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The microstructure of iron powders formed by high-energy, ballmilling is a function of processing conditions and processing time. In this study iron powder particles were processed in a high-energy ATTRITOR ball mill in a gaseous nitrogen environment. Total mechanically infused nitrogen concentration within the particles increased linearly with processing time. During the first 50 hr of ball milling, the mechanically processed powder developed a particle grain size of approximately 10 nm and a nitrogen concentration of approximately 0.9 wt. %. At 100 hr of milling, the nitrogen concentration exceeded 1.8 wt. % and, in addition to the nanocrystalline bcc-Fe phase, a second, finer, nanosize grain, bct-Fe phase had developed. X-ray diffraction and Mössbauer data were used to characterize and identify the nanocrystalline iron microstructure and to show that the majority of the mechanically infused nitrogen resided in grain boundaries. The nitrogen distribution and nanostructure were extremely stable, retaining the nitrogen concentration and the mechanically induced nanostructure until approximately the Fe–N α → γ eutectoid temperature. The extended thermal stability of the nanostructure suggests near-net-shape formation of nanocrystalline materials for commercial applications and material evaluation by superplastic deformation.

KEY WORDS: Iron; nitrogen; mechanical alloying; nanostructure.

1. INTRODUCTION

Material characteristics of nitrogen alloyed into iron are similar to those of carbon alloyed to iron. Both nitrogen and carbon alloy into iron as an interstitial solute and, as such, are very effective tensile strengtheners [1]. Nitrogen and carbon have a very limited solubility in bcc-Fe and readily form second-phase precipitates [2]. Both also have a much greater solubility in fcc-(γ)-Fe than in bcc-(α)-Fe, and both nitrogen and carbon help form and stabilize bct-Fe martensite when cooled through the fcc to the bct phase transition: γ → α′ [3]. However, unlike carbon, nitrogen is a gas and is not easily alloyed into iron. Nitrogen addition to bcc-iron has usually been accomplished through high-temperature, solid-state, surface diffusion nitriding [4, 5] or by melting under elevated nitrogen pressures [6, 7]. Recently, a new nitrogenating technology has been developed in which nitrogen concentration in excess of 1 wt. % can be added to bcc-iron powder: high-energy ball milling [8-11].

Studies of high-energy milling have shown that milling energy [12, 13], milling time [9], and processing environment [9, 10, 11, 14] influence the resulting powder particle microstructure [15].

Processing environment and conditions have been shown to affect the resulting microstructures when mechanical alloying nitrogen into iron. For example, processing iron powder in α-NH3 gas environment in a very high-energy “SPEX” mill resulted in an amorphous microstructure or in the development of Fe4N precipitate [16]. Similar results have been reported for iron powder processed in a planetary ball mill in a nitrogen gas environment [11]. However, iron powder processed in a nitrogen gas environment using a less energetic, “ATTRITOR,” ball mill [8, 9] for times in excess of...
250 hours resulted in an iron-nitrogen solid solution with nitrogen concentrations exceeding 7 at.% (more than 100 times the nitrogen equilibrium solubility concentration in bcc-Fe), and the development of bcc-Fe and bct-Fe nanosize grains [8].

Several previous studies of nitrogen supersaturated, cast, bcc-Fe alloys have started by forming nitrogen-rich, fcc-Fe solid solutions which were then quenched to form either a homogenous, nitrogen supersaturated bcc-Fe phase and/or a duplex microstructure of bcc-Fe and nitrogen stabilized bct-Fe martensite phase [17–20]. During subsequent thermal aging of these nitrogen supersaturated bcc-Fe and bcc-/bct-Fe microstructures, the nitrogen consolidated and formed a locally ordered, nano-size bct-(Fe,N) microstructure [17, 21] that was initially coherent with the matrix bcc-Fe phase. However, with continued thermal aging, the nitrogen continued to consolidate and evolve into localized regions with a highly ordered bct-Fe$_{16}$N$_2$ structure which subsequently became separate incoherent Fe$_{16}$N$_2$ precipitates, and, if aged at temperatures above 500 K eventually transformed this microstructure into bcc-Fe$_{4}$N precipitates. Thus, the nitrogen supersaturated bcc-Fe matrix evolved by the classically described Guinier-Preston sequence from a supersaturated iron-nitrogen alloy into two phase, bcc-Fe and iron nitride, microstructure.

Martensite or bct-Fe is a metastable phase formed from fcc-Fe. The more common means of forming and developing martensite (by temperature and/or stress induced lattice transformation from fcc- to bcc-Fe in carbon-iron and nitrogen-iron alloys) have been well characterized and explained [3, 19, 22–27]. For example, one form of bct-Fe martensite develops by directional shearing along select crystalline fcc-Fe planes. The resulting martensite microstructure has a definite directional orientation relationship with respect to the fcc-Fe matrix from which it formed.

In this study, for the first time nanocrystalline, bct-Fe martensite was produced from bcc-Fe by processing iron powder in a ball mill in a nitrogen gas environment. Nanosize bct-Fe grains were formed on the nitrogen-rich grain boundary; no phase orientation relationship between the bcc-Fe grains and the newly formed bct-Fe grains was observed. Mössbauer analysis of mechanically alloyed iron powder suggests grain boundary widths between 0.5 and 1.0 nm depending upon alloying element [28].

Also in this study, the formation of mechanically processed bct-Fe process is presented. Both the change in powder microstructure during ball milling and the infusion of nitrogen into iron powder during mechanical processing are shown to be essential in the formation of bct-Fe. Nitrogen infusion, X-ray diffraction, electron microscopy, and Mössbauer data from the milled particles are consistent with recently developed theoretical models of mechanical processing iron powder in gas environments [29].

During mechanical processing, iron particles underwent extensive cold-working, repeated fragmenting, and cold welding, resulting in near-spherical, micrometer-size particles with nanosize grains. Also, during milling, nitrogen gas was adsorbed onto the freshly created surfaces where it rapidly dissociated [30–33], and subsequently was incorporated into the iron particles during cold-welding. The infused nitrogen thus resided principally on grain boundaries. The low solubility of nitrogen in bcc-Fe limited the concentration of nitrogen that could diffuse into the grain. With continued cold-working, several microstructures developed: (i) as-received, annealed bcc-Fe, (ii) cold-worked bcc*-Fe, (iii) nitrogen-enriched bcc-Fe(N), and (iv) nitrogen-stabilized bct-Fe (N).

2. EXPERIMENTATION

Two runs of approximately 500 g of iron powder (99.9% pure) were placed in a high-energy ball mill (ATTRITOR) with a processing media of 5 mm diameter, 440C stainless steel balls. Ball-to-powder ratio was approximately 15:1. The ATTRITOR rotational speed was 300 rpm. During each ball-mill run, the processing tank was continuously flushed with nitrogen gas. In one run, approximately 10- to 25-g powder samples were removed at several stages during the 100-hr run. In a second iron-nitrogen run, the powder was processed without interruption for 100 hr.

