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Effect of Plasma Nitriding and Sensitization on the Microstructure and Microhardness of AISI 304 Austenitic Steel

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The article analyzes the influence of plasma nitriding and sensitization on the microstructure and microhardness of AISI 304 austenitic steel. The microstructure of AISI 304 austenitic steel in all states was observed on a Neophot 32 optical microscope. The initial structure consisted of polyhedral austenite grains of different sizes. The microstructure contained a large number of non-metallic MnS-based inclusions. After plasma nitriding, a continuous nitriding layer was formed under the steel surface, while the grain shape was preserved. Carbide chromium was excluded along the austenitic grain boundaries by the following processes: sensitization and plasma nitriding followed by sensitization. The nitriding layer began to deteriorate due to temperature and length of sensitization. Vickers microhardness measurement on a Zwick/Roell ZHμ machine proved that the nitriding layer is reaching the high hardnesses compared to the core of samples. After sensitization, the nitrided samples achieved only slightly increased microhardness compared to the core. Finally, EDX analysis of the nitriding layer was performed on the SEM and compared with the layer that was affected by the sensitization process.

Keywords: Austenitic stainless steel, Plasma nitriding, Sensitization, Microstructure, Microhardness

1 Introduction

Austenitic stainless steels are used as structural materials in aerospace, nuclear, transportation, chemical, and food industries [1, 2]. This grade of steel is also widely used in elevated temperature conditions because of its good mechanical properties, corrosion resistance, and formability [3]. Austenitic steel AISI 304 is one of the most usable stainless steels in its class, because it has a very excellent combination of corrosion resistance, weldability, and low cost. This steel is also suitable for use wherever non-magnetic properties are required. [4]. Due to the high chromium content of these steels, a passivation layer is formed on their surface, which ensures corrosion resistance in normal environments. When the oxidation environment changes, this type of steel is more susceptible to the formation of pitting corrosion [4, 5].

The disadvantage of these steels is their low abrasion resistance and hardness. Plasma nitriding technology is currently used to increase mechanical, tribological, and fatigue properties [6]. In the case of nitriding of austenitic steels above a temperature of 450°C, chromium nitrides are precipitated. These nitrides drain chromium from the material matrix, resulting in reduced corrosion resistance [7]. An experiment by Faltejsek et al. [5] demonstrated that plasma nitriding significantly increases the surface hardness and thus increases the abrasion resistance of austenitic steels. Furthermore, the research confirmed that molybdenum has adverse effects on the hardness and depth of the nitriding layer when the diffusion of nitrides is slowing down. Wang et. al. al [8] demonstrated a correlation between the nitriding thickness and the nitriding time when the nitriding layer grew with a longer nitriding process. The quality of the nitrided surface has a direct influence on the nitriding result. Generally, a surface that has lower roughness will achieve more nitriding depth and hardness [9]. Plasma nitriding is used in industry as the last step in the production of a component before its application in practice [10].

In the case of austenitic steels, care must be taken to avoid sensitization of the steel. This phenomenon occurs when the steel is processed in the temperature range of 400 - 800°C. Sensitization can also occur during welding or operation [3, 11]. During exposure to these critical temperatures, chromium carbides precipitate at the austenitic grain boundaries. This causes adjacent areas to be depleted of chromium, increasing the susceptibility of the steel to intergranular corrosion [4,12]. A study by Tavares et al. [13] showed that the sensitization of AISI304 at a temperature of 650°C promotes steel embrittlement. The degree of sensitization level can be demonstrated by rapid etching in oxalic acid.

2 Material and methods

The investigated material of AISI 304 austenitic steel was supplied in the form of square bars 10x10mm and 3000mm length long. The bars were produced by cold rolling. The chemical analysis of the austenitic steel used was carried out on a SPECTROMAXx spark emission spectrometer [14]. The results of the chemical analysis are shown in Tab. 1.

