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SURFACTANT EFFECT ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF Fe POWDERS PREPARED BY WET MILLING

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ABSTRACT. The effect of wet milling with benzene on the structural and magnetic properties of Fe powder was investigated. Average crystallite sizes of 14 nm and 7 nm were obtained for the dry-milled and wet-milled samples respectively. It was found that benzene reacts with the Fe powder during wet milling, carbon entering into the Fe structure. After annealing, the average crystallite sizes remained at 27 nm for dry-milled Fe and 25 nm for wet-milled Fe. Some of the benzene evaporated during annealing, however, a significant amount of benzene still remained in the powder mixture after annealing.

Keywords: *ball milling, surfactant, α-Fe, powders, crystal structure, microstructure.*

INTRODUCTION

Permanent magnets are used in a wide range of applications from small-scale electric and electronic devices to large-scale energy applications, becoming critical components for the development of advanced technologies. Recent developments in applications like the growing hybrid and electric car industry and in the energy sector with applications in wind turbine generators [1-3], where the quantity of magnetic materials is very high, have caused a strong increase in the demand for permanent magnets. Until recently, the lowest cost per energy-density unit was obtained for $Nd_2Fe_{14}B$-type permanent magnets [2-5]. However, a major disadvantage of rare-earth-based permanent magnets has emerged lately due to the high and fluctuating market price and unreliable supply of rare-earth elements [6, 7]. A proposed solution to this problem is to use magnets with

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reduced or no rare-earth content such as manganese based materials, soft/hard magnetic nanocomposites (spring magnets) [8] or the tetragonal distorted Fe based alloys or Fe-Co materials. For the new $Fe_{16}N_2$ phase obtained by chemical methods or in thin layers, the iron magnetic moment was reported to be 3.0 μ_B/Fe [9-11]. The problem, which remains to be solved, is given by the rather low coercivity and thermal stability. The introduction of atomic nitrogen in to the Fe structure is not a trivial task, as we want to avoid the formation of Fe-N chemical compounds. A proposed solution is to synthesise nitrided nano sized Fe powders by means of mechanical milling or annealing in a nitrogen rich atmosphere. The Fe crystallite size and distribution can be controlled through properly selected milling parameters, the most important ones being milling type, milling energy (speed and time), and process control agents (lubricants and surfactants) [12]. The use of a surfactant during milling minimizes cold welding between particles [12]. However, the surfactant can interact with the powder during milling, forming compounds which get incorporated into the powder particles during milling [12]. Hydrocarbons could introduce carbon into the powder particles, resulting in the formation of carbides [12]. In this work we investigate the effect of dry and wet milling on the structural and magnetic properties of Fe powders. The microstructure evolution and the elimination of the surfactant, used for wet milling, were investigated in annealed Fe powders.

EXPERIMENTAL DETAILS

The starting material used in this study was commercial NC 100.24 Fe powder (Höganäs product) below 40 μm. Two samples of milled Fe were prepared using a planetary mill (Fritsch Pulverisette 4). The first Fe powder sample was dry-milled in Ar for 4 h. The second sample was prepared by milling Fe powder mixed with 5 ml of benzene under Ar for 4 h. The milling vials (with a volume of 80 ml) and balls (diameter Ø = 15 mm) were made of 440C hardened steel. The ratio between the rotation speed of the disk and the relative rotation speed of the vials was Ω/ω=333/900 rpm with a ball-to-powder weight ratio of 10:1. Differential thermal analysis (DTA) was employed to study the structural transformations and phase transitions in the temperature range 100-700 °C under Ar atmosphere with a temperature ramp rate of 20 °C/min. A heat treatment was done at 400 °C for 1 h under vacuum. The structure and microstructure of the Fe powder samples were investigated using an Inel Equinox 3000 X-Ray diffractometer with Co K_α radiation and Bragg-Brentano focusing geometry. The average crystallite sizes of the powder samples were determined from the full width at half-maximum (FWHM) values of the diffraction peaks using the Williamson-Hall method [13]. The FWHM values were obtained by fitting the peaks using a normalized pseudo-

Voigt function. For the calculation of the average crystallite size, the instrumental contribution to the peak width was subtracted from the obtained FWHM values. The instrumental broadening was measured from the X-ray diffraction pattern of a reference sample. Magnetic susceptibility versus temperature measurements were recorded using a Faraday balance.

RESULTS AND DISCUSSIONS

The DTA curve of the 4 h wet-milled Fe sample shows two peaks centred around 330 °C and 550 °C respectively, which are not present in the dry milled samples, Figure 1. The 4 h wet-milled Fe sample annealed at 400 °C for 1 h shows only one DTA peak, around 550 °C. The absence of the peak at 330 °C in the annealed wet-milled sample could indicate the evaporation of benzene from the powder mixture. The peak at 550 °C corresponds to the decomposition of benzene into diphenyl [14]. The presence of this peak in the annealed wet-milled Fe sample indicates that while most of the benzene has evaporated, there is a significant quantity still mixed with the milled Fe powder. This fact proves the importance of the milling environment on the physical properties of milled powders.