Nitrogen analysis was determined using a LECO model TC 436 gas analyzer.

X-ray diffraction was used to characterize the nanosize microstructure, electron microscopy was used to characterize the submicrometer and nanosize microstructure, and Mössbauer analysis was used to characterize the interatomic microstructure. Using these techniques, the following were determined: (1) particle size distribution, (2) nitrogen and oxygen concentration, (3) phases present, (4) lattice d-spacing, (5) internal strain, (6) crystallite size, (7) atomic configuration surrounding the iron atoms, and (8) nitrogen distribution. X-ray line-shape analysis of the (110) bcc-Fe iron peak was used to determine the internal strain and crystallite size, and to characterize the microstructure. Electron microscopy was used to examine the nanosize microstructure. Möss-
bauer analysis was used to determine the local iron atomic arrangement and the position of the infused nitrogen, characterizing the atomic structure.

Three X-ray diffractions studies were conducted. In the first two studies, X-ray diffraction was conducted with monochromatic Cu-Kα radiation. Two X-ray scans were run on each sample. The first, 0–2θ scan (an extended scan used to determine the phases present) covered from 25° to 95° at a resolution of 0.02° with 1-sec sampling at each step. The second X-ray scan was a limited, higher resolution scan from 38° to 50° (the centroid of the (110)-Fe peak was at approximately 44.5°) at 0.02° resolution with 4-second sampling at each step.

X-ray diffraction patterns were analyzed for d-spacing, crystallite size, and internal strain using two different techniques: (i) Fourier single-line (i.e., the line shape is resolved into its Fourier components from which the instrument, stress, and strain effects are determined) and (ii) Warren-Averbach multiple line (plot of full-width-half-maximum, FWHM, versus line theta value for determination of crystallite size and internal strain). The difference in analytical results between the two techniques was within experimental error.

In the third study [34], Rietveld analysis was carried out on X-ray scans from 10° to 145° using the Reitan-Izumi program. For crystallite size-strain analysis, the Williamson-Hall technique was used.

Several high-temperature, thermal stability studies of powder mechanically processed in argon and nitrogen for 100 hr were conducted. Samples were placed on the X-ray hot-stage and X-ray diffraction scans were taken every 100 K from room temperature to 900 K after aging for 1 hr at each temperature. In a second set of high-temperature experiments, samples were aged for 100 hr (i) at 400 K to determine if Fe16N2 could be formed, and (ii) at 500 K to determine if Fe4N could be formed. Finally, thermal gravimetric analyses (TGA) were conducted on samples to measure nitrogen weight loss as a function of temperature.

Mössbauer analysis was conducted at three laboratories.

Researchers at the laboratories used mechanically processed powder from the same run. Each researcher used the analytical techniques that they were most familiar with, and although the interpretation of the results are nearly identical for the different laboratories, the analytical techniques used by each produce data which, although similar, are not identical. A summary of results is presented in Table VI.

Mössbauer spectra of as-received and ball-milled powder samples were recorded and analyzed at 300 K, using a 25-mCi source of 57Co/Rh at three laboratories: (1) Old Dominion University, Virginia, USA [Dr. Desmond Cook], (2) Institute for Metal Physics, Kiev, Ukraine [Dr. Vladimir M. Nadutov], and (3) Group de Spectrometrie Mössbauer, Nancy, France, [Drs. J. M. Genin and I. Fall].

Particle surface morphology and cross-sectional microstructure of the mechanically processed particles were obtained by electron microscopy: transmission (TEM) and scanning (SEM). All examinations were conducted on particles that had undergone 100 hr of processing. Surface morphology was obtained from as-received and processed particles. Intergranular structure was obtained from cross-sectional and replica mounts. Cross-sectional microstructure was determined from samples mounted in epoxy. The final polishing media used was 0.25-μm diamond. The same cross-sectional surface was also examined by both scanning electron microscopy and atomic force microscope. In addition, a carbon replica of the polished surface was made for TEM analysis. To examine the intragranular structure, samples were microtomed from the epoxy mounts and examined on a high-resolution transmission electron microscopy.

3. DATA AND ANALYSIS

Results of the analysis of the mechanically processed powder as a function of processing time are presented in Table I. For each stage of processing, the analysis includes (1) total nitrogen concentration, (2) particle size, (3) crystalline phase identification from the extended X-ray diffraction pattern, and (4) (110)-Fe X-ray line deconvolution analysis, including (a) lattice d-spacing, (b) FWHM for the deconvoluted lines, (c) grain (or crystallite) size and internal strain, and (d) relative intensity (as determined by the integrated area under the curve). Included in Table I are the results of the uninterrupted run of mechanically processed iron powder in nitrogen environment for 100 hr.

3.1. Nitrogen Concentration

As observed previously in ball-milling experiments of iron powder in a nitrogen environment [8], nitrogen concentration increased linearly with processing time (Fig. 1):

\[ N, \text{wt} \% = 0.018 \text{ (processing time, hours)} \]  \hspace{1cm} (1)

The effect of mechanical processing on particle size distribution (Fig. 2) of similarly prepared powder has pre-
Table 1. X-ray Diffraction Analysis As Function of Processing Time

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>0</th>
<th>4</th>
<th>9</th>
<th>16</th>
<th>24</th>
<th>36</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>100**&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>[N], wt. %</td>
<td>0.006</td>
<td>0.028</td>
<td>0.051</td>
<td>0.136</td>
<td>0.295</td>
<td>0.50</td>
<td>0.87</td>
<td>1.31</td>
<td>1.82</td>
<td>1.88</td>
</tr>
<tr>
<td>Phases</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;, α&lt;sup&gt;b&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;, α&lt;sup&gt;b&lt;/sup&gt;</td>
<td>α&lt;sup&gt;a&lt;/sup&gt;, α&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Part. size, μm</td>
<td>30.2</td>
<td>46.5</td>
<td>12.6</td>
<td>7.8</td>
<td>7.5</td>
<td>7.5</td>
<td>7.3</td>
<td>6.4</td>
<td>6.1</td>
<td>—</td>
</tr>
<tr>
<td>bcc</td>
<td>d-spacing, nm</td>
<td>0.2027</td>
<td>0.2026</td>
<td>0.2029</td>
<td>0.2029</td>
<td>0.2030</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>FWHM, 2θ</td>
<td>—</td>
<td>0.36</td>
<td>0.69</td>
<td>0.74</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>grain size, nm</td>
<td>—</td>
<td>27.6</td>
<td>19.1</td>
<td>16.9</td>
<td>14.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>strain, %</td>
<td>—</td>
<td>0.23</td>
<td>0.62</td>
<td>0.72</td>
<td>0.76</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>bcc&lt;sup&gt;a&lt;/sup&gt;</td>
<td>d-spacing, nm</td>
<td>—</td>
<td>0.2026</td>
<td>0.2034</td>
<td>0.2033</td>
<td>0.2033</td>
<td>0.2031</td>
<td>0.2033</td>
<td>0.2033</td>
<td>0.2033</td>
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<tr>
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<td>FWHM, 2θ</td>
<td>—</td>
<td>1.60</td>
<td>2.00</td>
<td>2.47</td>
<td>1.37</td>
<td>1.01</td>
<td>1.16</td>
<td>1.21</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>grain size, nm</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>12.0</td>
<td>10.4</td>
<td>7.1</td>
<td>5.8</td>
<td>5.2</td>
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<td>strain, %</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.87</td>
<td>1.00</td>
<td>0.80</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>rel. intens. %</td>
<td>—</td>
<td>0.005</td>
<td>0.03</td>
<td>0.04</td>
<td>0.34</td>
<td>1.00</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>bct</td>
<td>d-spacing, nm</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.2073</td>
<td>0.2085</td>
</tr>
<tr>
<td></td>
<td>FWHM, 2θ</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.18</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>rel. intens. %</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.05</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<sup>a</sup>α = bcc-Fe.
<sup>b</sup>α<sup>a</sup> = nitrogen-enhanced, cold-worked, bcc-Fe.
<sup>c</sup>α<sup>b</sup> = bct-Fe (martensite).
<sup>d</sup>** = second mechanical processing run.

