

Sintered High Nitrogen Stainless Steel Obtained using Pre-Mixed Powders

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Abstract Nitrogen alloying in martensitic stainless steels has been considered as an alternative to improve mechanical properties and corrosion resistance. The use of conventional melting and solidification processes is not the most efficient way to produce high nitrogen steels (HNS) since nitrogen solubility in melt is quite low. Nowadays, HNS is being produced by Powder Metallurgy and, in this case, the nitrogen is alloyed in the solid state, especially considering reactions between high nitrogen sintering atmospheres and pre alloyed pressed bodies. This paper investigates another possibility regarding the introduction of nitrogen in stainless steel, i.e., the use of high nitrogen chromium powders (nitrided powders) mixed with ordinary atomized iron powder. This mixture was pressed and sintered at 1350 °C for 2 and 8 hours. As reference, two other set of “nitrogen free” samples were produced and characterized: sintered pre-alloyed 434L stainless steel (commercial powder); sintered pre mixed Fe + “nitrogen free” Cr. The discussion was based on shrinkage during sintering, microstructural aspects and corrosion resistance.

Introduction

Martensitic stainless steel has been used in high strength applications combining hardness, toughness and corrosion resistance [1,2,3]. Different classes of martensitic stainless steels with different carbon content have been produced but, to improve corrosion resistance, the carbon present in this class of steels has been totally or partially replaced by nitrogen [3]. Production of HNS is difficult and expensive due to the low solubility of nitrogen in liquid iron (under atmospheric pressure). Different production routes for high nitrogen stainless steels have been previously investigated [4,5,6] and Powder Metallurgy can be considered as an attractive route due to the possibility of adding high nitrogen contents under low pressures [2,3,7], as can be seen in Fig. 1.

The route (A) was investigated previously [2,8] and it was concluded that the substitution of carbon by nitrogen in both as-sintered and full-density (hot isostatically pressed) stainless steels improves

their uniform corrosion resistance in acid environment. The beneficial effects of nitrogen on localized corrosion resistance depend on sintered density.

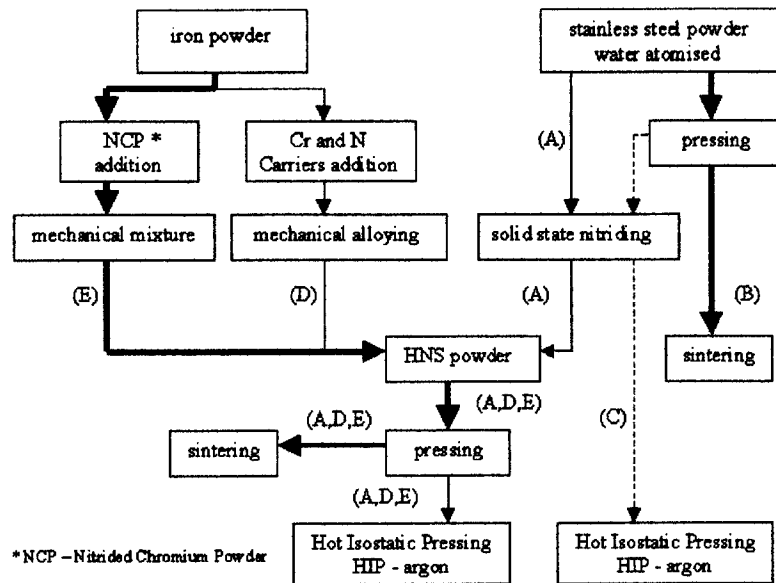


Fig. 1 – PM routes to produce sintered stainless steels.

Experimental Procedure

Three sets of specimens were produced (Fig. 2):

Group (E-PM): Pre-mixed (PM) powders processed through route E in Fig.1. Flakes of electrolytic chromium were milled and then nitrided in a tubular furnace at 1000°C, under 2.5 atm of pure N₂ for 30 min. The nitrided chromium was milled again and classified between 325 and 400 mesh. This NCP (nitrided chromium powder) was mixed with commercial atomized iron powder to produce a mixture with 18 wt.% Cr (route E in Fig. 1). As the nitrogen content of the NCP was 18.1 wt.%, the nitrogen content of the mixture was around 3.3 wt.%. The mixture was pressed at 700 MPa (cylindrical samples) and the sintering was carried out in a dilatometer at 1350°C (heating rate of 20°C/min) for 2 and 8h under dynamic atmosphere (N₂-10H₂). The cooling rate was 30°C/min.