Tab. 1 *Chemical composition of the experimental material*

Type of steel	The concentration of chemical elements [wt.%]									
	C	Cr	Ni	Mn	Si	Mo	S	P	N	Fe
AISI 304	0.046	18.53	7.79	1.72	0.36	0.47	0.05	0.022	0.103	balance

The micropulse plasma nitriding technology, developed at Röbig, was used for the nitridation of samples. Using thermocouples to regulate the temperature during the process, nitridation was carried out in the temperature range of 520-530°C for 24 hours. Austenitic steel AISI 304 after plasma nitriding is used in biomedical environments where high hardness, abrasion resistance, and at the same time a certain degree of corrosion protection is required.

Sensitization of the sample took place at the Department of Materials Engineering at the University of Žilina in Žilina. The sensitization was performed in an electric resistance furnace without a protective atmosphere. The sensitization temperature was 700°C with a duration time of 10 hours. This time was followed by cooling in the furnace.

For proper observation of the microstructure, samples of all states were metallographically prepared. The preparation consisted of grinding, polishing, and etching of samples (Tab. 2). The samples were etched using Kallings 2, which is made of 5g of $CuCl_2$, 100 ml of HCl, and 100 ml of CH_3CH_2OH. The etching time was approximately 15 seconds.

Tab. 2 *Grinding and polishing procedure for AISI 304 samples*

Step	Operation	Griding paper	Emulsion	Time [s]
1	Griding	Piano	Water	180
2		Largo	Water	300
3	Polishing	DAC	DAC	300
4		NAP	Dia Pro Nap-B	180
5		MD Chem.	OP-U	120

The metallographic preparation of samples was followed by microstructural analysis on a NEOPHOT 32 light microscope. NIS Elements 4 program was used for the photo documentation. The photo documentation was carried out at a magnification of 400x. EDX analyses were performed on a Tescan Vega LMU II scanning electron microscope using a Bruker spectrometer [15,16].

The microhardness was measured by Vickers static test on a Zwick/Roell ZHμ microhardness tester. For samples of the initial state, after plasma nitriding, sensitization, and plasma nitriding with sensitization, the load of HV 0.5 was chosen. Microhardness was measured on metallographically prepared samples from the edge of the samples to the core of the steel. For the measurement of the microhardness of the nitriding layers, a load of HV 0.01 was used. The lower load was chosen to maintain the required spacing between the indentations and thus prevent incorrect test execution. The loading time was 10 seconds at a temperature of ± 20°C.

3 Result and discussion

3.1 Microstructural analysis

3.1.1 Initial state analysis

The microstructure of AISI 304 austenitic steel is formed by polyhedral austenite grains of different sizes (Fig. 1a). In addition to the deformation martensite (DM), there is also a significant amount of annealing twins (AT) in the structure (Fig. 1b), which were created by the rolling process (the manufacturer states the production of the bars by cold rolling).

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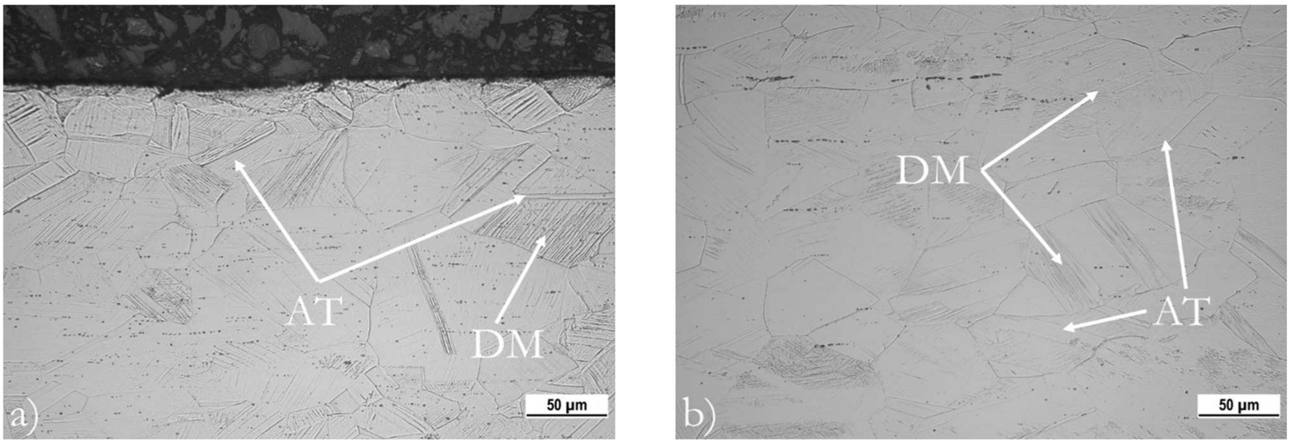