Previously been described [8]. Only average particle size is presented in Table I.

3.2. X-ray Analysis

The extended X-ray diffraction patterns (using Warrens-Averbak [35] and Williamson-Hall [36] analyses) of samples mechanically processed 100 hours in argon [8] and in nitrogen are presented in Table II. Microstructure analysis obtained from the extended X-ray scan and from the higher resolution limited scan (110)-Fe peak were compatible. Both techniques had similar results.

Analysis of the X-ray diffraction region surrounding the bcc-(110)-Fe peak (35°-55°) was used to obtain information about phase microstructure. As shown in Fig. 3, the line shape associated with the (110)-Fe peak increased its FWHM and shifted its peak position with increasing processing time. Line-shape analysis was used to deconvolute the (110)-bcc-Fe peak into separate line shapes which were then used to determine the presence of secondary phases and their individual crystallite size and strain (Table I).

Hot-stage X-ray diffraction results for the deconvoluted (110)-Fe peak are presented in Table III for iron powders processed for 100 hr in both argon and nitrogen.

Fig. 1. Nitrogen concentration as a function of mechanical processing time.

Fig. 2. Plot of particle diameter distribution as a function of processing time.
environments. Analyses include line-shape deconvolution for phase identification, crystallite size and internal strain.

3.3. Nitrogen Distribution

Nitrogen distribution for the different mechanically produced microstructures as a function of processing time is presented in Table IV. The nitrogen concentration within each phase was determined by subtracting the lattice $d$-spacing, determined from deconvoluted line shape X-ray analysis, from the corresponding as-received lattice $d$-spacing, and multiplying by the appropriate factor for lattice expansion due to interstitial nitrogen [3, 37, 38].

$$d = d_0 + k_0[N, \text{ at} \%] \quad (2)$$

for bcc phase: $d_0 = 0.2866 \text{ nm}$, $k_0 = 8.0 \times 10^4 \text{ nm/ at.} \% \text{ N}$; for fcc phase: $d_0 = 0.3572 \text{ nm}$, $k_0 = 7.8 \times 10^4 \text{ nm/at.} \% \text{ N}$. Determination of the excess nitrogen, the nitrogen not previously accounted for as interstitial nitrogen, is presented in Table IV.

Determination of nitrogen grain boundary concentration is presented in Table V. For the powders that had undergone extensive mechanical processing, i.e., those with a heavily cold-worked microstructure, the correlation relating the excess nitrogen concentration (weight percent) not accounted for as interstitial nitrogen (excess d, Table IV) as a function of inverse crystallite size ($d = \text{nanometers}$) was used to determine the nitrogen associated with the grain boundary (Fig. 4).

$$[N, \text{ wt} \%] = -0.71 + 12.3(1/d, \text{ nm}), \quad R^2 = 0.99^+ \quad (3)$$

The large negative constant, $-0.71$, in Eq. (3) is an artifact of the starting powder size which had no nitrogen on the surface. The nitrogen concentration associated with the grain boundaries is approximately one nitrogen atom per unit surface cell. Analysis suggests that the border surrounding the individual grains contains most of the infused nitrogen.

3.4. Mössbauer Analysis

Two approaches were used to understand the Mössbauer results. The first approach was qualitative, consisting of visual examination of the Mössbauer patterns (Fig. 5). Secondary Mössbauer features that were overwhelmed by the presence of the dominant $\alpha$-Fe pattern were determined by subtracting the Mössbauer pattern of unprocessed iron from the Mössbauer pattern of the mechanically processed powders. The effect of mechanical processing was also determined by subtracting iron powder processed in argon from iron powder processed in nitrogen (Fig. 6). In both cases, the subtracted patterns revealed that a definite substructure existed in the powders processed in nitrogen.

In the second approach, the Mössbauer spectra were
deconvoluted and the quadrupole splitting, the isomer shift, and the hyperfine field for different possible Fe–Fe and Fe–N atomic neighbor configurations were determined (Table VI). Powders were analyzed at three different facilities. Deconvolution results are highly dependent upon the technique (software) used in the analysis. The results from the different laboratories were similar and are consistent with the formation of a bcc-Fe phase in the powders processed in a nitrogen environment for times in excess of 50 hr.

3.5. Microscopy

Electron microscopy examination showed that during the initial phase of mechanical processing the particles underwent severe cold-working, resulting in particle flattening. With continued processing the particles began to fragment. Fragmented pieces were then cold-welded, resulting in micron-size, nearly spherical particles (Fig. 7). Cross-sectional examination of the processed particles showed the development of nanosize grains [52]. Grain size for particles processed for 100 hr, determined by TEM and X-ray diffraction, were similar: approximately 10 nm. In addition, the TEM analysis suggests a grain-boundary width approximately 1 nm in diameter [52].

4. RESULTS AND DISCUSSION

4.1. Microstructure

Results of microstructure analyses are presented in Tables I–VI.

