

Evaluation of nitriding process effects on cold worked AISI 304 and 316 austenitic stainless steels

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Abstract The nitriding behavior of austenitic stainless steels (AISI 304 and 316) was studied by different cold work degree before nitriding processes. The microstructure, thickness, microhardness and chemical composition were evaluated through optical microscopy, microhardness, scanning electron microscopy techniques (WDS microanalysis). It was observed that previous plastic deformations do not influence expressively on layer thickness. Two different layers can be identified as result of the nitriding process: the first due to the austenitic matrix expanded by nitrogen atoms, the second, a thinner layer expanded by carbon atoms.

1 Introduction

The austenitic stainless steels are plenty utilized in chemical processes equipment in pharmaceutical, foodstuff, textile, petroleum, cellulose industries, where these components are exposed at aggressive ambient conditions and low temperatures. These steels are also employed in orthopedic implant due to its biocompatibility [1].

The austenitic stainless steels, despite the elevated corrosion resistance, have low hardness and small tribological behavior. Those characteristics impede your application in wear strength. To surpass this problem there are alternatives studies with surfaces properties changes, without hinder other properties like, for example, the corrosion resistance. One alternative is the thermochemical process, the well-known nitriding process that basically can utilize one of the three methods: gaseous, salt bath or plasma. The nitride process, independent of the method, increases the surface hardness of austenitic stainless steels and promotes higher wear resistance [2].

The literature has shown that is possible utilize nitride process in austenitic stainless steels; one of the phases is formed with nitrogen in solid solution, increasing the hardness of the surface and the wear resistance without loss of corrosion resistance. This phase is the expanded austenite due to the nitrogen action and is called as Y_N or S phase. The phase identification is relating to the obtained x-rays diffraction reflections that are dislocated with low Bragg angles relating to the positions in a normal austenite phase [3].

The plasma nitriding allows the nitrogen introduction in steels with temperatures of 450°C, producing a harder structure and metastable phases resistant to the corrosion. Many literature define this phase formed at low temperature as a nitrogen supersaturate phase, with a distorted

crystalline FCC structure, nitride free, known as “S” phase or “ Y_N ” expanded austenite [4, 5, 6].

The austenitic stainless steels response to the conventional nitriding processes ($500^\circ\text{C} \leq T \leq 600^\circ\text{C}$) é surprising principally because a metal initially with hardness of 200 HV can surpass values of 1300 HV in the nitriding layer, that is the same order observed in carbides present in some tools steels. I. L. Singer was the first author to identify this layer as expanded austenite, but also is a phase called as “S phase” or “m phase”. The expanded austenite is a layer rich in nitrogen, obtained in austenitic stainless steels like the AISI 304 after nitriding in temperature of 500°C [7].

Structural analyses show that the modified layer is dominated by a cubic phase with a considerable expansion of the austenite lattice and in some cases a fine layer ($<0.1\mu\text{m}$) of CrN and α -Fe precipitates at the surface. The lattice parameters show that the expanded austenite could be described by a special triclinic crystalline structure [8].

The hardening can also modify the diffusion kinetics of nitriding process and consequently the nitride layer formation and until now there are few studies about it. This work shows a study of nitriding kinetics processing applied to the AISI 304 e AISI 316 stainless steels when initially submitted to different grade in cold work plastic deformation.

2 Materials and Methods

The austenitic stainless steels can have expressive deformation rate and hardening after cold work processing. In the present study were utilized cold worked and heat treated steels sheet (AISI 304 with 1,0 mm thickness and AISI 316 with 1,5 mm thickness).

The utilized sample deformation process in this work to produce plastic deformation was prepared by tensile test with a universal machine tensile test MTS810, with the ASTM E8MM-98 test procedure.

Table1. Chemical Composition (weight %) of the studied steels.