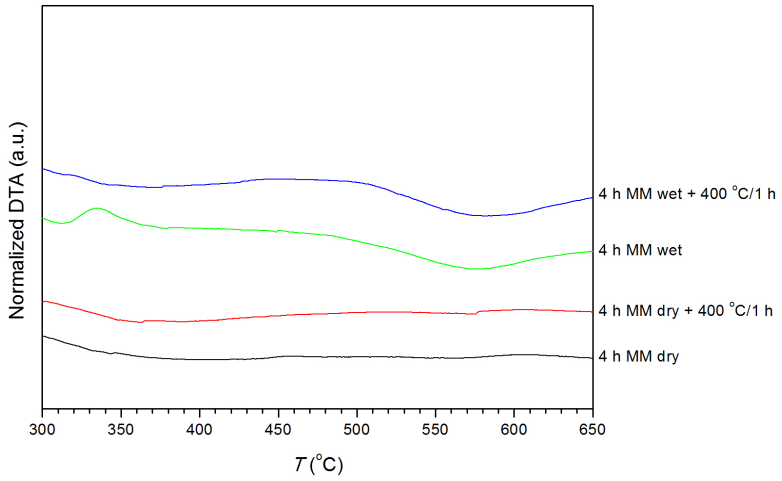

Fig. 1. Differential thermal analysis curves for the 4 h MM as-milled and annealed samples. For clarity, the curves were shifted vertically.

The X-ray diffraction (XRD) patterns for the as-milled and annealed Fe samples, along with the starting Fe sample are shown in Figure 2. The XRD peaks get broader after milling due to the smaller Fe crystallite sizes, Table 1, and the

presence of strain induced by milling. The Fe XRD peaks of the wet-milled sample are broader than those of the dry-milled one due to the smaller Fe crystallites of the wet milled sample. This is due to the reduced effect of cold welding during milling [12]. Because of the elimination of internal stress and crystallite growth after annealing, the XRD peak width diminishes. It is worthwhile to note that the annealed wet-milled Fe sample shows slightly smaller crystallite sizes compared to the annealed dry-milled one, Table 1.

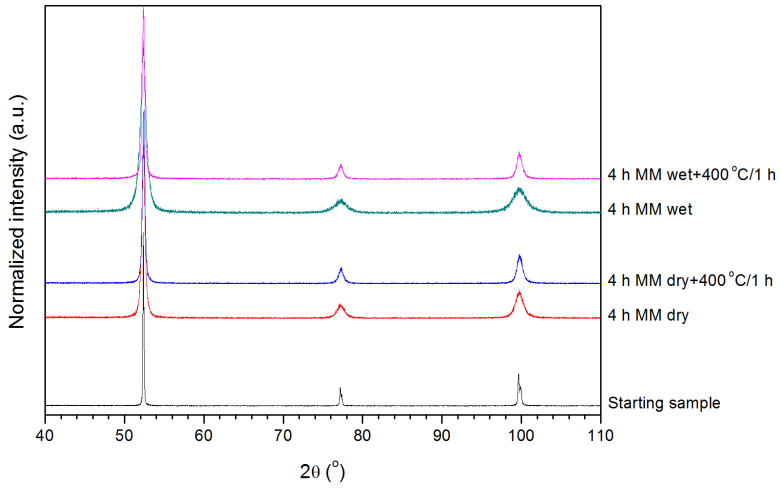

Fig. 2. X-ray diffraction patterns of the as-milled and annealed Fe samples. The XRD pattern of the starting Fe sample is shown for comparison. For clarity, the curves were shifted vertically.

Table 1 Average crystallite sizes, *d,* determined from XRD patterns for the as-milled and annealed Fe samples.

Sample	***d* (nm) ± 2 nm**
Fe 4 h MM dry	14
Fe 4 h MM wet	7
Fe 4 h MM dry + 400 °C/1 h	27
Fe 4 h MM wet + 400 °C/1 h	25

The thermomagnetic measurements for the as-milled samples, Figure 3, show that the 4 h dry-milled Fe sample shows almost no thermal hysteresis and a Curie temperature of about 765 °C. However, the 4 h wet-milled Fe sample shows a lower Curie temperature around 745 °C and a very broad thermal hysteresis. The lower Curie temperature of the wet-milled sample could be attributed to the

introduction of carbon in the Fe structure during milling due to the decomposition of benzene [12]. The broad thermal hysteresis could be attributed to the transformation of pearlite into austenite [15]. A similar behaviour was reported in the resistivity versus temperature curves for Fe containing 0.83% carbon, the pearlite to austenite transformation taking place around 730 °C and the reverse transformation occurring around 690 °C [15].

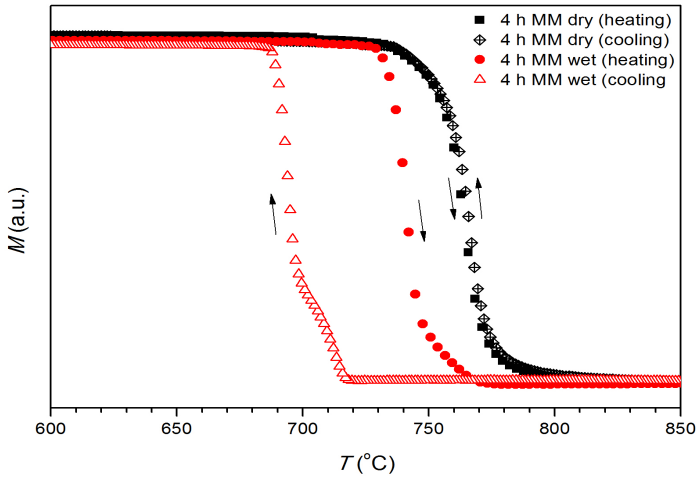

Fig. 3. Magnetization versus temperature curves during heating and cooling for the 4 h as-milled Fe samples.

CONCLUSIONS

The effect of dry and wet mechanical milling on the structural and magnetic properties of Fe powders was investigated. DTA investigations have shown that benzene evaporates during annealing, however, there was a significant quantity still mixed with the milled Fe powder after annealing. Milling with benzene led to smaller Fe crystallite sizes in both the as-milled and annealed samples. Thermomagnetic measurements indicated the entering of C in the Fe structure during wet milling, resulting from the decomposition of benzene.

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