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Effect of Heat Treatment at Different Temperatures on The Structural and Tribological Properties of Electroless Ni-B Coated 32CrMoV12-10 Alloy

Erdoğan Koray Özyurt[1] Muharrem Pul[2,*]

[1]*Department of Defense Technologies, Institute of Science and Technology, Kırıkkale University, Kırıkkale, Türkiye*
[2]*Kırıkkale Vocational School, Kırıkkale University, Kırıkkale, Türkiye*

ABSTRACT

In this article, Ni-B (nickel-boron) plating process was performed on 32CrMoV12-10 barrel material, which is widely used in the defense industry and produced by forging method, by electroless plating method in aqueous solution prepared in a bath. The coated samples were then heating process at 250, 300, 350 and 400°C temperatures. The effects of these heat treatments on tribological and microstructural properties were investigated. Cauliflower-like surface structure was formed on all coated samples. In XRD analysis, it was observed that an amorphous structure was formed in the sample heating processat 250°C in argon environment. The highest hardness was measured on the surface of the sample heating processat 350°C in argon environment, while the lowest hardness was measured on the surface of the sample with amorphous structure and heating process at 250°C in argon environment. It was observed that there was a notable increase in the wear endurance of the samples heating process at 300°C, 350°C and 400°C in argon environment. It was concluded that heat treatment in an open atmosphere causes oxidation at the steel interface, which prevents the diffusion of nickel into the steel in the plating process. The surface roughness of the sample heating process at 250°C in an amorphous argon atmosphere was higher than all other samples. The best surface roughness value was obtained at the argon atmosphere 350°C treatment conditions. When all the data supporting each other are brought together, it is determined that the most suitable heat treatment temperature is at 350°C in argon atmosphere instead of high temperature heat treatment after Ni-B plating process on an industrial scale.

Keywords: *32CrMoV12-10 alloy, Electroless plating, Nickel-Boron coating, Heat treatment, Mechanical properties, Tribology*

Farklı Sıcaklıklardaki Isıl İşlemin Akımsız Ni-B Kaplamalı 32CrMoV12-10 Alaşımının Yapısal Ve Tribolojik Özelliklerine Etkisi

ÖZET

Bu çalışmada, savunma sanayinde yaygın olarak kullanılan ve dövme yöntemi ile üretilen 32CrMoV12-10 namlu malzemesine, banyo içerisinde hazırlanan sulu çözeltide akımsız kaplama yöntemi ile nikel-bor (Ni-B) kaplama işlemi gerçekleştirilmiştir. Kaplanan numuneler daha sonra farklı sıcaklıklarda ısıl işleme tabi tutulmuştur. Bu ısıl işlemlerin tribolojik ve mikro yapısal özellikler üzerine etkileri incelenmiştir. Tüm kaplanan numunelerde karnabahar benzeri yüzey yapısı oluşmuştur. XRD analizi, argon atmosferinde 250°C'de ısıl işlem uygulanan numunenin yapısının amorf olduğunu göstermiştir. En yüksek sertlik değeri argon atmosferinde 350°C'de ısıl işlem uygulanan numunede, en düşük sertlik ise amorf yapıya sahip argon atmosferinde 250°C'de ısıl işlem uygulanan numunede ölçülmüştür. Argon atmosferinde 300, 350 ve 400°C'de ısıl işlem uygulanan numunelerin aşınma dirençlerinin önemli ölçüde iyileştiği görülmüştür. Açık atmosferde ısıl işlemin çelik ara yüzeyinde oksidasyona neden olduğu ve bu durumun kaplama işleminde nikelin çeliğe difüzyonunu engellediği sonucuna varılmıştır. Amorf argon atmosferinde 250°C'de ısıl işleme tabi tutulan numunenin yüzey pürüzlülüğü diğer tüm numunelerden daha yüksek bulunmuştur. En iyi yüzey pürüzlülük değeri argon atmosferinde 350°C işlem koşullarında elde edilmiştir. Birbirini destekleyen tüm veriler bir araya getirildiğinde endüstriyel ölçekte nikel-bor (Ni-B) kaplama işleminden sonra yüksek sıcaklık ısıl işlemi yerine argon atmosferinde 350°C'de en uygun ısıl işlem sıcaklığının olduğu belirlenmiştir.

Anahtar Kelimeler: *32CrMoV12-10 alaşımı, Akımsız kaplama, Nikel-Bor kaplama, Isıl işlem, Mekanik özellikler, Triboloji*

*Corresponding author, e-mail: mpul@kku.edu.tr

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1. INTRODUCTION

The historical evolution of weapons has taken place in parallel with technological advancements, resulting in the continuous improvement of the desired properties of weapons such as high durability, low weight, high wear resistance and corrosion resistance. Research has shown that weapon parts are subjected to high stresses and therefore manufacturing materials must have high durability. Therefore, it is important that the materials have high durability and impact resistance to achieve long life and high dimensional stability in weapon parts [1-3]. In recent years, due to the need to increase the firing life of weapons beyond the world standards, development studies on weapon parts such as barrels have gained importance. In order to extend the service life, it is emphasized that the factors affecting the service life of the parts, such as material selection, heat treatment applications and coating, should be selected at the optimum level [4].

Coating is the process of layering or deposition of another material, which is considered as a sub-material and on which functionality is desired to be imparted, so as to enhance the physical, chemical and mechanical properties of a material. The types of surface coatings known and applied to obtain surfaces with different types of characteristics include hard chrome plating, electroless plating, thermal spray, weld overlay, CVD, PVD, ion implantation and laser surface treatment [5]. Electroless coatings refer to a surface coating method based on the controlled reduction reaction of metal ions such as copper, nickel, silver, gold and similar metal ions, without the need for electric current, accompanied by the catalytic properties of the surface. Nickel-phosphorus and nickel-boron are the most important electroless deposition coatings for improving chemical and physical wear properties [6]. Electroless nickel plating is the deposition of nickel without the use of electric current. The plating takes place by autocatalytic chemical reduction of nickel ions by hypophosphite, amino borane or borohydride compounds. The process is carried out by immersing the material to be plated in a solution. The plating bath consists of aqueous solutions of chemical substances consisting of metal salt, reducing agent, pH level adjusting buffer solution and reaction rate adjusting catalysts. The reducing agent ensures the reduction of metal ions. Electroless nickel plating is based on electrochemical deposition in which the reducing agent acts as a catalyst and adheres to the material during the plating process [5, 6]. Electroless nickel plating is preferred in a wide range of industrial applications such as petroleum, chemical and plastic industries, optics, printing, mining, aviation, nuclear, automotive, electronics, computers, paper, textile and food machinery due to its superior technical properties such as excellent chemical and physical wear resistance, uniform coating thickness in all areas, solderability and weldability, excellent coating hardness and lubricity [5, 6].