AISI	%C	%Si	%Mn	%P	%S	%Ni	%Cr	%Mo
304	0.08	1.00	2.00	0.045	0.03	8.0 / 10.0	18.0 / 20.0	-
316	0.08	1.00	2.00	0.045	0.03	10.0 / 14.0	16.0 / 18.0	2.0 / 3.0

The applied deformation rates were: 0% (heat treated), 10%, 20%, 30%, and 40%. The three possible nitriding processes were explored. Each tested sample was divided in four identical samples (Figure 1):

- Samples 01: For characterization of initial condition;
- Samples 02: Gaseous nitriding at 570°C during 3.5 h;
- Samples 03: Plasma nitriding at 430°C during 5 h;
- Samples 04: Liquid Nitriding at 570°C during 2h.

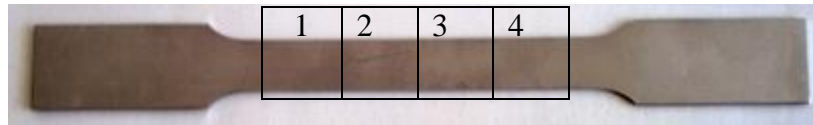


Figure 1: *Schema of distribution of each divided sample.*

After traditional steels metallographic preparation method (mounting, planar grinding, rough polishing, final polishing, and etching with Marble's reagent), all samples were observed in optical microscope Leica with A4iDocu image capture program. The nitriding layer of the steels samples was measured and also documented by photographic register.

For SEM observations the sample were completely re-polished, cleaned and a conductive Al layer. Samples pattern were utilized for the carbon concentration determination to compare with the evaluated samples. The N and C elements were quantified with a WDS MICROSPEC analyzer in a SEM PHILIPS Quanta 600. Starting at the surface of the analyzed samples the N and C chemical composition curves were determined obtaining analysis at points spaced out to 5 μm .

For steel matrix hardness measurements and also the hardness profile related to the layer depth were utilized Vickers hardness equipment with the following parameters: load = 50 g; Load halt time = 15 s.

3 Results and Discussion

The tensile test curves of the samples are presented in the Figure 2. The cold deformed austenitic stainless steels can induce martensite formation, which depends of the direct alloy chemical composition; for example the carbon presence tends to lower the temperature of the beginning of the martensite formation and consequently reduce also the possibility of the martensite induced by plastic cold deformation.

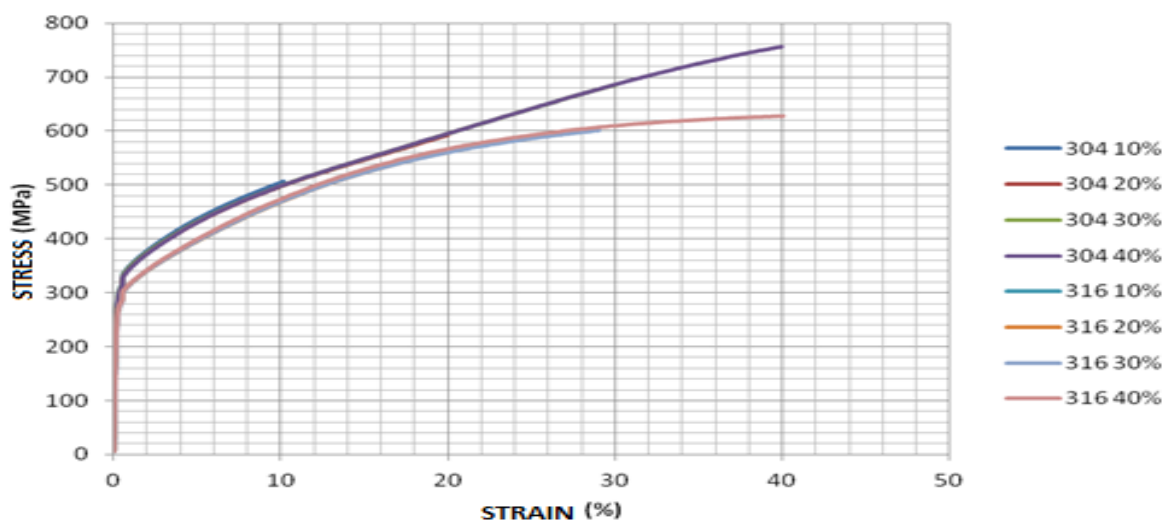


Figure 2 - *Stress- Strain Curves in deformed AISI 304 and 316 samples.*

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The AISI 304 steels show a strong tendency to the occurrence of martensite during the plastic cold deformation, principally in low carbon steels as 304L [9]. It is estimated a good crystal defects density to evaluate this influence in the kinetics study of the nitrogen diffusion during the nitriding processes.

