

High carbon–nitrogen iron alloys

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A new processing technique produces high carbon–high nitrogen iron alloys by melting iron-carbon steels in a hot isostatic pressing (HIP) furnace with nitrogen as the pressurizing gas. Furnace cooling O-1 tool steel with enhanced nitrogen concentrations resulted in the retention of the austenite phase without formation of carbide and nitride precipitates. The duplex austenite/ferrite structure has enhanced hardness, strength, and wear resistance.

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1. Introduction

Development of f.c.c.-Fe or austenite alloys has traditionally required the addition of expensive alloying elements such as nickel. In this study, the austenite phase was retained by alloying with a combination of only carbon and nitrogen. Previous experimental studies have shown that when alloys of greater than 0.4 wt % of both carbon and nitrogen are formed: (i) both carbon and nitrogen are retained as interstitials [1, 2], (ii) the f.c.c.-Fe phase is retained [3, 4], and (iii) the mechanical strength, hardness and wear properties are improved [4]. These results are in contrast to the thermodynamic calculations, which show that iron alloyed either individually with carbon or nitrogen or in combination, readily forms precipitates [5].

Nitrogen has been shown to improve the properties of austenitic stainless steels; the greater the nitrogen concentration the greater the strength, hardness, wear, corrosion, fatigue life, etc. [6]. Because interstitial nitrogen solubility in iron and steel alloys is limited, to increase the nitrogen concentration, the steel must be melted under elevated pressures [7–9]. By processing austenitic steels under elevated pressures, interstitial nitrogen concentrations approaching 1.0 wt % have been obtained. However, addition of nitrogen to b.c.c.-Fe or ferritic iron alloys is much more limited. Iron-nitrides begin to form when the interstitial nitrogen concentration is less than 0.05 wt %. Despite the difficulty in getting large concentrations of nitrogen into iron, the improved surface hardness and wear properties of nitrated iron has spurred the development of numerous surface nitridation techniques. In this study, nitrogen was added to an iron-carbon ferritic steel at elevated nitrogen pressure and temperature resulting in a uniform nitrogen concentration throughout the ingot from which bulk material properties could be measured.

2. Experimentation

Nitrogen was added to an O-1 tool steel (Table I) using the HIP-drip technique [10]. In the HIP-drip technique, the ingot to be melted is suspended in a crucible with a

hole in the bottom above a casting mold in a HIP furnace. The pressurizing gas is nitrogen. When the ingot is melted the molten iron drips into the cast mold and at the same time comes into equilibrium with the pressurizing nitrogen atmosphere. The nitrogen concentration in the molten phase is proportional to the square root of the nitrogen pressure (Sieverts's law) and can be predicted by thermodynamic calculations (e.g. THERMOCALC). Because of the reduction in nitrogen solubility of the liquid to solid phase transition, the pressure in the HIP furnace is raised just before solidification so that the nitrogen concentration in the liquid phase is now undersaturated but the nitrogen in the solid phase is in equilibrium with the nitrogen pressure. This elevation in pressure is done just prior to solidification so as to minimize the increase in molten iron nitrogen concentration.

In this study, four 10 kg ingots of O-1 tool steel were HIP melted. The first ingot was melted under 10 MPa using argon as the pressurizing gas to establish a baseline. Three HIP-drip melts were made at pressures of 40, 90, and 160 MPa. Just prior to solidification, the nitrogen pressure was increased by 50 MPa for all nitrogen HIP-drip melts. The ingots were furnace cooled (approximate cooling rates: at 900 °C ~21 °C min⁻¹, at 700 °C ~15 °C min⁻¹, at 500 °C ~8 °C min⁻¹).

Microstructure was determined from X-ray diffraction, and optical and electron microscopy. Bulk properties measured include hardness (HRC and HV), compression strength (120 mm diameter by 17.5 mm tall cylinders), and abrasive wear (pin-on-drum using 150 grit garnet), see Table II.

