

## CHARACTERISTICS OF THERMOCHEMICAL TREATED EN10090 X50 STEEL

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### ABSTRACT

*EN10090 X50 steel is commonly used for engine valves to withstand severe operation conditions involving high temperature and corrosion from fuel and combustion gas. Usually, to enhance wear performance, valves undergo nitriding thermochemical treatment by salt baths. The aim of this work is to produce diffusion layers at least 20 $\mu$ m thick with hardness higher than 700HV by plasma surface treatment with no continuous compounds layer using nitrogen and methane based atmospheres. Samples were characterized by laser Confocal and scanning electron microscopy, X-ray diffraction and Vickers hardness. Salt bath treatment induced formation of undesirable compounds layer at the surface and a diffusion layer thicker than 40 $\mu$ m, with hardness arising 1280HV<sub>0,010</sub>. Plasma surface treatment produced diffusion layer thicker than 40 $\mu$ m with no continuous compounds layer and mean hardness varying from 750 to 960HV<sub>0,010</sub>.*

**Keywords:** Plasma Surface Treatment, Salt Baths Nitriding, EN10090 X50 Steel, Engine Valves

## INTRODUCTION

Engines valves are usually assembled on Otto cycle internal combustion engines allowing the opening and closure of the fuel-air mixture stream into the combustion chamber. The thermodynamic of a four-stroke (four-cycle) engine encloses four separate strokes: intake, compression, power, exhaustion <sup>(1)</sup>. During power stroke, the combustion of the fuel-air mixture generates high temperature and pressure gases. Combustion occurs instantaneously, producing heat and light, consequence of the complete or partial oxidation reaction of carbon, hydrogen and sulfur from the fuel <sup>(2)</sup>.

Besides sealing combustion chambers, engine valves may resist to severe mechanical tension cycles aggravated by high temperatures and corrosion-erosion. Selected materials for engine valves request good mechanical properties at high temperatures (hardness and yield strength), corrosion resistance related to the fuel into de combustion chambers before and after combustion, good thermal conductivity and fatigue resistance. To withstand these severe conditions, alloyed steels and superalloy coatings are frequently required <sup>(3)</sup>.

The austenitic medium carbon steel according EN 10090 X50 is used to produce the head of exhaust valves due its mechanical properties at high temperature and corrosion resistance. To enhance wear resistance (erosion), fatigue at moderate tension levels and corrosion, steel engine valves undergo termochemical treatments, usually by salt baths <sup>(4)</sup>.

The valves are soaked in a molten salt bath consisting on cyanides mixtures at temperatures between 530 to 650°C during a period of time ranging from 0,5 until 20 h and then water cooled. The process is simple and has a very good cost and benefit rate. Among disadvantages, process presents low sustainability, high pollution level and poor control of nitriding layers, producing continuous compound layer at steel surface, usually undesirable due its brittle nature <sup>(5)</sup>.

An alternative to salt bath processing is the plasma surface treatment, consisting on placing features in a furnace with low pressure nitrogen rich ionized atmosphere at temperatures from 300 to 600°C for wide range of time periods. The well controlled atmosphere composition (partial and total pressure of nitrogen and

their potential) and the adequate sputtering rate (which depend on gas pressure, temperature, gas mixture and voltage) allows a better design of layers producing, for example, no brittle compounds layer<sup>(6, 7, 8)</sup>.

The aim of this work was to assess engine valves features treated by salt bath and compares it to plasma termochemical treatment. Conventional treatment was done in an industrial cycle and plasma treatment was carried out following two distinct cycles, both aiming to produce coatings with no brittle continuous compounds layer and diffusion layer thicker than 20µm with 700 HV<sub>0,01</sub> minimum hardness<sup>(1)</sup>.

## MATERIALS AND METHODS

This work studied EN 10090 X50 steel used to produce exhaust engine valves, Table 1.

Tab.1. Chemical composition of EN 10090 X50 steel, weight %<sup>(4)</sup>.