When the literature is reviewed, it is seen that similar studies have been carried out on the investigation of electroless coating and properties of different steel alloys. In the studies of Taha-Tijerina et al., the tribological properties of electroless Ni-B film were evaluated under extreme pressure conditions when D2 tool steel samples were coated with 3 μm, 6 μm and 12 μm coating thicknesses and heat treatment (200 °C for 90 minutes) were applied. The results showed that the chemical-free technology improved the coefficient of friction (COF) of tool steel with 3 μm and 12 μm coating by 15% to 30%, respectively. When this improvement was increased by applying heat treatment to the coated components, it was stated that improvements of 24-38% were shown between 3 mm and 12 mm, respectively [7]. In another study by Cies´lak et al.; a process scheme was developed for the production of Ni-B layers and composite coatings with nickel-boron matrix and a dispersant phase in the form of boron nanoparticles. In order to improve the performance of the produced coatings, a heating process was carried out at 400 ◦C and the performance of Ni-B and composite Ni-B/B coatings was investigated after the heat treatment process. When the results were evaluated, it was stated that the heat treatment of the coatings caused the crystallization of the amorphous matrix and significantly increased the hardness. On the other hand, the high hardness of the crystalline nickel boride phases was reported to contribute to the high brittleness and cracking of the coatings [8]. In a similar study by Arias et al., the tribological properties were evaluated before and after one hour of heat treatment at 450 °C in Ni-B autocatalytic coatings deposited on AISI/SAE 1018 carbon steel. According to the tribological evaluation, heat treatments applied to Ni-B coatings were found to improve their tribological performance. As a result of the research, it was stated that it was confirmed that the hardness and wear resistance of Ni-B coatings could be significantly improved by applying an adequate heat treatment [9]. In a study conducted by Çelik et al., the surface of commercially pure titanium (Grade 2) was coated with electroless Ni–B and then heat treated at 400 C for one hour. The analysis results showed that the electroless Ni–B coating had a significantly amorphous structure when deposited. In addition, it was determined that the coating structure crystallized after heat treatment and the wear resistance of pure titanium increased after chemical-free Ni–B coating. In particular, it was stated that the wear resistance and surface hardness of pure titanium increased significantly after heat treatment [10]. In the study of Bülbül et al., electroless Ni–B coating was deposited on AISI 316L stainless steel and its structural, tribological and corrosion properties were characterized. Microstructural analysis showed that the non-chemical Ni–B coating deposited on AISI 316L steel substrate exhibited a typical cauliflower-like structure and exhibited amorphous growth. From this study, it was concluded that this treatment could not only improve the hardness and wear resistance of 316L stainless steel, but also provide cathodic protection without losing the original properties of 316L stainless steel [11].

In this experimental study; 32CrMoV12-10 (1.7765) barrel material produced by forging method was used. Due to its good mechanical properties, 32CrMoV12-10 steel is mostly preferred in high temperature applications. However, some tools or work dies made of 32CrMoV12-10 steel may be subject to frequent wear. Therefore, distinct surface treatments are applied to improve the tribological features of 32CrMoV12-10 and similar tool steels and to increase their wear resistance [12]. Industrial reclaimed steels are steels used in machine manufacturing that are highly amenable to hardening due to their carbon content (0.25% C to 0.6% C). The reclamation process is defined as the hardening and subsequent tempering of steel materials to give them high toughness properties. These steels are used in the production of medium caliber weapons due to their superior mechanical properties after the treatment process. They are also widely used in the manufacture of machine parts, crankshafts, axle shafts and splined shafts [13]. 32CrMoV12-10 is a hot work tool steel with high thermal shock endurance, high thermal conductivity and high toughness over long periods of time. This steel is used in various applications such as pressure casting of heavy metals, hot forging and forming dies, extrusion dies of materials such as aluminum, copper, brass and gun barrel production [14]. Based on the literature researches and past studies, the stages of the processes to be carried out were determined; in order to determine the best conditions of the plating baths, chemicals that will use nickel ions as a source, complexing agents, stabilizing agents, plating bath solution mixing speed and bath pH value were determined. The samples were then coated according to this plan in an electroless Ni-B coating bath. The Ni-B coated materials were then heating process at 250, 300, 350 and 400°C in argon atmosphere and 400°C in open atmosphere respectively. Since oxidation is expected to increase with the increase in heat treatment temperature, the open atmosphere experiment was carried out at 400 °C, which is the highest temperature within the operating limit conditions. In the study in the literature, it is stated that the crystallization temperature of Ni-B coating is 300°C - 350°C [15]. In the study subject to this article, the values in the literature were taken into consideration and it was deemed appropriate to examine the lower and upper values of these values. In the first step during the characterization studies, the surface and cross-sectional images of the Ni-B coated samples subjected to heat treatment at different temperatures were observed using FE-SEM device and the thickness of the coating was measured and the structures occured on the surface were examined in detail. After determining that the coatings were successfully applied, XRD analysis, hardness, wear and surface roughness tests were performed on the samples and the tribological strength properties were examined parametrically depending on the heat treatment temperature differences in the coating.

The main purpose of this study is to develop a coating that can increase the service life of the weapon by increasing the mechanical properties of the barrel. Therefore, in this study, 32CrMoV12-10 barrel material, which is widely used in the defense industry and produced by the forging method, was prepared in the form of plate samples. Ni-B coating was applied to the prepared samples by the electroless coating method in the bath prepared in an aqueous solution. Subsequently, heat treatments were applied at different temperatures and the effects of heat treatment parameters on the tribological and microstructural properties of the final product were investigated comprehensively. The obtained data were evaluated and an attempt was made to determine the optimum parameter within the selected heat treatment parameters.

2. MATERIAL AND METHOD

2.1. Preparation of samples and electroless Ni-B coating

In this study, plate-shaped specimens with dimensions of 29×29×3 mm were prepared by wire erosion cutting method from 32CrMoV12-10, which is a material frequently preferred in gun barrel production as a base metal. Table 1 shows the chemical composition and some mechanical properties of 32CrMoV12-10 steel.

Table 1. Chemical combination and mechanical properties of 32CrMoV12-10 steel [16].

