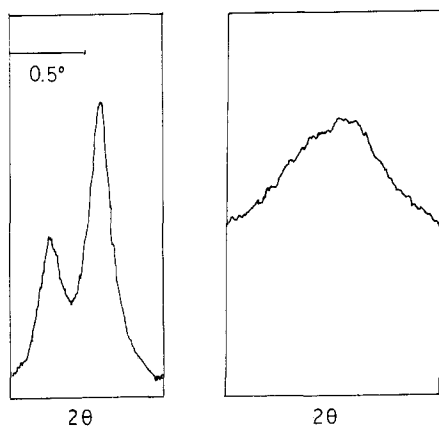


Figure 1 Influence of grinding on the broadening of the (3 1 1) peak of nickel.

for the dehydrogenation of formic acid in the vapour phase, using helium as carrier gas. The activity was measured in the range 350 to 450 °C; at lower temperatures, the blank reaction rate was approximately of the same magnitude as the total one. Decomposition products (CO₂ and H₂) were analysed by gas chromatography. Working conditions were chosen so that reactions followed a zero-order kinetics with regard to the partial pressure of formic acid.

3. Results and discussion

Fig. 1 illustrates, by way of example, the variation of the shape of the (3 1 1) X-ray profile of nickel as a function of the grinding time. It can be observed that the broadening of the peak increases on increasing the grinding time, in such a way that the K α doublet that appears well resolved on the XRD diagram of the unground sample becomes overlapping as the mechanical treatment progresses.

The values of the crystallite sizes and the microstrains calculated from the Williamson and Hall method for both the as-received and the ground samples of nickel are shown in Table I. These results show that the broadening of XRD peaks is mainly produced by the microstrains generated during the comminution, rather than by the diminution of the crystallites sizes.

TABLE I Crystallite size and microstrain of as-received and ground samples of nickel

Sample	D (nm)	ϵ
NiNG	120	1.3×10^{-5}
NiG3	100	3.8×10^{-4}
NiG30	100	8.1×10^{-4}

On the other hand, the SEM images of both NiNG and NiG30 samples included in Fig. 2 show that a diminution of particle size takes place during the comminution of nickel. This fact may be explained [11] by considering that the microstrains generated by the grinding of the material helps the contacts between the particles and, hence, their cold-welding.

Fig. 3 shows the changes in integral breadth, followed through the (3 1 1) reflection, of as-received and ground nickel powders after various 1 h annealing treatments at different temperatures. Peak broadening of the as-received powder is not affected by annealing in the temperature range studied. However, the line broadening of milled powders markedly decreases between 200 and 320 °C. Moreover, the starting temperature for recrystallization of the material decreases on increasing the grinding time in such a way that the mean X-ray peak broadening of the samples annealed at temperatures higher than 320 °C decreases according to the following trend: NiG30 < NiG3 < NiNG. In other words, Fig. 3 indicates that though the starting degree of crystallinity of the untreated nickel powder is initially higher than that corresponding to ground samples, the annealing-out of crystal defects in the temperature range at which the catalytic activity has been measured makes the previously milled powders more perfect materials than the original ones.

TABLE II Activation energy of the dehydrogenation of formic acid catalysed by the nickel samples

Sample	E(kcal mol ⁻¹) ^a
NiNG	8.2
NiG3	15.4
NiG30	20.7

^a4.19 J = 1 cal.

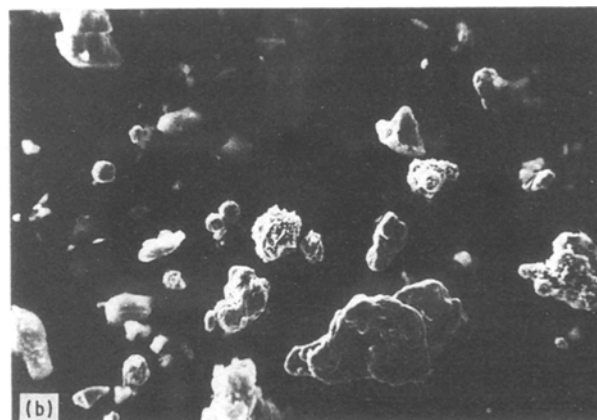
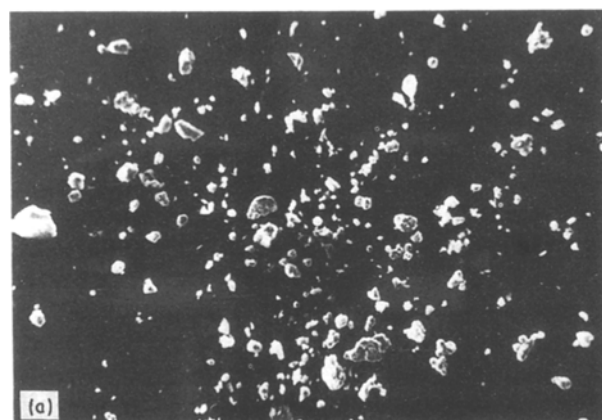


Figure 2 SEM images of nickel samples: (a) NiNG, (b) NiG30.

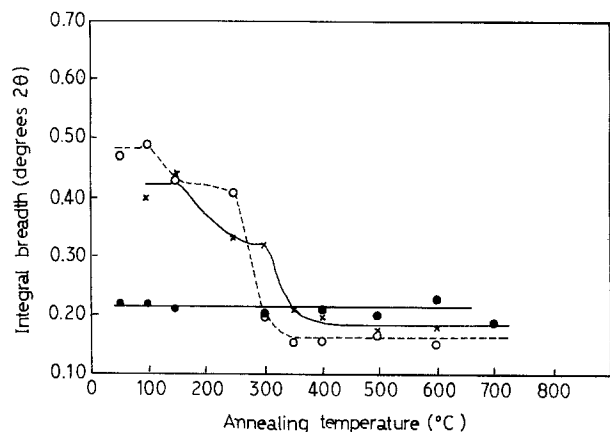


Figure 3 Influence of the annealing temperature on the integral breadth of the $K\alpha_1$ component of the (3 1 1) peak of nickel. (●) NiNG, (×) NiG₃, (○) NiG₃₀.

This fact has not been taken into account in the literature, and it explains why the activation energy for the catalytic dehydrogenation of formic acid is higher on NiG₃₀ than on NiNG, as the data shown in Table II indicate.

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