3. Results

The HIP-dripped ingots were solid and did not show any evidence of gas porosity resulting from nitrogen coming out of solution during solidification. The nitrogen concentration was uniform along the length and throughout the interior of the ingots. The nitrogen concentration was proportional to the square root of the HIP nitrogen pressure (Fig. 1) as was predicted by

TABLE I Chemical composition of O-1 tool steel

Fe	C	Mn	Si	Cr	Ni	W	V
Balance	0.91	1.20	<0.50	0.5	<0.3	0.5	<0.3

TABLE II Characterization of HIP-dripped Fe-C/N alloys

Melt pressure	As-received	40 MPa	90 MPa	160 MPa
Melt cooling	Furnace	Furnace	Furnace	Furnace
Nitrogen (wt %)	0.01	0.48	0.66	0.91
Microstructure				
f.c.c.-Fe (%)	0	12	27	55
d-spacing: 0.2075 ^a	—	0.2088	0.2090	0.2093
b.c.c./b.c.t. (%)	88	88	72	45
d-spacing: 0.2027 ^a	0.2028	0.2033	0.2037	0.2036
Fe ₃ C, (%)	12			
Hardness				
HRC	26	45	48	52
Vickers	210	495	510	576
Compression				
yield, (MPa)	417	1348	1442	1488
ultimate, (MPa)	1290	1707	1924	2046
elong, (%)	13	19	20	21
Wear				
pin-on-drum, (mm ³ Nm ⁻¹)				
150 g garnet	0.0145	0.009	0.0063	0.0058

^aLattice dimension values obtained from powder diffraction files for f.c.c.-Fe (1 1 1) peak and b.c.c.-Fe (1 1 0) peak carbon and nitrogen free iron alloys.

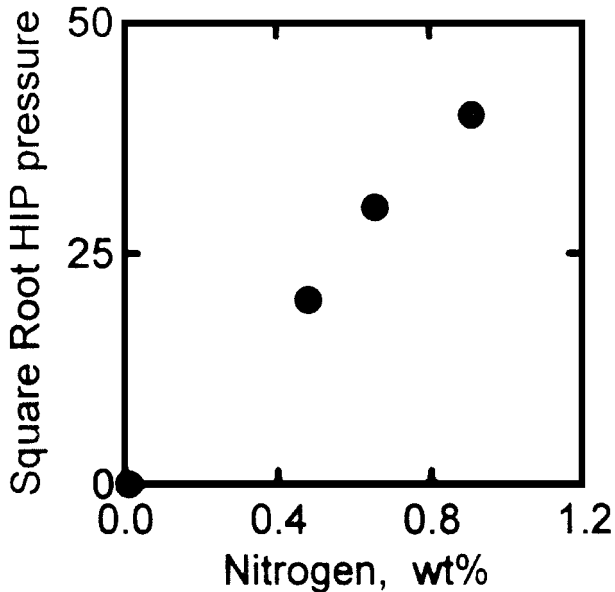
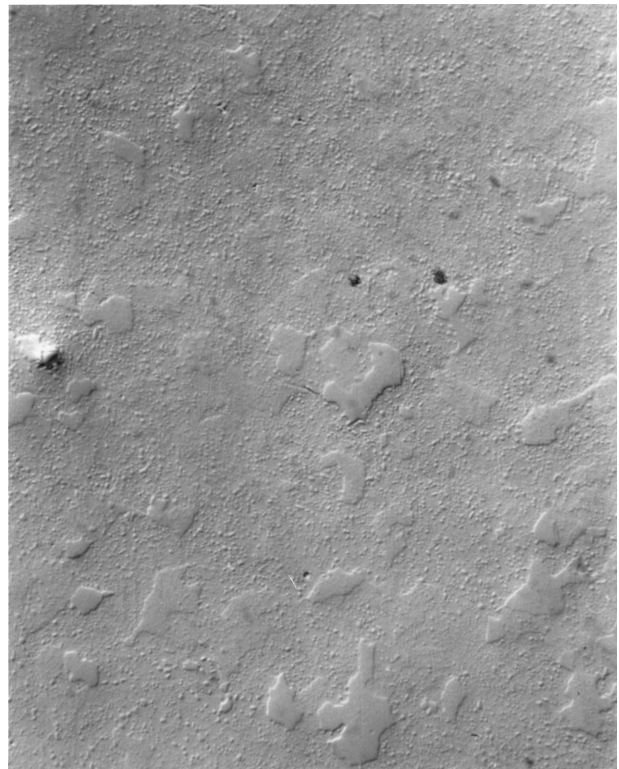
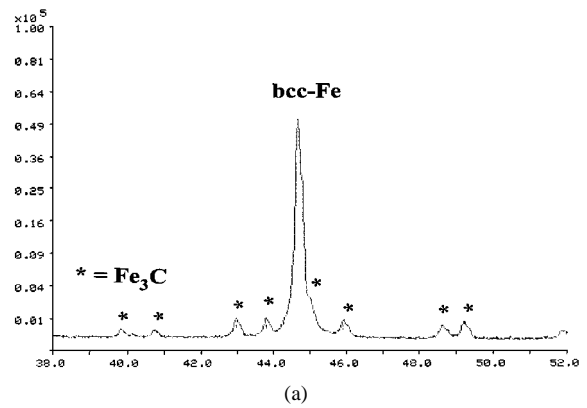


Figure 1 Nitrogen concentration in O-1 tool steel as a function of HIP-drip melting under nitrogen pressures of 40, 90, and 160 MPa.