Group (B-PA): Pre-alloyed powders processed through route B in Fig. 1. Commercial AISI 434L stainless steel powder (17 wt.% Cr, 0.02 wt.% C) was pressed under 700 MPa and cylindrical samples were produced. Pressed samples were sintered in a dilatometer at 1350°C for 2 or 8 hours under a dynamic atmosphere of N₂-10H₂.

Group (E-PM-NF): Pre-mixed (PM), nitrogen free (NF) powder, processed through the route E in Fig. 1. The same as group E but the chromium powder was not nitrided.

Dilatometric measurements were carried out in a 402S Netzsch dilatometer. Densities were determined geometrically. Microstructures were observed by optical microscopy. Cyclic polarization tests were performed in 0.5 M H₂SO₄ + 3.5% NaCl solution by a PAR 273 potentiostat with the reference of calomel electrode and platinum counter-electrode. The applied potential was changed at a rate of 1 mV/s, and all the specimens were prepared in emery paper up to a 600 grade

before the tests. Polarization Resistance (R_p) and Pitting Potential (E_p) parameters were computed from polarization data to analyze the generalized and localized corrosion resistance of the specimens respectively.

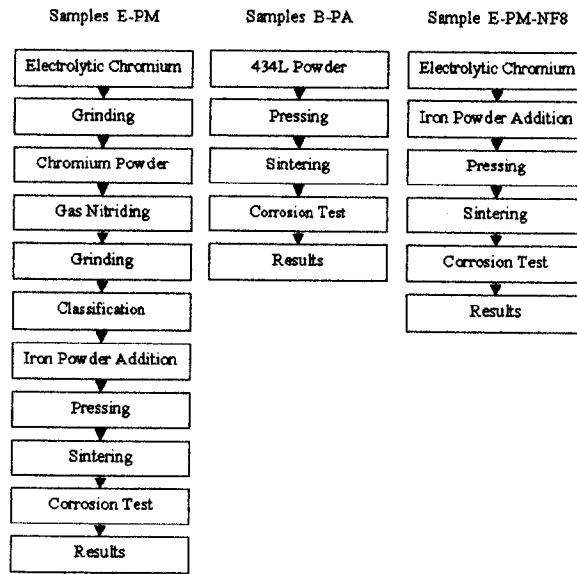


Fig. 2 – Experimental procedures: routes E-PM, B-PA and E-PM-NF.

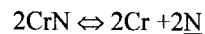
Results and Discussion

Table 1 shows some characteristics of three sets of samples. The green density is basically the same in all cases. The sintered densities for the pre-mixed powders (E-PM and E-PM-NF) were lower than pre-alloyed (B-PA), probably because the iron and chromium diffusion disturbed the neck growth between particles, thereby reducing shrinkage. The nitrogen content after sintering was reduced from 3.3 wt.% to around 0.5% wt.%.

Table 1: Density and chemical composition of the specimens.

Specimen	Sintering Time	Green Density [g/cm ³]	Sintered Density [g/cm ³]	N content [wt. %]
E-PM2	2 h	6.23	6.74	0.50
E-PM8	8 h	6.23	7.05	0.46
B-PA2	2 h	6.19	7.17	--
B-PA8	8 h	6.21	7.36	--
E-PM-NF8	8 h	6.44	6.88	--

Fig. 3 shows different dilatometric behaviors, especially during heating, for samples E-PM and B-PA sintered for 2 hours. Sample E-PM2 presented one transition at around 900°C that corresponds to $\alpha \rightarrow \gamma$ transition. The shrinkage related to neck growth between iron particles started at 1000 °C and it was observed sharp (step) shrinkage at around 1100 °C that could be related to the chromium nitride decomposition, which can be described by the reaction [1] and illustrated by the calculated phase diagram in Fig. 4.