Fig. 1 *Microstructure of AISI 304 austenitic steel in the initial state a) on the edge of the sample b) in the core of the sample*

There is a large number of inclusions in the microstructure. Using EDX analysis-mapping, these inclusions were identified as manganese sulfide (MnS). This sulfide has an elongated oval shape in the direction of the rolling rod (Fig. 2). Sulphur enters the steel from the ore. It weakens the cohesion of the austenitic grain, which causes a decrease in the fatigue limit, and toughness and increases the brittleness of the material. Manganese in steel increases strength without making the steel suffer in plasticity but increases grain coarsening. However, an important aspect of manganese is that it binds sulfur to itself, when the already mentioned manganese sulfide is formed, thereby limiting the degradation potential of sulfur on the material.

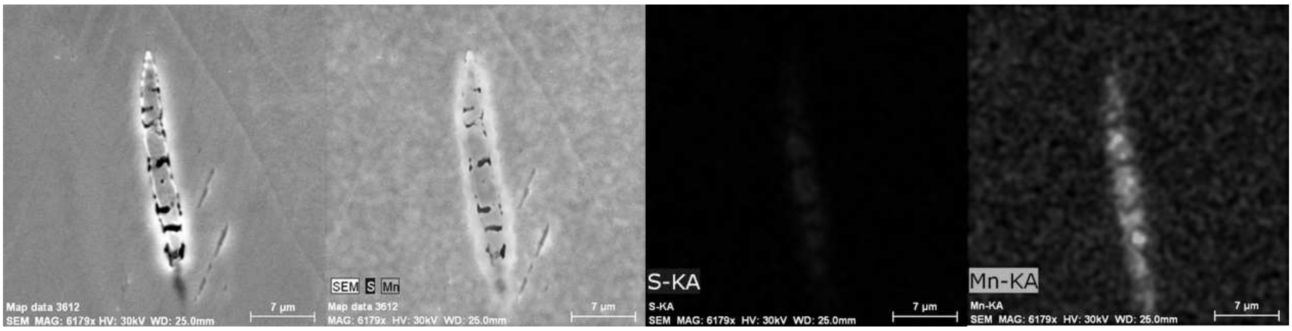

Fig. 2 *EDX analysis MnS – manganese sulfide*

3.1.2 Analysis after plasma nitriding

The plasma nitridation process did not affect the austenite grain shape and size (Fig. 3a). There, inclusions were not dissolved, due to plasma nitridation. Deformation martensite (Fig. 3b) as well as annealing twins were also preserved in the structure. This is evidence that the nitriding temperature was not high enough to dissolve the deformation martensite. On the surface of the sample, there is a nitriding layer, which was created by the process of plasma nitriding.