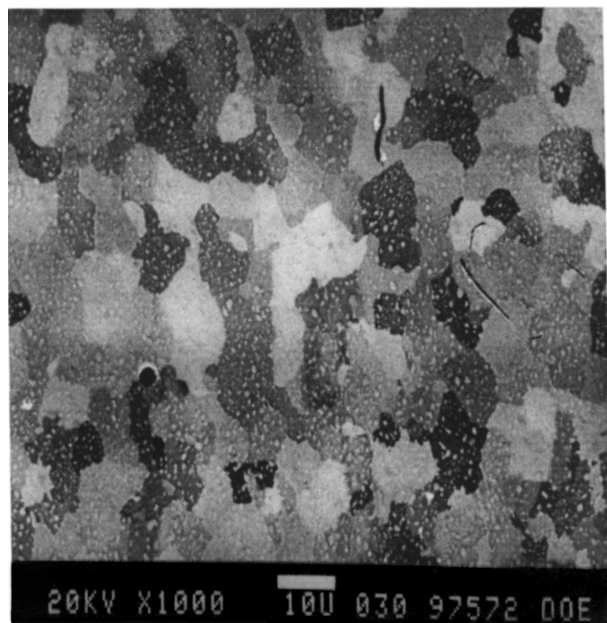
THERMO-CALC* for the nitrogen equilibrium concentration in the liquid phase just prior to solidification.

Microstructure of the argon HIP-dripped O-1 tool steel showed a fine grain structure with a uniform dispersion of Fe₃C. X-ray diffraction did not show the presence of any retained austenite (Fig. 2). The hardness values were typical of an annealed O-1 tool steel.

Microstructure of the nitrogen HIP-dripped O-1 tool steels showed the retention of the austenite phase and

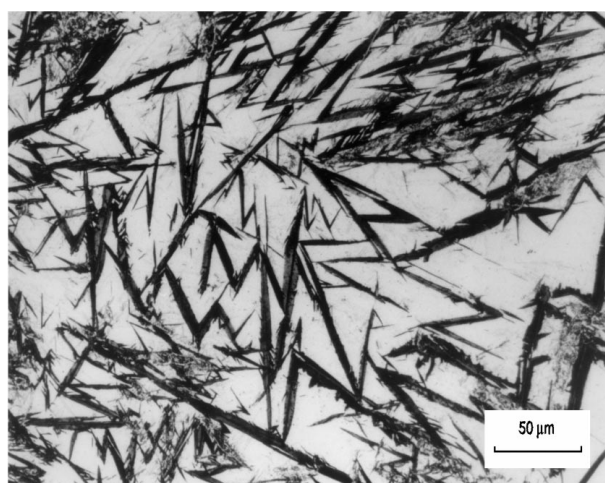
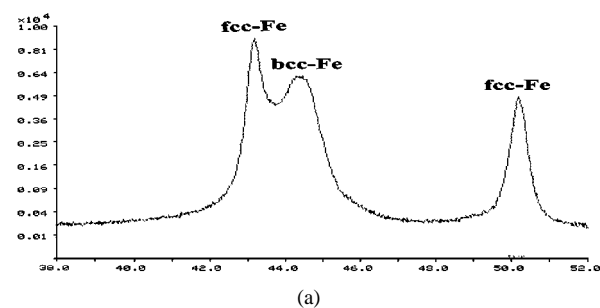


(b)

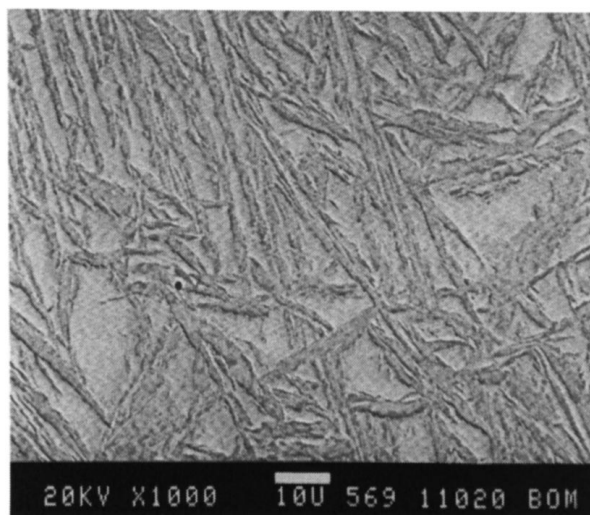


(c)

Figure 2 Microstructure characterization of as-received O-1 as-received: (a) X-ray diffraction, (b) optical, and (c) SEM micrographs.



