# Surface improvement of 42CrMo4 low alloy steel via nitrocarburization and electroless Ni-P plating: enhancing the surface hardness

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Article Info	Abstract
Article history: Received 12.12.2023 Revised: 22.04.2024 Accepted: 25.04.2024 Published Online: 26.04.2024	This research aims to improve the surface hardness of 42CrMo4 low alloy steel, which is a very important material in the defense industry and especially in the context of gun production. The enhancement is maintained through the application of nitrocarburization and electroless Ni-P plating processes. The resulting nitrocarburized surface revealed corresponding hardness and diffusion depth
Keywords: Materials science Nitrocarburization Electroless Ni-P plating Surface hardness Steel	values of 566 HV0.1 and 132.60 $\mu$ m, respectively. Then, electroless Ni-P coating process was carried out. For coating hardness, it was heat treated at 250°C for 4 and 8 hours. With the effect of heat treatment, the hardness value of 563±33 HV0.01 resulted in a significant increase to 715±24 HV0.01 and 852±42 HV0.01. Simultaneously, the nitrocarburization process caused a gradual decrease in hardness from 566 HV0.1 to core hardness, covering a distance of 132.60 $\mu$ m from the surface. This symbiotic integration results in a composite structure characterized by a flexible and wear-resistant surface superimposed on a subsurface that helps maintain the hardened coating.

## 1. Introduction

Low alloy 42CrMo4 steel is frequently used in the defense industry due to its superior temperability, niturability and possibility of design its mechanical properties by heat treatment. Despite its advanced properties, the surface of 42CrMo4 steel is modified for long life and stability in some defense industry applications. For example, in the use of 42CrMo4 steel in pistol applications, the properties demanded from the material are tough and impact resistant on the core and hard, wear and corrosion resistant on the surface.

Nitrocarburization and electroless Ni-P coating are among the methods used to improve the surface properties of 42CrMo4 steel. Nitrocarburization is a thermochemical surface treatment applied to steels, cast irons and sintered iron-based materials that improves wear, fatigue strength and corrosion resistance of part [1]. Nitrogen and carbon atoms are diffused simultaneously on the surface of the material by the nitrocarburization process, which can be applied in a pack, salt bath, gas, or plasma environment, and carbides and nitrides are formed on the surface and near the surface to increase the wear, corrosion, and fatigue resistance of the material [2-6]. As a result of the process, white layer consisting of  $\varepsilon$ -Fe<sub>2</sub>-3N -  $\gamma$ '-Fe<sub>4</sub>N is formed on the surface of steel materials and a diffusion zone just below this layer where nitrogen and carbon exist as solid solution in the steel material [7]. Although the compound layer on the surface of the material is quite hard, it is quite brittle due to the internal stresses in the boundary regions of the  $\varepsilon$ -  $\gamma'$  phases [8]. In addition, the surface formed is not desirable in applications where decorative appearance is important.

Electroless Ni-P plating is an autocatalytic coating method invented by Riddel in 1946 and generally applied to improve the surface properties of metallic materials such as surface hardness, wear and corrosion resistance [9, 10]. This technology produces coatings that do not require an external electrical source. As a result, coating thickness variations caused by regional current density in electrolytic coatings are not a concern in such coatings. Coatings with a uniform thickness distribution are produced [11]. It is also possible to apply electroless Ni-P plating to polymer and ceramic materials with appropriate surface treatments [12, 13]. It can also be used as an intermediate layer in multilayer coating applications [14]. In addition, electroless Ni-P coating has a desirable decorative appearance. The hardness of electroless Ni-P, which have an amorphous structure as coated, can be improved by the formation of a very hard Ni<sub>3</sub>P compound in the structure by applying appropriate heat treatments [15].

In this study, it was aimed to improve the surface properties of low alloy 42CrMo4 steel, which is used extensively in the production of handgun parts, by nitrocarburizing and electroless Ni-P coating. The hardness changes and diffusion depth occurring on the surface of 42CrMo4 steel with nitrocarburization process were investigated. The effect of nitrocarburization process combined with electroless Ni-P coating on the surface hardness of the material was investigated. The effect of heat treatment on the hardness of electroless Ni-P coating was evaluated.