C	Si	Mn	P	S	Cr	Ni	W	Nb + Ta	N
0,4 5-0,55	0,45	8, 00-10,00	0,045 <	0,03	20 ,00 -22,00	,50 - 5,50	0 ,80 -1,5	1, 8-2,5	,40- 0,60

Valves were treated using Durferrit<sup>®</sup> salt bath CR4 and REG1. The soaking time was 50 min at 540°C temperature and then cooled in heated water (80°C).

The two cycles of plasma treatment involved pre-heating and cleaning for 2h at 450°C within a mixture of 90% to 95% H<sub>2</sub> and 5% to 10% Ar. For the plasma cycle 01, specimens were exposed for 6 h at 500°C within 74%N<sub>2</sub>+23%H<sub>2</sub>+3%CH<sub>4</sub> plasma mixture and then remain at 500°C in 25%N<sub>2</sub>+75%H<sub>2</sub> for 4 h. For the plasma cycle 02, samples were exposed for 1 h at 550°C within 74%N<sub>2</sub>+23%H<sub>2</sub>+3%CH<sub>4</sub> mixture and then for 1 h within a 75%N<sub>2</sub>+25%H<sub>2</sub>. At the end, samples were cooled during 3 h in an inert atmosphere to avoid oxidation.

Samples were characterized by laser Confocal and scanning electron microscopy, X-ray diffraction analysis and Vickers hardness under 10 gf.

## RESULTS AND DISCUSSION

Specimen treated in salt bath showed superficial hardness up to 1200 HV<sub>0,01</sub> decreasing to the average hardness of 856 HV<sub>0,01</sub> after 12µm depth, figure 1. The higher hardness on the top is consistent with the formation of the continuous

compounds layer. Diffusion layer was formed leading to increase on hardness values from 10  $\mu\text{m}$  to 40  $\mu\text{m}$  when compared to the core.

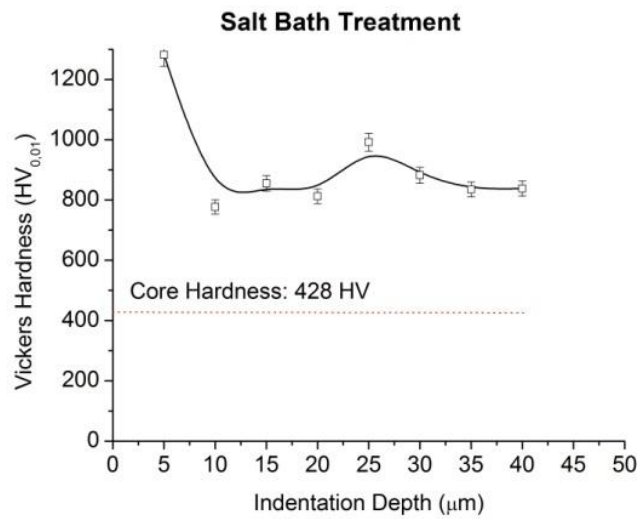


Fig. 1. Hardness depth profile of specimens after treatment using Durferit<sup>®</sup> salt bath.

For cycle 01 samples, figure 2(a), it can be noticed the absence of the hardness superficial peak, suggesting no compounds layer was formed. The average hardness of 960  $\text{HV}_{0.01}$  up to 40  $\mu\text{m}$  was measured and is related to the diffusion layer formed.

Specimens treated by cycle 02, figure 2(b), showed no superficial hardness peak. The average hardness was 750  $\text{HV}_{0.01}$ , lower than that obtained with the longer plasma treatment of cycle 01. As the treatment cycle 01 is longer than cycle 02, it is expected most effective nitrogen diffusing into steel specimens, providing nitrogen saturation and higher nitrides volume and, as a consequence, higher hardness.