C	Mn	Si	Cr	Mo	V	P	S	Fe
0,3 – 0,35	≤ 0,6	≤ 0,35	2,8 – 3,2	0,8 – 1,2	0,25 – 0,35	≤ 0,025	≤ 0,01	Remain

Yield Strength Rp 0.2 (MPa)	Tensile Stress Rm (MPa)	Elongation A (%)	Heat Treatment Condition	Brinell Hardness (HB)
≥ 740	≤ 1080	≥ 10	Tempering	Tempered 265–320

$NiCl_2.6H_2O$ (Tekkim ≥97 %), $C_2H_8N_2$ (Merck ≥99 %), $NaBH_4$ (Tekkim ≥97 %), $Pb(NO_3)_2$ (Tekkim ≥98 %) and NaOH (Tekkim ≥97 %) were used as plating bath components. The surfaces of the selected base metal samples were cleaned with acetone to remove unwanted impurities. The surfaces to be coated were first sanded with Silicon carbide paper abrasives with 120, 240, 400, 600, 800 and 1200 mesh abrasives and then polished using 3 µm and 1 µm diamond suspension. The base metal to be coated was then cleaned with acetone and washed with ethanol. The samples were then placed in 15% HCl solution by volume and 2% inhibitor for 90 seconds. Samples were then soaked in 5% H_2SO_4 solution by volume for 30 seconds and dried, which made the base metal ready for coating. Rinses were performed at regular intervals using distilled water. In order to evaluate the cross-sectional morphology and thickness of the coated samples, the samples were cut and then bakelined. After these treatments, they were subjected to sanding processes (120, 240, 400, 600, 800, 800, 1200 mesh abrasive) and polishing using diamond suspension (9 µm, 3 µm, 1 µm) [17].

In the second stage, the preparation of electroless Ni-B plating baths was initiated. Nickel chloride hexahydrate ($NiCl_2$-$6H_2O$) was selected as the nickel ion source and its solution was used at a concentration of 20 g/L. Ethylenediamine ($C_2H_8N_2$) was added at a concentration of 110 g/L as a complexing agent with the dissolution of nickel, i.e. to prevent a sudden decrease in the pH of the reaction medium and precipitation of the nickel ions to be reacted, and stirring was continued. Considering that the baths using $NaBH_4$ can easily decompose in acidic and neutral conditions, the plating baths must be in an alkaline environment. Therefore, sodium hydroxide (NaOH) solution was gradually added to the reaction solution at a concentration of 75 g/L to prevent decomposition due to low pH. After adding NaOH to the plating bath, the bath was heated. When the bath temperature approached the desired reaction temperature for plating, Lead (II) nitrate $Pb(NO_3)_2$ solution was added at a concentration of 0.026 g/L as stabilizer to maintain the stability of the plating bath and prevent decomposition. Sodium borohydride ($NaBH_4$) was dissolved in a different beaker with a concentration of 0.925 g/L and added to the plating bath as a reductant to realize the reduction of nickel in aqueous solution during the plating process. After the bath components were added, when the process temperature was reached (90±1°C), pH control was performed (pH >13) and the samples were dipped in the bath and coated for one (1) hour [17].

In this study, heat treatment was applied to the NiB coated surfaces at different temperatures and times in the final stage of the preparation of the test specimens. For this purpose, heat treatment was carried out in Protherm brand split furnace in argon atmosphere at temperatures of 250, 300, 350, 400°C and in Protherm brand chamber furnace in open atmosphere at 400°C for 1 hour. Since oxidation is expected to increase due to the increase in tempered temperature, the open atmosphere experiment was carried out at 400°C, which is the highest temperature within the operating limit conditions [17].

2.2. Characterization of Coatings

In order to determine the effects of heat treatment parameters on the tribological and microstructural properties of electroless Ni-B coated 32CrMoV12-10 (1.7765) barrel material, firstly, the cross-section and surface morphology of the coated samples were examined with "HITACHI SU 5000" SEM, (scanning electron microscope). XRD analyses were then performed to investigate the phase structure in the coated samples. The analyses were performed on a Malvern Panalytical Empyrean device using Cu Kα X-ray radiation with a wavelength of 1.54 Å in the range of 2θ=10°-90° and a scanning speed of 2°/min. Hardness measurements of the coatings were performed with Anton Paar Nanoindentation (NHT3) hardness tester by applying a maximum load of 30 mN for 10 s. At least five measurements from various locations were weighted and averaged to get the hardness values. In the second part of the mechanical tests, wear tests were carried out. For this purpose, abrasion tests were performed on UTS Tribometers brand abrasion tester with 6 mm diameter alumina ball, 2 N normal load, 20 (mm/s) sliding speed, 1 (Hz) frequency, 10 mm abrasion track spacing, 150 meters abrasion distance and 2500 seconds duration. In addition, the width measurements of the wear pits occured on the sample surfaces after the wear tests were performed on the Olympus GX51 brand metal microscope. Wear volumes were calculated according to the measured wear widths. The calculations were performed with the help of SolidWorks 3D design program. In the last stage of the experiments, roughness values, which are an indicator of the surface quality of the NiB coatings obtained, were measured. Surface roughness measurements were made on MahrSurfPS1 surface roughness device by taking measurements from 16 different regions on the coated surfaces and calculating the average surface roughness values [17].

3. RESULTS AND DISCUSSIONS

3.1. Microstructural Analysis

FESEM images of the surfaces of 32CrMoV12-10 specimens with electroless Ni-B coatings heating process at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere are given in Figure 1.