[1]

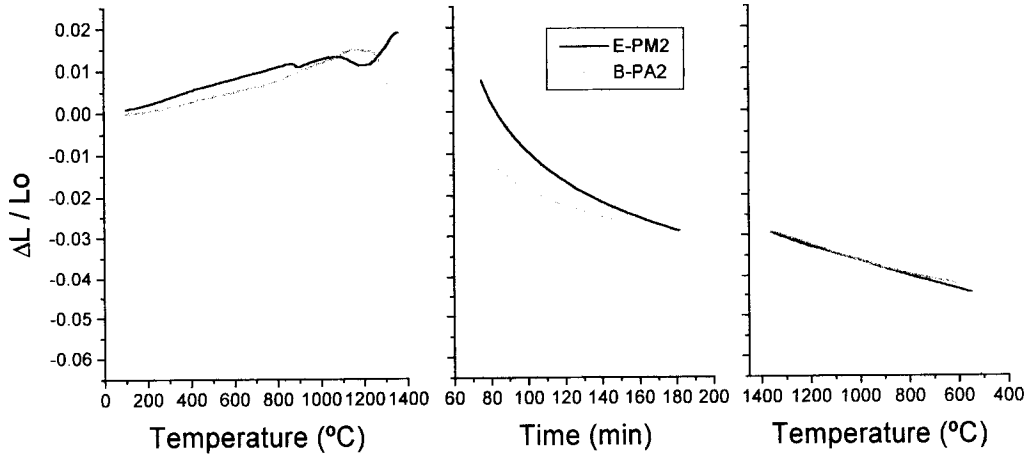


Fig. 3: Dilatometric curves of samples E-PM2 and B-PA2.

For the sample B-PA2 only the shrinkage (neck growth between 434L particles) at around 1200 °C was observed.

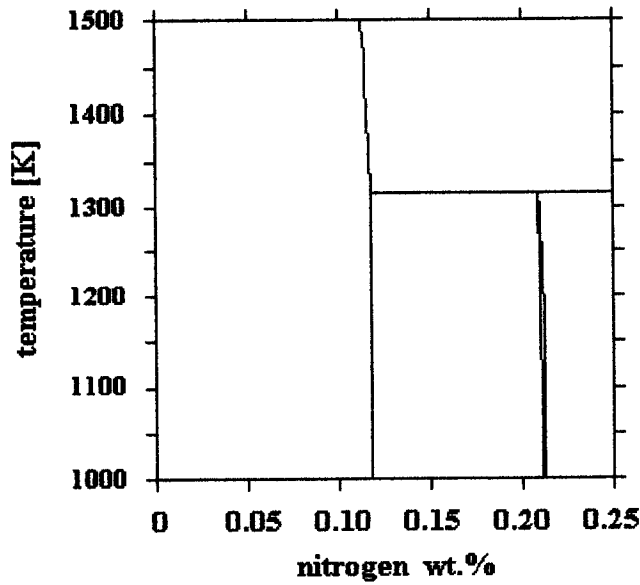


Fig. 4: Diagram CrN – 1 atm nitrogen gaseous.

Fig. 5 present dilatometric curves for samples sintered for 8 hours. The behavior of the samples E-PM and B-PA was the same. Sample E-PM-NF8 did not show shrinkage during heating.

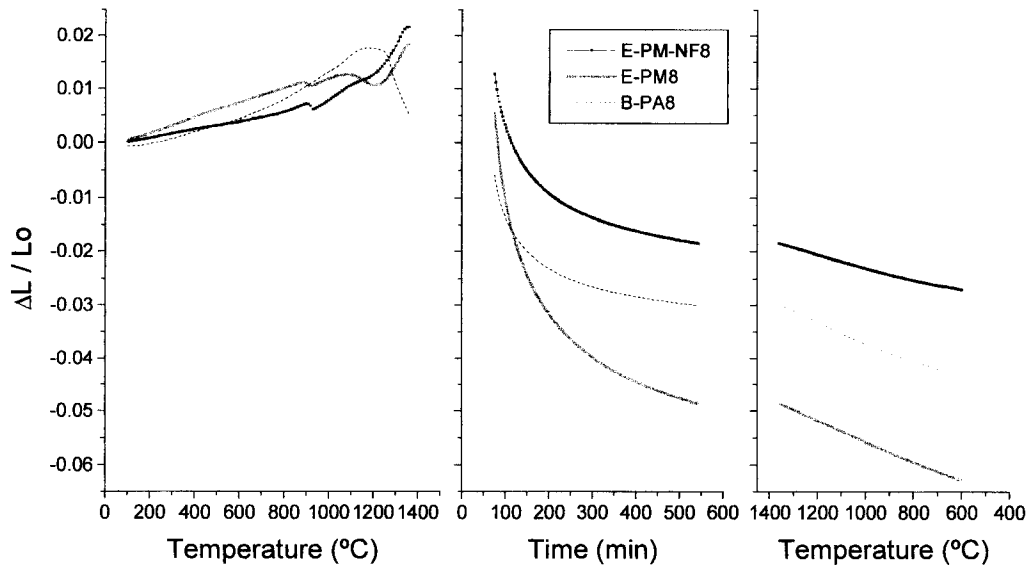


Fig. 5: Dilatometric curves of samples E-PM8, B-PA8 and E-PM-NF8.

