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SURFACE HARDENING BY NITRATION FOR SOME STAINLESS AUSTENITE STEEL TYPES

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ABSTRACT

Stainless austenite steel types have a good resistance to corrosion in different natural, industrial environments but their hardness and mechanical resistance are low enough. In order to assure an increased resistance to abrasion it is necessary to increase also the surface hardness. This thing is possible if the nitrogen concentration in the surface layer is increased by means of nitration.

The researches made on stainless austenite steel types pointed out a strong hardening tendency for the major part of steel types except for steel type 2CuMoNiCr200. The austenite in this has a very high degree of stability as a result of high content of alloying elements. When the nitrogen is diluted, the hardness is more reduced. Hardness strong increase in the other steel types is determined by complex nitrides separations favoured by nitrogen diffusion and increase of its concentration in the surface layer. The thickness of the hard layer increases depending on the period of nitration process from one hour to 3 hours and is influenced also by the characteristics of each sample.

KEYWORDS: austenitic stainless steel, nitration, corrosion, erosion

1. Introduction

Stainless austenite steel types have a good resistance to corrosion in different natural, industrial environments but their hardness and mechanical resistance are low enough. In man] cases industrial installations components are subjected both to corrosion and to erosion because the fluids are moving with relative high speeds, and the erosion is favoured by the presence of some hard particles in this fluids.

Such cases can be seen for example in the mining industry at the ore preparation installations, in soil fertilizers industry, in paper and cellulose industry etc.

The increase of facilities lifetime is possible by assuring a higher hardness degree that can be more resistant to erosion if this resistance to corrosion is maintained in reasonable limits.

It is well known that for normal steel types is possible to assure a surface hardness if a carburization thermo-chemical treatment followed by quenching and tempering is applied.

For stainless austenite steel types the increase of carbon content determines, in certain temperature conditions, the precipitation of chrome carbides to the limit of austenite grains and implicitly, to decrease of resistance to inter-crystalline corrosion.

In order to remove this inconvenience, it is recommended to replace the carburization with nitration.

Nitration as well as carburization, assures an increase of surface hardness without affecting the resistance to inter-crystalline corrosion.

Nitrogen alloying extends austenite stability domain even if the carbon content is higher, diminishing the danger of chrome carbides precipitation, of decreasing the chrome content in austenite and its de-homogenization, these being the main reasons for inter-crystalline corrosion.

2. Experiments

The materials subjected to research were stainless austenite steel types Cr-Ni and Cr-Ni-Mo with low carbon content %C<0.03, with higher carbon content %C=max.0.12 and even higher and stabilized with Ti or Nb. The chemical composition of these steel types is presented in table 1. The samples were made from rolled plates, the austenite structure being obtained after a quenching treatment of adding into solution. They were cut-off at 60x20x3 mm, by chipping and with abundant cooling. Samples quality surface is important because it may influence the nitration process. A polished surface assures an uniform layer but a slow development of the process.

Table 1

Steel code	**Related mark**	**C**	**S**	**P**	**Mn**	**Si**	**Cu**	**Cr**	**Ni**	**Mo**	**Ti**	**V**
		[%]										
1	12NiCrl80	0.12	0.028	0.055	1.24	1.64	0.06	23.	9.8	0.11	0.01	0.02
2	10TiNiCrl80	0.06	0.008	0.036	1.55	0.65	0.08	17.	9.3	0.05	0.60	
3	2NiCr1 85	0.03	0.005	0.028	1.27	0.42	0.19	18.	8.95	0.15	0.01	0.02
4	2MoNiCrl75	0.02	0.005	0.039	2.06	0.78	0.27	20.	8.8	2.7	0.03	0.03
5	10TiMoNiCrl75	0.045	0.012	0.031	0.96	0.54	0.16	18.	11.6	2.04	0.32	
6	2CuMoNiCr200	0.02	0.008	0.027	1.12	0.41	0.70	20.	18.1	6.1		0.2

Too much roughness may lead to a non-uniform layer. As a result of this remark, samples surface have been finely adjusted on metallographic paper with grains of 280-320, and the edges rounded.

