OPTIMIZATION OF THE SYNTHESIS PARAMETERS OF NANOCRYSTALLINE FE

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ABSTRACT

In this study work we have investigated in detail by X-ray diffraction the crystal refinement, the development of the microstructure and the optimization of the synthesis parameters of nanocrystalline Fe. Furthermore, the ball-milled Fe powders have been characterized in more detail with respect to their thermophysical properties using differential scanning calorimetry. The process of ball milling on powders of pure Fe has been particularly effective in determining a strongly reduction of the average grain size $<D>_v$ (~10 nm) and a high degree of structural disorder, like indicated from the results of X ray diffraction and differential scanning calorimetry.

Keywords: *Nano-Fe, Ball-Mill, Grain Size, XRD, DSC*

INTRODUCTION

It is of technological interest to investigate the evolution of the microstructure and the thermal stability of nanocrystalline materials [1,2]. In this study work we have investigated in detail by X-ray diffraction the crystal refinement, the development of the microstructure and the optimization of the synthesis parameters of nanocrystalline Fe. Furthermore, the ball-milled Fe powders have been characterized in more detail with respect to their thermophysical properties using differential scanning calorimetry.

MATERIALS AND METHODS

Pure iron powder (Alfa products, 99.999% purity) with a particle size of 5 μm was subjected to mechanical attrition by ball milling at room temperature for selected times, up to 16 h, in a hardened tool steel vial with a SPEX mixer mill model 8000. The weight of the mixed powder was about 6 g, and the powder/sphere mass ratio was 1/5. Than the mass of mixed powder was changed to about 3.5 g, and the powder/sphere mass ratio was 1/8. After different milling times (4, 8 and 16 h), the process was interrupted and a small quantity of the milled powder was removed. In the following, the different iron powder will be denoted just by means of the respective milling time.

Secondly, DSC was performed with a DSC 2010 CE with Thermal Analyser Instruments at heating rate 10 C/min from 40 ^{0}C up to 600 ^{0}C under steady Ar flow with a flow rate 40 cm^3/min using about 20 mg of the sample powder sealed hermetically in Al pans. The temperature and heat flow were calibrated using indium standard. For the determination of the total heat released during a DSC scan, a second run was performed on the samples and subtracted from the curve of the first run.

RESULTS

a) Optimization of milling parameters and evolution of the microstructure during milling.

The average grain size $<D>_v$ and the root-mean-squared strain $<\varepsilon^2>^{½}$ (microstrain) were evaluated by x-ray diffraction (XRD) through Warren Averbach analysis method [3,4]. The results are shown in Table 1.

Milling time (h)	Ratio m_p/m_s	Grain Size $\langle D \rangle_v$ (nm)	Microstrain $\langle \varepsilon^2 \rangle^{1/2}$ 1×10^{-3}
4	1/5	18.7	3.3
8	1/5	13.4	5.2
16	1/5	12.4	5.5
8	1/8	10.2	6.6

Table 1: Average grain size $\langle D \rangle_v$ and microstrain $\langle \varepsilon^2 \rangle^{1/2}$ in function of milling time, as obtained by Warren Averbach analysis method.