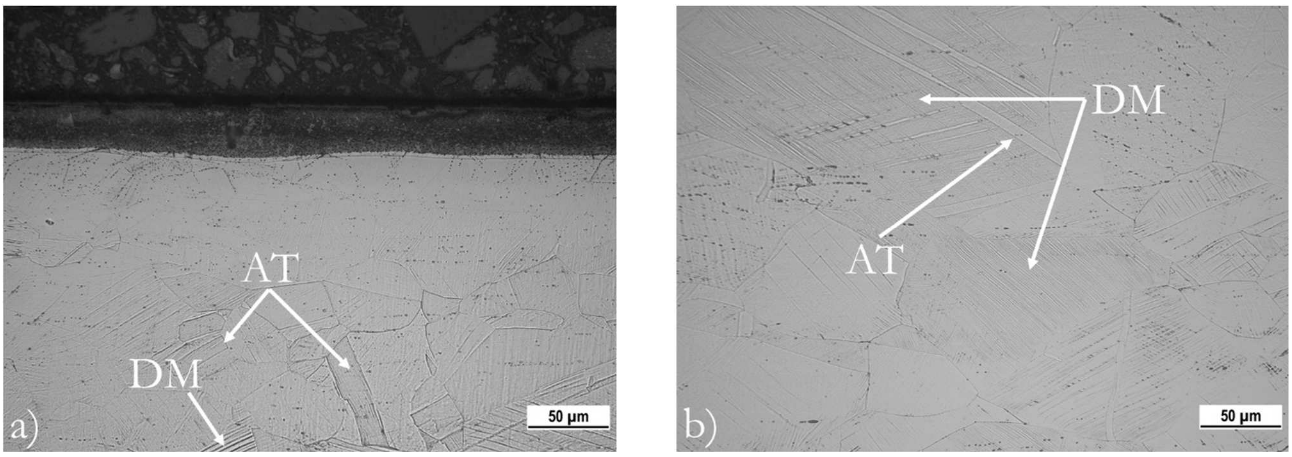

Fig. 3 *Microstructure of AISI 304 austenitic steel after plasma nitriding a) on the edge of the sample b) in the core of the sample*

Line-scan analysis was performed on a scanning electron microscope to analyze the nitrogen content of the sample (Fig. 4). The transition of the nitrogen content between the nitriding layer (NL) and the base material (BM) was monitored. The sample was wrapped in aluminum foil (AF) before metallographic preparation, for better conductivity.

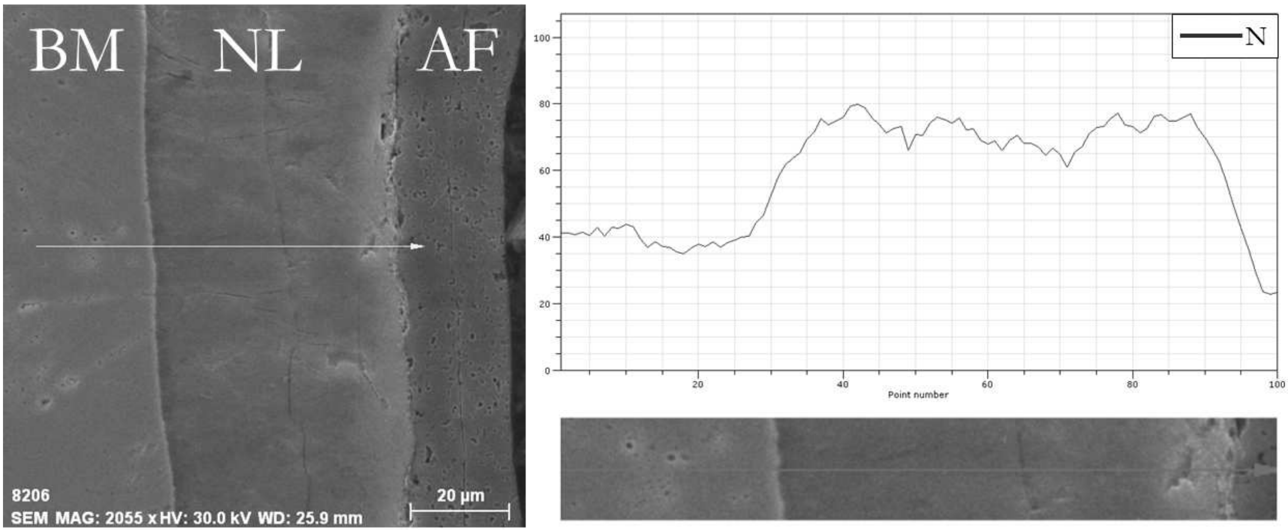

Fig. 4 *Line-scan analysis of nitriding layer formed on AISI 304 austenitic steel*

The thickness of the nitriding layer was also measured on an optical light microscope. Compared to the research by Sing et al. [9], where they compared the thickness of the nitriding layer formed on AISI 304 austenitic steel depending on the surface roughness, their results showed that on the ground sample (Ra = 1.2), the thickness of the nitriding layer was approximately 50 μm. On the sample used in the experiment, the nitridation layer's thickness was similar (48 μm). Samples used in the experiment did not have a mechanically processed surface, similar layer thickness was achieved.

