

Microstructure and Corrosion Resistance of Simultaneous Nitrided and Sintered AISI 434L Powder

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Abstract: Water atomized AISI 434L (17%Cr-0.02%C) powder was compacted and then simultaneously sintered and gas nitrided. The specimens were treated in the 1273K-1473K range under Nitrogen pressures between 0.15 and 0.36 MPa during 3 to 9 hours, and then cooled down with a maximum cooling rate of 200K/min. Under 1373K treatment sintered high Nitrogen stainless steels were obtained, the Nitrogen content ranging between 0.7%N and 1.3%N, similar to the carbon contents of conventional AISI 440 A, B, C. The samples were analyzed by Optical and Scanning Electron Microscopy and by X-ray diffraction. Martensite plus retained austenite and some chromium nitrides were found in the microstructures of the 1373K and 1473K specimens. A maximum density of 88% of the theoretical was obtained after the 1473K treatment. Corrosion tests were carried out in the sintered plus nitrided samples. The specimens with the greatest amount of chromium nitrides showed poor resistance to generalized and pitting corrosion. Samples where the microstructure was composed mostly by martensite plus retained austenite showed a better generalized and pitting corrosion resistance.

Introduction

Nitrogen bearing stainless steels have been studied during the last years, due to improvement in properties this element promotes when in solid solution. Austenitic stainless steels with high Nitrogen contents can be used to manufacture surgical implants and many different components for chemical, petrochemical and mining industries [1,2]. In some cases, Nitrogen and Manganese are used to replace Nickel, with the purpose of obtaining low allergenic materials [3]. High Nitrogen martensitic stainless steels, on the other hand, can be used in many components of pumping and conveying systems, hydroelectric and gas turbine installations, aircraft industry and other applications where simultaneous corrosion and wear resistance are required, together with good mechanical resistance and high strength/weight ratio [1,2,4].

Nitrogen addition to steel can be made directly on liquid alloy by pressurized molten metallurgy techniques [1], but the process is expensive and very difficult to carry out in laboratory. Solid state diffusion is used to obtain case hardened steels, with high Nitrogen concentration gradients from surface to nucleus. Powder metallurgy, conversely, can be used to obtain Fe-Cr-N alloys with an even distribution of Nitrogen over the volume. Nitrogen can be added to the powder before compaction, during sintering or in a final full-density process like Hot Isostatic Pressing (HIP). When nitriding is simultaneously done with sintering the surface of the steel is put in contact with gaseous Nitrogen at high temperature. Dissociation of the gaseous bi-atomic molecules occurs and individual Nitrogen atoms can cross over the surface of the particles. Under equilibrium conditions there is a maximum quantity of Nitrogen that can be absorbed by the solid at each temperature and gas pressure. This maximum Nitrogen content may be the result of different reactions each one with a specific equilibrium constant [5]. Nakamura *et al.* and Toro *et al.* observed that, in the 1273-1473K range, the saturation Nitrogen content of Fe-17%Cr [6] and Fe-23%Cr [7] powders after

three hours treatment decreased with the increase in treatment temperature during simultaneous sintering and nitriding processes. In contrast, some authors have shown that for the same alloys the Nitrogen solubility in austenite increases with temperature [8,9].

Nitrogen can enhance some important corrosion and mechanical properties when added to stainless steels. When Nitrogen is in solid solution fatigue and creep resistances of some austenitic stainless steels can be increased [2,10] while wear and corrosion-wear resistances are improved when in martensitic stainless steels [11,12,13,14]. Nitrogen-alloyed stainless steels can be highly passivated and repassivated when compared to carbon-alloyed stainless steels with equivalent interstitial elements contents, and MN and M₂N type nitrides promote less matrix sensitization than M₂₃C₆ and M₇C₃ type carbides [11,15].

The main purpose of this work was to study the microstructure and corrosion resistance of high Nitrogen AISI 434L stainless steels obtained by simultaneous sintering and gas nitriding applied to pressed specimens.

Experimental

Material

AISI 434L stainless steel powder was used as raw material in this investigation. Table 1 shows the nominal composition and some physical characteristics of the AISI 434L powder.

