INFLUENCE OF GAS MIXTURE COMPOSITION ON THE LOW TEMPERATURE PLASMA CARBURIZING OF AISI 420 MARTENSITIC STAINLESS STEEL

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Abstract. *Plasma-assisted carburizing is a process that takes advantage of glow discharge in order to introduce carbon atoms on the surface of a metallic material, consequently, these atoms will diffuse into the bulk. Mechanical and metallurgical properties of the modified layer are dependent of the operation variables applied during the process, including the gas mixture composition. In this context, this work presents the study of the gas mixture influence on the properties of the layers obtained by low temperature plasma-assisted carburizing treatment. The process was performed on samples of AISI 420 martensitic stainless steel at 723 K for a period of 14.4 × 10^3 s (4 hours). The content of methane was varied from 0.25 to 1.00% in a gas mixture containing 20% Ar and 80% H_2, at a flow rate of 1.67 × 10^{-6} m^3s^{-1} (100 sccm – standard cubic centimeters per second), under a pressure of 400 Pa (3 Torr). The obtained layers were characterized by optical and scanning electron microscopy, X-ray diffraction and microhardness measurements. The results indicate that the variation in the proportion of CH_4 in the gas mixture leads to changes in the properties of the carburized layer. For high methane concentration soot deposition was observed what can be detrimental to the process.*

Keywords*: Low temperature Plasma treatment, Carburizing, AISI 420 stainless steel.*

1. INTRODUCTION

The use of plasma-assisted techniques in the field of materials thermochemical processing has increased steadily in recent years. The possibility of altering the material's surface characteristics by varying the process parameters has led to the development of different research works on its influence on the properties of the modified surface. For example, recent published studies for different plasma-assisted techniques investigate the influence of temperature and time parameters (Corengia *et al.* (2004); El-Hossary *et al.* (2001); El-Hossary *et al.* (2009); Figueroa *et al.* (2005)), power (Marins *et al.* 2009; Raaif *et al.* (2008)), gas pressure (El-Rahman *et al.* (2004); Liang *et al.* (2000)), gas flow (Brunatto and Muzart, 2007), gas mixture composition (Allenstein *et al.* (2010), Skonieski, *et al.* (2008), Zhao Cheng *et al.* (2005)) on the treated surface properties.

As pointed out by the literature (Zhang and Bell, 1985; Ichii *et al.* (1986); Sun and Bell (1991), Davis (1994); Menthe *et al.* (1995), Czerwiec *et al.* (2009)), plasma-assisted techniques are important tools to carry out thermochemical treatments and improve the wear and frictional properties, as well as corrosion and fatigue resistance of parts. In addition to excellent mechanical/metallurgical properties obtained by applying these treatments, it is also to be considered that it can be performed in industrial scale remaining, in general, non-polluting. Moreover, the process presents high treatment quality, high repeatability and easy automation.

For industrial application, plasma-assisted processes have been employed in order to improve the surface properties of different materials, optimizing its properties and expanding their application field. This has been observed in the treatment of stainless steel, which results in an increase in its surface hardness and corrosion resistance. Thus, several plasma-activated thermochemical surface modification techniques have been extensively studied and tested. Among these processes, the plasma carburizing has shown good results in practical applications, as described by Edenhofer *et al.* (2001). This technique allows surface hardening by interstitial diffusion of carbon atoms, providing an improvement of their properties. However, the traditional plasma carburizing process, held at elevated temperatures (austenitic phase), causes deterioration of corrosion resistance of stainless steels. As an alternative method, research has shown that the performance of plasma-assisted carburizing process, when realized at lower temperatures, provided similar results to those obtained by the process conducted at elevated temperatures (with respect to obtaining mechanical properties), without, however, reducing the corrosion resistance properties. (Ernst *et al.* (2007); Gobbi *et al.* (2006); Souza *et al.* (2009); Sun (2005), Sun and Bell (2002); Sun (2009); Tsujikama *et al.* (2008)).

