Nitrogen Addition to bcc-Fe by Attrition Milling

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Abstract:

To enhance the nitrogen solubility in bcc-Fe, iron powder and blends of iron and iron nitride powders were attrition-milled in nitrogen gas. X-ray diffraction and Mössbauer spectroscopy were used to characterize the milled microstructure and to characterize the nitrogen distribution. After processing for 150 hours, the infused nitrogen was determined to be interstitial (locally deforming the bcc-Fe lattice to a bct-Fe lattice) and associated with the outer layer of the bcc-Fe nanograin. Nitrogen stabilized the milled grain structure but at elevated temperatures rapidly came to thermodynamical equilibrium transforming from bcc-Fe(N) to bcc-Fe and Fe₃N.

Introduction:

Thermodynamic calculations and experimental results show that nitrogen solubility in bcc-Fe is limited at atmospheric pressure. And, because nitrogen is a gas, it is not easily alloyed into bcc-Fe. Several studies reported in previous HIGH NITROGEN STEEL CONFERENCES have shown that nitrogen solubility can be increased by processing under elevated nitrogen pressures (SEVIERTS' Law), processing in reactive nitrogen gas environments, or ion implant. The first two processes require elevated temperatures. The resulting microstructure is usually in thermodynamic equilibrium and the nitrogen is in the form of nitride precipitates at room temperature. Recently it has been shown that mechanically processing bcc-Fe in nitrogen rich environments will also increase the nitrogen solubility in bcc-Fe far in excess of thermodynamical equilibrium without forming nitrides [1,2,3].

In this study, mechanically infused nitrogen was added using two techniques: (i) processing in a nitrogen gas environment, and (ii) alloying blends of iron and iron-nitride powders. The milled powder microstructures and nitrogen distributions were characterized using X-ray diffraction and Mössbauer spectroscopy. The infused nitrogen concentrations greatly exceeded nitrogen bcc-Fe solubility but did not produce nitride precipitates. The thermal stability of these milled powders was studied and several different powder consolidation techniques were attempted.
One rationale for trying to enhance the nitrogen solubility in bcc-Fe is the observation that nitrogen greatly enhances magnetic properties of iron. All previous attempts to produce the highly desirable magnetic Fe₁₅N₂ phase required a nitrogen supersaturated bcc-Fe(N) phase as a precursor. However, because the Fe₁₅N₂ phase rapidly decomposes above 200°C, to date the technique used to produce Fe₁₅N₂ has been to quench nitrogen in the bcc-Fe phase and then conduct long term aging at reduced temperatures [4]. Mechanical infusion of nitrogen into bcc-Fe might offer an alternative technique to forming the Fe₁₅N₂ precursor.

Experimentation:

Powder processing was done in a 5 liter Szegvarc attritor ball-mill at an armature speed of 300rpm. The processing media was 5mm diameter 440C stainless steel balls. The powder to ball weight ratio was 1 to 20. Approximately 500 grams of 30-50 micrometer diameter 99.9+ pure iron powder was used. The processing environment was commercial grade (99.95% pure) argon or nitrogen gas maintained under a slight positive pressure by running the processing chamber outlet gas at a constant gas flow rate of 1.2 liters per hour through a hose that was immersed under silicon based oil to a depth of approximately 10 cm. A LECO model CS244 was used for carbon analysis and LECO model TC430 for nitrogen and oxygen analysis. A L&N Automatic Surface Area Analyzer model 4200 was used for powder surface analysis. A L&N Microtrac Particle Analyzer model 7991-3 was used for particle size analysis. A Θ-2Θ Philips powder diffractometer using monochromatic Cu Kα radiation was used for X-ray diffraction analysis. Diffractographs were analyzed using single-line Fourier analysis of the bcc-Fe (110) peak for (i) peak position, (ii) grain size, and (iii) rms-strain. Transmission Mössbauer spectra were recorded at room temperature using 20 mg of sample pressed into boron nitride binder and irradiated using a 25mCi ⁵⁷Co/rhodium foil moving at constant acceleration. Spectra were fitted using the transmission integral method. The Mössbauer data include hyperfine magnetic field strength and site defect configuration: A(nn,nnn) where nn=nearest neighbor site and nnn=next nearest neighbor site defects, e.g., A(0,0) would be an iron atomic site with no defect site -- a perfect bcc-Fe lattice site. D* is the designation for a defect site that results from tensile straining the local lattice [5,6]. Thermal stability was measured using hot-stage X-ray diffraction and differential scanning calorimetry. Additional information on experimental techniques can be found in references 1, 2, and 3.

Data and Analysis:

TABLE I contains a summary of powder analysis from (i) six similar runs of iron processed in argon, Fe-[Ar], (ii) ten runs of iron processed in nitrogen, Fe-[N], and (iii) eight runs of blends of pure iron powder and iron nitride powders, processed in argon or nitrogen, Fe-Fe₅N₅-[Ar/N]. The table lists the extremes of the data range, e.g., the highest nitrogen concentration in a iron powder processed in nitrogen was 2.02 wt%, the (110) bcc-Fe lattice d-spacing for this sample was 0.2034 nm, grain size was 4.5, etc. Extended tables of X-ray diffraction and Mössbauer data from which TABLE I was derived can be found in references 1, 2, and 3.
The iron powder milled in argon is presented as base-line data against which the nitrogen attrition-milled powder data can be compared. The data is a summary of 6 similar runs. After milling for 150 hours, the powders reached an asymptotic limit for surface area, particle size, grain size, and rms-strain [3]. There was little variation in powder characteristics between runs. The measured increase in uniform lattice strain (from 0.2026 in the as-received powder to 0.2029 nm in the milled powder) and localized or rms-strain (from 0.01 to 0.55%) was attributed to the presence of localized dislocation structures on the grain boundary [7]. Direct evidence for the role of grain boundary influence on the milled microstructure comes from relationships between the (inverse) grain size and (i) the uniform lattice strain (Fig.1), (ii) the rms-strain, (iii) the concentration of defect free iron lattice sites (Fig.2), and (iv) grain boundary defect structure, $D^*$ (Fig.3). Previous studies have shown that the oxygen is on the particle surface and not in the grains or particles interior [1,2].