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**Table IV. Nitrogen Concentration Analysis (Wt. %)**

<table>
<thead>
<tr>
<th>Processing, hr</th>
<th>16</th>
<th>24</th>
<th>36</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.30</td>
<td>0.50</td>
<td>0.87</td>
<td>1.31</td>
<td>1.82</td>
</tr>
<tr>
<td>Total measured [N]</td>
<td>0.12</td>
<td>0.11</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Analysis for interstitial bcc-Fe nitrogen</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>As-received: bcc [N]</td>
<td>0.02</td>
<td>0.19</td>
<td>0.50</td>
<td>0.87</td>
<td>1.31</td>
</tr>
<tr>
<td>3</td>
<td>Excess (a)</td>
<td>0.01</td>
<td>0.11</td>
<td>0.23</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>Cold-worked: bcc* [N]</td>
<td>0.01</td>
<td>0.08</td>
<td>0.27</td>
<td>0.59</td>
<td>0.98</td>
</tr>
<tr>
<td>Analysis for nitrogen clusters: bcc**</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>Cluster: bcc** [N]</td>
<td>0.01</td>
<td>0.08</td>
<td>0.27</td>
<td>0.59</td>
<td>0.63</td>
</tr>
<tr>
<td>7</td>
<td>bct [N]</td>
<td>0.01</td>
<td>0.08</td>
<td>0.27</td>
<td>0.59</td>
<td>0.95</td>
</tr>
<tr>
<td>Analysis for nitrogen stabilized martensite: bct</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>Grain boundary [N]</td>
<td>0.00*</td>
<td>0.13</td>
<td>0.29</td>
<td>0.54</td>
<td>1.01</td>
</tr>
<tr>
<td>11</td>
<td>Excess (c)</td>
<td>0.00</td>
<td>−0.05</td>
<td>−0.02</td>
<td>0.05</td>
<td>−0.06</td>
</tr>
</tbody>
</table>

**Table V. Determination of Nitrogen Surface Concentration**

| Surface area for crystallite after 50 hr of processing: $x^2 = x(5.0, \text{nm})^2$ | 785 nm$^2$ |
| Surface area of bcc-Fe unit cell: $(0.2866, \text{nm})^2$ | 0.818 nm$^2$ |
| Number of surface cells on crystallite | 960 |
| Volume of crystallite after 50 hours of processing: $(4/3)x^3 = (4/3)x(5.0, \text{nm})^3$ | 524 nm$^3$ |
| Volume of bcc-Fe unit cell: $x(0.2866, \text{nm})^3$ | 0.0235 nm$^3$ |
| Number of bcc-Fe cell in crystallite | 22300 |
| Number of Fe atoms per crystallite: 2 atoms per unit cell | 44600 |
| Atom percent excess nitrogen (Eq. (1)): $\approx 4\text{wt. \%}$ $[N] = 0.71 + 0.022 \times 44600$ | 2.16 at. % |
| Total number of excess nitrogen atoms associated with crystallite: $0.022 \times 44600$ | 980 atoms |
| Number of nitrogen atoms per unit surface cell $\approx 1$ | — |
Nitrogen concentration increased linearly (Fig. 1) and both the particle size and the crystallite or grain size (listed as grain size in Table I) decreased (Fig. 8) with processing time. Mechanical processing of iron powder for 100 hr in a nitrogen gas environment resulted in a nitrogen concentration in excess of 1.8 wt.% nitrogen. The shape and morphology of iron particles changed with increased processing (Fig. 7). X-ray diffraction, TEM analysis, and Mössbauer analysis did not detect the presence of iron-nitrides.

4.2. X-ray

Deconvolution of the (110)-bcc-Fe peak as a function of processing time and environment is shown in Fig. 9.

X-ray diffraction analysis of powders processed for the first 25 hr detected only the bcc-Fe phase. The line shape associated with the (110)-Fe peak was composed of two X-ray lines at approximately the same lattice d-spacing but with different line shapes, i.e., different FWHM values, characteristic of a single-phase material with grains of different crystallite sizes, strains, and/or alloy composition. Line centroids at approximately the same peak position indicate that both peaks are associated with identical phase structure (in this case bcc-Fe) and similar lattice parameters (Table I). The small shift in lattice d-spacing between the deconvoluted lines indicated either that some particles or local regions within the particles had higher interstitial nitrogen concentrations and/or that some regions of the particle had uniform strain.
The two deconvoluted line shapes were analyzed for crystallite size and interior strain. The line with the smaller FWHM value (< 1.0) was determined to have larger crystallite size and lower strain, i.e., less cold work, indicative of the unprocessed, as-received, annealed particles. The line with the larger FWHM (> 1.0) was associated with particles that had undergone mechanical processing and had undergone extensive plastic deformation, resulting in smaller crystallite (grain) size and greater strain than the as-received powder grains.

Note. Computer line-shape analysis used in this study assumes a constant, uniform alloy composition. There is a possible, and reasonable assumption, that part of the line shape may result from nonuniformity in the nitrogen concentration within the particle. The presence of heterogeneous nitrogen concentration within different grains would broaden the line shape and thus would affect the crystallite size and internal strain. Although the possible heterogeneity in nitrogen concentration problem is recognized and acknowledged, no analysis of the concentration effect was attempted. It should be noted, however, that even at room temperature the diffusion rate of nitrogen is sufficiently rapid that an interstitial atom of nitrogen can diffuse approximately 30 nm in 24 h [39, 40]. Therefore, the nitrogen distribution within the particle can be considered to be in "quasi-equilibrium" during the mechanical alloying. All X-ray and Mössbauer analyses were conducted on the powder samples several hundred hours after they were removed from the ATTRITOR, giving nitrogen atoms sufficient time to diffuse throughout the particle to their most stable position within the particle. Thus, at the time of analysis, the infused nitrogen atom distribution was considered to be in its most favorable thermodynamically stable position.

After 36 hr, the particles developed a uniform cold-worked microstructure as indicated by the presence of...
only a single, broad X-ray peak with a lattice d-spacing of 0.2033 nm and a FWHM value slightly greater than 1.0 θ-value. The measured bcc-Fe lattice d-spacing, 0.2033 nm, was considerably less than the lattice expansion predicted, 0.2045 nm, for a nitrogen concentration of 0.87 wt.% (Fig. 10, Ref. 38). The measured lattice expansion could accommodate only a 0.31-wt.% concentration of interstitial nitrogen. Thus, because no nitrides were formed, the remaining measured 0.56 wt.% nitrogen must be associated with grain boundaries.

X-ray analysis of the powders processed in excess of 50 hr (Fig. 9) showed, in addition to the single, broad peak associated with powders processed for 36 hr, the development of a second, even broader peak (FWHM > 4.0 θ) with a (110)-bcc-Fe lattice d-spacing at approximately 0.2080 nm (i.e., the lattice parameter of 0.2080 nm for the (110) plane is approximately 0.2918 nm for the (001) plane of the tetragonal c-axis of bct-Fe in Table II). The formation of this new peak was unique to iron powder processed in a nitrogen environment and was not observed for iron powder similarly processed in argon [8]. Analysis of this new line shape determined the grain diameter was at best a couple of nanometers and the grain was free of strain (Table II). The lattice d-spacing for this line was consistent with the formation of either a coherent (202)-bct-Fe martensite/(110)-bcc-Fe microstructure [26] or the formation of nitrogen enriched bcc**-Fe clusters.

