

High-pressure nitrogen gas alloying of Fe–Cr–Ni alloys

Part II *Mechanical properties*

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The melting of Fe–Cr–Ni alloys under 200 MPa nitrogen pressure has shown that nitrogen significantly improves the mechanical properties. Tensile strengths of these high-nitrogen alloys were found to be proportional to interstitial nitrogen concentration. The tensile strengths of nitrogen-alloyed steels could be significantly increased over comparable carbon-alloyed steels. The increase in tensile strength was found to be proportional to the square root of the interstitial nitrogen concentration indicating that the strengthening may be controlled by thermal effects.

1. Introduction

Nitrogen steel is currently being suggested as a substitute for carbon steel because of improved mechanical, physical, and chemical properties. Commercial nitrogen steels are formed by adding metal nitrides to the melt. The metal nitrides dissolve in the melt and enter into the solid metal matrix as interstitial solute atoms. Nitrogen concentration is controlled by the alloy composition [1] and crystallinity [2]. Chromium and manganese increase the nitrogen solubility, nickel and carbon decrease nitrogen solubility [1]. Nitrogen solubility in the austenite phase (fcc) is nearly an order of magnitude greater than nitrogen solubility in the ferritic phase (bcc) [2]. Nitrogen solubility also can be increased by increasing the nitrogen pressure during melting [3–6]. Nitrogen concentrations approaching 1.0 wt% have been achieved using 4.2 MPa nitrogen pressure [7].

Increasing the nitrogen concentration in steels alters their mechanical, physical, and corrosion properties [1, 3]. Several current theories predict that mechanical properties of nitrogen alloys, such as tensile strength, are increased by the effects of interstitial nitrogen atoms [7–10]. In a detailed study, Byrnes *et al.* [11] demonstrated there are two components, thermal and athermal, in steel alloys with interstitial nitrogen that increase tensile strength. The athermal component of flow stress increases linearly with increasing nitrogen concentration, while the thermal component increases as the square root of the nitrogen concentration. The shear and elastic moduli increased with increasing nitrogen concentration.

Tensile data from commercial and experimental nitrogen austenitic steels indicate that both the tensile and yield strengths of nitrogen steels are proportional to interstitial nitrogen concentration [4, 7–12] (Fig. 1). The tensile properties of nitrogen steels at room temperature for nitrogen concentrations less than

0.3–0.4 wt% are approximately linearly proportional to the nitrogen concentration. For higher nitrogen concentrations, the tensile strength deviates from linearity, suggesting that the mechanism of nitrogen strengthening is influenced by the thermal component. Thermal strengthening occurs when the dislocation stress field interferes with the short-range order of highly stable nitrogen–chromium atom clusters. (It has also been observed that nitrogen steels have a higher elastic modulus resulting from nitrogen clusters that increase the stress needed for the dislocation movement [13].)

Mechanical properties of nitrogen-alloyed steels are independent of the technique that is used to obtain the particular concentration of nitrogen, whether that technique is addition of metal nitrides or application of nitrogen pressure. Through either technique, the tensile strengths are directly proportional to the nitrogen concentration [8]. Because no metal nitrides have been reported in these steels, all the nitrogen is presumed to be present as interstitial nitrogen.

In the present study, nitrogen concentration in the alloys was increased through nitrogen-high-pressure melting, N-HPM, with the total nitrogen concentration in the resulting N-HPM Fe–Cr–Ni alloys substantially above 0.5 wt% of commercial steels; the nitrogen solubility limit was reached and metal-nitrides formed. Through this study it will be shown that nitrogen solubility and, hence, tensile strengths of ultra-high-nitrogen steels are a function of alloy composition and possibly second-phase precipitates.

2. Experimental procedure

Ten Fe–Cr–Ni alloys were prepared as 100 g ingots by melting 99.9% pure elemental powders under high-pressure nitrogen gas, fabricated, and evaluated for mechanical properties. Granular chunks were loosely