**FIGURE -1-**  (110) bcc-Fe lattice dimensions versus inverse grain size for different nitrogen concentrations

**FIGURE -2-**  Defect free lattice site concentration, A(0,0), versus inverse grain size. Also plotted are the defect free concentration for grain boundary widths +1 = one lattice cell wide
+2 = two lattice cell wide

**FIGURE -3-**  Grain boundary defect concentration, $D^*$, versus inverse grain size for iron processed in argon, A, and iron processed in nitrogen, N.
Iron powder milled in nitrogen did not show the presence of nitrides. However, both X-ray diffraction and Mössbauer analysis showed the presence of a nanostructured bct-Fe phase consistent with nitrogen being mechanically infused into the bcc-Fe lattice. As the nitrogen concentration increased both the bcc-Fe and the bct-Fe lattice dimensions increased (Fig.4). Analysis of the Mössbauer spectra suggests that the nitrogen is concentrated within the outer one to two lattice cells of the grain with the interior of the grain being free of interstitial nitrogen (Fig. 2 and 3). As the nitrogen concentration increases, the bcc-Fe lattice dimensions increase due to the grain boundary strain resulting from the infusion of nitrogen into the bcc-Fe lattice locally deforming the bcc lattice to bct-Fe. The milled bcc-Fe grain size decreased with increasing nitrogen concentration and the rms-strain increased (Fig.5).

![Figure 4](image1.png)  ![Figure 5](image2.png)

**FIGURE 4** - (110) bcc-Fe (circles) and bct-Fe (squares) d-spacing versus nitrogen concentration

**FIGURE 5** - Nitrogen concentration versus inverse grain size for both Fe-[N] and Fe-Fe₃N₂-[Ar/N]

The milling blends of iron and iron-nitride powder processed in argon or nitrogen broke-up the iron nitrides and formed a microstructure that was similar to that of the iron powder processed in nitrogen. After 150 hours of attrition milling, neither X-ray diffraction nor Mössbauer analysis detected the presence of nitride precipitates. There was a continuous gradient of bcc-Fe lattice dimension, grain size, and rms-strain with increasing nitrogen concentration, regardless of the means of nitrogen addition: either processing in a nitrogen gas environment or by processing blends of iron and iron nitride powders.

Thermal stability of the milled nanostructure was determined by hot-stage X-ray diffraction. Because the nitrogen solubility in iron is limited, there is little tendency for the nitrogen to leave the grain boundary and diffuse into the grain's interior. At low thermal aging temperatures, less than 200°C, the bct-Fe(N) nanostructure is stable and shows no sign of transforming into the Fe₁₆N₂ microstructure or iron-nitrides. At modest temperatures, 300-550°C, bct-Fe(N) is unstable and will transform to bcc-Fe and fcc Fe₃N. The nitride precipitates are on the grain boundaries and stabilize the bcc-Fe nanograin against growth. At temperatures, greater than 600°C, the nitrogen rapidly diffuses out of the powders above 600°C resulting in rapid bcc-Fe grain growth.
FIGURE 6 - Thermal stability: grain size versus temperature for Fe-[Ar] and Fe-[N]

Discussion:

Attrition milling of iron powder produces a cold-worked microstructure. The continuous generation of dislocations produce dislocation forests that eventually transform into nanosize cells. The grain boundary structure resulting from the cold-working does not completely eliminate all the dislocations. Some remain associated with the grain boundary and give rise to localized, rms-strain. The presence of the dislocations on the grain boundary form a ring around the individual grains that produce a uniform strain on the grain lattice [7]. In attrition milling, the cold-worked particles fragment and these fragments are subsequently cold-welded together further refining the microstructure.

When the attrition milling is done in a nitrogen gas environment, the nitrogen reacts with the freshly generated metal surfaces that are produced during cold-working. Nitrogen gas molecules become attached to the particle surface, rapidly dissociate [8], and the atoms are infused into the grain during the cold-welding of the fragmented particles. The amount of fresh surface exposed to the processing environment is directly proportional to the processing time. Thus, the milled nitrogen concentration is directly proportional to the processing time. Because nitrogen has a very limited solubility in bcc-Fe, it does not diffuse into the grain interior. Thus, the mechanically processed nitrogen is restricted to the grain surface.

When attrition milling iron powder with iron-nitride powder, the iron-nitride powder is broken up and is welded to the outside of the iron powder particles. With continued milling, the nitrides are further broken up. Eventually the nitride particle size is reduced until the particle's structure becomes unstable and the nitride dissolves. The iron atoms become part of the bcc-Fe grain structure and the nitrogen becomes part of the bct-Fe lattice sites on the grain boundary. The bct-Fe structure of this process is indistinguishable from the bct-Fe structure described above for iron processed in nitrogen gas.
REFERENCE:


TABLE I: Data summary table for 150 hour attritor milled powders.
(Complete data for each attritor run can be found in references 1, 2, and 3.)

|                | Fe -- [Ar]    | Fe -- [N]   | Fe-Feₐₙₐₑₐₙₐ_sₐ₄₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ_-