Three different means of developing this bct-Fe or bcc**-Fe nanostructure are feasible: (i) development of nitrogen rich, bcc-Fe (N) microstructures clusters or regions, (ii) nitrogen diffusion, consolidation, and localized ordering resulting in the development of coherent bct-Fe regions within the bcc*-Fe lattice, eventually leading to separate grains of martensite, and (iii) local atomic rearrangement from bcc*-Fe to bet-Fe at the nitrogen-rich grain boundaries to reduce stress resulting from mechanical processing and high concentration of nitrogen.

4.2.1. Nitrogen-Rich, bcc-Fe

If the 0.2080-nm d-spacing were due to the formation of nitrogen rich clusters, bcc**-Fe, the change
Fig. 7. SEM micrographs of mechanically processed powder as function of processing time: (a) as-received powder; (b) processed 8 hrs: ball-milling impacts have caused the particles to lose their spherical and random structure of (a) and start to flatten; (c) processed 25 hrs: particles continue to flatten and due to the extensive amount of cold-working begin to fragment; (d) processed 50 hrs: flattened particles and fragments begin to be cold-welded together forming thicker particles; (e) processed 75 hrs: with continued fragmentation and cold welding the particles begin to develop equiaxed microstructure; (f) processed 100 hrs: particles now a bimodal distribution of submicron particle fragments and of micron-size highly refined particles.
Fig. 7. Continued.
in lattice $d$-spacings would then be a measure of the local nitrogen concentration (Table IV [17, 24, 38]). The formation of these nitrogen rich regions would have resulted from continuous nitrogen diffusion (and consolidation), resulting in certain regions losing nitrogen and in other regions a gradual concentration of nitrogen into clusters. Thus, the (110)-bcc*-Fe (nitrogen rich clusters) peak would gradually evolve out of the bcc*-Fe (cold-worked) peak, i.e., the (110)-bcc*-Fe peak would gradually develop an asymmetric shape indicative of the development of nitrogen-rich bcc*-Fe regions within the particle. The appearance of the 0.2080-nm peak after 50 hr of processing is not consistent with this model of nitrogen redistribution. Note: Because of the low nitrogen solubility in the bcc*-Fe matrix, the nitrogen diffusion and consolidation must occur in the grain boundary region. More will be said about grain boundary nitrogen below.

Fig. 8. Particle size and grain size as a function of processing time.

Fig. 9. Deconvolution of X-ray diffraction peaks: (a) X-ray diffraction of Fe-[Ar] at 100 h: line analysis required no deconvolution, the line shape could be fitted to a small grain, cold-worked microstructure; (b) X-ray diffraction of Fe-[N] at 16 h: line shape required deconvolution into two peaks at approximately the same lattice $d$-spacing, one line identified with the as-received microstructure, the second with a cold-worked microstructure; (c) X-ray diffraction of Fe-[N] at 50 h: line shape analysis was similar to that of (a), a single line shape of small-grain, cold-worked microstructure; (d) X-ray diffraction of Fe-[N] at 100 h: line shape analysis again showed the presence of two line one associated with the cold-worked microstructure, the other was shifted to lower 2-$\Theta$ values.
4.2.2. Nitrogen Diffusion to Form bct-Fe

Jack [17] has shown that the low solubility and the rapid diffusion of nitrogen supersaturated bcc-Fe can result in the formation of a coherent bct-Fe/bcc-Fe duplex microstructure, which he designated the nitrogen-rich region bct-Fe structure: Fe₅N (x > 10). (It is important to note in his study the supersaturated bcc-Fe was obtained from quenched nitrogen rich fcc-Fe.) In this Fe₅N structure the nitrogen atoms are arranged along a preferred lattice direction (commonly designated the c- or z-direction). As a result of this interstitial nitrogen-matrix alignment, the clustered nitrogen atoms cause a local, preferred lattice expansion. The greater the nitrogen concentration, the greater the lattice expansion in the z-direction. The other two lattice bct-Fe dimensions in this nitrogen rich region remain essentially unchanged, i.e., the same as the adjacent bcc*-Fe lattice dimensions. This developing two phase microstructure is the interstitial equivalent of the more common, solid solution formation and development known as Grunniern-Preston precipitation.

In Table II the 0.2918-nm lattice parameter was assigned to the c-dimension of the bct-Fe lattice, whose other two dimensions are coherent with the bcc*-Fe lattice, 0.2877 nm. The Fe₅N microstructure has been shown to be very unstable, and with time and/or thermal aging, the nitrogen continues to coalesce and consolidate into incoherent iron precipitates, either bct-Fe₁₆N₂ or fcc-Fe₅N [3]. No iron-nitride precipitates were observed in the nitrogen rich mechanically processed powder either after mechanical processing or thermal treatment (400 and 500 K for 100 hr [thermal analysis presented below]). Therefore, the formation of the observed bct-Fe microstructure was not believed due to nitrogen diffusion and coalescence.

4.2.3. Mechanically Induced Grain Boundary Formation of bct-Fe

A third explanation for the observed change in line shape predicts the formation of bct-Fe as a natural consequence of mechanical processing in nitrogen. Deconvolution results for the extended X-ray diffraction pattern for iron processed for 100 hr in argon and nitrogen is presented in Table II. Results of the deconvolution are consistent with the presence of two phases, bcc-Fe and bct-Fe. One phase was a heavily cold-worked, bcc*-Fe lattice with a lattice parameter of 0.2876 nm. This lattice parameter is characteristic of iron powder processed in either argon or nitrogen environments, i.e., the bcc*-Fe crystallite structure resulting from ATTRITOR ball milling. The strains in the bcc*-Fe phases are about the same for iron powder mechanically processed in either nitrogen or argon, approximately 0.9%. The small difference in the lattice d-spacing between the powder processed in argon and in nitrogen is consistent with the low concentration of nitrogen in bcc-Fe.

The second lattice parameter, 0.2918 nm, was attributed to the c-axis of the bct-Fe (or α'-Fe [17] or martensite) lattice. Line shape results show this phase to have nanometer dimensions and to be strain free. Formation of a strain-free, bct-Fe, nanometer precipitate and the change in bcc*-Fe crystallite size (from 10 to 7 nm with the formation of the nanometer bct-Fe) [Table I] suggests that the formation of the bct-Fe phase is the result of very local shear deformations, most likely at the bcc*-Fe grain boundaries where the greatest stress is concentrated and the majority of the nitrogen is located (Table IV). Formation of nanosize bct-Fe grain boundary precipitates would simultaneously reduce the local strain, accommodate a high local nitrogen concentration, and decrease the bcc*-Fe grain size.