Table 1. Nominal composition and some characteristics of AISI 434L stainless steel powder

Cr (%)	Mn (%)	Si (%)	Mo (%)	C (%)	N (%)	D _{apparent} (g/cm ³)	Mean particle diameter (μm)*	Microstructure
17.0	0.20	0.90	1.0	0.02	0.018	2.66	68	Ferrite

*Measured by laser interferometry method

Carbon-alloyed stainless steels

AISI 434L stainless steel powder was mixed with graphite powder and then compacted. Identification of specimens was made according to its carbon content as follows: 440A (0.6%C), 440B (0.9%C), 440C (1.0%C). The pressed specimens were sintered in a 0.15MPa Argon atmosphere at 1473K during 6 hours, and then cooled down to room temperature with a cooling rate of 200K/min.

Nitrogen-alloyed stainless steels

Cylinders made of green compact with 78-80% of the theoretical density were obtained by pressing AISI 434L powder at 700MPa. Simultaneous sintering and gas nitriding was performed in a tubular furnace where high purity Nitrogen was introduced. After the treatment, cold Nitrogen was blown on the specimens placed in the radiation-isolated front end of the furnace. Equilibrium constants for the overall reaction calculated in a previous work [6] allowed calculation of optimum experimental conditions used in the treatments. Some of the alloys obtained, 440AN, 440BN and 440CN, have Nitrogen contents equivalent to the Carbon contents of the conventional stainless steels 440A, 440B and 440C, respectively. Table 2 indicates the sintering + nitriding conditions.

Table 2. Experimental conditions for simultaneous nitriding and sintering treatments

Sample	T (K)	P _{N₂} (MPa)	Time (hours)	Cooling Rate (K/s)	Sample	T (K)	P _{N₂} (MPa)	Time (hours)	Cooling Rate (K/s)
440AN	1373	0.15	6	3.3	440BN-T1	1373	0.25	3	0.8
440AN-CR	1373	0.15	6	0.8	440BN-T2	1373	0.25	9	0.8
440AN-T1	1373	0.15	3	0.8	440CN	1373	0.36	6	3.3
440AN-T2	1373	0.15	9	0.8	440CN-CR	1373	0.36	6	0.8
440AN-HD	1473	0.25	6	1.6	440CN-T1	1273	0.15	3	3.3
2489G	1473	0.15	6	3.3	440CN-T2	1273	0.15	9	3.3
440BN	1373	0.25	6	3.3	440CN-HN1	1273	0.25	6	3.3
440BN-CR	1373	0.25	6	0.8	440CN-HN2	1273	0.25	6	0.8

X-Ray diffraction and microstructure characterization

Diffraction tests were performed in a PW1710 PHILIPS Diffractometer, with a Copper anode tube and scanning angles between 20° and 120°. Optical and Scanning Electron microscopes were used to characterize the microstructure of all the specimens.

Corrosion Tests

Cyclic polarization curves for 440A, 440B, 440C, 440AN, 440BN and 440CN samples were obtained in a *Princeton Applied Research* potentiostat model 273, with saturated calomel reference electrode (SCE) and Platinum counter electrode. The electrolyte used was 0.5M H₂SO₄ + 3.5% NaCl and the tests were performed at (23±2)°C. All the samples were polished in emery paper up to grade 600, cleaned in ultrasonic device, rinsed with alcohol and dried with warm air before the tests. All the curves were obtained at a potential scan rate of 1mV/s, with starting point at 300 mV below the established corrosion potential. The samples were immersed in the solution for 5 min before starting the test.

Results And Discussion

Solid state alloying

The sintering + sintering + nitriding treatments produced alloys with chemical compositions and microstructures indicated in **Table 3**.

Table 3. Chemical composition and microstructure of investigated materials

Sample	%C	%N		Microstructure	Sample	%C	%N		Microstructure
		(a)	(b)				(a)	(b)	
440A	0.6	-	-	M+A+C↓	440BN-CR	-	0.89	0.91	F+M+N↑
440B	0.9	-	-	M+A+C↑	440BN-T1	-	0.87	-	F+A+N↓
440C	1.0	-	-	A+M+C↓	440BN-T2	-	0.88	-	F+A+N↓
440AN	-	0.66	0.66	M+A	440CN	-	1.31	1.35	M+N↑
440AN-CR	-	0.62	0.68	F+M+N↓	440CN-CR	-	1.25	1.30	F+M+N↑
440AN-T1	-	0.63	0.68	M+A	440CN-T1	-	1.50	-	M+N↑
440AN-T2	-	-	0.65	M+A	440CN-T2	-	1.45	-	M+N↑
440AN-HD	-	0.60	0.65	M+F+A	440CN-HN1	-	2.57	-	M+N↑
2489G	-	0.40	0.45	M+A	440CN-HN2	-	2.50	-	M+F+N↑
440BN	-	0.89	0.92	M+A+N↓					