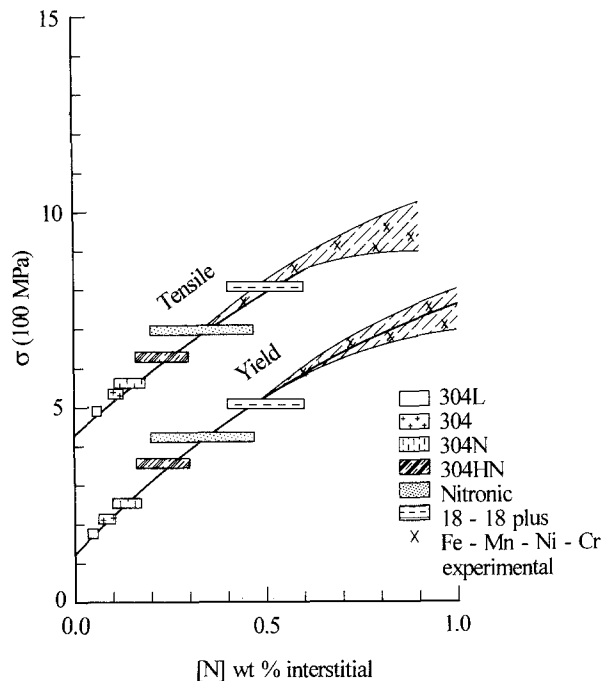


Figure 1 Yield and tensile strength of commercial nitrogen-containing steels and N-HPM steels.

packed in Al_2O_3 crucibles and placed in a hot-isostatic-pressure furnace that was heated to 1650 °C and pressurized to 200 MPa (2000 atm) using nitrogen. The temperature and pressure were held constant for 30 min, after which the pressure was held constant while the temperature was reduced significantly below the melting temperature before the pressure was reduced (Fig. 2). Detailed analysis of the microstructure and chemical composition were described in a previous publication [14].

The as-cast samples were metallographically sectioned. Rockwell hardness tests (HR_A) were conducted on these as-cast alloys (Table I). The pure iron and the Fe-Ni alloys were hot-worked at 800 °C, and Fe-Cr and the Fe-Cr-Ni were hot-worked at 1000 °C. Total work reduction was approximately 50% in 10% reduction steps. Owing to the thickness of the hot-worked sheets, Knoop hardness tests were conducted (Table I).

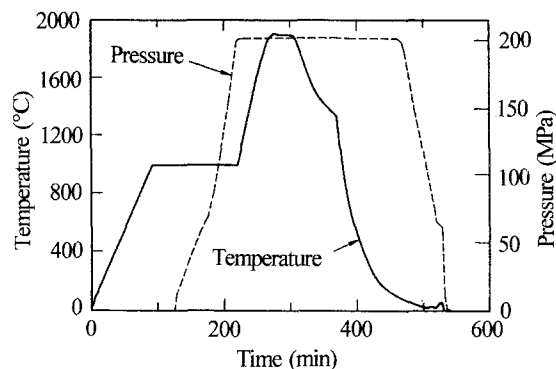


Figure 2 Schematic drawing of the N-HPM pressure/melting cycle profiles of time, temperature and pressure.

Subsized tensile samples were machined from the hot-worked sheets. Total sample length varied between 50 and 75 mm; sample width was 12 mm. The reduced test sections varied between 25 and 45 mm in length and were 6 mm × 1 mm in cross-section. Tensile tests were conducted in accordance with ASTM E-8. Equipment limitations did not allow for accurate determination of the yield strength or reduction in area. Only tensile strengths are reported in Table I.

Fractured surface, and cross-sectioned and metallographically polished hot-worked samples were examined with an SEM.

3. Results and analysis

Tensile tests, hot-working results, and hardness data are presented in Table I. Phase identification of the N-HPM materials are presented in Table II.

X-ray analysis shows that the iron and Fe-15Ni steels form iron nitrides. Those steels that contain chromium form CrN. Nitrogen analysis indicates that the nitrogen concentration depends strongly on the alloy composition. Increasing the nickel concentration lowers the nitrogen concentration. Increasing the chromium concentration increases the nitrogen concentration, both total nitrogen and interstitial nitrogen. SEM-EDX analysis in the metal matrix region showed a significant reduction in chromium concentration due to the formation of chromium nitrides.

TABLE I Alloy composition, fabrication history, and mechanical properties

Sample	Fe (at %)	Ni (at %)	Cr (at %)	Hot-working ^a	Tensile strength (MPa)	Hardness	
						As-cast HR_A	Hot-worked (Knoop)
1	100	—	—	8-51 OK	745	59.9	813
2	84	16	—	8-45 OK	896	61.3	370
3	69	31	—	8-52 OK	565	34.7	208
4	83	—	16	10-47 OK	472	64.5	635
5	65	—	34	10-46 OK	560	77.4	770
6	68	15	17	10-48 OK	776	58.4	266
7	54	15	31	Not-rolled	—	60.3	243
8	55	30	15	10-65 OK	529	52.3	197
9	39	28	33	10-47 poor	—	52.1	310
10	70	11	19	10-59 OK	882	68.5	480

^a XX-YY ZZ: XX = hot-working temperature (8 = 800 °C, 10 = 1000 °C), YY = total % reduction, ZZ = rolled sheet quality.