Although there are many papers reporting the application of low temperature plasma-assisted carburizing in austenitic stainless steels, the authors didn't have found any work describing the adoption of this technique for the treatment of martensitic stainless steels. So this issue requires a detailed investigation. Likewise, the possibility of

investigating the influence of plasma treatment parameters on the properties obtained represents a broad research field. Considering the above mentioned, this work presents the study of gas mixture composition influence on final surface properties of the AISI 420 martensitic stainless steel treated by low temperature plasma-assisted carburizing.

2. EXPERIMENTAL DETAIL

2.1. Material

Cylindrical samples of AISI 420 martensitic stainless steel with 10 mm in height were cut from a 9.5 mm commercial rod, austenitized at 1323 K (1050 °C) for 3.6×10^3 s (1 h) and oil quenched. After the thermal treatment, the samples were grounded using wet SiC paper from 240 down to 1200-grit and mechanically polished using a felt disc and 1 μm Al_2O_3 abrasive solution. Finally, the samples were cleaned with alcohol in an ultrasonic bath and introduced into the plasma chamber.

2.2. Processing

In order to remove the native oxide layer formed on the specimens surface and for cleaning the sample holder, before treatment the specimens were sputter-cleaned in 80% H_2 + 20% Ar atmosphere at 573K (300°C), under a pressure of 400 Pa (3 Torr) for 1.8×10^3 s (0.5 h). The plasma-assisted carburizing process was carried out at 723 K (450 ºC) for 14.4×10^3 s (4 h), at flow rate of 1.67×10^{-6} $m^3 s^{-1}$ (100 sccm – standard cubic centimeter per second), under a pressure of 400 Pa (3 Torr), and for gas mixture composition of 80% H_2 + 20% Ar with CH_4 content varying from 0.25 to 1.00%. After the completion of the carburizing process, the specimens were cooled in the processing chamber down to the room temperature in the presence of H_2-Ar flowing gas atmosphere.

The equipment used in the experimental work consists of a pulsed DC power supply and a vacuum chamber of 350 mm in diameter and 380 mm high stainless steel cylinder attached to steel plates sealed with silicone o-rings at both ends (see Fig. 1). The system is evacuated down to a residual pressure of 1.33 Pa (10^{-2} Torr) using a double stage mechanical pump. The gas mixture and flux of H_2, Ar and CH_4 was adjusted by three mass flow controllers, two of 8.33×10^{-6} $m^3 s^{-1}$ (500 sccm) and one of 8.35×10^{-8} $m^3 s^{-1}$ (5 sccm), respectively.

Aiming to carburize three samples per treatment, an AISI 1020 steel support with external diameter of 55 mm was constructed, consisting of three holes of 10 mm in diameter symmetrically placed 20 mm from the support center (Fig. 1). This sample holder worked as the cathode of the discharge, being negative biased using a square wave pulsed power supply. The peak voltage was set to 700 V. The mean power transferred to the plasma was adjusted by varying the switched on time (*t*on*)*. The applied pulse period was 240 μs. The temperature was measured by means of a chromel–alumel thermocouple (K-type of 1.5 mm diameter) inserted 8 mm depth into the sample support and it was controlled by adjusting the switched on time of the pulsed voltage (a non reported study was carried out to evaluate the thermal gradient through the sample support showing that it is negligible). The pressure in the vacuum chamber was measured by a capacitance manometer of 1.33×10^4 Pa (100 Torr) in full-scale operation and adjusted by a manual valve.