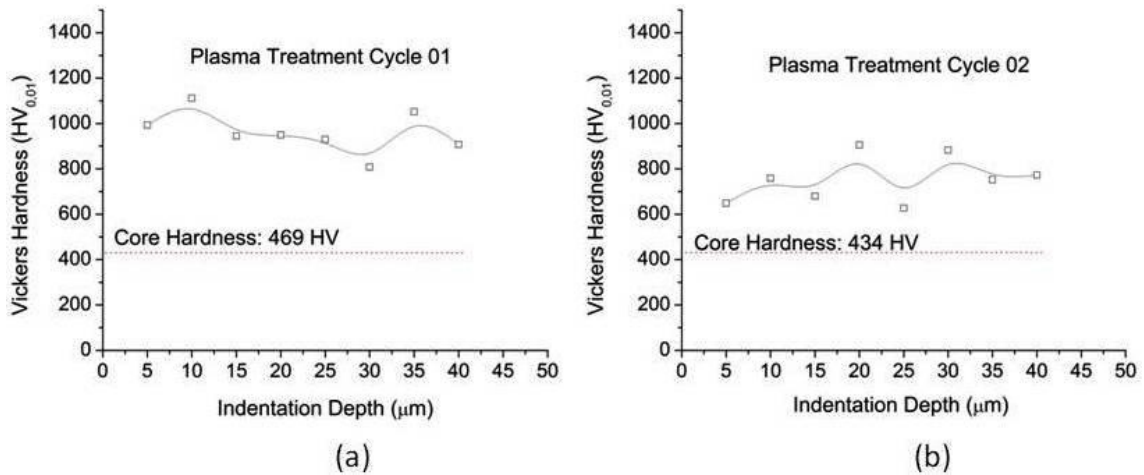


Fig. 2. Hardness profiles of plasma treated samples: (a) cycle 01 and (b) cycle 02.

The microstructure of salt bath treated X 50 steel showed continuous compounds layer at the surface, which induced higher surface hardness, figure 3a. As nitrogen contents overcame solubility level, precipitation of acicular nitrides with fibrous morphology on diffusion layer occurred <sup>(7)</sup>.

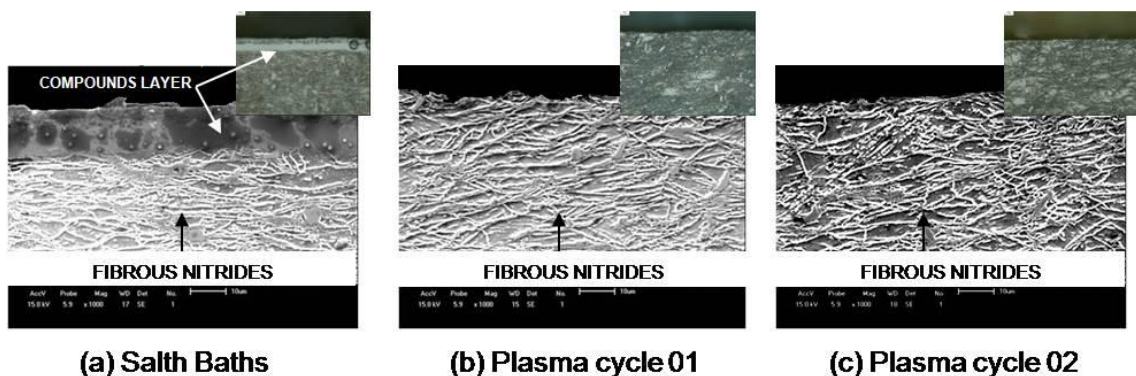


Fig. 3. Scanning electron microscopy and laser Confocal microscopy on samples treated by: (a) salt baths, (b) plasma cycle 01 and (c) plasma cycle 02.

Plasma treated samples, Figure 3 (b) and 3 (c), exhibited microstructure with fibrous morphology containing acicular nitrides on diffusion layer and no compounds layer. These microstructures are consistent with the absence of superficial hardness peak on tested samples, confirming the ability of plasma surface treatments to produce best controlled surfaces <sup>(7, 8)</sup>.

The fibrous morphology observed on diffusion layer was previously reported for alloying carbides. This can be better described as the conversion of a fine dispersion of CrN (chromium nitride) with high interfacial energy to an aggregate of acicular CrN

in austenitic matrix. The reduction of the interfacial free energy is the driving force for such morphology formation <sup>(9)</sup>.

X-ray diffraction analyses, showed very similar phases for all treatments, confirming the formation of Fe<sub>3</sub>N, NbN / NbC, and CrN / Cr<sub>7</sub>C<sub>3</sub> hardening phases, as reported in the literature, figure 4 <sup>(10)</sup>.

