The microstructural properties of highly nitrogenated iron and iron–aluminum powders

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A study has been made of highly nitrogenated pure iron and iron–aluminum alloy powder containing 2 wt.% Al (Fe–2Al) using Mössbauer spectroscopy and X-ray diffraction. The samples were prepared by high-temperature, high-pressure diffusion of nitrogen. They were prepared in a hot-isostatic-pressure (HIP) furnace at 1000 °C at nitrogen pressures up to 200 MPa. The alloy powders contained up to 8 at.% nitrogen as determined by vacuum fusion analysis. XRD analysis indicates that for the pure iron powders, the lattice spacing remained independent of nitrogen concentration, but that for the Fe–2Al powders, it decreased with increasing nitrogen concentration. Mössbauer analysis showed that for the pure iron powders, most of the nitrogen was associated with the formation of the iron nitride Fe₅N. For the alloy powders containing less than 5 at.% nitrogen, all of the nitrogen was contained interstitially. The presence of nitrogen completely eliminated the conduction-electron spin-density oscillations observed in many ferromagnetic alloys.

1. Introduction

Powder metallurgy is an important technological research field of materials science due to the potential industrial advances that can be made through improved materials properties. In particular, it is important to manufacture materials which have increased hardness and wear resistance. In addition to the unique industrial processing capabilities of powders, it is possible to produce powders with compositions and/or microstructures that cannot be produced by conventional metal processing techniques. It is well known that although mechanical and chemical properties of iron alloys are improved by the addition of nitrogen, the maximum bulk nitrogen concentration in pure iron is less than 0.1 at.%. However, nitrogen concentration in iron alloys is a function of alloy composition and the concentration of nitrogen in a metal can be increased through knowledge of the interactions between the nitrogen and the substitutional elements. Alloying elements such as Al, Cr and Mn
increase the nitrogen concentration, whereas C and Ni decrease the nitrogen concentration [1]. At the same time, Al and Cr also have a strong tendency to form metal-nitrides at very low nitrogen concentrations. Infusion of nitrogen in solid iron is by interstitial atomic diffusion, whose rate is several orders of magnitude faster than solid solution diffusion of substitutional alloy elements. Because the diffusion distance in iron powders is small and there is a large difference in diffusion rates between interstitial nitrogen and substitutional elements in solid iron, it is possible to choose conditions of temperature and time that allow for nitrogen to completely diffuse throughout a powder particle while limiting the diffusion distance of substitutional alloying elements. Several nitrogen alloying techniques exist in which nitrogen infusion into powders can be made to significantly exceed the nitrogen solubility in the bulk material. High-temperature, high-pressure diffusion is one method we have used to greatly increase the nitrogen concentration in iron and several iron alloys. This paper reports the results of highly nitrogenated iron and iron–aluminum powders produced using this method. The study provides insight into the nitrogen concentration and distribution in the iron and iron alloy powders.

2. Sample preparation and experimental procedure

The powders studied were pure iron and bcc iron–aluminum alloy containing 2 wt.% aluminum, Fe–2Al. The latter alloy was chosen because at 2 wt.% (4 at.%) the aluminum is in solid solution and has a strong affinity for nitrogen. The powders were produced by gas atomization using helium as the melt atmosphere and as the atomizing gas. They were sieved and only particles less than 100 microns were kept. The average particle size was between 30 and 50 microns. High-temperature, high-pressure diffusion was conducted in a hot-isostatic pressure (HIP) furnace at 1000 °C for 900 s at pressures up to 200 MPa (2000 atm), using nitrogen as the pressurizing gas. The powders were placed in alumina crucibles during heating. The diffusion temperature and time was chosen to ensure that nitrogen would be able to diffuse across a 100 micron diameter powder. At 1000 °C, Fe and Fe–2Al are both fcc, which has a greater nitrogen solubility than the bcc structure. The nitrogen diffusion distance in iron for this temperature and time is approximately 110 microns and aluminum diffusion is approximately 25 microns. Samples were diffused at ten different pressures of 0.1, 1.0, 2.5, 5.0, 10.0, 22.5, 40.0, 100.0, 150.0 and 200.0 MPa of nitrogen. Following diffusion, the powders were analyzed for total nitrogen concentration by vacuum fusion analysis in a nitrogen-oxygen determinator. X-ray diffraction was conducted on the powders in order to monitor the lattice parameters and to identify any precipitates present. Mössbauer spectra of the powders were recorded at 300 K, using a 25 mCi source of $^{57}$Co/Rh, in order to monitor changes in hyperfine parameters and to identify any iron precipitates as well as their fraction.
3. Results and discussion