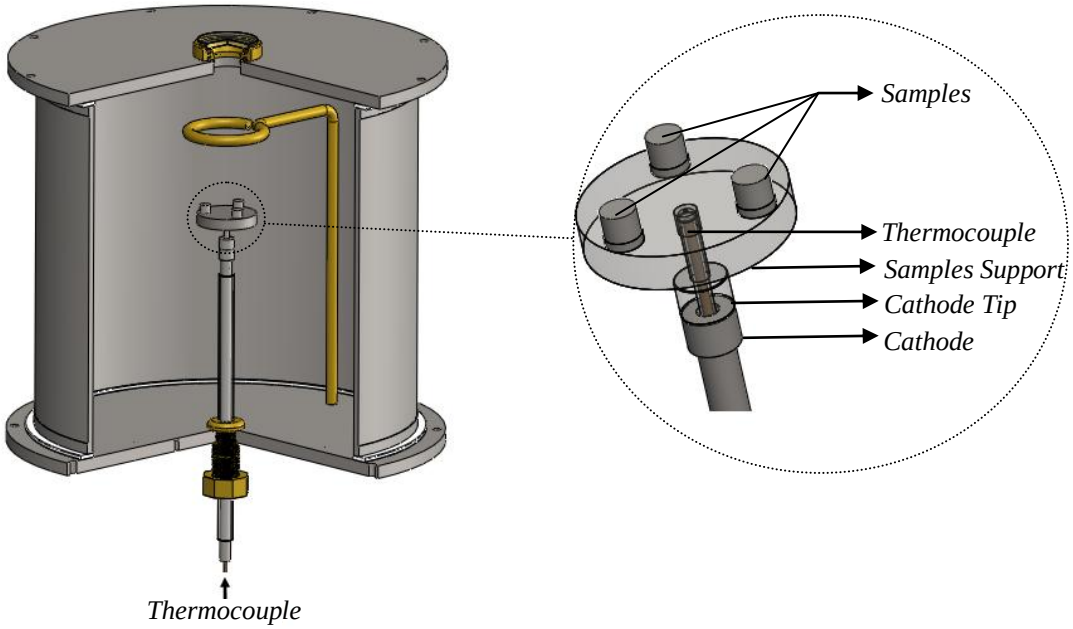

Figure 1. Schematic representation of the vacuum chamber and of the sample support configuration applied in the plasma carburizing treatment.

2.3. Characterization techniques

For metallographic analysis, the plasma carburized specimens were cross-sectioned, fine-grounded, polished and etched with Aqua Regia reagent. Samples were examined by optical and scanning electron microscopy, with an Olympus BX51M optical microscope and a Philips XL30 scanning electron microscope, respectively. The phase evolution was studied by X-ray diffraction analysis using a Shimadzu XDR7000 x-ray diffractometer with a Cu $K\alpha$ X-ray tube, using a scan speed of 1 deg/min. Microhardness measurements were performed on the treated surface, on the non-treated surface (sample base) and on the samples cross-section with a Shimadzu Micro Hardness Tester HMV-2T, applying a load of 300 gf for a peak-load contact of 15 s. The mean of five measurement points were taken to determine the microhardness value.

3. RESULTS AND DISCUSSION

3.1. Metallographic observation

In Fig.2(a-d) SEM micrographs from cross-sectioned samples, carburized at different gas mixture composition (0.25, 0.50, 0.75 and 1.00% CH_4, respectively), are presented. It can be seen that the carburized layer presents resistance to the etchant used to reveal the microstructural features of stainless steel presenting a nearly homogeneous thickness. This is similar to the precipitation-free structures observed on the surface of a low temperature nitrided martensitic stainless steel (Corengia *et al.* (2004); Figueroa *et al.* (2005); Kim *et al.* (2003); Xi *et al.* (2008 [a])). In SEM images, non reported in this paper, realized using backscattered electrons detector (BSE) the carburized layer presents the same gray scale tonality of the bulk, indicating that their density are similar.

In Fig. 3 the evolution of the carburized layer thickness as a function of the CH_4 content in gas mixture is shown. It may be noted that the CH_4 percentage can enhance thickness of the plasma carburized layer. The obtained thicknesses were 1.04, 1.22, 1.25 and 1.79 μm for the conditions of 0.25, 0.50; 0.75 and 1.00 % CH_4, respectively, demonstrating that de methane ratio is an important processes parameter. Nevertheless, for 1.00% CH_4, slight soot formation on the treated surface was observed, what could be non desirable for industrial application.