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## 2. Materials and Methods

Low alloy 42CrMo4 steel with dimensions of 1000 mm x 500 mm x 10 mm was supplied from Asil Çelik, Turkey. In order to verify the chemical composition of the steel material, a 50 mm x 50 mm x 10 mm piece was cut and optical spectrography (Arun Technology, Artus 8, England) was performed. The determined weight percent chemical composition is shown in Table 1. In order to determine the initial hardness of the test material, a piece of 10 mm x 10 mm x 10 mm was cut and mounted. Sanding operations were carried out with 320, 600 and 1200 sandpaper. 6  $\mu$ m and 1  $\mu$ m diamond abrasive suspension and broadcloth were used for polishing. Microhardness measurement was carried out with a load of 100 grams using a Vickers penetrating tip (Emcotest, DuraScan 20 G5, Austria).

In order to carry out the nitrocarburization and electroless Ni-P plating processes, 50 mm x 50 mm x 10 mm samples were cut from the test material. Samples are coded as shown in Table 2. All samples were sandblasted in a pressure blasting cabinet using  $Al_2O_3$  abrasive particles with particle sizes of 90-125  $\mu$ m. Ferritic nitrocarburization was applied to the samples in a salt bath prepared with commercial chemicals at 570 °C for 60 minutes. In order to determine the diffusion depth after the nitrocarburization process, a 10 mm x 10 mm x 10 mm piece was cut from the sample N and mounted. After the metallurgical specimen preparation, the diffusion depth was measured according to the DIN 50190 standard with a load of 100 grams by applying the Vickers microhardness measurement method [17]. The core hardness of the material was determined by making three microhardness measurements at a distance of 500 µm from the surface. Determination of diffusion depth was

performed using Equation 1. Diffusion depth is the depth at which the microhardness value corresponding to the result obtained from equation 1 is determined in the material.

Diffusion Depth=(Actual Core Hardness+50)HV<sub>0.1</sub> (1) [17] For other samples, before the electroless Ni-P plating process, the compound layer formed on the material surface during the nitrocarburization process was removed from the structure by pressure sandblasting using Al<sub>2</sub>O<sub>3</sub> abrasive particles. The electroless Ni-P plating process was carried out for 45 minutes at 90 °C using proprietary chemicals. In order to increase the hardness of the electroless Ni-P coating, EN-2 and EN-3 samples were subjected to heat treatment at 250°C for 4 hours and 8 hours, respectively. Heat treatment was not applied to the sample EN-1.

For coating microhardness and coating thickness measurements, 10 mm x 10 mm x 10 mm pieces were cut from EN-1, EN-2 and EN-3 samples and mounting processes were carried out so that the cross-sectional area could be seen. After sanding and polishing, coating thickness and coating microhardness measurements were carried out. Microhardness measurements were carried out with a Vickers indenter tip using a load of 10 grams. Coating thickness measurement was performed on an Olympus GX-53 metallurgical microscope using Stream Essentials software.

## 3. Results and Discussion

The microhardness of the test material in its as-received state is shown in Figure 1. As can be seen in Figure 1, the initial microhardness of the material on the surface is  $303.4\pm12.3$  HV<sub>0.1</sub>.

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	Element	С	Si	Mn	Р	S	Cr	Mo	Fe
	DIN EN 10083-3 -	0,38-	Max.	0,60-	Max.	Max.	0,90-	0,15-	Balance
	42CrMo4	0,45	0,40	0,90	0,025	0,035	1,20	0,30	
	Measured Values	0,41	0,15	0,61	0,037	0,005	1,12	0,25	Balance

Table 2. Test samples and procedures applied to the samples						
Sample	Nitrocarburization	Electroless Ni-P Plating	Heat Treatment			
Ν	570 °C – 60 min.	-	-			
EN-1	570 °C – 60 min.	90 °C – 45 min.	-			
EN-2	570 °C – 60 min.	90 ⁰C – 45 min.	250°C – 4 h			
EN-3	570 °C – 60 min.	90 ⁰C – 45 min.	250°C – 8 h			



Figure 1. Initial surface microhardness of low alloy 42CrMo4 steel



Figure 2. Microhardness and diffusion depth measurements on low alloy 42CrMo4 steel following the nitrocarburization process



Figure 3. Coating microhardness and coating thickness measurements of the sample EN-1



Figure 4. Coating microhardness and coating thickness measurements of the sample EN-2

The diffusion depth measurement performed on the sample N is shown in Figure 2. As can be seen in Figure 1 and Figure 2, the surface hardness of low alloy 42CrMo4 steel was increased from  $303.4\pm12.3$  HV0.1 to 566 HV<sub>0.1</sub>, resulting in an 86.55% increase in hardness with the nitrocarburization process.