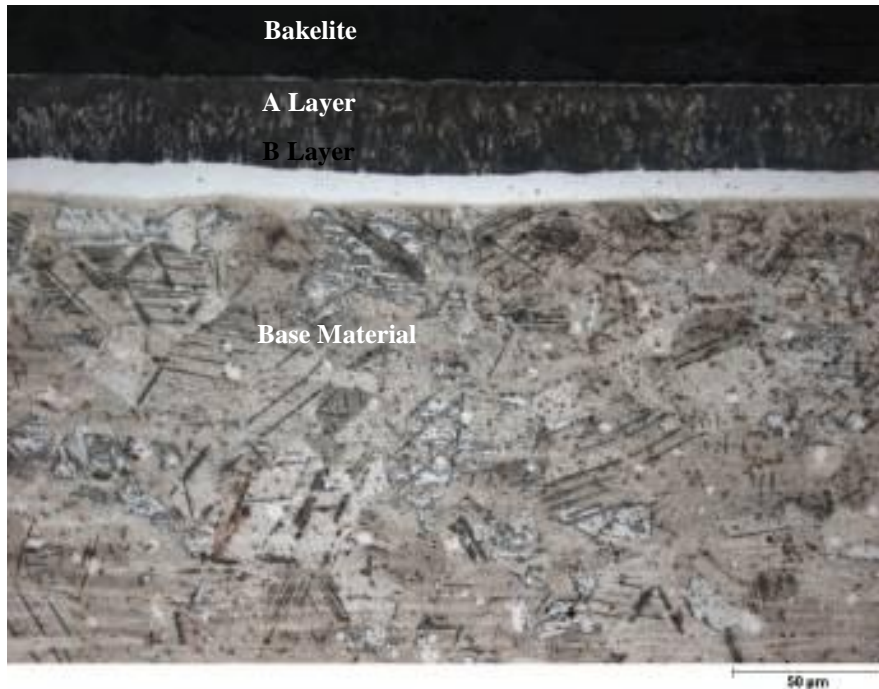


Figure 3 - Reference for the nitride layer thickness measurements.