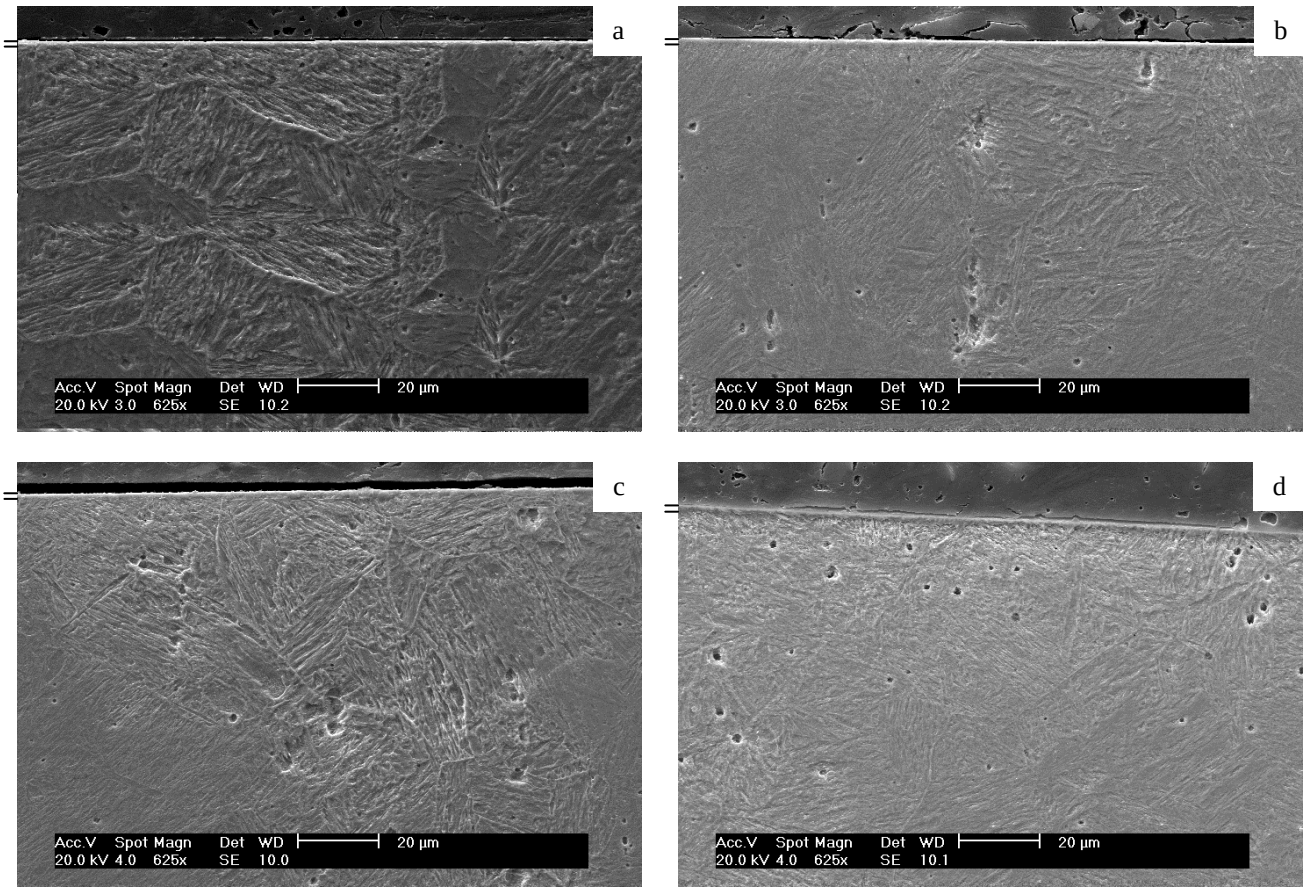

Figure 2. SEM cross-section images of treated samples at variable gas mixture composition: (a) 0.25% CH_4, (b) 0.50% CH_4, (c) 0.75% CH_4 and (d) 1.00% CH_4. Samples treated at 450 °C for 4 h at gas flow of 100 sccm. The extent of the treated layer is marked outside the micrograph.