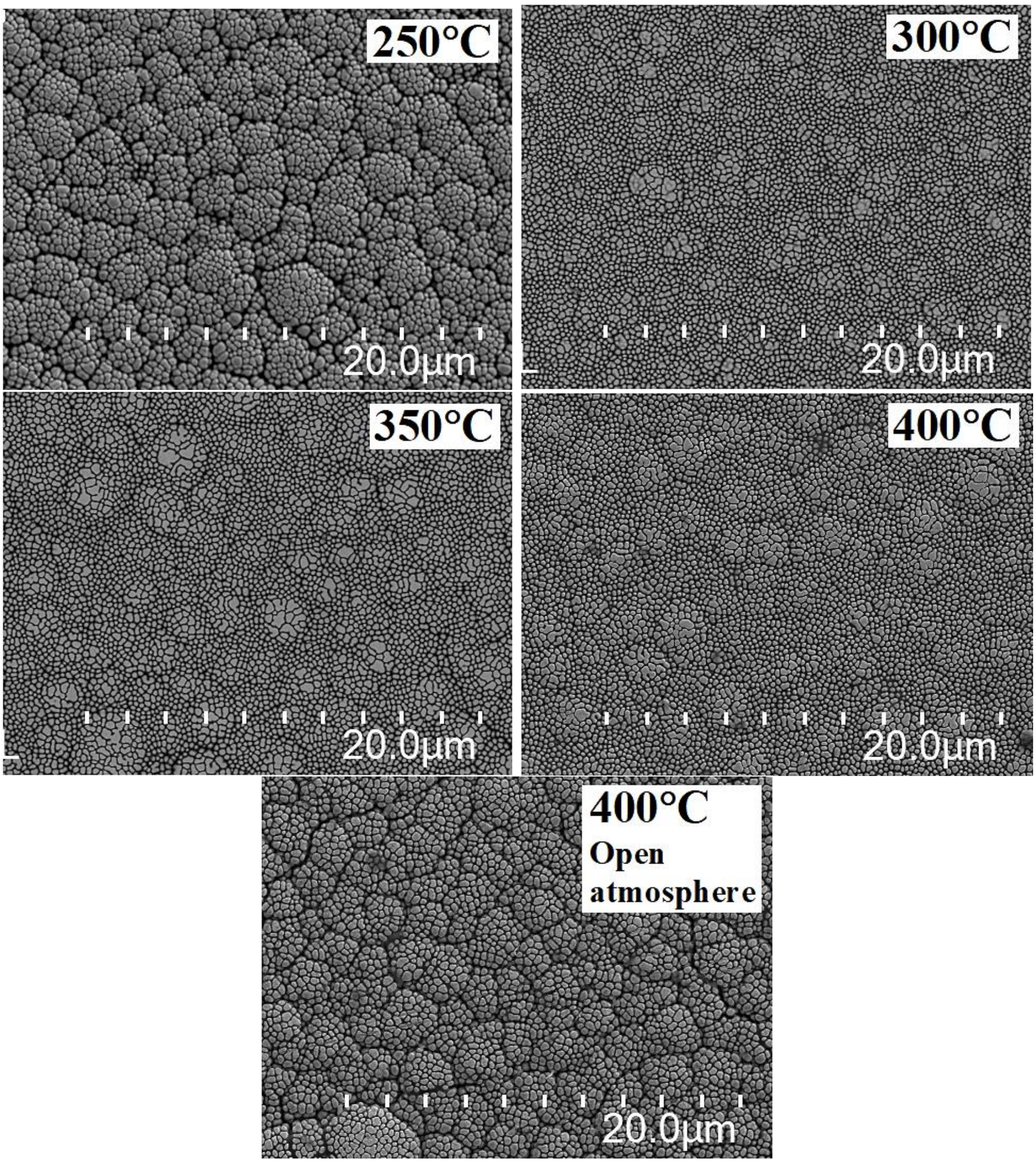

Figure 1. Surface micrographs of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17, 18].

Looking at the BSE images in Figure 1, it is seen that changes in heat treatment temperatures lead to differences in the surface morphology of Ni-B coatings. In electroless Ni-B coatings, a columnar structure is expected due to the growth mechanism and nodular growth starts as a secondary layer. The cauliflower-like structure in the coatings is also due to the growth mechanism (Figure 1) [19]. When the surface morphologies of the obtained coatings were examined; a regular cauliflower-like microstructure occurred in all of the Ni-B coating samples heating process at different temperatures. This is a desired morphological feature. Doğan et. al. reported that the formation of a similar surface structure [20].

In the sample heating process at 250°C in argon atmosphere, the nodules are more open and the rough structure on the surface is noticeable. At this temperature, the opening between the nodules is clearly visible.

With the increase in heat treatment temperature, the increased regularity in nodule formation created a tighter structure, resulting in a smoother and more distinct appearance. In parallel with the literature, it is expected that the surface roughness will gradually decrease with increasing heat treatment temperature. However, the surface roughness is in a similar value range at close heat treatment temperatures [7]. When the images were carefully examined, it was observed that a tighter nodule structure and a smoother surface were obtained in the heat treatment performed above 250°C in an argon atmosphere. It is evaluated that the surface morphology becomes blacker with increasing heat treatment temperature. However, it is observed that the nodules expanded, i.e. the tight structure of the nodules started to separate from each other under open atmosphere 400°C heat treatment conditions (Figure 1). In experiments under open atmosphere conditions, oxygen in the environment enters between the nodules and forms oxide layers there. The oxide formed on the surface causes the volume of the nodules to expand, which causes the nodules to appear more discrete. As a result, the stable structure is disrupted. FESEM images taken to examine the thickness and coating morphology of the realized coatings are given in Figure 2.

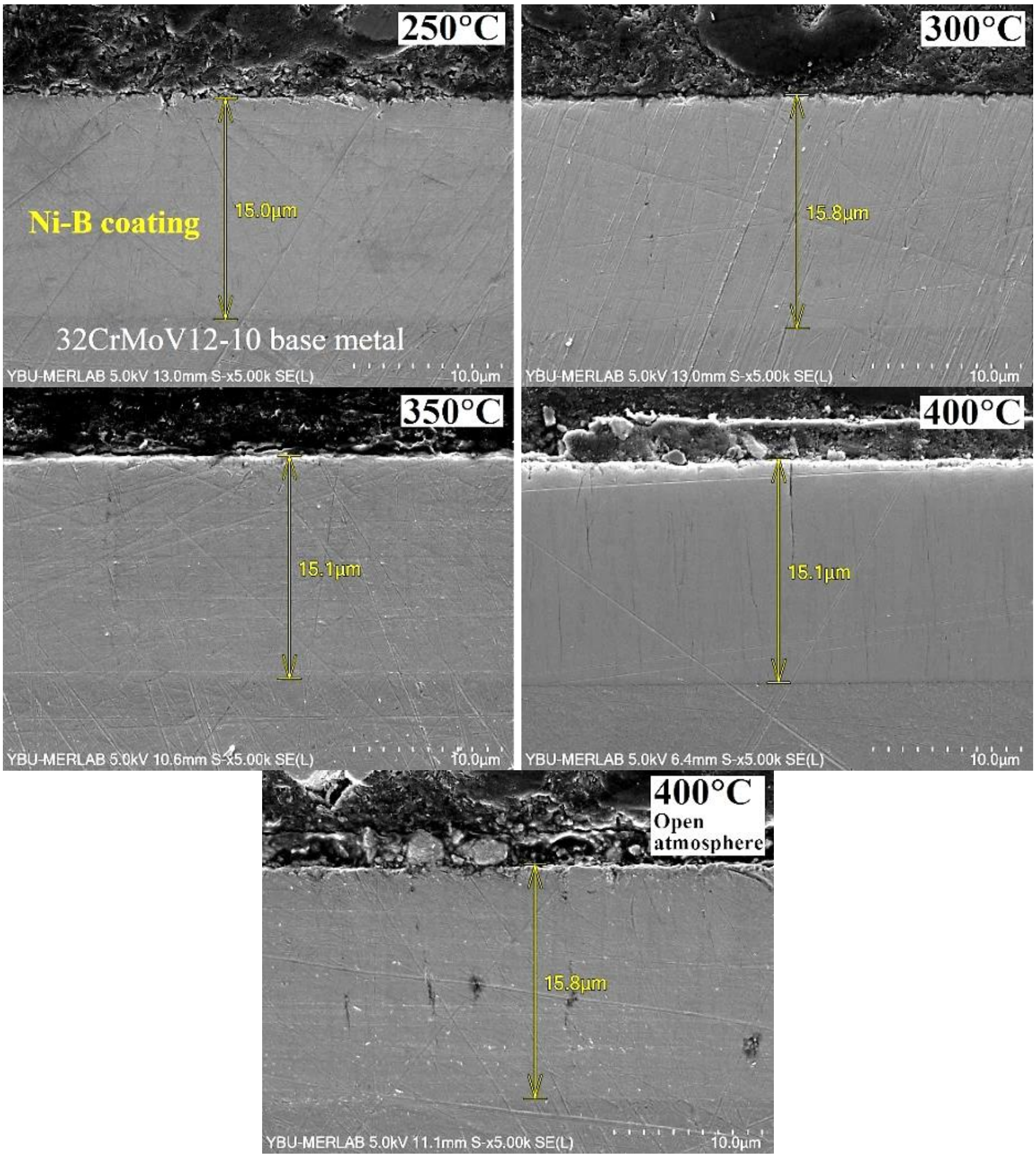

Figure 2. Cross- Sectional images of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17].

