

# INFLUENCE OF THE CHEMICAL COMPOSITION ON THE BEHAVIOR OF AUSTENITIC STAINLESS STEEL IN FLUID LAYER NITRIDING PROCESS

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## ABSTRACT

The main factors that influence the stainless steel behavior to the nitriding process are: chemical composition, nitriding temperature, treatment time. Researches have revealed that, with low temperature nitriding, the chemical composition expressed directly by the alloying elements or indirectly by the austenite or ratio  $E_{Cr}/E_{Ni}$  stability index decisively influences the characteristics of the nitride layer. The high alloyed steels having over 50% alloying element and high stability index S=30, produce a diffusion layer of a low nitrogen concentration, below the saturation limit, and hardness less than 500 HV<sub>005</sub>. The usual stainless steels CrNi, CrNiMo of low stability index S=17.5-24 at 500°C, within the sensitive temperature range form high hardness combinations (1200-1400 HV<sub>005</sub>) and at temperatures of 450°C under the sensitive range, diffusion layers of high nitrogen concentrations close to the saturation limit, featuring high hardness 1100-1200 HV<sub>005</sub> and slightly lower depths, tens of microns.

KEYWORDS: nitriding process, stainless steel, austenite

### **1. Introduction**

Due to the large variety of austenitic stainless steels subject to nitriding process it is compulsory to investigate their behavior under the specific technological conditions of the nitriding treatment and fluid layer process.

Under similar nitriding conditions, i.e. nitriding atmosphere consisting of nitrogen and 30% ammoniac, gas pressure able to provide smooth fluidization, the enclosure characteristics, it was found that the major factors nitriding behavior depends upon are: the steel chemical composition, nitriding temperature and time.

The chemical composition of the austenitic stainless steels is an extremely important factor which is characterized directly from the concentrations of the chemical elements or indirectly from the austenite stability index S or  $E_{\rm Ni}/E_{\rm Cr}$  ratio. Table 1 gives the chemical compositions, the values of the stability index S and  $E_{\rm Ni}/E_{\rm Cr}$  ratio for six austenitic stainless steel grades which undergo the nitriding treatment.

Steel	Steel	С	Cu	Cr	Ni	Mo	Ti	V	S	E <sub>Cr</sub> /E <sub>Ni</sub>
code	SR: EN 10283-98	[%]								$\mathbf{L}_{Cr}/\mathbf{L}_{Ni}$
1	X2CrNi18.8	0.12	0.06	23.2	9.8	0.11	0.01	0.02	24	1.78
2	X6CrNi18.10	0.06	0.08	17.1	9.3	0.05	0.60		19	1.26
3	X2CrNi18.9	0.03	0.19	18.9	8.95	0.15	0.01	0.02	17.5	1.95
4	X2CrNiMo17.11.2	0.02	0.27	20.0	8.8	2.7	0.03	0.03	21.6	2.23
5	X6CrNiMoTi17.12.2	0.045	0.16	18.1	11.6	2.04	0.32		22.6	1.48
6	X1CrNiMoCu20.18.7	0.02	0.70	20.1	18.1	6.1		0.2	29.8	1.40

Table 1.



# 2. Results and discussion

Nitriding process was carried out at  $450^{\circ}$ C and  $500^{\circ}$ C for 3 hours. With the steel code 6-X1CrNiMoCu20.18.7 having a concentration of the alloying elements of 50% and a very high austenite stability index S=29.8, the behavior to nitriding was different from that of the other steels, irrespective of temperature or exposure times.

At low temperatures,  $450^{\circ}$ C and  $500^{\circ}$ C, the layer hardness was about 500HV<sub>005</sub> or even lower and the layer depth of tens of microns.

Even lower values of the layer hardness and depth were reported with temperatures below 450°C. This result is accounted for by the low velocity of nitrogen diffusion into the high-alloyed steel and high concentration of Ni and Cu which increase the Ni austenitezed effect.

The high stability index of the austenite prevents the formation of combination layers at all treatment temperatures applied. The diffraction diagram analysis made on DRON confirms the presence of the diffusion layer of austenitic structure for the steel code 6-X1CrNiMoCu20.18.7. The aspect of the diffraction diagram in case of steel code 6 is similar to that of the initial austenitic stainless steel with some modifications determined by the occurrence of phase  $\gamma_{\rm N}$ . Figure 1 illustrates the presence of drops according to the diffraction angles as determined by the gamma phase  $\gamma_{Fe}$ . With the austenitic stainless steel, the gamma phase is a solid carbon solution in the Fey which is highly alloyed with Cr Ni Mo etc. It can also be seen the drops of the phase  $\gamma_N$  diffraction angles, which is nitrogen enriched austenite by its diffusion into the inter-atom spaces which cause a slight expansion of the crystalline mesh.



Fig 1. Diffraction diagram, nitrated sample steel code 6-X1CrNiMoCu20.18.7.

The austenite nitrogen enrichment results in increased hardness, to a large extent this is also due to the small amount of nitrogen. The max value of hardness reported was  $500 \text{ HV}_{005}$ .