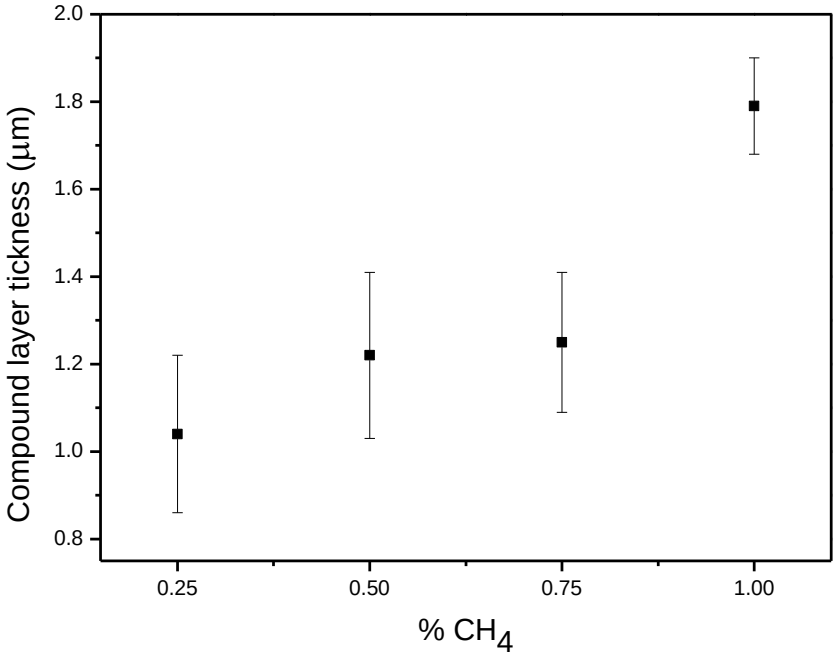

Figure 3. Evolution of the layer thickness as a function of CH_4 content in gas mixture. Samples treated at 450 °C for 4 h at gas flow of 100 sccm.

3.2. X-ray diffraction analysis

X-ray diffraction patterns of untreated and treated AISI 420 samples, at different carburizing gas mixture conditions, are presented in Fig. 4.

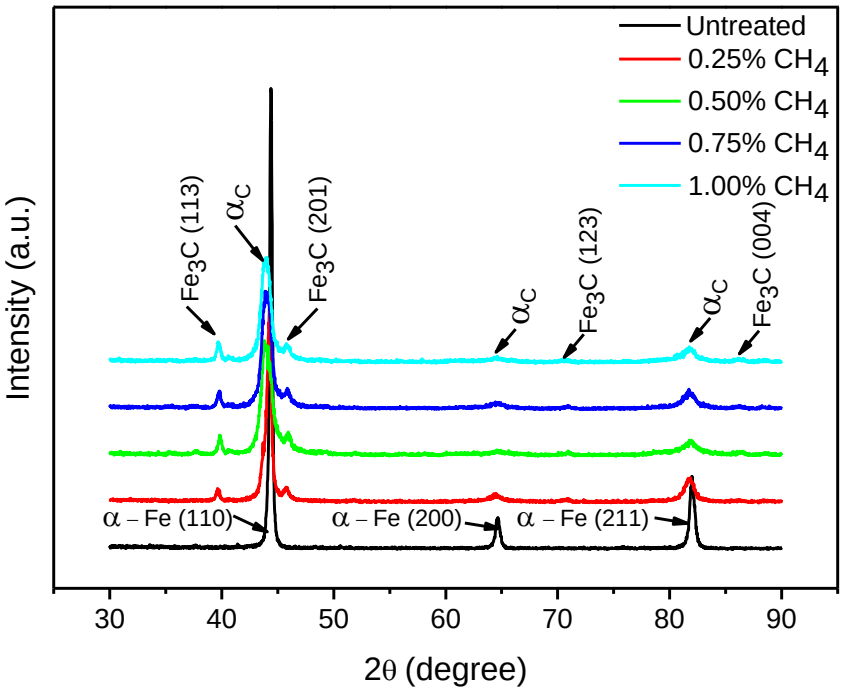

Figure 4. Evolution of the XRD patterns for different gas mixture composition (0.25%% CH_4, 0.50% CH_4, 0.75% CH_4 and 1.00% CH_4). Samples treated at 450 °C for 4 h at gas flow of 100 sccm.

From Fig. 4, it can be observed by comparing the XRD patterns obtained for the different gas mixture compositions and for the untreated material that martensite peaks presents a offset to the left, ie, for smaller angles, associated with a decrease in its intensity, suggesting an expansion of crystalline lattice occurred due to the superior amount of carbon

introduced in solid solution. According to Cheng *et al*, (2005), this shift shows that the *S*-phase is an expanded phase in austenitic stainless steel, so in the case of martensitic stainless steel the expanded phase is called, by analogy, expanded martensite (α_N) by Kim *et al.* (2003), Manova *et al.* (2005), Xi *et al.* (2008)[a] and Xi *et al.* (2008)[b]. This is characteristic of phases with oversaturation.