3.1.3 Analysis after sensitization

Sensitization on AISI 304 stainless steel samples was used to examine the resistance to intergranular corrosion. This material is particularly susceptible to it during welding and slow cooling. This heat treatment resulted in the exclusion of carbides along the grain boundaries (Fig. 5a), but also resulted in the exclusion of carbides inside the grain (Fig.5b). Carbides were precipitated uniformly along the grain boundaries and formed a continuous carbidegrid.

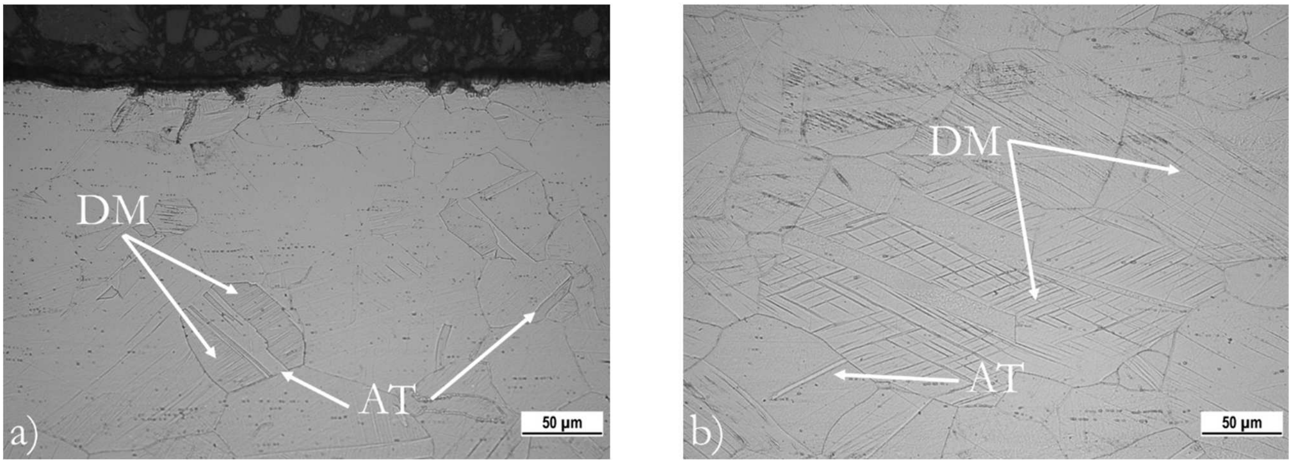

Fig. 5 *Microstructure of AISI 304 austenitic steel after sensitization a) on the edge of the sample b) in the core of the sample*

3.1.4 Analysis after plasma nitriding and sensitization

After the nitriding and sensitization process, we observe polyhedral austenite grains (Fig. 6a), which are depleted of chromium. Chromium precipitated in the form of chromium carbide along the grain boundaries and formed a significant carbide path (Fig. 6b). The nitriding layer did not affect the formation of carbides at the grain boundaries.