To a lesser degree is visible the phase CrN, the chrome nitrides looking like scarce points in the vicinity of the surface. As mentioned before the steel code 6-X1CrNiMoCu20.18.7 features over 50% alloying elements, a high austenite stability index S=29.8 consequently, the nitrogen gets dissolved into austenite without causing nitride separations but in very small, negligible amounts.

The structure, however, is still austenitic due to the small concentration of dissolved nitrogen. The metallographic analysis carried out on nitrated samples of this steel, figure 2, does not seem to show a distinct layer structure; the layer proved to be a diffusion austenitic layer made up of phases such as  $\gamma_{Fe}$  -austenite and  $\gamma_N$  -nitrogen enriched austenite, whose mesh has a slightly high parameter because the mesh expansion is determined by the penetration of interstitial nitrogen atoms.



**Fig 2.** Microstructure of the nitrated layer at 500°C steel code 6-X1CrNiMoCu20.18.7 x400



The other steels code 1 -X10CrNi18.8, code 2 -X6CrNiTi18.10, code 3 -X2CrNi18.9, code 4 -X2CrNiMo17.11.2, code 5 -X6CrNiMoTi17.12.2 features a totally different behavior as compared with steel code 6 - X1CrNiMoCu20.18.7 but somehow similar among them. With nitriding at 500°C they formed an external hard layer, hardness varying

between 1200-1400  $HV_{005}$ , consisting of nitrogenenriched austenite and strong nitrides separations CrN,  $Fe_4N$ , etc. of high hardness.

The nitride layer could be seen by metallographic analysis figure 3 and figure 4 featuring a distinct structure due to the existing combinations of tens of micron depths.



Fig 3. Microstructure of the nitrated sample of steel code 2-X6CrNiTi18.10



Fig 4. Microstructure of the nitrated sample of steel code 4–X2CrNiMo17.11.2 x400



Fig 5. Diffraction diagram for sample steel code 2-X6CrNiTi18.10



Depth is different from one steel to another; the depth of steel code 2–X6CrNiTi18.10 and steel code 3–X2CrNi18.9 is higher by almost 40 microns as these steels have austenite stability indexes smaller of about  $S_2=19$ ,  $S_3=17.5$ .

With steel, nitrogen diffusion takes place under more favorable conditions.

The analysis of the diffraction diagram for steel code 2–X6CrNiTi18.10 figure 5 indicates the presence of drops corresponding to Fe<sub>4</sub>N, CrN and to a smaller extent the presence of gamma phase  $\gamma_N$ . Both nitrides and solid phases in nitride based austenite determine considerable increase of hardness above 1200HV<sub>005</sub>.



Fig 6. Diffraction diagram sample steel code 4–X2CrNiMo17.11.2.

The aspect of the diffraction diagrams is similar for the first five steels except that drop intensity corresponding to phase  $\gamma_N$  takes a larger or smaller value depending on its stability. Figure 6 presents the diffraction diagrams for steel code 4-X2CrNiMo17.11.2 with an austenite stability index higher than steel code 2. It can be noted that the relative drop intensity of phase  $\gamma_N$  is higher as well. The decrease in the nitriding temperature of these steels results in a spectacular change. The metallographic analysis fails to reveal the presence of a surface layer of distinct structure figure 7. The structure is of diffusion type consisting of nitrogen austenite with nitride punctilious enriched segregations. The hardness reported in the nitrated layer takes values over 1100HV<sub>005</sub> which indicates a higher concentration of nitrogen, almost close to the saturation limit. Figure 8 makes a comparison between the diffraction diagrams for the samples of steel code 4–X2CrNiMo17.11.2.in initial state and under nitriding process at 450°C.



**Fig 7.** Microstructure of steel code 4–X2CrNiMo17.11.2.nitrated at 450°C





*Fig 8.* Diffraction diagrams of the samples of steel code 4–X2CrNiMo17.11.2.in initial state and under nitriding process at 450°C.

On the diffraction diagram of the initial sample drops corresponding to phase angles  $\gamma_{Fe}$  can be seen, featuring an austenitic structure as well. On the diffraction diagram of the sample nitrated at 450°C it can be seen large amplitude drops corresponding to the diffraction angles of phase  $\gamma_N$ , nitrogen enriched austenite and smaller amplitude drops for the diffraction angles corresponding to the CrN phase. This indicates that the structure contains small amounts of CrN nitrides along with nitrogen enriched high alloyed gama solid solution. The presence of the two phases accounts for the increase in the pregnant hardness to be found with the nitriding layer at 450°C.

#### 3. Conclusions

Low temperature nitriding of high alloy austenitic stainless steels fails to result in harder layers since austenite stability does not allow for nitrides separation. At the same time the high concentration over 50% of the alloying elements limits nitrogen diffusion and keeps it well below the saturation limit. The highest influence is that of the Ni concentration over 18% and copper of about 1% which increase the Ni austenitezed effect. With usual austenitic stainless steels nitriding at 500°C results in layers of separate nitride combinations inside the nitrogen enriched austenitic volume as a consequence of the low stability index, the deepest depths being reported with low index steels. Decreasing the nitriding temperature to 450°C under the austenitic stainless steel sensitivity limit leads to diffusion layers made up of nitrogen enriched austenite of high nitrogen concentration which is close to the saturation limit.

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