TABLE II Alloy metal chemical composition, matrix and precipitate phases, analysis of substitutional and precipitate chromium and nitrogen composition distribution

Sample	Alloy composition			Phases			Nitrogen concentration		
	Fe (at %)	Ni (at %)	Cr (at %)	Determined by X-Ray		Second-phase precipitate	Predicted		
				Matrix (%) bcc fcc	Matrix (%) bcc fcc		Schaeffler diagram ^a	Interstitial (at %)	Total (at %)
1	100	—	—	100	—	Fe ₄ N, Fe ₂ N	F-M	2.6	4.9
2	84	16	—	40	60	Fe ₄ N	A-M	1.7	2.3
3	69	31	—	—	100	—	A	0.9	1.2
4	83	—	16 (0.2) ^b	100	—	CrN (15.99) ^c	F-M	0.4	16.3
5	65	—	34 (8.6)	100	—	CrN (25.6)	F-M	0.8	26.4
6	68	15	17 (2.3)	20	80	CrN (14.2)	A-M	0.6	14.8
7	54	15	31 (11.2)	—	100	CrN (19.9)	A	1.1	21.0
8	54	39	15 (2.9)	—	100	CrN (21.1)	A	0.4	12.5
9	39	28	33 (13.9)	—	100	CrN (19.3)	A	0.9	20.2
10	70	11	19 (2.4)	40	60	CrN (16.2)	A-M	0.7	16.9

^a A = austenite, F = ferrite, M = martensite. (X) minor phase, < 15%, phase present.

^b Total chromium concentration of as-cast alloy, (XX) = chromium concentration of metal matrix with the Cr in the CrN subtracted.

^c Atomic per cent of chromium tied-up in CrN.

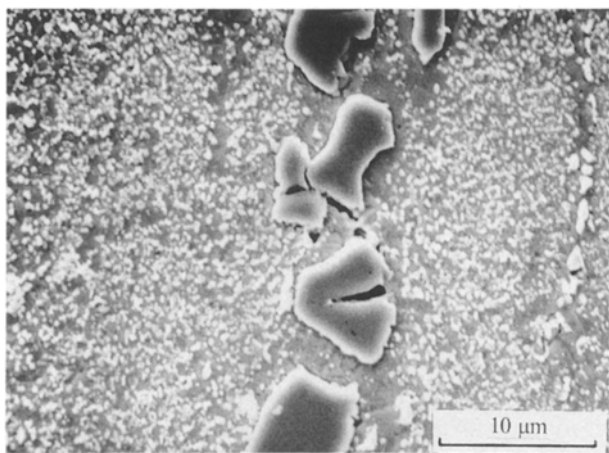


Figure 3 Cross-section of hot-worked material. The fine precipitates are the broken up eutectic CrN dendrites. The large chunks are broken up primary dendrites.

Fabrication temperatures and reduction procedures generally used to fabricate commercial stainless steel steels with little or no nitrogen can be used to successfully fabricate N-HPM steels.

SEM examination of cross-sectioned N-HPM material after hot-working and annealing shows that the CrN microstructure is broken up and the eutectic CrN precipitates are uniformly distributed throughout the metal matrix (Fig. 3). Primary CrN dendrites are also broken up. There are no holes or microcavities resulting from fragments being pulled out during polishing, indicating the CrN fragmented particles are strongly bonded to the metal matrix. Also, the quantity and size of the CrN fragments near the outer metal surface are similar to the CrN in the interior of the hot-worked sheet, indicating that CrN does not easily dissociate and diffuse out as a result of hot-working.

When the hardness of as-cast and hot-worked samples are compared, the alloy values are higher after hot-working suggesting that the material was not