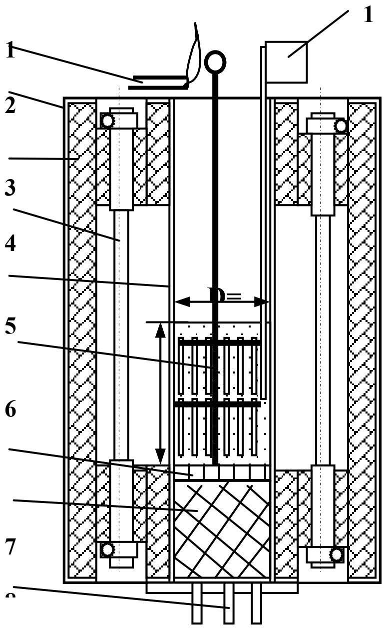

Fig. 1. *Furnace for fluidized bed nitration. 1 - methane gas hose for look - out flame, 2 -plate house, 3 - insulation, 4 - heating elements, resistors, 5 - refractory ceramic tube, 6 -wire support for suspending the samples, 7 - ceramic grid for separating the fluidized bed, 8 -gas homogenization chamber, 9 - lower cover for gas blast, 10 - thermocouple, D, H -fluidized bed dimensions.*

At one end, a hole was drilled into the sample so hat they can be suspended on a stainless steel wire support. This support allowed the samples o be arranged vertically inside the nitration installation, at equal distance, and this made possible for a great number of samples to be treated simultaneously in identical conditions. Before being treated the samples were washed and de-greased together with the wire support, by means of agitation and immersion in carbon tetrachloride, then dried with air.

In order to make this research, it was used the fluidized bed nitration method, made of quartz sand washed and dried, with uniform grains having dimensions between 0.1 and 0.16 mm. Like the classical methods for thermo-chemical treatment, temperature, time and nitration environment composition are the base parameters of the process.

This method assures a high speed for carrying out the process when the temperature is low, between 500 -1000°C and even at the lower limit of the interval. The trials were made at a temperature of 550°C for 1, 2 or 3 hours. The gaseous nitration environment made of N_2 mixed with dissociated 30%NH_3 was obtained directly in the fluidized bed which represents also the heating environment of the samples. This way, the properties of the fluidized bed are valorised such as: great uniformity of temperature, high coefficient of mass and heat, good dynamics of the process. A heating furnace with electric resistances was used for nitration. Its scheme is presented in Fig. 1.

3. Samples analysis

In order to point out how the hard nitrated layer is formed, a hardness trial on the exterior layer was made by Vickers method, with low loads HV_{02} for which the pressure force was 200gf. For this trial, the surfaces were polished with metallographic paper, the size of grains being 800, so as to remove the grey-brown surface layer formed by oxides and other compounds. The results have shown a great increase of hardness, so the existence of a very hard but thin surface layer. In a previous hardness trial Vickers HV_5 with the pressure force of 5Kgf, the hard layer for which the thickness increases at the same time with the process duration could be pointed out.

The values of hardness does not characterize the surface layer which has a small thickness if we compare to the prints depth and it offers only qualitative information. The results of these trials are presented in table 2.

Table 2

Steel code	**Related mark**	**HV_5 hardness Kgf/mm^2**				**HV_{02} Nitration for 3 hours**
		Initial samples	**Nitrated samples**			
			1 hours	**2hours**	**3 hours**	
1	12NiCr180	198	246	277	317	1310
2	10TiNiCr180	202	260	289	258	1180
3	2NiCr185	188	268	296	321	1315
4	2MoNiCr175	180	244	251	336	1320
5	10TiMoNiCR175	202	286	296	362	1170
6	2CuMoNiCr200	182	190	210	270	500

For the study of hardness variation in the layer section some samples have been made in order to estimate correctly the hardness and thickness of nitrated layer. They were cut-off with an abrasive disk with abundant cooling. The samples have been incorporated in resin, grinded and polished. In order to point out the layer and the structure, in general, the samples have been subjected to electrolytic attack, in a fresh solution with 50% HNO_3 at a voltage of 1.5 - 2 V_{cc} for 15-20 seconds.

As the thickness of nitrated layer is believed to reach tens of microns, a Vickers hardness test with very small loads was considered to be necessary, so as to obtain very small prints, respectively HV_{005} for which the pressure force is 50gf. The tests were made for all the 6 types of steel, for the three nitration conditions with duration of 1, 2 and 3 hours. The results of these tests are presented in tables 3, 4, 5, 6, 7, 8.