The development of extended grain boundary dimensions in mechanically processed iron powder has been shown to be related to the alloying element [28]. The decrease in grain size by approximately 1 nm when the iron powder was mechanically processed in nitrogen versus processing in argon (Table II) is consistent (i) with the mechanically infused or alloyed nitrogen being concentrated on/in the grain boundary, (ii) with the formation of a nitrogen-rich, extended grain boundary of approximately 1 nm around the mechanically alloyed grains, and (iii) with the eventual development of nitrogen stabilized bct-Fe nanosize grains within the extended grain boundaries.

As further support of the hypothesis that the new
phase was associated with a new lattice structure and not localized nitrogen enrichment, the change in lattice d-spacing as a function of nitrogen concentration was examined. If the 0.2080-nm X-ray peak was related to the formation of a bct-Fe lattice, the change in lattice d-spacing could again be used to determine the nitrogen concentration associated with bct-Fe lattice (Table IV, Refs. 17, 19, 24). Previous studies of nitrogen addition to martensite bct-Fe in cast bcc-iron alloys have reported a change in lattice spacing of 0.20268 nm + 0.0020 nm/wt.% nitrogen for the bct-Fe, (101)-plane [19, 24]. In this study the observed change in lattice d-spacing from 50 hr to 100 hr with respect to the measured change in nitrogen concentration was 0.0023 nm/wt.% consistent with the observed nitrogen-spacing change.

4.3. Thermal Stability

Thermal aging (for 100 hr at 400 and 500 K) of mechanically processed iron powder showed that the nitrogen enhanced nanosize microstructures were very stable [52]. Only small difference in X-ray line shape before and after thermal aging was observed, indicating little change in microstructure, nanocrystalline size, and internal strain. This small change in nanostructure is in spite of the fact that at the experimental temperatures and hold time, interstitial nitrogen atoms could have diffused a distance of approximately 4 μm [39], many times the average crystallite diameter and approximately halfway across an average particle. And, while iron atom diffusion within the bcc-Fe grain at these temperatures is essentially nil, iron atom diffusion along grain boundary is tens of millimeters [40]. In studies by Jack [17], similar aging conditions of nitrogen-super saturated bcc-Fe have resulted in the formation of iron-nitride precipitates. However, as previously stated, in this study no iron-nitrogen precipitates were formed during thermal aging, indicating that the nitrogen present in the mechanically processed powder must be in a stable configuration.

Thermal stability experiments from room temperature to 875 K (Table III) of the 100-hr mechanically processed powder also showed that the nanosize structure was stable (Fig. 11). X-ray diffraction in situ experiments showed that a trace amount of Fe₃N started to form at approximately 700 K (Fig. 12). Above 700 K, the concentration of bct-Fe and Fe₃N slowly increased with increasing temperature. Not until approximately 800 K did the bct-Fe and Fe₃N precipitate phase begin to grow rapidly. Above approximately 875 K, the concentration of bct-Fe phase decreased rapidly and eventually disappeared. The 900 K was the same temperature at which the thermal-gravitational-experiments showed that nitrogen rapidly diffused out of the powder and is approximately the α → γ eutectoid temperature for the Fe–N system (Fig. 13).

4.4. Mössbauer

Mössbauer analysis showed a significant differences in the local environments of the iron atoms depending upon mechanical processing time and environment. The raw Mössbauer spectra show a distinct but hard to quantify difference between processing conditions (Fig. 6a). Two different analytical approaches were used to interpret the Mössbauer spectra: (i) computer-aided deconvolution of the Mössbauer patterns into components characteristic of different Fe–Fe and Fe–N atomic configurations (Fig. 6 and Table VI), and (ii) spectra subtraction which presents a visual verification of the presence of secondary features (Fig. 5).

4.4.1. Spectral Deconvolution

Figure 6b (provided by Dr. V. M. Nadutov) shows the computer-analyzed Mössbauer spectra of pure iron and iron mechanically processed in nitrogen for 16 and 100 hr. Component 1 is the sextet for bcc-Fe. Components 2 and 3 are sextets associated with increasing amounts of cold-working and were identified from previous studies of Fe–N and Fe–C alloys as belonging to bct-Fe, i.e., with iron atoms with nearest- and next-nearest-neighbors nitrogen atoms [41]. Results of Mössbauer spectra for iron powder processed for 100 hr in argon and nitrogen analysis by Drs. Genin and Fall are (Table VI) provided qualitative in-
formation as to the amount of each different local structure present. In their analysis, the iron processed in argon showed a local environment that was dominated by the bcc-Fe lattice structure. A small portion of the lattice (approximately 16%) was associated with a more open structure. The iron processed in nitrogen had a smaller quantity of bcc-Fe iron atoms with no nitrogen nearest or next-nearest neighbors. The difference in Fe–Fe nearest neighbors for iron powder processed in argon and in nitrogen is consistent with the change in volume to surface ratio predicted for the difference in grain size measured by X-ray diffraction for processing in argon and nitrogen environments (Table II). The ratio of iron atoms with nearest- and next-nearest-neighbors nitrogen atoms is consistent with formation of nitrogen-assisted bct-Fe (42).

The computer analysis by Dr. Desmond Cook is in close agreement with Drs. Genin and Fall’s results (Table VI). The concentration of bct-Fe phase determined by Drs. Genin and Fall’s, and by Dr. D. Cook’s Mössbauer analysis is similar to that predicted by the X-ray diffraction analysis (Table I).

The Mössbauer spectra did not show the single peak in the center of the bcc-Fe sextet characteristic of fcc-Fe. And, in the analysis of the Mössbauer spectra, the hyperfine field associated with the nearest and next-nearest nitrogen neighbors is about 300 kOe. If Fe$_{16}$N$_2$ had formed the field would have been about 400; had Fe$_4$N formed the field would have been about 200 kOe, neither of which were observed [42].

4.4.2. Spectral Comparison

Although the above Mössbauer analysis provides quantitative data, examination of the mechanically processed Mössbauer spectra is dominated by the Fe–Fe spectra. To help clarify the presence of substructure, i.e., to be certain that the measured Mössbauer spectra contained information of the Fe–N interaction, the dominate Fe–Fe spectra has to be removed from the mechanically processed Mössbauer spectra.

To obtain a visual understanding of the effects of mechanical processing, the Mössbauer spectrum of an
unprocessed powder was subtracted from the Mössbauer spectrum of iron powder processed in argon for 100 hr (Fig. 5a). The resulting spectra showed only a random pattern. To characterize the effect of mechanical processing in nitrogen, the pure iron spectrum was subtracted from the spectrum of iron powder processed in nitrogen for 25 hr (Fig. 5b). The difference between the subtracted spectra (Fig. 5a, b) also indicated that there was no significant difference in the local iron environment during the initial stages of mechanical processing in nitrogen and in the local iron environment of heavily cold-worked iron powder in argon.