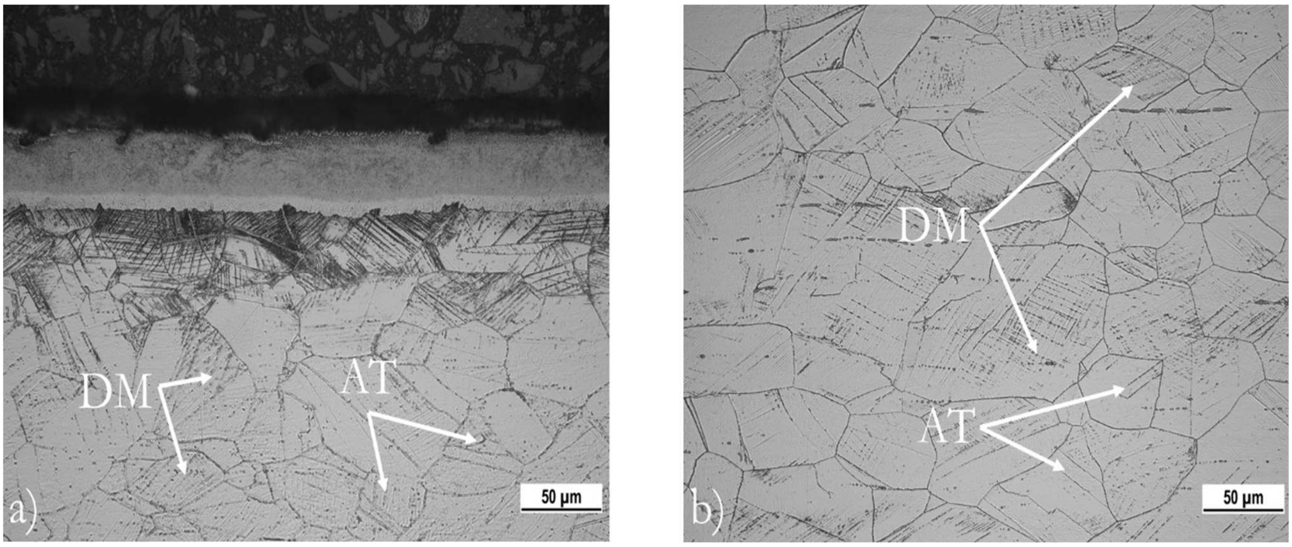

Fig. 6 *Microstructure of AISI 304 austenitic steel after plasma nitriding and sensitization a) on the edge of sample b) in the core of the sample*

Even in this experimental steel condition, a line-scan was performed to analyze the nitrogen content in the nitriding layer of the sample (Fig. 7). A very thin oxide (O) layer was visible on the sample after sensitization, which was formed on the surface of samples after sensitization

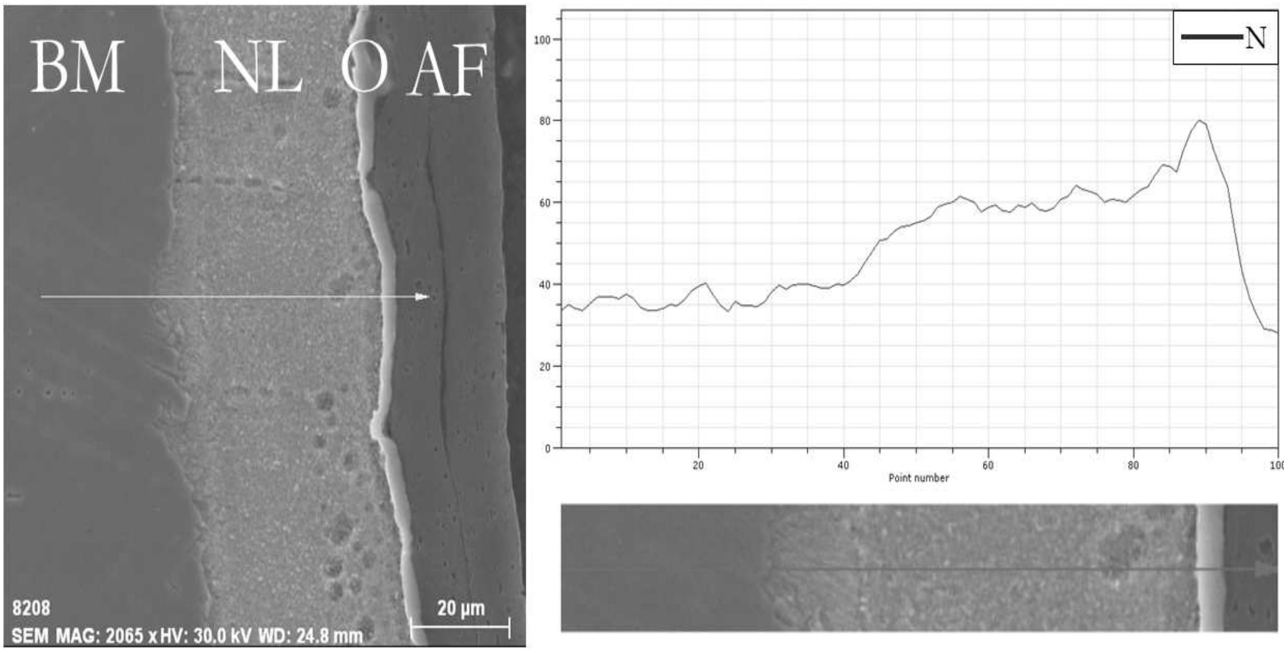

Fig. 7 *Line-scan analysis of nitriding layer after sensitization on AISI 304 austenitic steel*