Looking at the cross-sectional images in Figure 2, it is seen that a uniform coating is obtained in all of the samples at the coating thicknesses. The difference between the lowest and highest thickness measured is 0.8 µm. With this situation, it was observed that the coating thicknesses were maintained in heat treatments performed at different ambient and heat treatment temperatures. A coating thickness of 15 to 15.8 µm was obtained on all samples. Taha-Tijerina et al. reported that 12 um coating thickness was obtained in 60 minutes [7]. Therefore, the 15 um coating thicknesses obtained were considered to be successful and compatible with the literature. It is understood that different temperatures applied in heat treatments do not cause any significant difference on the coating thickness of the samples.

3.2. XRD Phase Analysis

The graph created according to the values obtained from the XRD analysis of the electroless Ni-B coated 32CrMoV12-10 test specimens heating process at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere is given in Figure 3.

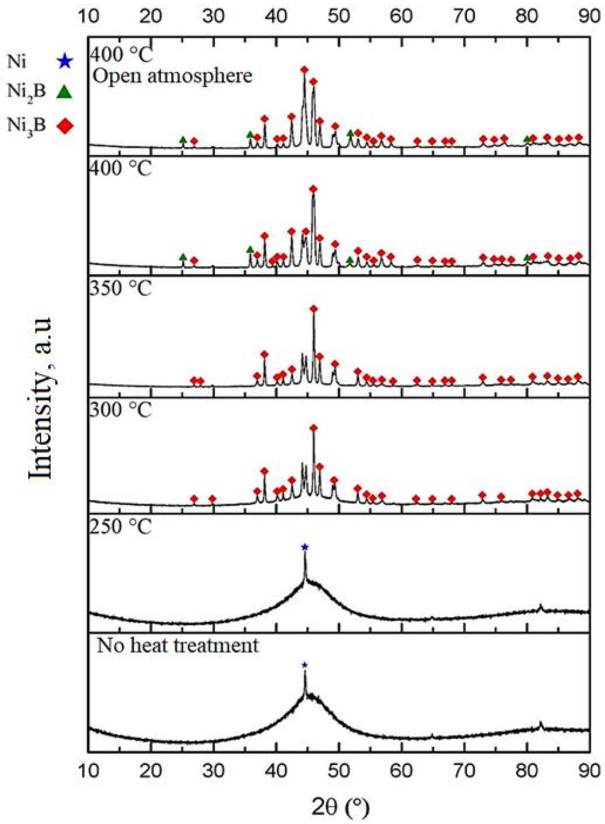

Figure 3. XRD diagram of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17].

When Figure 3 is examined; it is understood that in Ni-B coatings, the structure of the sample without heat treatment and the sample heating process at 250°C in argon atmosphere is amorphous and there is no crystalline order. At 300°C and above, the samples subjected to heat treatment show crystal structure formation. Ni3B phases developed throughout the sample heating procedure at 300°C and 350°C. Unlike the others, Ni2B peaks were observed at 25.1 2θ (°), 35.8 2θ (°), 51.8 2θ (°) and 80.0 2θ (°) in addition to Ni3B phases in samples heating process at 400°C in argon atmosphere and 400 °C in open atmosphere. In 2007, Anik et al. [21] reported in their XRD analysis of Ni-B coated 304 stainless steel materials that Ni2B phases did not form below 400°C and Ni2B and Ni3B phases formed above 400°C, and similar results were obtained in our current study. According to XRD phase analysis, it was observed that the structure of the coatings was generally affected by different heat treatment conditions.

3.3. Hardness Investigations

In hardness measurements, a weighted average of the values obtained after taking measurements from at least 5 different points for each sample was taken. Figure 4 shows an optical microscope image taken from a sample for which hardness measurements were made, and Figure 5 shows a graph based on the average values obtained from the hardness measurements.

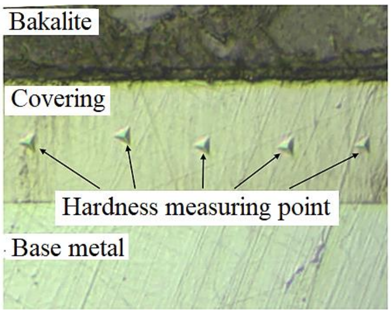

Figure 4. Hardness measurement points [17].

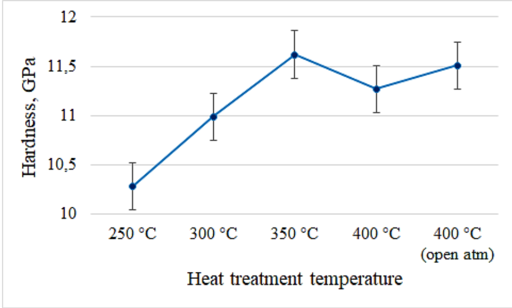

Figure 5. Hardness values of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere.

Examining Figure 5, it can be demonstrated that the sample heating method at 250°C in an argon environment yields the lowest hardness value. Because of the amorphous nature of this sample, the XRD examination shows that the lowest value in the hardness test findings was reached at 250°C in an argon environment. The creation of the Ni3B phase in the structure as a result of heat treatment at 300°C in an argon environment was found to improve the hardness value in comparison to other hardness values. According to Çelik et al., heat treatment causes the coating's amorphous structure to crystallize, and the resulting Ni2B and Ni3B phases raise the hardness values [22]. The sample heated to 350°C in an argon environment produced the greatest hardness value. Subsequently, a significant decrease was observed in the hardness values measured as a result of heat treatment at argon atmosphere 400°C and open atmosphere 400°C compared to the heat treatment conditions at argon atmosphere 350°C. This hardness reduction was more pronounced in the 400°C open atmosphere than in the heating process specimen. Pal et al. reported that in the hardness test on Ni-B coated samples on mild steel, the lowest hardness value was obtained in the amorphous sample, while the highest hardness value was obtained at 350°C. After 350°C, a downward graph was observed in the hardness value [23]. With this result, it was observed that similar results were found with the literature. In addition, the high hardness value at 400□C in the open atmosphere can be attributed to the presence of Fe_2O_3 (iron oxide) formed on the coating. Because Fe2O3 (iron oxide) formed on the coating surface in the open atmosphere has a hardness of approximately 70 HRC. However, the hardness value of the 35CrMoV12-10 alloy used in this study is an average of 300 HB. This value corresponds to 32 HRC. Therefore, it can be stated that one of the reasons for the difference between the hardness values is oxidation.