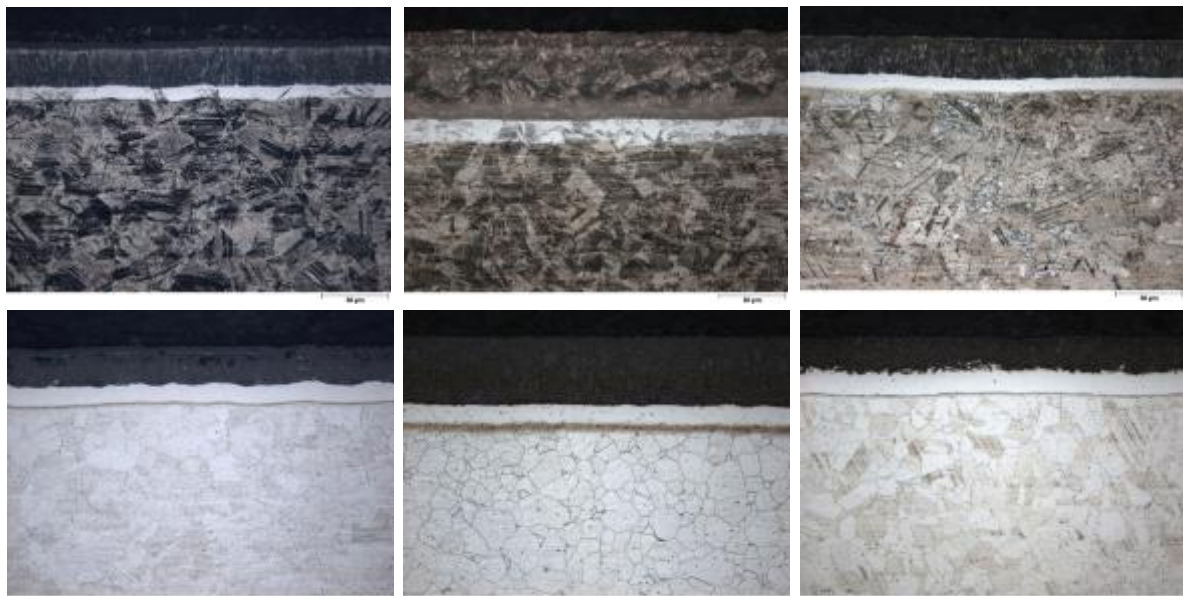


Figure 4 - AISI 316 (a) liquid nitriding process; (b) gaseous nitriding process; (c) plasma nitriding process. AISI 304 (a) liquid nitriding process; (b) gaseous nitriding process; (c) plasma nitriding. (Marble etching).

With optical microscopy it is observed two sub layer inside the nitride area in sample (Figures 3 and 4). Moreover, the thickness variations were random (Table 3) and do not suggest any tendency relating to the influence in nitride thickness due to the samples pre deformation.

Table 3 - Thickness of the nitride layer (μm) relating to the Figure 3.

AISI	Deformations	A Layer			B Layer		
		Gaseous	Plasma	Liquid	Gaseous	Plasma	Liquid
304	0%	71	33	34	16	10	10
	10%	67	29	33	15	13	10
	20%	65	34	33	13	9	10
	30%	66	26	32	17	11	10
	40%	71	26	33	18	12	10
316	0%	51	29	28	12	17	11
	10%	48	20	23	12	18	10
	20%	50	27	22	15	13	9
	30%	47	28	24	15	17	10
	40%	51	20	26	14	18	10

4 Chemical Analysis by WDS (Scanning Electron Microscopy)

It can be observed the nitrogen and carbon concentration, illustrated in Figures 5, obtained by wave dispersive X-rays spectrometry (WDS) using SEM, which the first layer has a nitrogen concentration of 5.5% and the second layer shows a 1% carbon concentration peak. Both steels have 0.08 weight % of carbon and with the exception of the liquid nitriding process, the gaseous and plasma processes are carbon free. This indicated that probably occurs in this region a decarbonization with nitrogen diffusion and these carbon atoms are diffusing to regions just below the real nitride layer, forming a second layer with a bigger carbon concentration. In this way originates two layers, the first a matrix of austenite expanded by nitrogen atoms, followed by another layer formed by matrix of austenite expanded by carbon atoms.

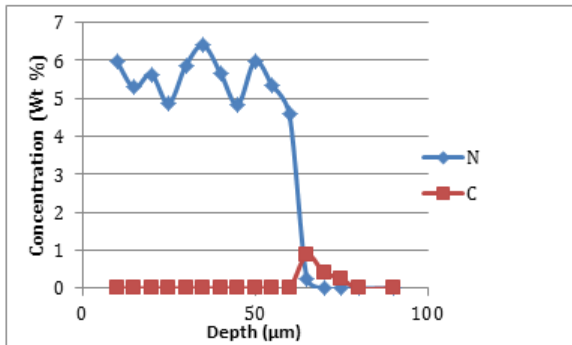
The figure 6 shows the hardness value of the samples with different degree of cold work before nitriding processes. There is a considerable hardness increase, more with the AISI 304 steel, possibly due to the strong tendency to the occurrence of martensite induced by plastic cold work. The figure 7 shows the hardness curves of samples after nitriding process; it can observe, with the data, that the applied pre cold work shows a little influence in all the utilized diffusion processes. Regarding that both AISI 304 and 316 were nitrated together, that is in same conditions, it is observed that more high hardness values in AISI 304 samples depth.

