Grain-Size and Alloying Effects on the Pressure-Induced bcc-to-hcp Transition in Nanocrystalline Iron

Jianzhong Jiang¹, Janus Staun Olsen² and Leif Gerward^{1, *}

¹Department of Physics, Technical University of Denmark, Fysikvej 307, DK-2800 Kgs. Lyngby, Denmark

²Niels Bohr Institute, H. C. Oersted Laboratory, University of Copenhagen, DK-2100 Copenhagen, Denmark

The pressure-induced bcc-to-hcp phase transformation has been studied by x-ray diffraction for bulk iron as well as nanocrystalline iron and a Fe₉₀Cu₁₀ alloy. The nanocrystalline material has a lower onset pressure and a larger pressure hysteresis than bulk iron. The non-random orientation of the nanocrystals is sensitive to shear stress in the high-pressure cell.

(Received February 26, 2001; Accepted June 8, 2001)

Keywords: phase transformation, transition pressure, nanocrystals, iron

1. Introduction

Three polymorphic phases of iron have been recognized at normal pressure: bcc α -Fe is stable below 906°C, fcc γ -Fe is stable between 906°C and 1401°C, and bcc δ -Fe is stable between 1401°C and the melting point at 1530°C at ambient pressure. The α phase has a Curie temperature of 769°C where the material changes from a ferromagnetic to a paramagnetic state. Based on shock wave research, Bancroft *et al.*⁽¹⁾ postulated the existence of a hcp high-pressure phase above 13 GPa at room temperature. This phase, which is called ϵ -Fe, has since then been verified in x-ray diffraction experiments by Takahashi and Bassett⁽²⁾ and others. Iron, one of the most abundant elements in the universe, is a prime candidate for materials constituting the earth's core, and it has been suggested that the inner core is composed of hcp ϵ -iron.

Several investigators have reported that the bcc-to-hcp transformation in iron occurs over a wide range of pressures and is apparently very sluggish. It has been suggested that the transformation is martensitic. Using x-ray diffraction, Giles *et al.*⁽³⁾ have found that with increasing pressure, the hcp phase becomes evident at about 13 GPa but the bcc phase persists to about 16 GPa. Upon decompression, the amount of hcp iron gradually decreases until the hcp completely disappears at about 4.5 GPa. The large hysteresis between forward and reverse transformation and the large range over which the two phases coexist are indicative of a martensitic transformation. Because of this hysteresis it is difficult to determine a unique transition pressure that represents the thermodynamic equilibrium between the two phases, *i.e.* the phase boundary in the pressure-temperature diagram.

Von Bagen and Boehler⁽⁴⁾ have demonstrated that the pressure range of the bcc-to-hcp transformation varies with increasing shear strength of the pressure medium. Moreover, they postulate that the hysteresis width is correlated to the crystal size of the sample. Accordingly, a single crystal would transform to the high-pressure phase more rapidly than a polycrystalline aggregate, since the latter contains more grain boundaries and other crystal defects. The aim of the present work is to study the grain-size effect on the bcc-to-hcp trans-

formation in iron by performing *in situ* high-pressure x-ray diffraction using synchrotron radiation and comparing bulk and nanocrystalline material. In addition, the alloying effect on the bcc-to-hcp transformation in ball-milled nanocrystalline Fe₉₀Cu₁₀ is investigated.

2. Experimental

Powders of bulk iron were obtained commercially (purity 99.9%). Nanocrystalline material was prepared in a planetary ball mill (Fritsch Pulverisette 5) using hardened stainless steel vial and balls as described by Jiang *et al.*⁽⁵⁾ After a milling time of 50 hours, the average grain size was about 15 nm (range 10–30 nm).

High-pressure x-ray diffraction spectra were recorded by the white-beam energy-dispersive method using synchrotron radiation. High pressures were obtained in a Syassen-Holzapfel type diamond-anvil cell. The sample and a small ruby chip were enclosed in a hole of diameter 0.2 mm in an Inconel gasket. Silicone oil was used as the pressure transmitting medium. The pressure was determined by the ruby fluorescence method. The Bragg angle associated with each series of diffraction spectra was determined from a zero-pressure spectrum of a NaCl powder in the diamond-anvil cell.

The relative volume V/V_0 of the sample can be described by the Birch⁽⁶⁾ equation of state

$$P/B_0 = \frac{3}{2}(x^{-7/3} - x^{-5/3}) \left[1 + \frac{3}{4}(B'_0 - 4)(x^{-2/3} - 1) \right] \quad (1)$$

where $x = V/V_0$, V being the volume at pressure P , and V_0 the zero-pressure volume. The parameters B_0 and B'_0 are the isothermal bulk modulus and its pressure derivative, both evaluated at zero pressure. Values of B_0 and B'_0 are obtained by a least-squares fit of eq. (1) to the experimental pressure-volume data.