Fig. 6 and 7 show microstructural aspects (optical microscopy) for samples E-PM2 and B-PA2. Sample E-PM2 shows large rounded pores and a martensitic microstructure, due to the presence of nitrogen. Sample B-PA2 presents rounded pores inside ferritic grains, which is an indication of grain growth and that densification was limited by bulk diffusion.

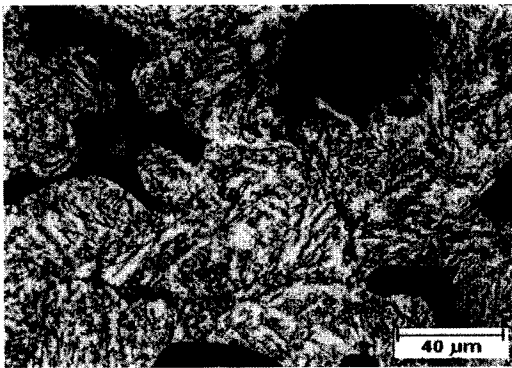


Fig. 6: Optical micrograph of the sample E-PM2. Kalling.



Fig. 7: Optical micrograph of the sample B-PA2. Kalling.

Fig. 8, 9 and 10 show typical polarization curves for some of the steels produced, and Table 2 indicates the Polarization Resistance (R_p) and Pitting Potential (E_p) parameters of the specimens. The AISI 434L steel (B-PA8) showed better localized corrosion resistance than the nitrided samples (E-PM), but this behavior was probably influenced by the differences in densities, 7.36 compared with 7.05 and 6.84 g/cm^3 (table 1). On the other hand, the R_p parameter had its highest value for sample E-PM8, which indicates the beneficial effect of nitrogen on uniform corrosion resistance when this element is homogeneously distributed in the steel, even with low densities.

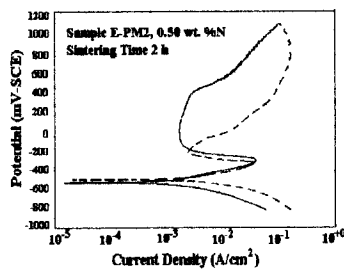


Fig. 8: Cyclic Polarization Curve of Sample E-PM2

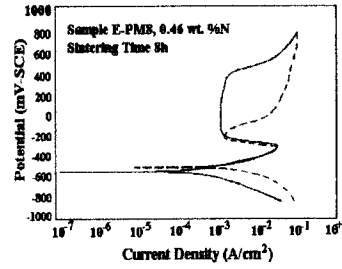


Fig. 9: Cyclic Polarization Curve of Sample E-PM8

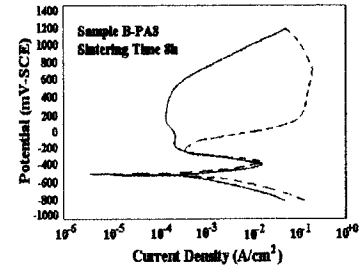


Fig. 10: Cyclic Polarization Curve of Sample B-PA8

Table 2: Polarization Resistance (R_p) and Pitting Potential (E_p).

Sample	R_p ($\Omega \cdot \text{cm}^2$)	E_p (mV-SCE)
E-PM2	44.0 ± 5	402 ± 16
E-PM8	61.4 ± 3	430 ± 14
B-PA8	58.9 ± 5	460 ± 21

Conclusions

The shrinkage of pre-alloyed steels was higher than that of the pre-mixed ones.

A martensitic microstructure was obtained in all the nitrogen alloyed specimens.

The pre-alloyed steel AISI 434L "nitrogen free" showed better localized corrosion resistance than the nitrogen-alloyed samples, but this behavior was probably influenced by the differences in density between the specimens.

Nitrided samples showed good generally corrosion resistance.

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