3.4. Wear Behavior

3.4.1. Determination of friction coefficient

Ball-on-disk wear tests of Ni-B coated specimens were performed using alumina balls. As a result, the time-dependent variation of the coefficient of friction was determined and the results are shown in Figure 6.

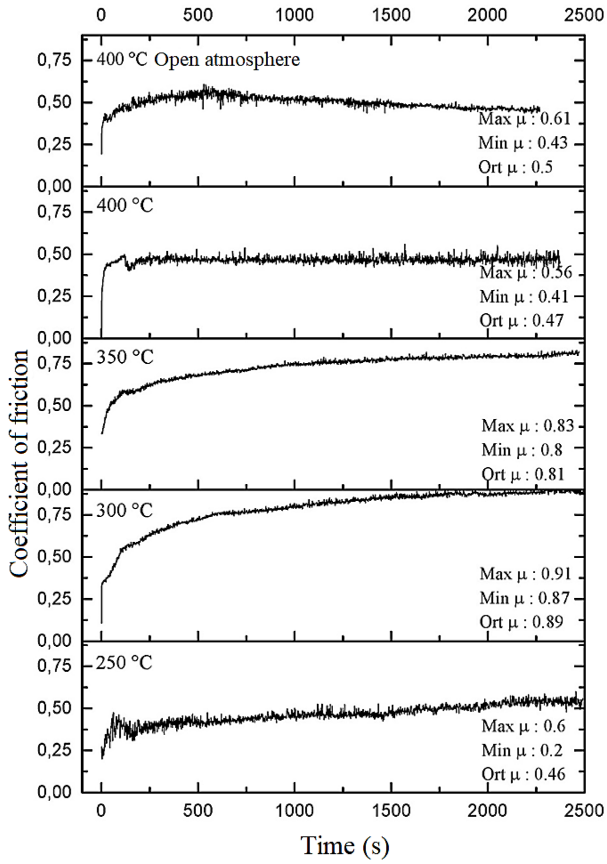

Figure 6. Change of friction coefficients of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17].

3.4.2. Analysis of wear surfaces and calculation of wear volume

Optical microscope images of the widths of the scars formed after wear are given in Figure 7. When the graph in Figure 6 is examined, it is seen that the lowest coefficient of friction value is 0.43 in the sample heating process in 400°C in argon atmosphere and the highest coefficient of friction value is 0.89 in the sample heating process in 300°C in argon atmosphere. Arias et al. reported that similar coefficient of friction values were obtained in NiB coated and heating process steel material at 400°C [24]. Looking at the widths of the wear track in Figure 7, it is understood that the lowest width is formed in the sample heating process at 350°C in argon atmosphere and the maximum width of the wear track is formed in the sample heating process at 400°C in open atmosphere. In this case, it is seen that the heat treatment temperature has an effect on the coating structure and changes the friction coefficient values and wear volume amounts in the wear tests. Zhao et al. emphasized that the best mechanical performance was obtained from the heating process sample at 350°C [25].

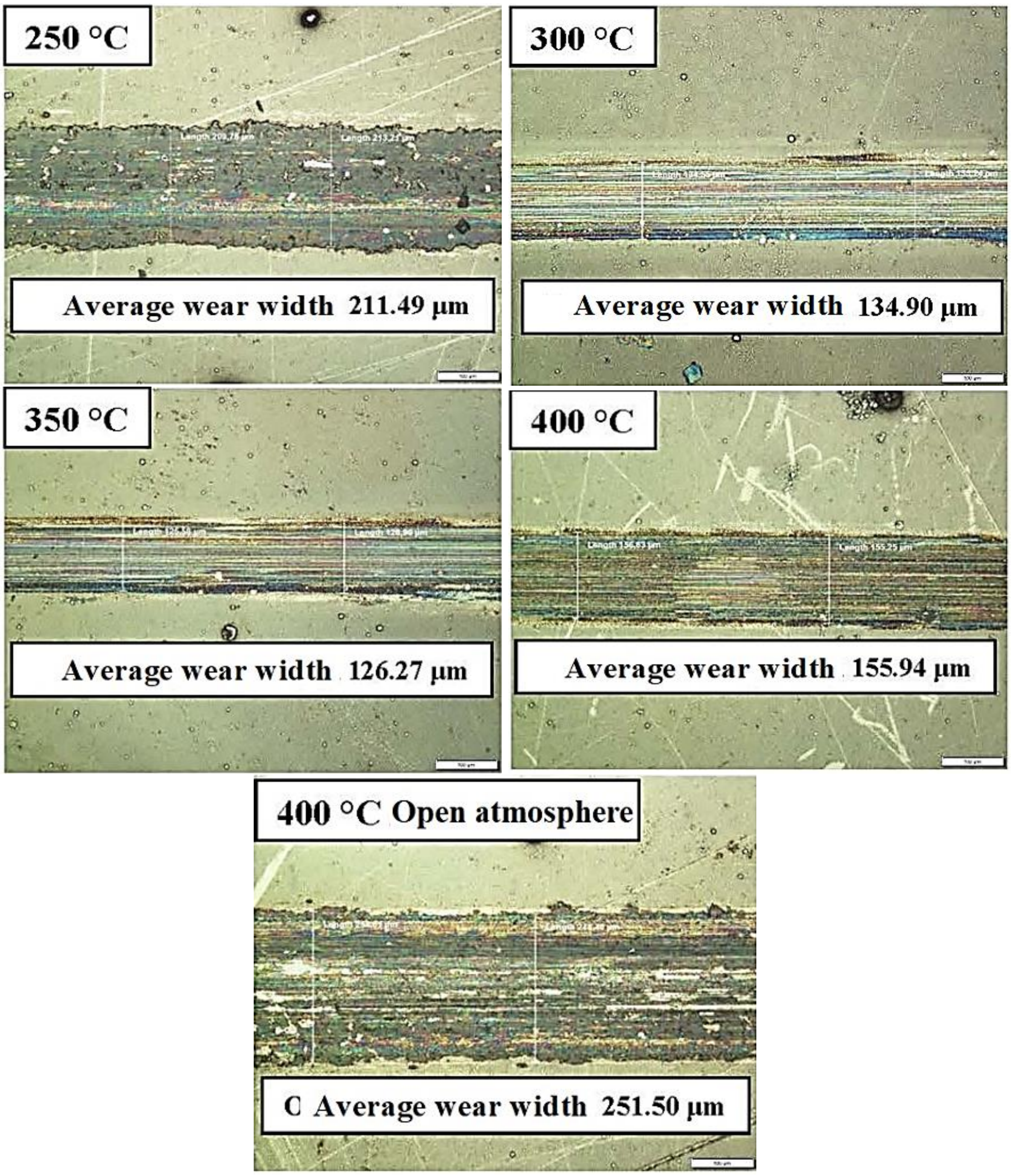

Figure 7. Wear widths of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17].