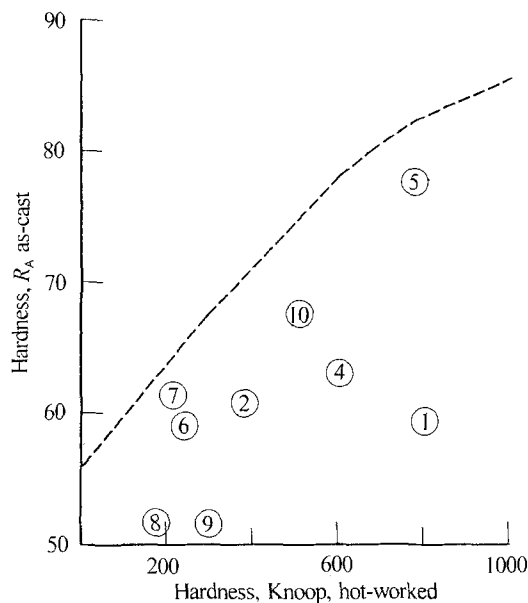


Figure 4 Comparison of as-cast and hot-worked hardness data. Data point symbols given in Table II. (---) One-to-one relationship equating HR_A and Knoop hardness values.

annealed and that some nitrides had dissociated and the nitrogen had dissolved into the matrix and strengthened the material (Fig. 4).

When tensile strengths are plotted as a function of hot-worked hardness, three distinct groupings are observed. Within the austenite phase, one grouping was associated with the austenitic phase (high nickel concentration), another with the austenite-martensite phase (low nickel concentration), and one with the (bcc)-martensite phase (no nickel) (Fig. 5). The greater the martensite phase content, the higher the hardness and the tensile strength. As expected, lower hardness values are associated with the austenite phase. Increasing the nickel concentration decreases the tensile strength and the hardness.

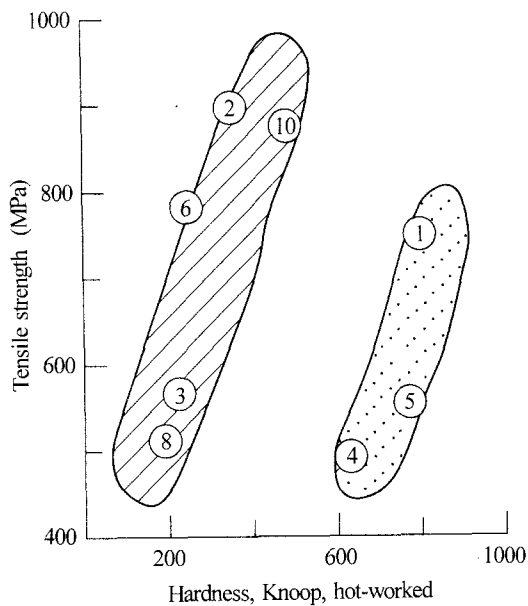


Figure 5 Tensile strength versus Knoop hardness. Data point symbols are given in Table II. The cross-hatched region has fcc structure. The dotted region has bcc structure.

Tensile strengths for the ultra-high nitrogen N-HPM steel are proportional to the square root of the interstitial nitrogen concentration. When tensile strengths of N-HPM alloys are compared to interstitial nitrogen concentrations, two data regions are observed (Fig. 6). One is associated with the austenite–martensite dual structure, the other with the single-phase pure martensite or pure austenite alloys.

4. Discussion

High concentrations of interstitial nitrogen and metal nitrides formed by melting Fe–Cr–Ni alloys under high nitrogen pressures improve mechanical and physical properties.

Hot-working properties of N-HPM steels are unaffected by large concentrations of interstitial nitrogen and the presence of metal nitride. The metal nitrides are readily broken-up and evenly distributed throughout the metal matrix. There is limited indication that metal nitrides dissolve at hot-working temperatures.

Hot-working the pure iron alloy (and possibly also the Fe–Ni alloys) increases the hardness much more than does hot-working the Fe–Cr alloys. This difference in hardenability may be related to the higher level of interstitial nitrogen measured in the as-cast material of these alloys. The N-HPM process increases nitrogen concentration substantially above nitrogen solubility at atmospheric pressure. Hardness data suggest that, during hot working, the supersaturated nitrogen attempts to reach equilibrium by forming submicrometre-sized metal nitride precipitates. Both interstitial nitrogen and the submicrometre-sized metal nitrides contribute to increasing resistance to plastic deformation and, therefore, to increasing hardness.