Figure 5c shows the result of subtracting a pure iron Mössbauer spectrum from a spectrum of an iron powder processed for 100 hr in nitrogen. The development of a distinct underlying pattern was now apparent. Finally, to provide a visual understanding of the effect of mechanical processing in a nitrogen environment, Fig. 5d shows the result of subtracting a Mossbauer spectrum of iron powder processed in argon for 100 hr from a Mossbauer spectrum of iron powder processed in nitrogen for 100 hr. The resulting spectrum revealed the presence of a distinct underlying pattern that was consistent with previously characterized Mössbauer spectra of martensite bct-Fe (Fig. 5d) [42, 43].

Both X-ray diffraction and Mössbauer analysis of iron powder mechanically processed in a nitrogen gas environment showed that a new phase was present after 50 hr of processing and that this phase was not fcc-Fe, or an iron-nitride precipitate but was consistent with the formation of nitrogen bct-Fe martensite.

4.5. Nitrogen Distribution

During milling fresh iron surfaces are constantly being produced by either plastic deformation or fragmentation. Nitrogen has an adhesion energy on iron of 11.9–14.3 kJ/mole [44] and thus readily became adsorbed onto freshly created iron surfaces. The rate of dissociative nitrogen adsorbed onto the iron was very rapid and occurred almost instantaneously upon being adsorbed onto the iron surface [45–47]. Thus, as a result of the high-energy nature of mechanical alloying and the creation of fresh iron surfaces, the majority of the nitrogen concentration was infused into the iron particles by becoming part of the highly deformed, disordered, and disturbed microstructure associated with the nanocrystalline grain boundary region.

The measured total nitrogen concentration, which increased linearly with processing time (Fig. 1), was determined to be distributed in the various microstructures that developed during mechanical processing: (a) in the matrix as interstitial nitrogen, (b) in the heavily damaged region of the particles, (c) in the grain boundaries and near surface regions of each grain, and (d) eventually in the bct-Fe phase.

During the initial stages of mechanical processing, the particles were cold-worked and developed a duplex as-received/cold-worked bcc-Fe microstructure. When the mechanical processing exceeded 50 hr, the microstructure began to produce a distinct second phase that was identified as bct-Fe. The nitrogen concentration in the different microstructures could be determined from the lattice d-spacing and the relative concentration of the phase from integrated X-ray diffraction line intensity [20, 38].

Table IV presents an accounting of the nitrogen concentration as a function of processing time and microstructure. Examination of powders in a scanning electron microscope showed that after 8 hr of processing, a small but significant fraction of powder still had not undergone any cold-working (Fig. 7). (See relative intensity row in Table I.) However, after 25 hr of mechanical processing, most of the powder appeared to have been cold-worked.

Line 1 in Table IV is the measured total nitrogen concentration as a function of processing time. Line 2 is the nitrogen concentration accounted for by interstitial nitrogen that had diffused into the undamaged region of the particle (bcc-Fe). Line 3 is the difference between the measured nitrogen and that accounted for by the nitrogen associated with interstitial bcc-Fe phase.

By the time the powder had been processed for 36 hr all of the particles had been cold-worked (Fig. 7). Line 4 is the nitrogen associated with the heavily cold-worked phase (bcc*-Fe). The percentage of nitrogen associated with this cold-worked phase continued to increase with increased processing time, accounting for approximately 40% of the total nitrogen concentration after 50 hr. Line 5 is the nitrogen not accounted for by interstitial nitrogen associated with the bcc-Fe and the bcc*-Fe phase. The nitrogen concentration associated with the cold-work bcc*-Fe phase saturates after 36 hr, at the same point in processing that the amount of internal strain saturated.

Because of the different possible interpretations of the X-ray diffraction data for the new microstructure that developed after 50 hr of mechanical processing, two approaches were taken to describe the nitrogen distribution in the nanocrystalline microstructure: (i) The newly created nanocrystalline structure was associated with nitrogen rich, randomly substituted nitrogen, bcc*-Fe clusters. Determination of the nitrogen concentration for the bcc*-Fe with the associated change, in d-spacing is
given in Table V, line 6. The excess nitrogen not associated with interstitial nitrogen concentration, line 7, now shows that with increasing processing time, all additional mechanically infused nitrogen went into formation of the newly created nitrogen rich bcc*-Fe clusters.

(ii) The newly created phase was analyzed as bct-Fe. Line 8 is the nitrogen concentration calculated for a bct-lattice with measured d-spacing [20]. Line 9 is the nitrogen not accounted for as being part of a grain matrix of either bcc*-Fe or bct-Fe. In this scenario, only a small portion of the mechanically infused nitrogen became part of the newly formed bct-Fe microstructure.

To account for the placement and distribution of the “excess (d)” nitrogen, the mechanism whereby the nitrogen became infused into the particle was reexamined. The hypothesis for nitrogen infusion into particles is that during mechanical processing, nitrogen adheres to the freshly exposed metal surface. During subsequent processing particles are reformed by cold-welding. The surface-adhered nitrogen is now imbedded in the interior of the particle and has become part of the newly created grain boundary. With increasing time, particle fragmentation and cold welding produces ever smaller grains (Table I), and thus, an ever-increasing total grain surface area. The nitrogen associated with the increasing grain boundary area continues to increase with increasing processing time. Note, that nitrogen rapidly diffuses through bcc-Fe matrix and even faster along grain boundaries. Therefore, grain boundaries formed from dislocation cell walls would rapidly be saturated with nitrogen due to disordered microstructures attraction for nitrogen [20].

Figure 4 is a plot of the reciprocal crystallite size versus excess nitrogen (for the bct-Fe nitrogen scenario, Table III, line 9). The slope of the line is related to the surface nitrogen concentration. The y-intercept for a particle with infinite grain size is the matrix interstitial nitrogen concentration. The observed linear relationship between the “excess” nitrogen and grain diameter (proportional to the grain boundary surface area) suggests that the nitrogen, not accounted for as part of the grain matrix, was part of the interface region between grains, i.e., grain surface. Line 10 is the nitrogen calculated from the statistically derived equation, Eq. (3), associated with grain surface region.

Determination of the surface nitrogen concentration from the empirical relationship (Eq. (2)) is presented in Table V. Figure 4 shows the relationship between nitrogen concentration and grain size. Calculations predict approximately one nitrogen atom associated with each unit lattice cell in the near-surface region of the grain interface. This result is consistent with the above scenario in which nitrogen atoms became attached to the newly created surface during cold-working and were subsequently incorporated into the interior of the particle by cold welding. The bottom line of Table IV is the result of subtracting the grain boundary nitrogen from the excess nitrogen and shows there is no unaccounted for nitrogen.