*Corresponding author: E-mail: gerward@fysik.dtu.dk

3. Results and Discussion

3.1 Bulk iron

Figure 1 shows an energy-dispersive diffraction spectrum of hcp bulk iron at 19.2 GPa. The indices hkl of each reflection are given in the figure. All the lines of hcp ϵ -Fe (100, 002, 101, 102, 110, 103 and $2\bar{1}2$) are observed. In Table 1 the corresponding diffraction data are given. The refined unit cell dimensions are $a = 0.24532 \pm 0.00006$ nm and $c = 0.39372 \pm 0.00011$ nm, where the uncertainties are the standard deviations of the least-squares fit. These values are in good agreement with Takahashi and Bassett²⁾ who give $a = 0.245 \pm 0.001$ nm and $c = 0.393 \pm 0.001$ nm for the same pressure 19.2 GPa. It is noted that Takahashi and Bassett give $d = 0.184$ nm for the hcp 101 reflection. However, our value 0.187 nm is in better accordance with the given lattice constants as seen in Table 1. The observed intensities roughly agree with the calculated ones.

The observed lattice plane spacings d are shown as functions of pressure in Figure 2, where the bcc-to-hcp phase transformation is obvious from the appearance of new lines at high pressure. Also the large hysteresis in reverse transformation is evident (open symbols). In Figures 3 and 4 we show the compression curves for the lattice constants and the sample volume. At the transition, the sample volume is reduced by 5.0%. A least-squares fit of eq. (1) to the experimental pressure-volume data of bcc iron gives $B_0 = 169 \pm 2$ GPa and $B'_0 = 4.00$ (constrained) in good agreement with literature data.⁷⁾ The fit was limited to the pressure range $P < 14$ GPa

Fig. 1 Energy-dispersive x-ray diffraction spectrum of bulk hcp Fe at 19.2 GPa. Bragg angle $\theta = 5.925$ deg. The $2\bar{1}2$ peak partially overlaps with the $W K\alpha$ line.

Table 1 Observed and calculated d spacings of hcp iron at 19.2 ± 0.2 GPa and room temperature. Also rough estimates of the intensities are included. Refined unit cell dimensions $a = 0.24532 \pm 0.00006$ nm and $c = 0.39372 \pm 0.00011$ nm, $c/a = 1.605 \pm 0.001$.

d_{obs}/nm	$d_{\text{calc}}/\text{nm}$	hkl	I_{obs}	I_{calc}
0.21254	0.21245	100	40	30
0.19706	0.19687	002	50	40
0.18697	0.18697	101	100	100
0.14433	0.11440	102	5	12
0.12267	0.12266	110	5	15
0.11166	0.11166	103	3	15
0.10402	0.10411	$2\bar{1}2$	2	14

to avoid any problems with possible non-hydrostatic pressure (cf. below).

3.2 Nanocrystalline iron

The lattice plane spacings are shown in Figure 5 as functions of pressure. At the onset of the phase transformation, all the lines of hcp ϵ -Fe (100, 002, 101, 102, 110, 103 and $2\bar{1}2$) are observed. However, the intensity of the 002 reflection is found to decrease rapidly with increasing pressure, and for $P > 18$ GPa the hcp 002 reflection is absent (Figure 6). Such behavior of hcp metals is common and has recently been explained by an alignment of crystallites with the c -axis parallel to the load direction of the diamond anvil cell.^{8,9)} It is not believed that the disappearance of the 002 reflection is associated with another structural phase transformation, since the other hcp lines are still present at the expected positions. Moreover, there are no new lines that cannot be explained by the hcp structure, as has been reported for high-pressure, high-temperature studies.¹⁰⁾ The alignment effect is noticeable also for bulk iron, but not as strong as for the nanocrystalline material (the 002 intensity decreases with increasing pressure but will not vanish completely for the bulk sample).

Fig. 2 Lattice plane spacings d of bulk iron as functions of pressure. Squares denote the bcc phase and triangles the hcp phase. Filled symbols denote compression and open symbols decompression. Note the large hysteresis between forward and reverse transformation. Bcc indices are given to the left and hcp indices to the right.

Fig. 3 Lattice constants of bulk iron as functions of pressure. The notation is as for Fig. 2.

Fig. 4 Compression curve of bulk iron. The notation is as for Fig. 2. V is the unit-cell volume ($Z = 2$ atoms per unit cell) at pressure P , and V_0 is the zero-pressure volume of the bcc unit cell.