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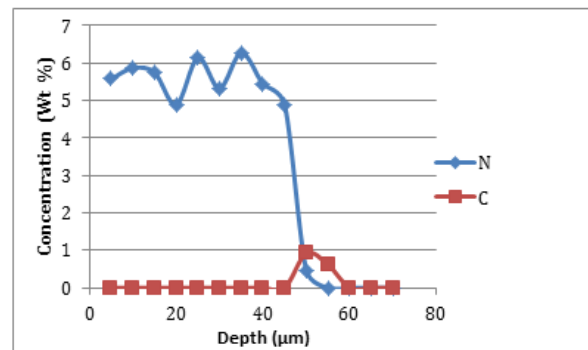
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Besides higher values were obtained in samples with plasma nitriding processes, probably due to the applied process temperature (plasma, $T = 430^{\circ}\text{C}$; Gaseous and Liquid, $T = 570^{\circ}\text{C}$).



(a)



(b)

Figure 5: Nitrogen and carbon distribution (weight %) regarding to the layer depth in (a) AISI 304 steel and (b) AISI 316 steel.

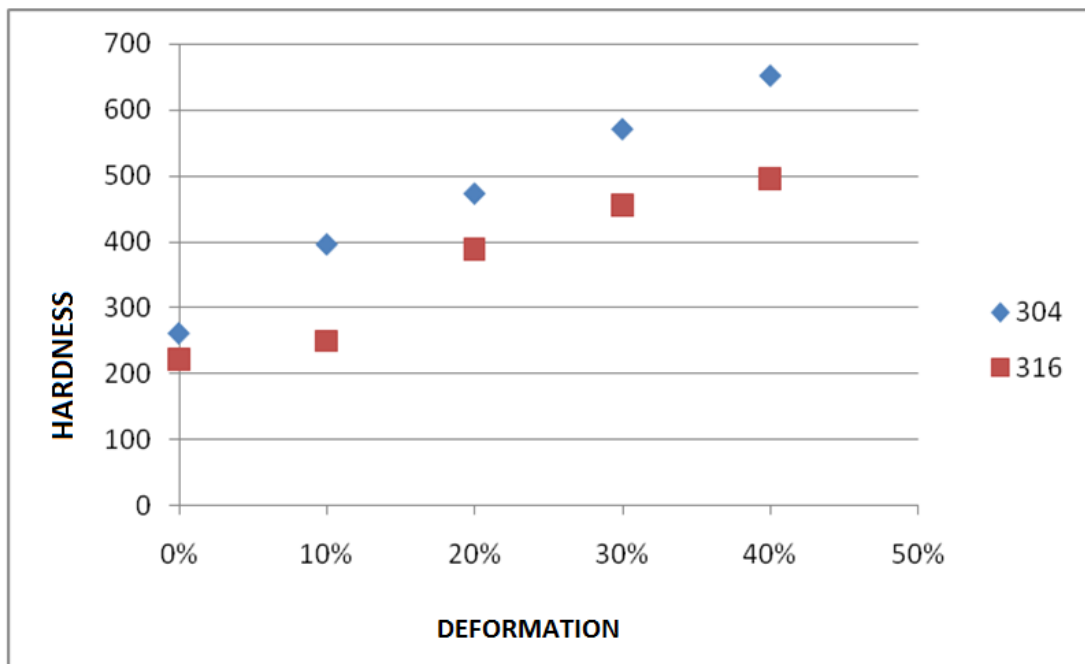


Figure 6: Hardness Values of the cold work samples of AISI 304 and 306 steels.