According to the measured wear widths, wear volumes were calculated using SolidWorks 3D design program. The values of the calculated wear volumes are shown in Table 2 and the graphs created according to these values are shown in Figure 8.

Table 2. Wear volume results of coatings [17].

Samples Wear	Volumes [mm^3]
250°C Argon Atmosphere	26.3×10^{-4}
300°C Argon Atmosphere	6.9×10^{-4}
350°C Argon Atmosphere	5.6×10^{-4}
400°C Argon Atmosphere	10.6×10^{-4}
400°C Open Atmosphere	44.3×10^{-4}

When the time-dependent change graphs of the friction coefficients given in Figure 6 and the images of the wear surface widths shown in Figure 7 are evaluated in more detail;

Although the coefficient of friction is low; when the wear widths are examined under the heat treatment condition at 250°C in argon atmosphere, it is seen that the coating is lifted from the surface and the coating is broken (Figure 7). It was evaluated that diffusion at the interface was not sufficient due to the amorphous structure and therefore adhesion was not good. As a result, it is seen that the wear volume is high with a high wear width.

When the wear widths are examined under the heat treatment conditions at 300°C and 350°C in argon atmosphere, it is seen that the adhesion improves without fractures with the increase in heat treatment temperature. It is clearly seen that the wear resistance has improved according to the test performed under the heat treatment condition at 250°C in argon atmosphere. This is due to the hard Ni3B phase formed on the surface. It was observed that the wear volume decreased between 36% and 40% with the formation of the Ni3B phase. When we look at the friction coefficient results, it is clearly seen that the friction curve is not smooth and shows significant fluctuations in the heat treatment condition at 300°C and 350°C in argon atmosphere. During the abrasion test, hard coating particles are accumulated due to the load. As a result of the compression of these particles between the surface of the abraded ball and the surface of the sample part, an increase in friction occurs. The reason for this fluctuation can be attributed to this phenomenon.

When the wear widths of the sample heating process at 400°C in argon atmosphere were examined, an increase of nearly 30 μm was observed in the wear width compared to the sample heating process at 350°C in argon atmosphere. However, there was an 89% increase in the wear volume values. The reason for this is interpreted as the material wears more due to the decrease in the hardness value of the material as a result of the formation of Ni2B particles in the argon atmosphere at 400°C temperature heat treatment condition. Looking at the friction coefficient result, it showed a very rapid increase at the beginning of the wear test and then remained stable throughout the test.

Considering the results of open atmosphere heat treatment at 400°C; Compared to the sample heating process at 400°C in argon atmosphere, there was a significant increase in wear width and wear volume and fractures occurred in the wear scar. It is thought that when heat treatment is carried out in an open atmosphere, the steel interface is oxidized as a result of oxygen coming to the surface, and the diffusion of nickel into the steel is prevented. Therefore, diffusion may be prevented, reducing adhesion. To understand the reason for this situation, the interface needs to be examined in more detail. A similar comment can be made for the friction coefficient results. An uneven friction curve and significant fluctuation are clearly visible.

Looking at the results of the open atmosphere 400°C heat treatment condition; compared to the sample heating process at 400°C in argon atmosphere, there was a significant increase in wear width and wear volume and fractures occurred in the wear track. When heat treatment is performed in an open atmosphere, it is thought that the steel interface is oxidized as a result of the oxygen coming to the surface, which prevents the diffusion of nickel into the steel. Therefore, diffusion may be prevented in between, reducing adhesion. For the cause of this situation, the interface needs to be examined in more detail. A similar interpretation can be made for the friction coefficient results. A non-uniform friction curve and significant fluctuation is clearly visible. Mukhopadhyay et al. evaluated the tribological behavior of heat-treated coatings at room temperature, 100°C, 300°C and 500°C. It was observed that wear resistance and COF were better in 300°C than in 100°C and 500°C. This was attributed to the synergistic effects of various phenomena occurring in 300°C, such as the formation of the tribo-oxidative layer, the mechanically mixed layer composed of compacted debris patches, phase transformation occurring during the wear process, wear mechanism and microstructure [25].

3.4.3. Surface roughness investigations

The graph created according to the values obtained from surface roughness measurements made at 16 different points on Ni-B coated surfaces is shown in Figure 9. When the graph in Figure 9 is examined, the differences in the roughness measurements made from the surface of the same sample are striking. According to these values, it can be said that the surface is not of the same thickness throughout the coating. Looking at the differences between the measurement values, it is understood that there are indentations or protrusions on the Ni-B coating surface.

In order to examine the surface morphology in more detail, a cross-sectional BSE microstructure image is shown in Figure 10. When looking at Figure 10, the rough structure on the coating surface can be seen very clearly. The average roughness values (Ra) determined by calculating the arithmetic mean of 16 surface roughness measurements made for each sample are given in the graph in Figure 11.

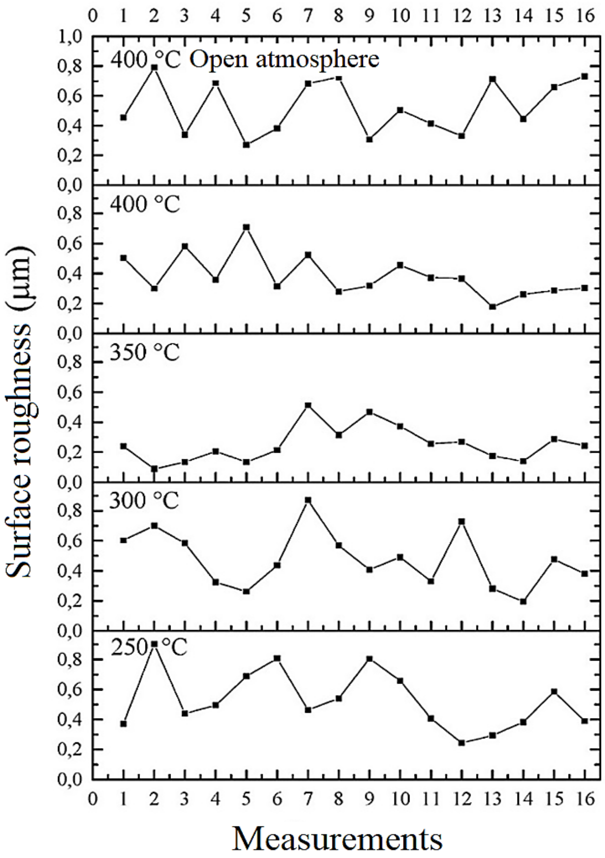

Figure 9. Roughness measurement values from 16 different regions of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17].