Electron microprobe analysis on the powders showed that the nitrogen concentration within a particle was uniform and did not vary substantially from the surface to the middle except where nitride precipitates were observed. Measured nitrogen concentrations for the Fe and Fe–2Al powders are plotted as a function of diffusion pressure in fig. 1. For pure iron powders, fig. 1(a), the fraction of nitrogen present approximates Sieverts' law and reaches a maximum of 4 at.% at the diffusion pressure of 150 MPa. For the Fe–2Al powders however, fig. 1(b), the
nitrogen concentration increases rapidly up to 4 at.% at low pressures and then increases at a rate similar to that of pure iron at higher pressures. A total of 8 at.% nitrogen is found in the sample diffused at 150 MPa. X-ray diffraction analysis of the nitrogenated iron powders indicated that at high and low nitrogen pressures, the lattice parameter remained constant at 2.867 Å, the value expected for pure iron. For pressures of 10 and 22.5 MPa, it was slightly less at 2.865 Å. The X-ray diffraction patterns identified the presence of small amounts of the iron nitride Fe₄N in the powders produced at pressures greater than 5 MPa. For the Fe–2Al powders, the lattice parameter was measured to be 2.872 Å for the as-received material. This is higher than for pure iron due to the substitution of the aluminum into the iron matrix. We measured an immediate drop in the lattice parameter to 2.868 Å for the powder diffused at 0.1 MPa, and a decrease to 2.867 Å for the powders produced at 10 MPa and above. Once again, X-ray diffraction shows the presence of the iron nitride Fe₄N in samples produced at pressures greater than 10 MPa. Careful analysis of the diffraction spectra failed to reveal the presence of any pure aluminum nitrides in any of the Fe–2Al powders.

Mössbauer spectra were recorded for the powders of Fe and Fe–2Al diffused in the HIP furnace at nitrogen pressures of 0.1, 22.5, 40.0, 100 and 200 MPa. The fitted spectra are shown in fig. 2. For the pure Fe powders, fig. 2(a), only a single sextet, $H = 330.0$ kOe, was observed for preparation pressures of 0.1 and 22.5 MPa. In the three spectra recorded for samples prepared at 40, 100 and 200 MPa, the iron precipitate Fe₄N was found to be present. The spectrum for the 200 MPa sample has been enlarged in fig. 2(a) in order to more easily observe the presence of the Fe₄N. The Mössbauer parameters characterizing the nitride indicate the presence of three iron sites, Fe I–A, Fe II–A and Fe II–B, in the ratio of 1:2:1 and whose magnetic fields are 34.1, 21.1 and 21.8 T, respectively. Our parameters are in close agreement with previously published data on Fe₄N [2,3]. The fraction of nitride present increased with nitrogen diffusion pressure. The fraction of Fe₄N present in each sample was determined from the subspectral area and, without making allowances for different recoilless fractions at the iron sites, we have calculated the percentage of nitrogen associated with the nitride. No other nitrides were identified through the X-ray or Mössbauer analyses and we therefore infer that the remaining fraction of nitrogen is interstitial. Plotted in fig. 1(a) are the data showing the percentage of nitrogen associated with nitride formation and the percentage contained interstitially. It can be seen that the majority of nitrogen in the pure iron powders has formed iron nitride and that the concentration of interstitial nitrogen remains fixed at about 0.3 at.% for pressures above 50 MPa. This fraction is only slightly larger than the normal solubility limit of nitrogen expected for a bulk sample of pure iron.

The Mössbauer spectra for the nitrogen-diffused Fe–2Al powders, fig. 2(b), show that the presence of 2 wt.% aluminum affects the local magnetic hyperfine field at the iron site. The change in magnetic field is controlled by the fraction of substitutional aluminum, as is the subspectral area of different iron sites that form in the bcc structure. Early theories attribute the phenomenon to spin–density oscillations
due to polarization of the 4s conduction electrons [4]. The as-received powder was fitted to four sextets whose hyperfine parameters agree with the many previous reports on aluminum-substituted iron alloys [5,6]. Subspectral areas and magnetic fields agreed closely with those computed using the binomial distribution for 4 at.% Al, the results of which will be the subject of another publication. The spectra of fig. 2(b) indicate that iron nitride is detected in the samples produced at 100 and 200 MPa. Spectral fits show that once again the nitride is Fe₄N, the fraction of which increases with pressure. It can also be seen from the spectra that as the diffusion pressure increases, the magnetic field distribution due to the substitutional aluminum is no longer observed. The presence of nitrogen has eliminated the spin-density oscillations, possibly as a result of clustering of the aluminum in the form of iron–aluminum nitrides.

Once again, the subspectral area of the nitride has allowed us to determine the fraction of interstitial nitrogen present in the powders. This is plotted in the graph of the nitrogen concentration, fig. 1(b), together with the percentage of nitrogen associated with the nitride. In comparison with the pure iron powders, the fraction
of nitride present increases with pressure and asymptotes to a maximum value of 2 at.\%, which is less than that observed in the pure iron. However, it can now be seen that the total fraction of interstitial nitrogen present is much greater and remains constant at about 5 at.\%, independent of diffussion pressure. In comparison with the pure iron samples which contain 1 at.\% of interstitial nitrogen, the Fe–2Al samples contain about 4 at.\% more. Knowing that these latter samples also contain 4 at.\% of aluminum, it may be suggested that there is approximately one interstitial nitrogen atom associated with each substitutional aluminum atom.

4. Conclusion

It has been shown that metal alloy powders can be highly nitrogenated by atomic nitrogen diffusion in an HIP furnace at high temperatures and pressures. The fraction of interstitial nitrogen found in the powder, however, depends on the alloying elements and their affinity for nitrogen. In pure iron powders, it is difficult to increase the fraction of interstitial nitrogen over the normal solubility limit found in bulk iron. For alloyed powders, nitrogen diffusion in an HIP furnace allows samples to be produced with higher nitrogen concentration than is found using conventional means. We have shown that for Fe–2Al up to 5 at.\% interstitial nitrogen can be obtained, a concentration only presently matched by mechanical alloying methods.

References