Table 3. *Hardness variation HV_{005} in the nitrated layer, sample code 1 - steel type 12NiCrl 80*

Nitration duration	Surface distance µm											
	7.5	9	10.5	12	16.5	18	22.5	30	36	46.5	55.5	Centre
1 hour	1006		486				286					251
2 hours				1144		412	340		251			243
3 hours		1313			584			412		340	276	251

Table 4. *Hardness variation HV_{005} in the nitrated layer, sample code 2 - steel type 1 TiNiCrl 80*

Nitration duration	Surface distance µm											
	7.5	9	10.5	13	17.5	21	27	36	39	45	54	Centre
1 hour		643			612		353		251			251
2 hours			1144			643	317	286				268
3 hours				1054			1184	643		380	268	268

Table 5. *Hardness variation HV_{005} in the nitrated layer, sample code 3 - steel type 2NiCrl85*

Nitration duration	Surface distance µm											
	7.5	10.5	11.5	12.5	20	22.5	25.5	33	36.5	42	48	Centre
1 hour				1006	557			286				251
2 hours		1224				340			259			259
3 hours			1314				1144		562	402	306	243

Table 6. *Hardness variation HV_{005} in the nitrated layer, sample code 4 - steel type 2MoNiCr175*

Nitration duration	Surface distance µm											
	8	9	12.5	13.5	15	24	26	27.5	33	45	52.5	Centre
1 hour	1224				752		259					251
2 hours		1314		1144		353			350			259
3 hours			1314		1144			508		306	386	251

Table 7. *Hardness variation HV$_{005}$ in the nitrated layer, sample code 5 steel type 10TiMoNiCrl 75*

Nitration duration	Surface distance µm											
	8	9	10.5	14	20	24	25.5	30	36	43.5	54	Centre
1 hour	557			713		340						268
2 hours		1006			584			340		306		270
3 hours			1172		891		584		380		286	260

Table 8. *Hardness variation HV$_{005}$ in the nitrated layer, sample code 6 - steel type 2CuMoNiCr200*

Nitration duration	Surface distance µm					
	9	22.5	34.5	39	55.5	Centre
3 hours	508	500	508	412	306	243

Hardness variation curves on the depth of the nitrated layer are presented in fig. 2, 3, 4, 5, 6, 7, for the thermo-chemical nitration treatment of 1, 2 respectively 3 hours, in fluidized bed.

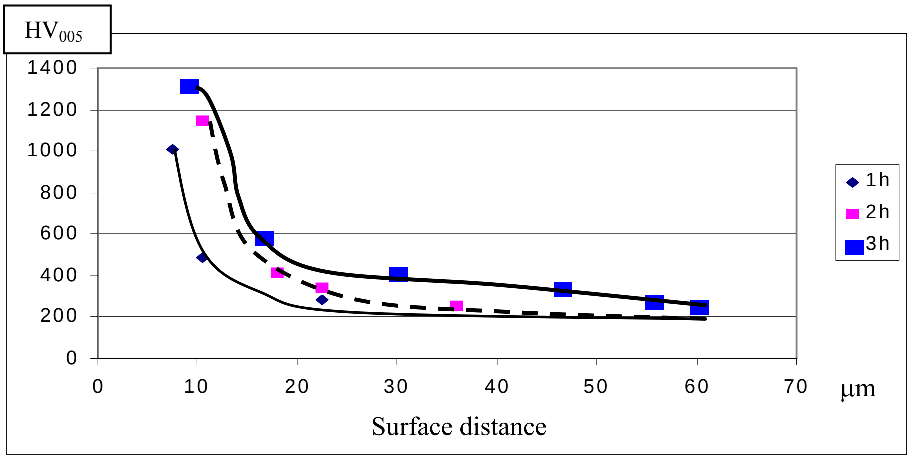

Fig.2. *Hardness variation HV$_{005}$ in nitrated layer, sample code 1, steel type -12NiCr180*

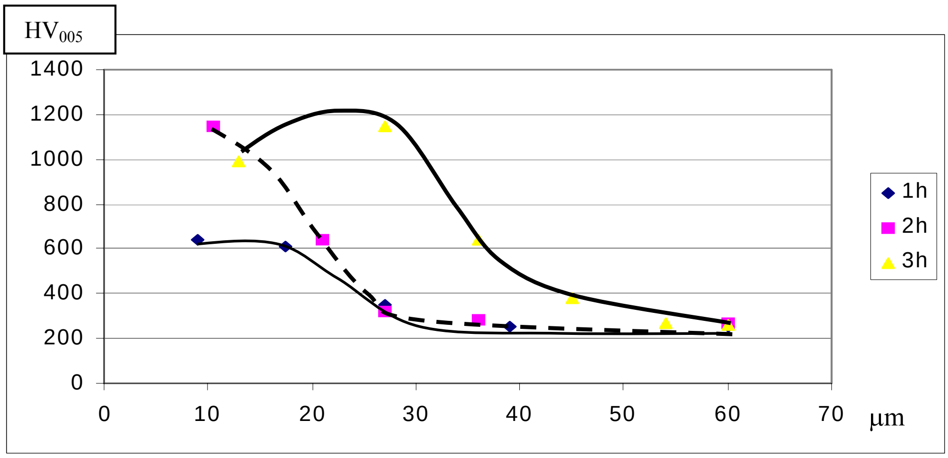

Fig.3 *Hardness variation HV$_{005}$ in nitrated layer, sample code 2 steel type 10TiNiCr180*