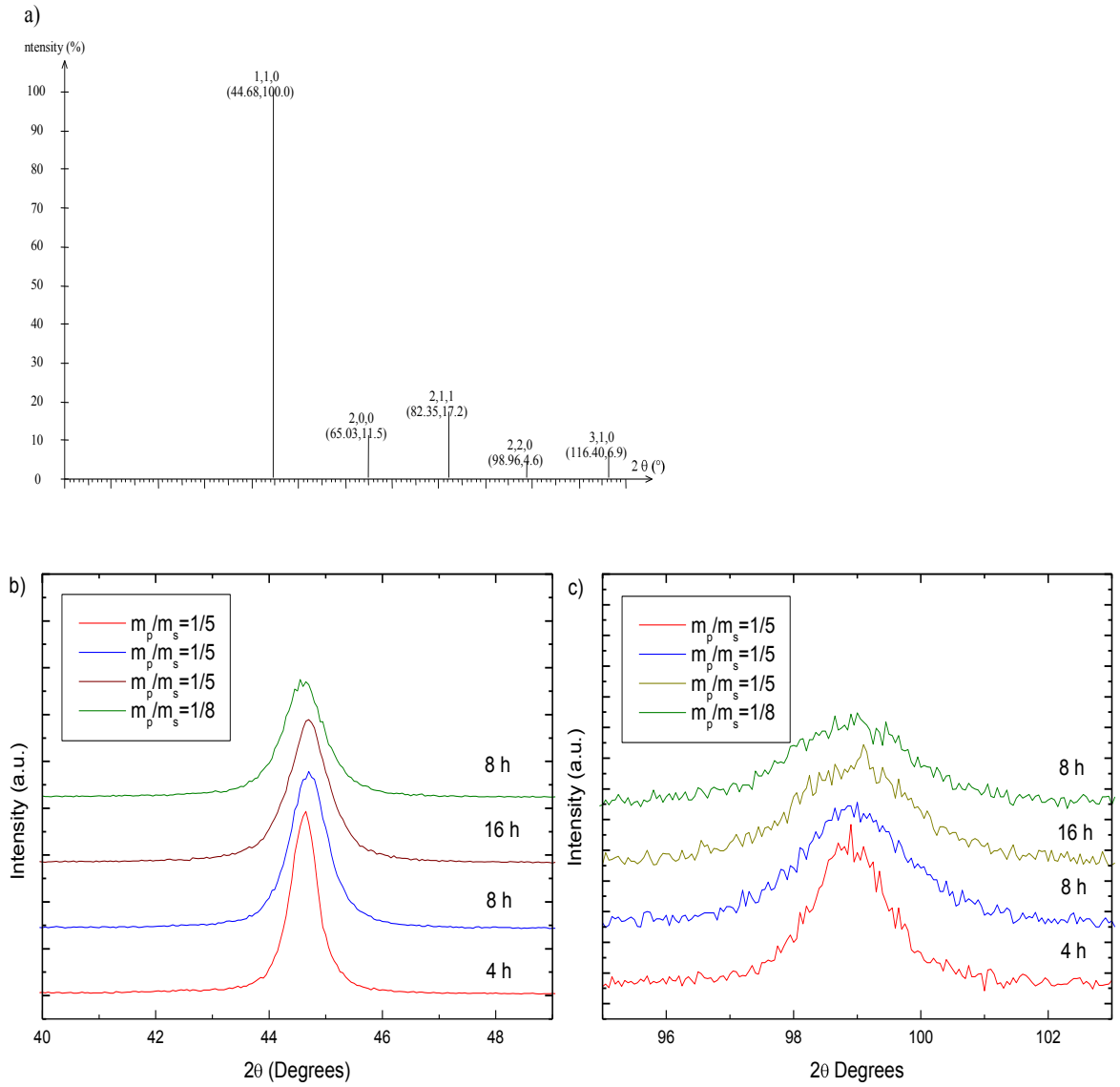

Figure 1: XRD a)peaks of un-milled Fe powders, b) (110) peaks of as-milled Fe powders, c) (220) peaks of as-milled Fe powders.

A strong grain size reduction is experienced in the first hours of the mechanical attrition. Changing the powder/sphere mass ratio to 1/8, a size reduction difference is investigated in comparison of the powder/sphere mass ratio 1/5.

The microstrain, due to the deformation induced by ball milling, strongly increases at short milling times and tends to a constant value for times in excess of 16 h milling (Table 1).

The microstrain and grain-size evolution during ball milling are in agreement with those reported by other authors.