The above nitrogen distribution analysis indicates that approximately half to two-thirds of the total nitrogen concentration is associated with the mechanically produced, nanocrystalline grain boundaries. The grain boundary width is the result of mechanically infusing nitrogen in/on the outer couple grain boundary lattice sites.

5. SUMMARY

Several high-energy milling studies have been conducted with iron powders in nitrogen-rich gas environ-
ments [8, 11, 16]. In these studies, the impact energy (using either a “SPEX” or planetary ball mill) was sufficient to form nanocrystalline microstructures, then with continued milling an amorphous microstructure, and finally iron-nitrides [11, 16]. The mechanical processing apparatus used in this study, an ATTRITOR mill, had sufficient energy to produce a highly deformed nanocrystalline microstructure but did not produce any amorphous material or second-phase precipitates [8].

Nitrogen infusion into iron powder during mechanical processing resulted from nitrogen gas adhesion to and dissociation on the freshly created metal surfaces that were formed during particle plastic deformation and fragmentation, and the subsequent nitrogen entrainment into the interior of the particle during cold welding [29].

Formation of a highly disturbed grain boundary surrounding nanocrystalline grains was consistent with previous reported nanocrystalline microstructures resulting from mechanically alloying iron powder [20, 28, 48]. In these studies of mechanically alloyed iron powders, X-ray diffraction and Mössbauer analysis were used to show that the thickness of the grain boundaries depended upon the alloying element but was generally between 0.5 and 1.0 nm [28]. Studies have also shown that if the iron lattice is sufficiently disordered, as for example by ion implanting [21] or by extensive cold-working [20], infused nitrogen becomes trapped in the dislocated lattice in energy wells that limit nitrogen mobility. The presence of nitrogen in the dislocation stabilizes the local disorder and increases the nitrogen concentration.

As a result of high-energy impacts, the powder particles underwent a number of microstructural changes (Fig. 16). The initial series of impacts increased the amount of cold-working leading to a highly disordered microstructure, increasing the nitrogen concentration, and eventually leading to particle fragmentation. These fragments then underwent a repeated series of cold work and further fragmentation resulting in micron-size particles with a nanosize grain microstructure [49–51].

Calculations have predicted [29] and experimental studies have shown that nitrogen concentration increases linearly with mechanical processing time [7]. This study shows that the majority of the infused nitrogen was associated with the highly deformed microstructure associated with grain boundaries.

When the grain size was reduced to approximately 10 nm, the total alloyed nitrogen concentration was approaching 1.0 wt.% and internal strain was approximately 1%. X-ray diffraction analysis showed that with subsequent mechanical processing, a second nanosize grain microstructure formed. Two possible explanations were examined: (1) formation of localized regions of high nitrogen concentration, i.e., nitrogen clusters (nitrogen diffusion, however, was inconsistent with subsequent experiments), and (2) formation of nitrogen stabilized bct-Fe. For a number of reasons, including Mössbauer analysis, the nanometer microstructure was determined to be bct-Fe. (Bct-Fe was theorized to form either by localized shearing or by nitrogen diffusion.)

The mechanically infused nitrogen concentration and mechanically induced nanostructure was shown to be thermally stable until near the eutectoid phase transition temperature. This stability was hypothesized to result from the formation of nitrogen-stabilized, bct-Fe nanosize grains on the grain boundaries of cold-worked bcc-Fe nanocrystalline grains that restricted grain growth of the bcc-Fe grains (Fig. 17). The extended thermal stability of the mechanically processed, nitrogen satu-

Fig. 15. Change in crystallite size with heat-treatment temperature for Fe-[Ar] and Fe-[N] powders (which contained both bcc-Fe and bct-Fe phases) processed for 100 hr.

Fig. 16. Hall-Petch relationship, hardness versus grain size for a number of compacted and heat-treated mechanically processed powders. Compaction techniques include explosive compaction and HIP. To obtain variation in grain size, the explosively compacted samples were heat-treated at 77 K for 60 min and 1325 K for 10 mins.
### Table VII.

<table>
<thead>
<tr>
<th>Processing</th>
<th>Fe\textsubscript{powder}</th>
<th>Fe-{Ar}\textsubscript{100}</th>
<th>Fe-{N}\textsubscript{100}</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing of the [110] planes of α-Fe (nm)</td>
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<td>0.2032</td>
<td>0.2038</td>
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<td>Mechanical alloying</td>
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<td></td>
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<td>0.2035</td>
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<tr>
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<td></td>
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<td>7.6</td>
<td>5.3</td>
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</tr>
<tr>
<td>Nitrogen concentration (wt.%)</td>
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<td></td>
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<tr>
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<td>789</td>
<td>999</td>
</tr>
</tbody>
</table>

The nanostructured microstructure suggests that the possibility of consolidating these powders while retaining their nanocrystallinity. Near-net-shape formation of nanocrystalline materials for commercial application and for the evaluation of material properties may now be possible.

To date, the only mechanism to consolidate and retain nanocrystalline microstructure of mechanically processed nanocrystalline iron powder has been by explosive compaction [52]. Compaction of nanosize particles formed by vapor condensation has been accomplished by die pressing using ultrahigh pressures (∼3 GPA) at temperatures as low as 600 K [53]. Explosive compaction significantly reduced the lattice spacing, indicating a significant reduction in the cold-work disorder within the nanosize grains with no significant change in the crystalline size and no loss in the nitrogen concentration (Table VII). The measured hardness of these compacts was directly related to the crystallite size, indicating that the Hall-Petch relationship remained valid down to the nanocrystalline dimensions (Fig. 16).

Recent studies have shown that nanocrystalline powders can have superplasticity properties at room temperature [54]. Other recent studies have shown micrometer- and submicrometer-size grain Fe–C alloys to be superplastic at temperatures slightly above the nanocrystalline stability temperature of the iron-nitrogen nanocrystalline particles produced in this study [55–58]. Because superplasticity is related to grain size, the superplastic forming temperature for these nanocrystalline Fe–N powders might be below the temperature at which rapid grain growth was observed.

### 6. CONCLUSION

This study shows that by controlling mechanical processing parameters, i.e., gas environment and ball-milling energy, it is possible to add large quantities of nitrogen to iron powder without forming iron-nitride precipitates. Nanosize grain microstructures were developed in micron-size particles with nitrogen concentrations up to 1.8 wt.% (7 at.%). Mechanically processing iron powder in a nitrogen gas environment for 50 hr reduced the crystallite size to approximately 10 nm with a nitrogen concentration of approximately 1 wt.%. With further mechanical processing, the particles developed a second nanometer bct-Fe phase. Bct-Fe formation in iron has previously been observed only as the result of the transformation from the fcc-Fe phase. The bct-Fe formed in this study was not formed by stress or temperature transformation of fcc-Fe but from the combination of localized strain reduction and localized nitrogen clustering in the grain boundary of nanocrystalline bcc-Fe grains.

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