(a) Measured by Fusion under Inert Gas Analyzer

(b) Measured by weighing the mass of the samples before and after the treatments

C↑=High volume fraction of carbides, C↓=Low volume fraction of carbides, N↑= High volume fraction of nitrides, N↓= Low volume fraction of nitrides, F=ferrite, M=martensite, A=austenite

Results showed that the saturation Nitrogen content decreases when the temperature increases in the range 1273K-1473K. Through an adequate selection of Nitrogen pressure for each temperature it was possible to get alloys with Nitrogen contents around 0.7, 0.9 and 1.3%N. At 1473K it was not possible to obtain the alloys with 0.9 and 1.1%N, due to the high pressures needed, above 0.9MPa, beyond the furnace capacity.

Microstructure characterization



a) 440A, OM

b) 440B, OM

c) 440C, OM

Figure 1. Microstructure of the 440A, 440B and 440C stainless steels sintered specimens. Etchant: a) and b): Kalling's 1, c) Vilella.

Table 3 and **Fig. 1** show that austenite stability increases with Carbon addition to the AISI 434L powder. The alloy with 0.6%C (440A) showed a microstructure composed by martensite, retained austenite and precipitated carbides; while the alloy with 1.0%C (440C) showed an austenitic microstructure with few precipitated carbides. **Fig. 1** shows the microstructure of the three carbon-alloyed stainless steels. In figure 1c, taken from the 1.0 % C specimen, martensite plates can be seen in some austenite grains. Microstructures of the Nitrogen-alloyed steels were dependent on the Nitrogen content, nitriding + sintering temperature and cooling rate. The samples treated at 1473K and cooled at 200K/min, with Nitrogen contents varying from 0.40 to 0.65%N, showed microstructures composed by martensite, retained austenite and few precipitated nitrides. On the other hand, specimens nitrided and sintered at 1273K and cooled at 50K/min (sample 440CN-HN2), with Nitrogen contents up to 2.5%N, showed profuse precipitation of nitrides in a mainly ferritic matrix. When the cooling rate increased the amount of nitrides was still high, but the matrix was composed by a greater volume fraction of martensite (sample 440CN-HN1). In samples sintered and nitrided at 1373K, with 0.7 to 1.3%N, it was observed that the increase in Nitrogen content led to an increase in the amount of precipitated nitrides and a decrease in the volume fraction of martensite, even for the highest cooling rate. **Fig. 2** shows the microstructure of some of the high-Nitrogen stainless steels obtained in this work.