Fig. 5 Lattice plane spacings d of nanocrystalline iron as functions of pressure. The notation is as for Fig. 2. Note the complete disappearance of the hcp 002 line above 18 GPa.

Fig. 6 Energy-dispersive x-ray diffraction spectrum of nanocrystalline hcp Fe at 19.7 GPa. Same Bragg angle as for Fig. 1. Notice the disappearance of the 002 peak.

Apparently, nanosize crystallites are able to orient themselves preferentially more easily than larger crystallites in a non-hydrostatic stress field.

Because of the preferred orientation described above, any analysis based on integrated intensities in the diffraction pattern is uncertain. The determination of the lattice con-

Fig. 7 Lattice constants of nanocrystalline iron as functions of pressure. The notation is as for Fig. 2.

Fig. 8 Lattice constants of nanocrystalline $\text{Fe}_{90}\text{Cu}_{10}$ as functions of pressure. The notation is as for Fig. 2.

stants, however, is based solely on peak positions. Figure 7 shows the unit-cell parameters of the bcc and hcp phases as functions of pressure. The precision of the experimental pressure-volume data for the nanocrystalline material is not high enough to produce a unique set of values for B_0 and B'_0 in the least-squares treatment of the data.

3.3 Nanocrystalline iron-copper alloy

The nanocrystalline Fe-Cu alloy follows the same pattern as pure iron, and in Figure 8 we content ourselves with showing the unit-cell parameters as functions of pressure. The alloy is found to be less sensitive to the alignment effect related above and the relative intensities of the hcp reflections are those of a random orientation of the crystallites in the sample. We interpret this behavior as an alloying effect.

3.4 Onset pressure and hysteresis

In the hard sphere representation, the interplanar spacings of the bcc (110) and hcp (002) planes are identical. Accordingly, the bcc 110 line of the low-pressure phase continues as the hcp 002 line of the high-pressure phase (*cf.* Figs. 2 and 5). We have followed the bcc-to-hcp transformation by observing the intensities of the reflections belonging to the hcp 100, 002 and 101 triplet (*cf.* Fig. 1). In Fig. 9 we plot the ratio $(N_{100} + N_{101})/N_{110/002}$, where N_{100} and N_{101} are

Fig. 9 Onset of the bcc-to-hcp transformation. N_{100} and N_{101} are the numbers of counts in the hcp 100 and 101 peaks, respectively, and $N_{110/002}$ is the number of counts in the bcc/hcp 110/002 peak. Filled squares denote bulk iron, open squares nanocrystalline iron, and filled triangles nanocrystalline $\text{Fe}_{90}\text{Cu}_{10}$ alloy. The full lines have been drawn through the data points to determine the onset pressures.

Table 2 Pressure hysteresis of the $\alpha \leftrightarrow \epsilon$ transformation. Pressures are given in GPa.

	Bulk Fe	Nano Fe	Nano $\text{Fe}_{90}\text{Cu}_{10}$
Start of $\alpha \rightarrow \epsilon$	13	11	9
Finish of $\alpha \rightarrow \epsilon$	17	14	16
Start of $\epsilon \rightarrow \alpha$	8	7	6
Finish of $\epsilon \rightarrow \alpha$	5	1	5

the numbers of counts in the hcp 100 and 101 peaks, and $N_{110/002}$ is the number of counts in the bcc/hcp 110/002 peak. The ratio is zero in the bcc low-pressure phase and it is supposed to grow to a saturation value in the hcp high-pressure phase. As mentioned above, the crystallites in the hcp phase tend to orient themselves with a strongly preferred orientation, in particular in the nanocrystalline material, and therefore the intensity ratio does not follow the expected behav-

ior. In fact, for nanocrystalline iron the ratio goes to infinity, since the hcp 002 reflection vanishes at the highest pressures (*cf.* Fig 6). However, the intensity ratio can be used to monitor the bcc-to-hcp transformation in a small pressure range around the transition. In particular, it is possible to get a fairly well defined value for the onset pressure of the transition as seen in Figure 9. The pressure hysteresis between forward and reverse transformation is evident in Figures 2–5 and 7–8. Table 2 summarizes the results for the bulk and nanocrystalline materials used in the present work.

Acknowledgements

We thank HASYLAB-DESY for permission to use the synchrotron radiation facility. Financial support from the Danish Natural Sciences Research Council (through DAN-SYNC) and the Danish Technical Research Council is gratefully acknowledged. The project was supported by the IHP Programme “Access to Research Infrastructures” of the European Commission under contract nr. HPRI-CT-1999-00040.

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