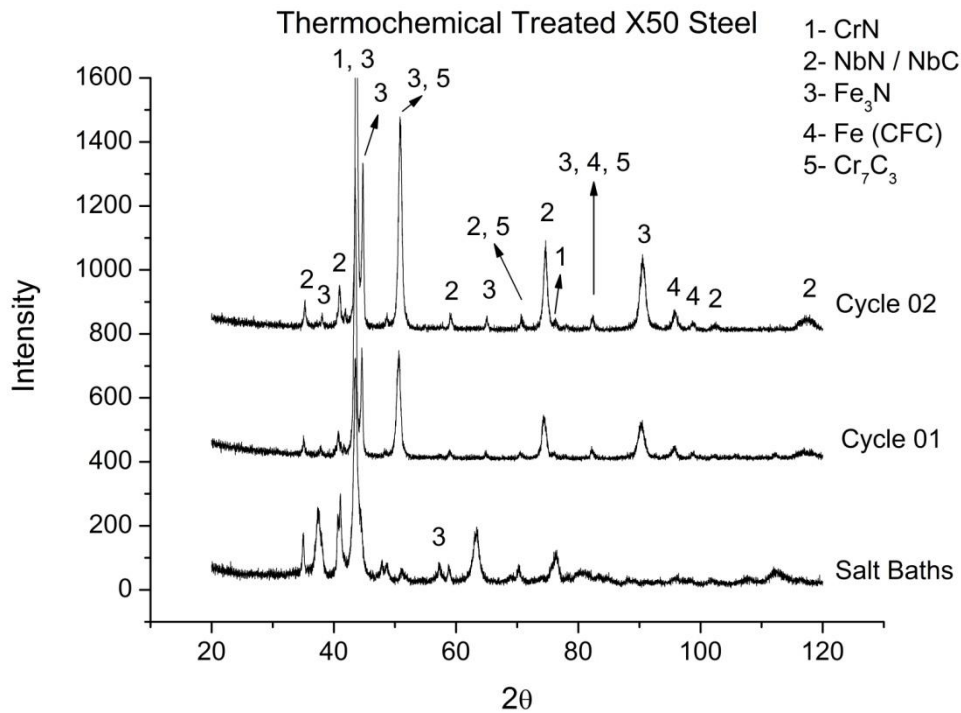


Fig. 4. X-ray diffraction analysis on treated samples.

As expected, chromium and niobium alloying are strong nitrides and carbides formers, carbides and nitrides with these elements on thermochemical treated EN 10090 X50 steel were identified, increasing significantly the hardness of diffusion layer.

CrN type chromium nitride was identified, differently as indicated in literature. According to previous research, the kind of nitride formed during thermochemical treatment carried out between 500 and 1000<sup>0</sup>C is hardly dependant on steel chromium content. Chromium level up to 20 wt% leads to the formation of CrN nitride and higher amounts induces Cr<sub>2</sub>N formation <sup>(10, 11)</sup>. Considering chromium content of X 50 steel (20 to 22 wt), Cr<sub>2</sub>N is expected to form, but this was not observed, probably because chromium free in solid solution was lower than 20 wt%, enabling CrN formation.

## CONCLUSIONS

Plasma and salt bath treatments showed to be efficient to enhance the surface hardness within specified requirements (hardened thickness higher than 20 $\mu$ m and hardness higher than 700 HV).

Plasma treatment produced surface hardening with no compounds layer and average hardness from 750 HV<sub>0,01</sub> and 960 HV<sub>0,01</sub> for a diffusion layer at least 40 $\mu$ m thick. On the other hand, salt baths formed high hardness 12 $\mu$ m thick compounds layer and a diffusion layer with an average hardness of 856 HV<sub>0,01</sub> from 12 to 40  $\mu$ m.

Plasma surface engineering confirmed the possibility of design nitrided layers, resulting in no compounds layer formation. Plasma treated atmosphere and time influenced directly on nitrides volume fraction, being the longer cycle 01 responsible for the harder layer.

The chemical composition of X 50 steel induced formation of chromium and niobium nitrides (CrN and NbN), with different dispersed phase as a fibrous morphology. This precipitated hardening phases induced important hardness increase on diffusion layer for X 50 steel.

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