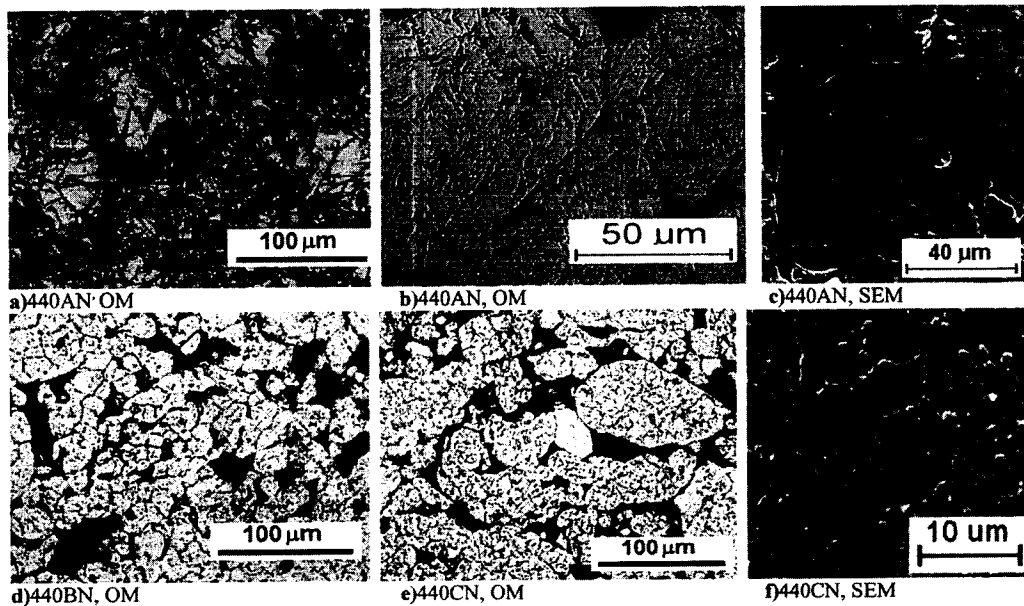


Figure 2. Microstructure of high-Nitrogen stainless steels obtained by simultaneous sintering + nitriding process. Etchant: Kalling's 1.

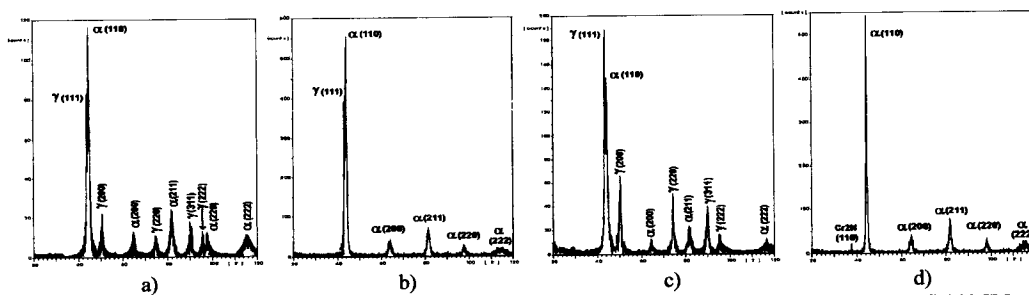


Figure 3. X-Ray diffractograms of some of the obtained alloys. a)440A, b)440AN, c)440C, d)440CN.

Figure 3 shows X-ray diffractograms for some of the studied alloys. Generally speaking, the carbon-alloyed specimens showed high intensity austenite peaks and smaller ferrite (martensite) and carbide peaks. The Nitrogen-alloyed specimens showed high intensity ferrite (martensite) peaks and smaller nitride and austenite peaks.

Corrosion tests

Table 4 shows the general results of corrosion tests, and Figure 4 shows typical cyclic polarization curves of 440A, 440AN, 440B, 440BN, 440C and 440CN specimens.

Table 4. Results of cyclic polarization tests

Sample	Polarization Resistance ($\Omega \cdot \text{cm}^2$)	Pitting Potential (mV,SCE)	Protection Potential (mV,SCE)	(% of theoretical density)	% C or N	Microstructure
440A	(15±6)	(452±15)	(-483±6)	88	0.60	M+A+C
440B	27	484	-487	88	0.90	M+A+C↑
440C	(10±3)	(441±26)	(-484±1)	88	1.00	A+C
440AN	(34±5)	(465±8)	(-529±8)	82	0.66	M+A
440BN	(58±7)	(381±18)	(-532±3)	81	0.89	M+A+N↓
440CN	(16±3)	≤-524 (Corr. Potential)	≤-524 (Corr. Potential)	81	1.31	M+N↑