In figure 1 are shown uncorrected diffraction peaks (110) and (220) of Fe powders in four different conditions: 3 samples milled for 4, 8 and 16 h with the powder/sphere mass ratio 1/5, and one sample milled for 8 h with the powder/sphere mass ratio 1/8. The initially sharp diffraction lines of the structure of Fe (Figure 1a) are significantly broadened after 16 h of ball milling. This broadening of Bragg peaks is caused by both the small size of the diffracting grains and by atomic level strain. Sophisticated Fourier techniques, such as the Warren-Averbach method, have been developed to separate these two effects, but this has required very careful measurements of peak profiles in order to determine grain size and strain values with high accuracy. Often, sufficient information about the changes in grain size and microstrain can be gained from the full width at half maximum (FWHM) of the peaks.

Figure 1b,c shows the reduction of grain size with increasing milling for Fe powders. In the early stages of milling the crystal size decreases rapidly to less than 30 nm. Further refinement proceeds slowly, and the grain size finally reaches a steady-state value of about 12 nm after 16 h of milling in the case of the powder/sphere mass ratio 1/5 (Figure 2). Also, as it is evident from Table 1, increasing the powder/sphere mass ratio to 1/8 the grain size decreases more rapidly during the milling process (about 10 nm after 8 h of milling). In this last as-milled state the powder was found to have a grain size of about 10 nm and an atomic level microstrain 6.6×10^{-3}, as measured by XRD.

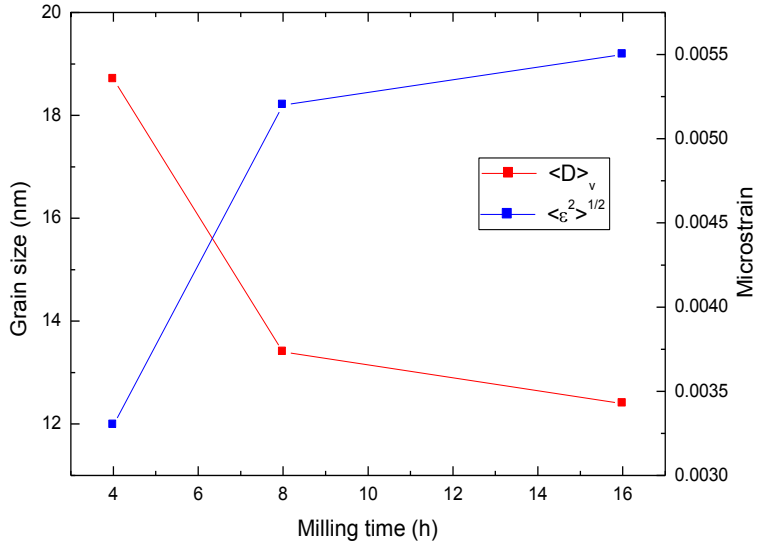

Figure 2: Evolution of the Grain size and microstrain in function of milling time (powder/sphere mass ratio 1/5).

b) Thermal stability of the as-milled powders.

The thermal stability of the powders was examined by DSC [5]. The DSC trace given in figure 3 shows an exothermic heat release starting at 360 K and extending over the whole

temperature range of the DSC scan. The broad exothermic reaction, characteristic for relaxation, recovery and recrystallization processes, is almost completed at 870 K. Integration of the exothermal signal during isorate heating (10K/min) corresponds to the energy stored in the sample and released during heating. Total amount of heat released during the scan in all samples is presented in Table 2.

Milling Time	m_p/m_s ratio	ΔH (kJ/mol)
4	1/5	0.5
8	1/5	1
16	1/5	1.2
8	1/8	1.74

Table 2: Total amount of heat release during scan in function of milling time.