The high levels of nitrogen solubilities produce substantial quantities of metal nitrides. Metal nitride, especially CrN, forms a lightweight, high-strength, high-elastic moduli composite phase that bonds tight-

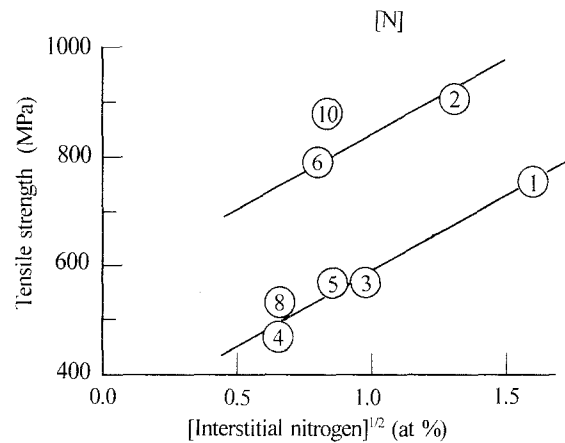


Figure 6 Tensile strength versus interstitial nitrogen. The upper line is associated with dual matrix phase structure. The bottom line is associated with single matrix phase.

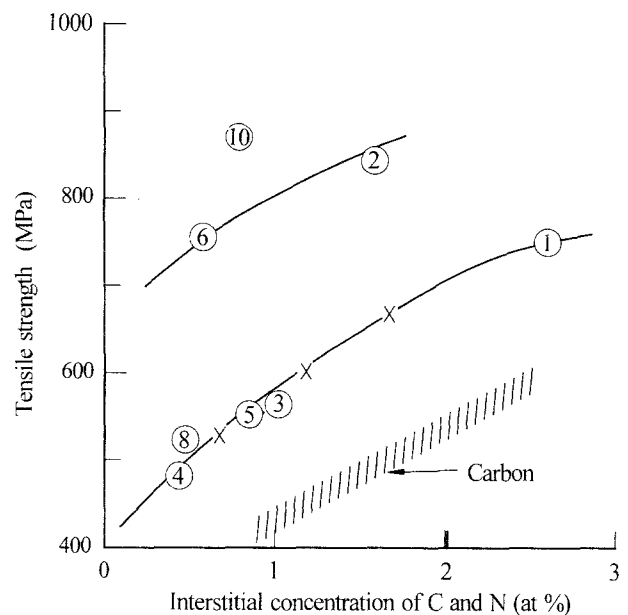


Figure 7 Comparison between tensile strength and interstitial nitrogen and carbon. Data point symbols are given in Table II. Note: atom for atom, nitrogen has approximately twice the strengthening power as does carbon.

ly to the metal matrix. Because CrN is less dense than iron–alloys, the iron–metal nitride composite density is reduced. Examination of the microstructure of the hot-worked material shows that metal nitride fragments remain tightly bonded to the metal matrix.

Increasing the interstitial concentration of nitrogen or carbon directly increases tensile strength (Fig. 7). However, atom for atom, nitrogen provides a much more efficient means of increasing tensile properties than does carbon [15]. Increasing interstitial nitrogen increases tensile strength properties. N-HPM data for high-nitrogen steels are consistent with the theoretical prediction that the increase in tensile strength should be proportional to the square root of the nitrogen concentration [11]. Note, higher carbon concentrations appear to increase tensile properties linearly.

The quantity of metal nitrides present in N-HPM alloys does not significantly alter tensile properties. However, the presence of these nitrides, up to 25 vol %

might affect other physical properties. The density of the N-HPM alloys results from a combination of the metal matrix and of the lighter, less-dense metal nitrides. Thus, the specific strengths of these N-HPM alloys are higher than those of similar nitrogen steels without metal nitrides. Note: we have shown that tensile strength of as-cast N-HPM metals is significantly stronger than the tensile strength of hot-worked metal and it increases linearly with increasing total nitrogen concentration [16].

In summary, the concentration of interstitial nitrogen is controlled by the alloy composition and, for Fe–Cr–Ni alloys, is approximately 1.0 at %. Any further nitrogen results in the formation of metal nitrides. The tensile strength for hot-worked N-HPM alloys is proportional to the square root of the interstitial nitrogen concentration. The formation of metal nitrides does not improve tensile strength, but does increase the specific tensile strength.

5. Conclusions

By varying Fe–Cr–Ni alloy composition, the nitrogen solubility resulting from nitrogen high-pressure melting can be controlled. The tensile strength of Fe–Cr–Ni alloys prepared by N-HPM are similar to tensile strengths of nitrogen alloys prepared by adding metal nitrides and with comparable interstitial nitrogen concentrations. However, melting under high nitrogen pressures can produce significantly higher interstitial and total nitrogen concentration. The higher nitrogen solubility resulting from N-HPM often results in the formation of metal nitrides. The tensile strength of nitrogen steels is directly related to the interstitial nitrogen concentration. For a given matrix crystal structure (austenitic, ferritic, or martensitic), the higher the interstitial nitrogen concentration, the higher is the tensile strength.

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