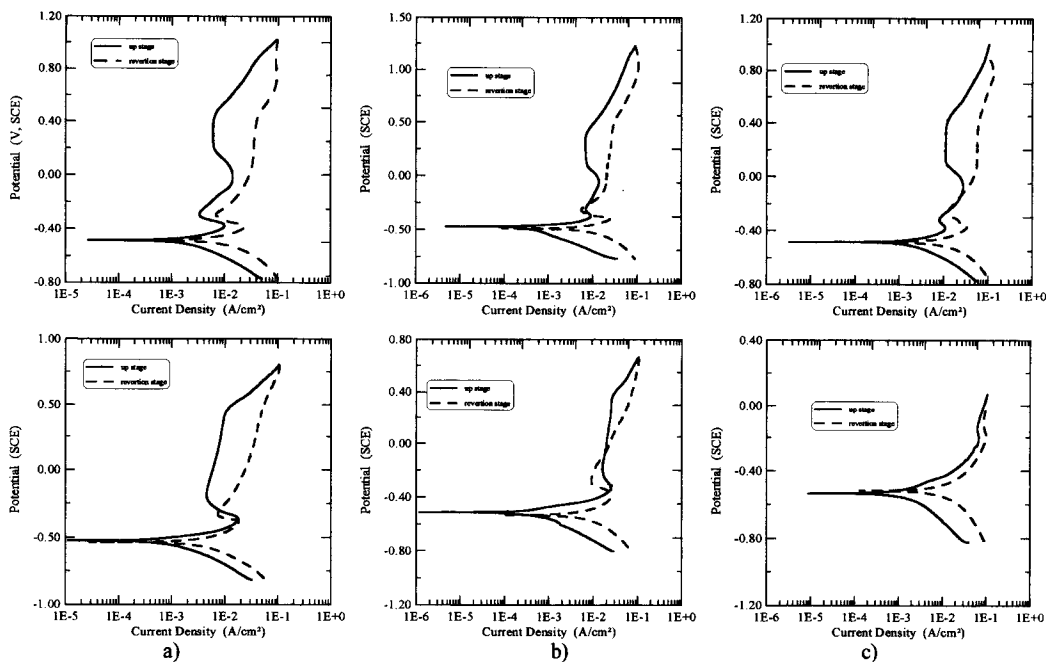


Figure 4. Typical cyclic polarization curves of the studied materials. a)440A (above) and 440AN (below); b)440B (above) and 440BN (below),c)440C (above) and 440CN (below). 0.5M H₂SO₄ + 3.5% NaCl solution

Cyclic polarization curves of all the studied materials (Figure 4), with the exception of the 440CN specimen, showed similar cathodic (hydrogen reaction), active and passive regions, with pitting and protection potentials clearly established. Protection corrosion is low for all the samples, being practically coincident with the corrosion potential. However, two particular characteristics can be observed in curves of Carbon-alloyed samples: 1)A second peak of anodic current density is present in all the curves, probably due to the existence of Chromium-impoverished regions in metallic matrix, as a consequence of Chromium carbides precipitation [16], and 2)Near to critical current, the current density values in the reversion stage are higher than in the up stage, probably indicating an increase in area during the up stage. This fact was observed in sensitized AISI 410 and 420

martensitic stainless steels [17,18]. Curves of Nitrogen-alloyed samples did not show these two characteristics. This fact can indicate that Nitrogen-alloyed samples are more resistant to intergranular corrosion than Carbon-alloyed samples.

It can be seen that the resistance to uniform corrosion in acid environment of Nitrogen-alloyed samples is better than Carbon-alloyed samples with equivalent interstitial contents, as indicated by the Polarization Resistance values in Table 4. This beneficial effect of Nitrogen was also observed in AISI 420 martensitic stainless steels modified with nitrogen by ONO *et al.* [12.,19]. The comparison between the Nitrogen-alloyed and Carbon alloyed specimens is valid due to the little influence of sample density on polarization resistance, as it was shown in a previous work [16]. On the other hand, Nitrogen addition caused a decrease in pitting potential (E_p) probably as a consequence of a decrease in the Chromium content of metallic matrix, promoted by the precipitation of Chromium nitrides. Only the 440AN sample, with 0.66%N, had a pitting resistance slightly higher than equivalent Carbon-alloyed sample 440A (0.6%C). However, it must also be considered that density of samples has significant influence in this case, due to the dependence of pitting corrosion with porosity. It was shown in a previous work that in simultaneously sintered and nitrided stainless steels, the higher the porosity the lower the pitting potential (E_p) [16].

Conclusions

- Nitrogen bearing stainless steels with controlled Nitrogen contents were obtained by a simultaneous nitriding and sintering treatment. Through an adequate selection of Nitrogen pressure for each temperature it was possible to get alloys with Nitrogen contents around 0.7, 0.9 and 1.3%N.
- Increasing treatment temperature led to higher densification and lower Nitrogen absorption in the range 1273K-1473K.
- Nitrided samples with Nitrogen contents up to 0.9 % showed microstructures composed by ferrite (martensite), austenite and few precipitated nitrides. When the Nitrogen content was greater than 1.1 % the amount of nitrides strongly increased and the volume fraction of ferrite (martensite) decreased.
- Substitution of Carbon by Nitrogen in 440A and 440B type stainless steels improves the uniform corrosion resistance in acid environment. The beneficial effect of Nitrogen could be more significant in samples with higher density.
- Both Nitrogen-alloyed and Carbon-alloyed steels showed low pitting repassivation capacity.

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