The total amount of heat released during the scan in the best sample (powder/sphere mass ratio 1/8) was ΔH=1.74 kJ/mol which is comparable to the 2 kJ/mol determined by Fecht et al. for ball-milled Fe [6]. The latter value correspond to 15% of the enthalpy of fusion of Fe of 14 kJ/mol. Moelle and Fecht found a heat release corresponding to 20% of the enthalpy of fusion. This higher value of stored enthalpy is conceivable since the vial temperature during the milling of these powders was kept 278 K, while the vial temperature in this study was considerably higher. In the steady state the milling process will consist of an equilibrium between the creation and the recovery of structural defects in the milled powder. Stored energy will cause the broad exothermic reaction in the DSC trace. The heat released during the DSC scan can be used to calculate the specific grain boundary enthalpy assuming that the stored energy within the crystalline regions is negligible, but this is out of scope of this work. The total excess enthalpy due to grain boundaries is given by [7]:

$$\Delta_g = \frac{3V_m\gamma_H}{\frac{D}{2}}$$

where g is a geometric factor taken as 1.67 and V_m is the molar volume.

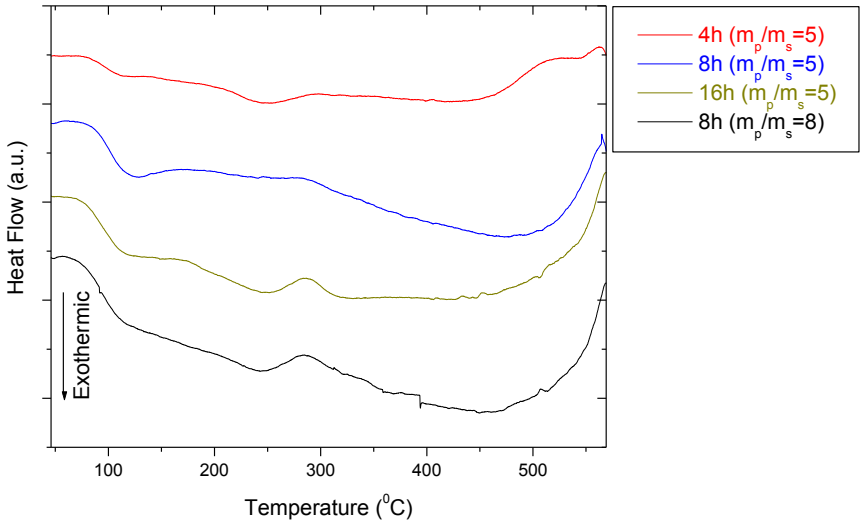

Figure 3: DSC trace of the as-milled Fe powders at a heating rate 10 K/min

DISCUSSION AND CONCLUSIONS

We have shown that mechanical attrition of pure Fe reduces the grain size and increases the lattice strain considerably. The final grain size is about 10 nm. Further refinements seems to be difficult to achieve. This was explained by considering the Hall-Petch relation:

$$\sigma_y = \sigma_0 + kd^{-\frac{1}{2}}$$

describing the dependence of the yield stress σ_y on the grain size d (σ_0 and k are constants for a given element). Although several recent studies reported controversial results on the validity of the Hall-Petch relation for nanocrystalline materials, it seems to be established now that the strength or the hardness of nanocrystalline solids increases with decreasing grain size.

Ball milling enhances the lattice strain considerably. The strain increases rapidly in the early stages of milling and reaches a maximum at the minimum grain size. Presumably, the main contribution to lattice strain in ball-milled powders is the dislocation density. In the early stages of milling the dislocation density increases rapidly due to the severe plastic deformation.

The observed enthalpies stored during ball milling are large compared with those reported for conventional techniques. For these techniques the stored enthalpy never exceeds a small fraction of the enthalpy of fusion. For the ball-milled powders the stored enthalpy reaches values up to about 40% of the enthalpy of fusion.

The process of attrition on powders of pure Fe has been particularly effective in determining a strongly reduction of the average grain size $<D>_v$ (~10 nm) and a high degree of structural disorder, like indicated from the results of X ray diffraction and differential scanning calorimetry.

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