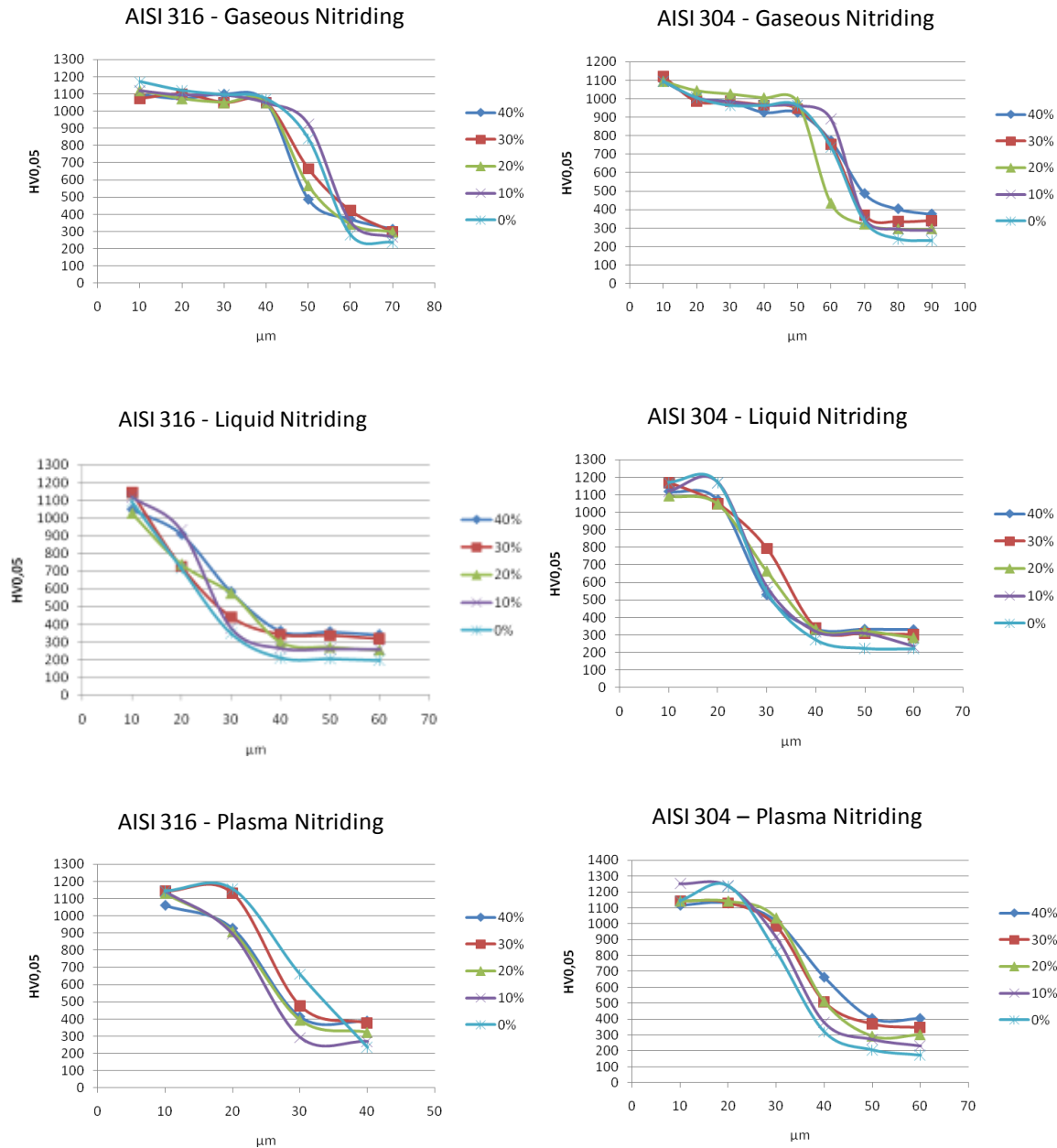


Figure 7: Hardness Curves in samples after different nitriding processes.

5 Conclusions

The applied hardening does not show special influence in nitriding kinetics. Two distinguished layers are observed, one made with a matrix of austenite expanded by the presence of nitrogen atoms followed by a second layer formed with austenite expanded by the presence of carbon atoms. The gaseous and liquid nitriding processes showed hardness values in the layers of 1100 HV and the plasma nitriding process 1200 HV. It is also observed bigger diffusion kinetics occurrence with the AISI 304 steel.

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7 References

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