The black curve (Fig. 4) shows that the untreated sample has three diffraction peaks of α-Fe (110), α-Fe (200) and α-Fe (211) in the range of 30°–90° (44.9º, 64.9º and 82.2º, respectively), in accordance with Xi *et al.* (2008)[a], Xi *et al.* (2008)[b] and Pinedo (2000). As can be seen, all these peaks were displaced for new 2θ angles on the order of 43.9º, 64.7º, and 81.6 º for the treated samples, corresponding to martensite enriched peaks. This statement is also supported by the fact that these peaks can not be matched with any other possible phases including iron, iron carbides, and chromium carbides in the present study. So, in the present work this carbon alloyed phase is termed carbon expanded martensite (α_C).

The peaks occurring at 39.8º, 45.9º, 71.33º and 86.11, in consonance with El-Rahman *et al.* (2004), El-Hossary *et al.* (2001) and El-Hossary *et al.* (2009), correspond to cementite (Fe_3C), as shown in Fig. 4.

The non-existence of peaks from chromium carbide is an indication that at the temperature of 450°C (723 K) it doesn't precipitate for the studied conditions, which ensures the maintainability of the corrosion resistance property for the material.

3.3. Microhardness

The microhardness measures obtained for samples carburized in the different tested conditions are presented in Fig. 5. These measurements were made on the treated surface and at bottom (non-treated) of samples. For comparison, the average microhardness of the untreated material in the quenched and annealed conditions is also shown in Fig. 5. All presented values correspond to the mean of five measurements. Comparing the value of microhardness obtained on the sample surface before (in quenched condition) and after plasma carburizing treatment, it can be observed that the value of microhardness of the material increased significantly. The lower microhardness value obtained in samples bottom, after plasma carburizing process, compared to quenched conditions, is justified because of sample bottom isn't exposed to plasma, and so there are no carbon enrichment in this face. Also, the lower microhardness value occurs as a consequence of the tempering process which occurs during treatment, once the process is performed at 450°C (723 K).

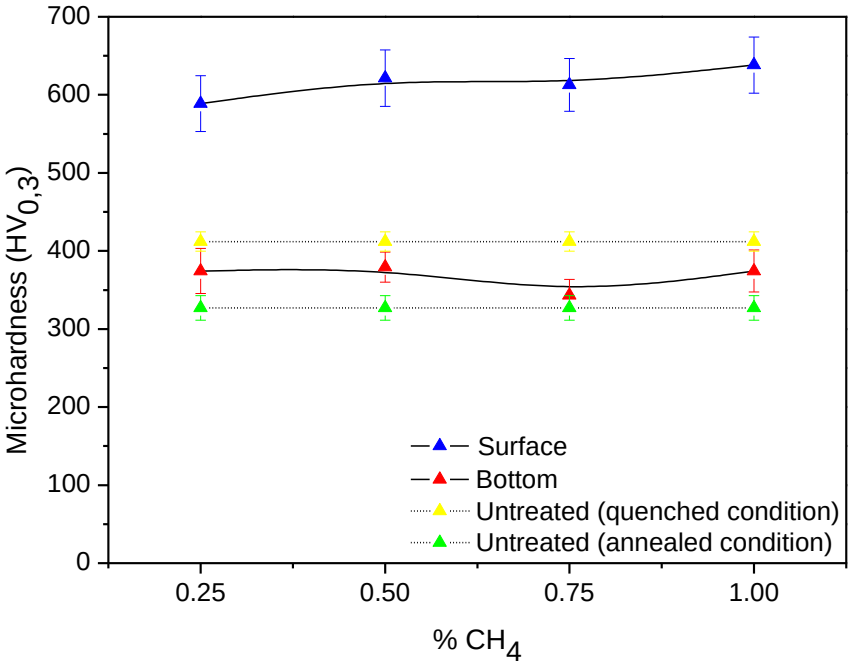

Figure 5. Surface microhardness of plasma carburized AISI420 martensitic stainless steel samples for different methane content in the gas mixture. Samples treated at 450 °C for 4 h at gas flow of 100 sccm.