Additionally, the hardness of the material was increased by the diffusion of carbon and nitrogen atoms from the steel surface to a depth of 132.60  $\mu$ m. Microhardness and diffusion depth values obtained by nitrocarburization are similar to the study by Doan et al., in which they applied nitrocarburization to low alloy 42CrMo4 steel [18].

Microhardness and coating thickness measurements performed on the sample EN-1 to which electroless Ni-P coating was applied are shown in Figure 3. In the sample EN-1, the microhardness of the as deposited electroless Ni-P coating was determined as  $596\pm33$  HV<sub>0.01</sub> and the coating thickness was  $11.50\pm0.59$  µm.

Coating microhardness and coating thickness measurements of sample EN-2 and EN-3, which were heat treated for 4 and 8 hours at 250 °C, respectively, are shown in Figure 4 and Figure 5. As can be seen in Figure 4, after a 4-hour heat treatment at 250°C, the hardness of the electroless Ni-P coating on the sample EN-2 was measured as  $739\pm24$  HV<sub>0.01</sub> and its thickness was measured as  $12.78\pm2.03$  µm.



Figure 5. Coating microhardness and coating thickness measurements of the sample EN-3

As can be observed in Figure 5. in the sample EN-3, where the heat treatment time was increased to 8 hours by keeping the temperature constant, the coating microhardness value was  $867\pm27$  HV<sub>0.01</sub>. The coating thickness on the sample EN-3 was determined as  $11,24\pm0,77$  µm.

The microhardness values of the coatings were enhanced to  $739\pm24$  HV<sub>0.01</sub> and  $867\pm27$  HV<sub>0.01</sub> by applying heat treatments to EN-2 and EN-3 samples at 250°C for 4 and 8 hours, respectively. These values are parallel to the microhardness values obtained by Apachitei et al. in their study [19]. The increase in hardness achieved by heat treatment in electroless Ni-P coatings can be explained by the formation of a hard Ni<sub>3</sub>P compound in the amorphous coating layer at temperatures above 220°C [20]. No significant changes due to heat treatment were observed in the coating thickness of EN-1, EN-2 and EN-3 samples.

#### 4. Conclusions

The surface hardness of low-alloyed 42CrMo4 steel has been enhanced through nitrocarburization and electroless Ni-P coating processes. The outcomes following surface treatments are summarized as follows:

- Initially, the surface hardness measuring  $303.4\pm12.3$  HV<sub>0.1</sub> was elevated to 566 HV<sub>0.1</sub> through nitrocarburization treatment, achieving a gradual hardness transition extending 132.60  $\mu$ m from the surface towards the center, thus preparing the material for subsequent surface coatings.
- An electroless Ni-P coating was applied to the nitrocarburized surface, resulting in a 0.5% increase in surface hardness, reaching 596±33 HV<sub>0.01</sub>.
- Applying a heat treatment at 250°C for 4 hours to the electroless Ni-P coating led to a 23.99% increase in surface hardness, reaching 739±24 HV<sub>0.01</sub>.
- Further heat treatment for 8 hours at 250°C on the electroless Ni-P coating resulted in a 45.46% increase in surface hardness, reaching 867±27 HV<sub>0.01</sub>.
- The combination of nitrocarburization, electroless nickelphosphorus coating, and an 8-hour, 250°C heat treatment on the EN-3 sample has yielded a wear-resistant coating with a desired hardness exceeding 800 HV for light firearms, along with an underlying surface that complements this coating.

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## **Author Contribution**

Uğur Temel Yildiz: Writing - original draft, Conceptualization, Data curation, Formal Analysis, Methodology

- Temel Varol: Supervision, Writing original draft, Conceptualization, Validation, Writing - review & editing
- Burak Berk Day: Methodology, Conceptualization, Data curation, Writing review & editing
- Büşra Kandemir: Visualization, Data curation, Writing review & editing

Furkan Alptekin: Writing - review & editing, Data curation Ahmet Fuat Günaçar: Writing - review & editing

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