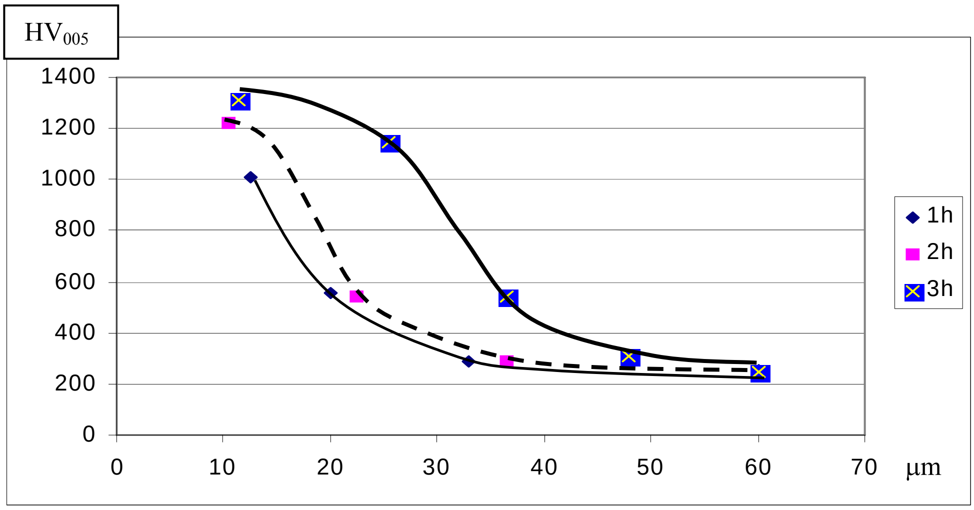

Fig.4 *Hardness variation HV$_{005}$ in nitrated layer, sample code 3 steel type 2NiCr185*

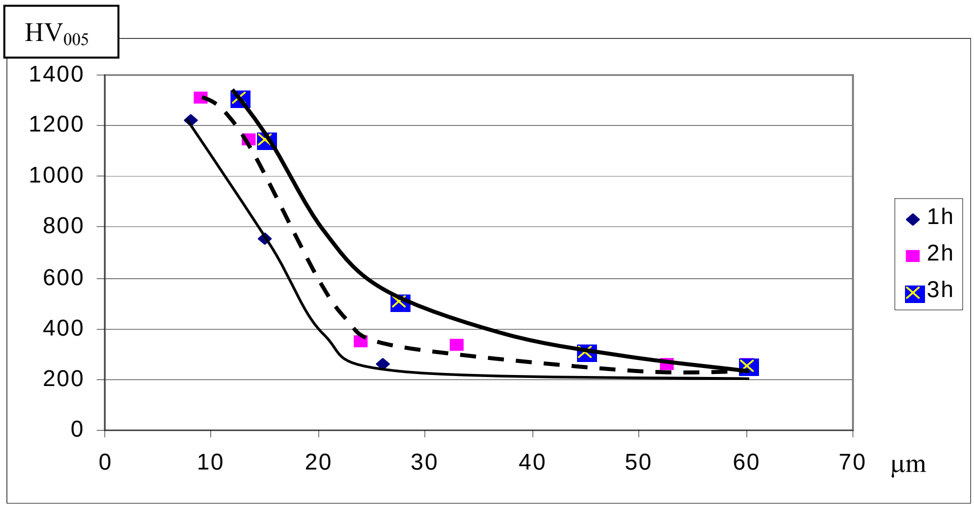

Fig.5 *Hardness variation HV$_{005}$ in nitrated layer, sample code 4 steel type 2MoNiCr175*