It is worth mentioning that the microhardness measurements were performed with a load of 300 gf, which represents a significant value. Considering the thin thickness of the layer obtained, possibly the microhardness on the surface shows higher values, since, for the load used, the indentation depth is approximately 5 μm, and thus the obtained values represent the microhardness of the transition region between the generated layer and material core, in oder words an aparent hardness.

Figure 6 shows the microhardness profiles of processed samples as a function of the plasma gas mixture composition. The obtained hardness profiles indicate typical hardness variation for diffusion layers. Hardness values of 565, 636, 627 and 769 $HV_{0.01}$ at depth of 3 to 3.5 μm, inside the compound layer, were measured for samples treated at 0.25, 0.50, 0.75 and 1.00% CH_4, respectively. For all studied conditions, measurements performed at 55 μm depth indicated values on the order of 370 $HV_{0.01}$, which comprise the hardness of the substrate bulk.

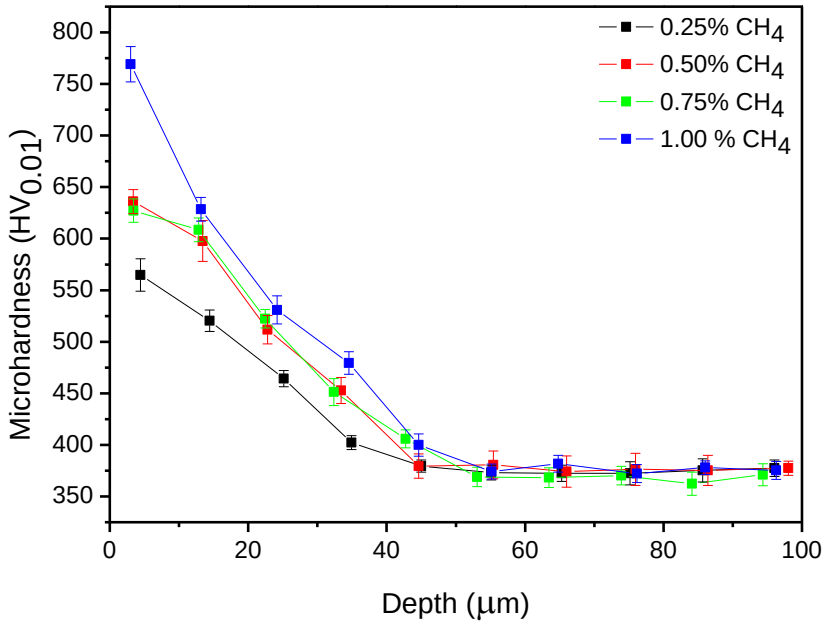

Figure 6. Microhardness profiles of treated samples showing the influence of the plasma gas mixture composition. Samples treated at 450 °C for 4 h at gas flow of 100 sccm.

4. CONCLUSIONS

By the obtained results, it can be concluded that:

1. Plasma carburizing can improve the surface hardness of AISI 420 martensitic stainless steel;
2. Carbon can be dissolved in the martensite lattice during plasma carburizing process, forming a carbon supersaturated solid solution;
3. The metallographic examination of cross-section has revealed that the low temperature carburized layer is more resistant to etching than the substrate, indicating the potential of the process to enhance the corrosion resistance of martensitic stainless steel, and indicating also that no precipitation of chromium carbides occurred;
4. The influence of CH_4 rate upon the carburized layer is clear and within the studied range of 1%. However, for this condition it was observed the occurrence of soot formation, which leads to the isolation of the sample probably preventing the carbon diffusion;
5. The percentages of 0.50 and 0.75 of methane showed similar values with respect to hardness and layer thickness, being both more appropriate conditions of treatment, since the ratio of 0.25% CH_4 was that presented significantly lower values of hardness and thickness of the carburized layer, and
6. All results indicate that the variation in the proportion of CH_4 in the gas mixture, leads to changes in the properties of the carburized layer and in the kinetics of the process.

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