3.2 Evaluation of microhardness

3.2.1 Measurement of microhardness from surface to core

By comparing the microhardness of all states, it can be concluded that samples in the initial state (IS) and samples after plasma nitriding (PN) had approximately the same course along the entire length of the measurement (Fig. 8). The minimum microhardness on samples in the initial state was 252 HV 0.5 and the maximum was 326 HV 0.5. On samples after plasma nitriding, the microhardness ranged from 262 HV 0.5 to 436 HV 0.5 at the edge of the sample. The microhardness of the sample after sensitization (S) decreased throughout the measurements (191 HV 0.5 to 284 HV 0.5), which can be attributed to a decrease in dislocation density and a decrease in the proportion of deformation martensite in the steel. Samples after plasma nitriding and sensitization (PN+S) had a similar character of microhardness course as the nitrided samples (240 HV 0.5 to 430 HV 0.5). On the nitrided samples, the microhardness was increased at the beginning of the measurement (below the surface).

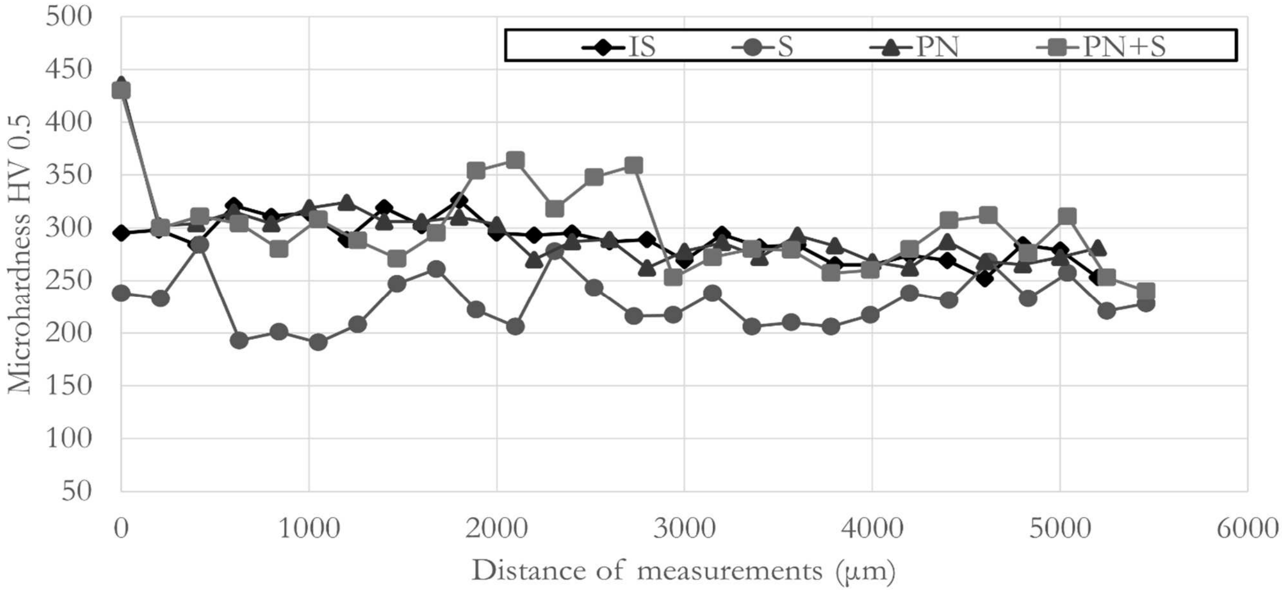

Fig. 8 *Comparison of microhardness from the surface to the core of the sample*

3.2.1 Measurement of microhardness on nitriding layers

Measurements of the microhardness of the nitriding layer showed that sensitization had a significant effect on the microhardness of the layer. The microhardness of the nitriding layer ranged from 1020 HV 0.01 to 1291 HV 0.01, followed by a steep transition to the softer part of the sample (core). The sample after plasma nitriding and with subsequent sensitization reached a microhardness of 551 HV 0.01. This means that in this sample there was not such a steep transition towards the core.