(b)



(c)

Figure 3 Microstructure characterization of 160 MPa HIP-dripped O-1 + 0.9 wt % N (a) X-ray diffraction, (b) optical, and (c) SEM micrographs.

no iron-carbide precipitates (Fig. 3). The appearance of the retained austenite in the X-ray diffraction study and in the micrographs is consistent with results from previous studies that suggested that a minimum of 0.4 wt % nitrogen is needed to begin retaining austenite [1, 2, 4]. X-ray data also show the presence of a b.c.c.-Fe phase and deconvolution of the f.c.c./-b.c.c.-Fe peaks revealed the presence of a third peak that was identified as b.c.t.-Fe(N). Optical micrographs also suggest the presence of a martensite microstructure. The shifts in peak positions for these three peaks were consistent with a uniform distribution of interstitials within each phase and similar carbon and nitrogen concentrations in all three phases.

Bulk properties were strongly correlated with nitrogen concentration and retained austenite. The compression yield strengths of these nitrogen-enhanced, annealed steels were three or four times that of the as-received nitrogen-free O-1 tool steel. The hardness of the nitrogen enhanced HIP-dripped O-1 alloys increased by a factor of two over the as-received material and increased linearly with increasing nitrogen concentration. Wear characteristics of the nitrogen enhanced O-1 also was significantly improved.

4. Discussion

HIP-drip processing produces iron-carbon ingots with high nitrogen concentrations. The technique greatly reduces the processing time by eliminating the need for nitrogen to diffuse through a molten ingot to reach a uniform concentration.

Both carbon and nitrogen have been shown to be austenite phase stabilizers, and are the strongest contributing elements in the “nickel equivalent” equation used to generate the Schaeffler stainless steel diagram. However, thermodynamics and practical experience have shown that both carbon and nitrogen individually have limited solubility in iron and readily form iron precipitates. Because of the difficulty in producing high nitrogen steels, little attention has been given to the possibility that the kinetics of high carbon and high nitrogen iron alloys might favor the retention of the austenite phase, even though numerous studies have shown that increasing the carbon concentration in iron alloys pushes the “knee” of the time-temperature-transformation (T-T-T curve) diagram to longer cooling times.

Because there is little solubility of carbon in iron nitrides and nitrogen in iron carbides as the solid cools down, both the carbon and nitrogen concentrations form a random interstitial solution in the austenitic phase. When the ratio of carbon-to-nitrogen reaches a certain level, the random distribution and diffusion motion of the carbon and nitrogen atoms interacts resulting in no local clustering of similar atoms and thus preventing formation of iron-precipitates which would reduce the local interstitial concentration and favor the austenite to ferrite transition. The retention of the austenite phase with increasing nitrogen (and carbon) concentration is consistent with previous studies [1, 2, 4]. The greater the nitrogen concentration the greater the retained austenite concentration. The expansion of the ferrite and retained austenite lattice dimensions are consistent with the measured total carbon and nitrogen concentrations being all interstitial [11, 12].

As with previous studies of nitrogen enhanced austenitic stainless steels [6, 13], the yield and ultimate strength increased with increasing interstitial nitrogen concentration (and with increasing retained austenite phase). Even with the increase in strength, the elongation at ultimate strength increases significantly over the argon processed O-1 steel. The wear properties are consistent with the increase in hardness. However, there was a change in material removal wear mechanisms. For the argon processed O-1 material, there was

numerous chipping of fine particles, whereas with the nitrogen enhanced O-1 with the retained austenite, there was significant plastic deformation of the material and no indication of chipping.

5. Conclusion

High-pressure HIP-dripped melting of high-carbon iron alloys in a HIP furnace using nitrogen as the pressurizing gas results in a duplex austenite/ferrite composition that is free of iron carbides and iron nitrides. As an interstitial solid solution, the co-operation of the carbon and nitrogen concentrations stabilizes, or helps to retain, the austenitic phase and strengthens the alloy. The interaction between carbon and nitrogen prevents, or hinders, formation of carbides and nitrides. Increasing the interstitial carbon and nitrogen concentration increased the retained austenite and increased the strength, hardness, and wear resistance.

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