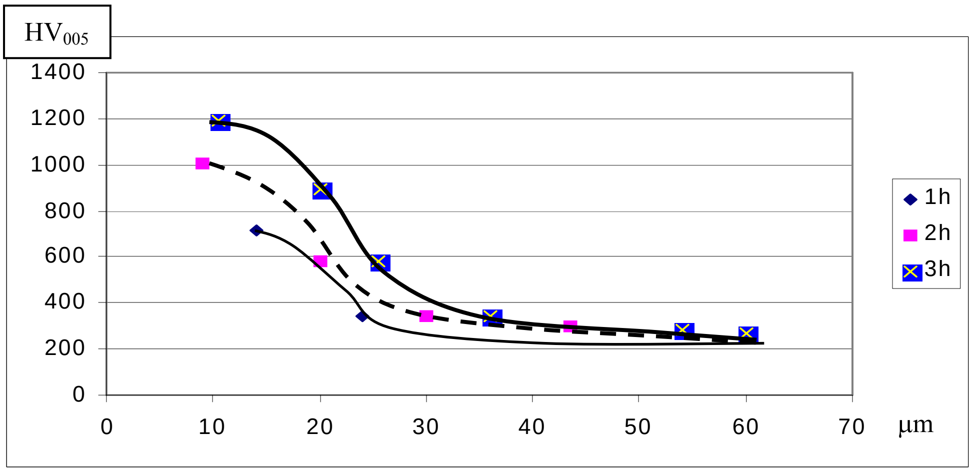

Fig.6 *Hardness variation HV$_{005}$ in nitrated layer, sample code 5 steel type 10TiMoNiCr175*

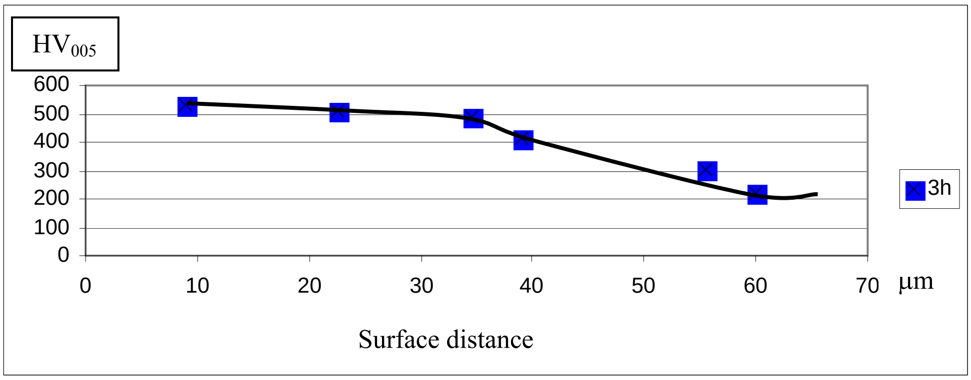

Fig.7 *Hardness variation HV$_{005}$ in nitrated layer, sample code 6 steel type 2CuMoNiCr200*

4. Conclusions

The analysis of hardness tests results shows that after one hour of fluidized bed nitration treatment the surface layer hardness reached very high values for the first 5 steel types, approx. 1000 HV$_{005}$. The layer was very thin, 10µm, discontinuous and non-uniform. In certain areas there are present only small islands of hard nitrated layer and this alternates with areas which have an austenite structure enriched with nitrogen and reduced hardness. This aspect is explained by the fact that on the surface there are more favorable dissociation, absorption and diffusion areas compared to others. After 2 hours of treatment, the layer expands to the entire surface, having the tendency to become uniform and after 3 hours of treatment the layer becomes thicker, the values are 20-40µm and even more. For steel type code 6 2CuMoNiCr200, highly alloyed with Cr, Ni, Mo, Cu, which has a very high index for austenite stability, the increase in hardness is smaller, with a value of 508 HV$_{005}$ and a layer depth of 35-40um. This shows that nitrogen diffusion process is more reduced in a highly alloyed austenite, mainly because of high nickel concentration, over 18%. At the same time, the great stability of austenite stops the separation of hard complex nitrides. Table 9 presents the values of austenite stability S indices and, in parallel, the depth of nitrated layer harder than 500 HV$_{005}$ for the steel types that have been analyzed. $S=E_{Ni}+0.4Ec_r$ in which:

E_{Ni}=30x(%C+%N)+0.5x%Mn+%Ni;
E_{Cr}= %Cr+%Mo+%Si

Table 9. *Values of austenite stability S indices*

Steel type	1	2	3	4	5	6
S	24	19	17.5	21.6	22.6	29.8
Thickness of nitrated layer [µm]	19	40	38	3	28	35

We can see that nitrogen diffusion and formation of hard nitrated layer depends on the concentration of alloying elements present in the steel types, on the austenite stability indices. Steel types code 2 and code 3 which have the smallest stability indices have the deepest hard nitrated layer and are being followed by steel types code 3 and code 4. On the 5 position there is steel type code 1 with a very thin layer, approx. 19µm. Steel type code 6 has a special behavior and, as we showed before, has an external layer about 500 HV$_{005}$- . The small value for the achieved hardness compared to nitrated layers hardness from the other steel types is explained by the lack of combinations and nitrides layer and formation of a diffusion layer. The external layers will be pointed out in the next paper by analyses of the structure.

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