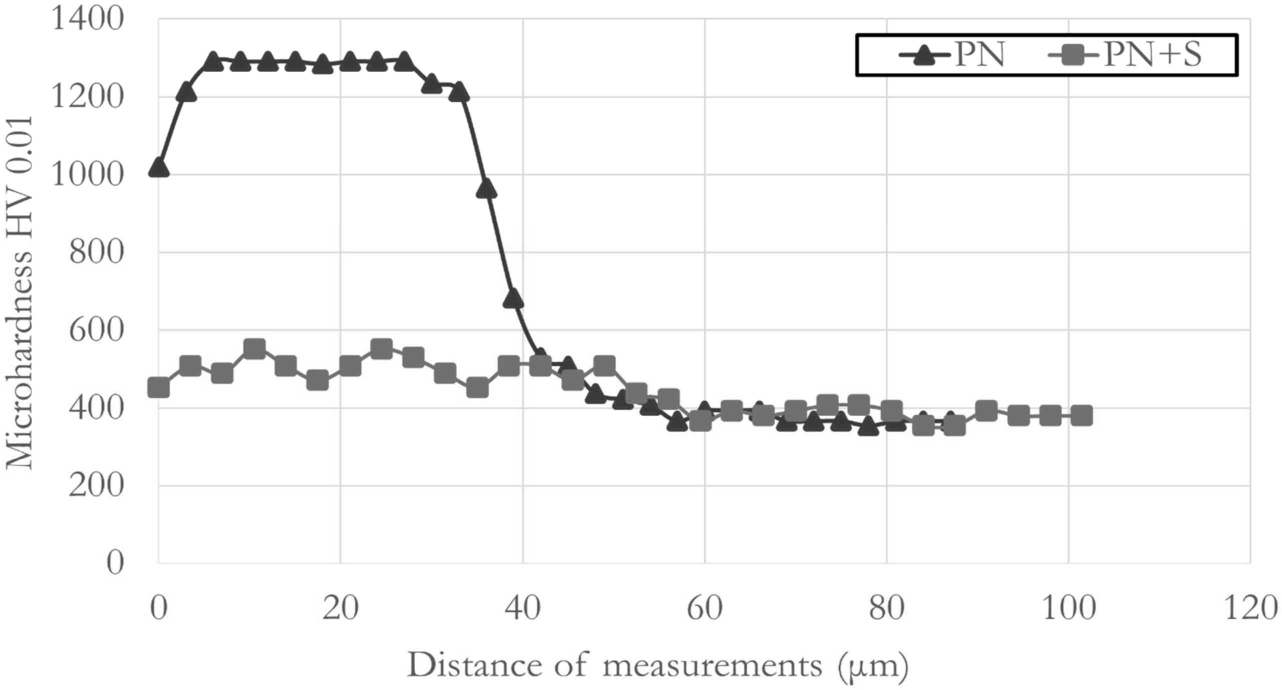

Fig. 9 *Comparison of microhardness of nitriding layer*

Research by Castillo et al. [17] achieved comparable microhardness of the nitriding layer with the nitriding layer on our experimental samples. The depth of plasma nitriding can also be compared with this research, when the transition from the layer to the core was approximately at the same distance from the surface and the microhardness of the steel core was approximately the same. Compared to the research by Castillo et al., there are differences in the plasma nitriding length and the nitridation temperature. The plasma nitriding used in the experiment lasted for 24 hours and was nitrided at a temperature of 520-530°C, while Castillo et al. nitrided for 15 hours at a temperature of 400°C.

4 Conclusion

From the analysis, which was focused on the effect of plasma nitriding and sensitization on AISI 304 austenitic steel, we can draw the following conclusions from the experimental results:

- In all evaluated states, the microstructure was formed by polyhedral austenite grains with different grain sizes. Inclusions in the steel were identified as manganese sulfide, by EDX analysis. In all states, deformation martensite was present in the microstructure. The nitriding layer could be distinguished from the base material and was also observable even after being affected by the sensitization process.
- The microhardness of the core of AISI 304 austenitic steel in the initial state and after plasma nitriding was approximately the same. The highest microhardness was measured on the nitriding layer.
- From the EDX line-scan analysis, it appears that due to the application of temperature sensitization on the nitriding layer, resulted in an equalization of the nitrogen content between the layer and the core of the steel.

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