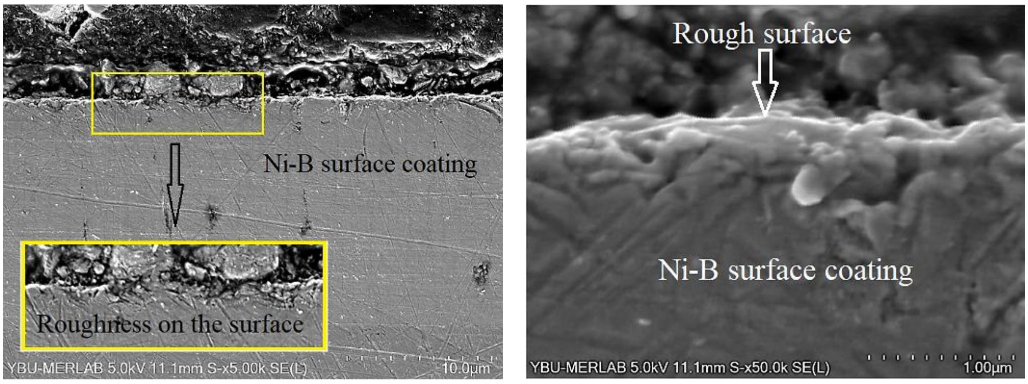

Figure 10. Ni-B coating cross sections at different magnifications [17, 18].

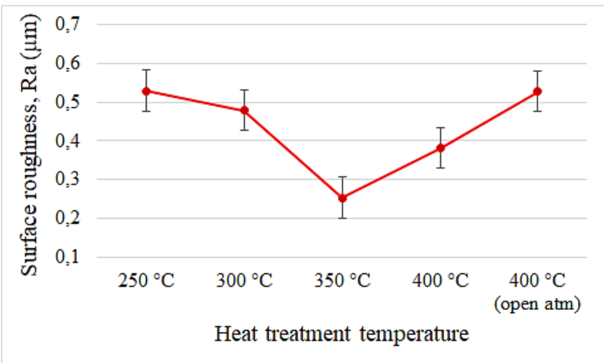

Figure 11. Average (Ra) roughness measurement values of Ni-B coated samples heat treated at 250°C, 300°C, 350°C, 400°C in argon atmosphere and 400°C in open atmosphere [17, 18].

When Figure 11 is examined, it is clearly seen that the heat treatment after coating has an effect on surface roughness. When the heat treatment was increased to the temperature conditions of 300°C in argon atmosphere, an improvement in surface roughness was observed. As in all the data obtained from previous examinations and supporting each other, the lowest roughness value of 0.253 microns was obtained from the sample heating process at 350°C in argon atmosphere. The highest roughness values occurred in the irregular and amorphous 250°C and 400°C samples treated in an open atmosphere. In order to support these evaluations with XRD analysis, the graph in Figure 12 is given.

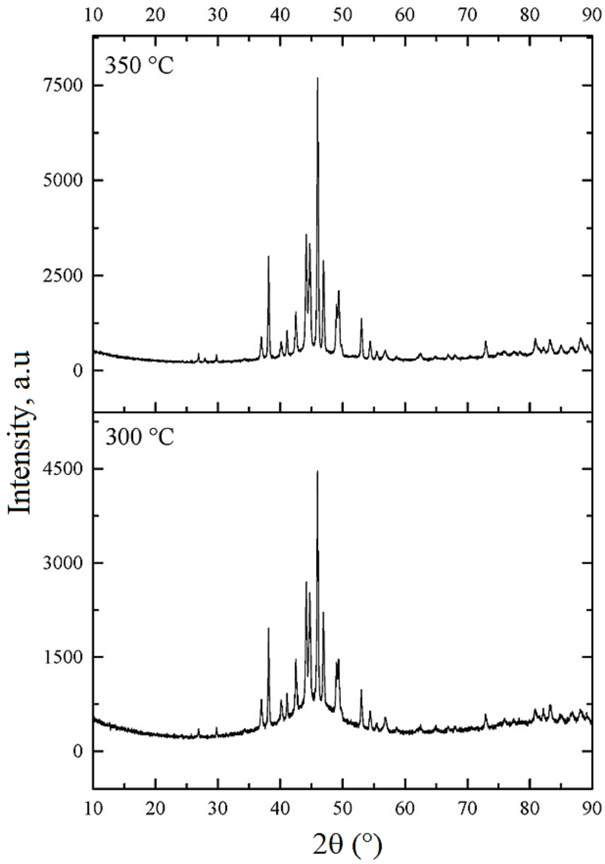

Figure 12. XRD analyzes of argon atmosphere 300°C and 350°C [17].

When the XRD patterns in Figure 12 are examined, it is seen that the peak intensities of the sample treated at 350°C in argon atmosphere are higher than the sample treated at 300°C in argon atmosphere. This indicates that the crystallinity in the Ni3B phase increases with increasing temperature. The increase in crystallinity caused a decrease in surface roughness. When the temperature is further increased, Ni2B phase also starts to form in the structure. It is thought that the Ni2B phase in the structure increases the surface roughness of the samples treated in argon atmosphere 400°C and open atmosphere 400 °C.

4. CONCLUSIONS

The results obtained from this experimental study, in which NiB was coated on 32CrMoV12-10 alloy, which is also used as barrel material, by electroless method and heat treatment was performed at different environments and temperatures, are summarized below:

- Cauliflower-like surface structure was formed on all coated samples. The cauliflower-shaped nodules formed on the surface of the samples heat-treated at 300°C, 350°C and 400°C in argon atmosphere were seen to be tighter. Samples heat-treated at 250°C argon atmosphere and 400°C open atmosphere showed a rough surface structure with more discrete and larger nodules.
- XRD analysis showed that the structure was amorphous due to the inadequacy of the heat treatment at 250°C argon atmosphere. Ni3B phases were formed in the samples heating process at 300°C and 350°C in argon atmosphere. In addition to Ni3B phases, Ni2B phases were also observed in the samples heating process at 400°C in argon atmosphere and 400°C in open atmosphere.

- As a result of hardness measurements, the highest hardness value occurred in the sample heating process at 350°C in argon atmosphere and the lowest hardness value occurred in the sample treated at 250°C with amorphous structure.
- In the abrasion tests, it was observed that the coating lifted from the surface and the coating was broken due to insufficient diffusion in the argon atmosphere under 250°C temperature conditions. Accordingly, the wear width and volume also increased. It was clearly seen that the wear resistance of the samples heating process at 300°C, 350°C and 400°C in argon atmosphere increased. It was concluded that this was due to the hard Ni3B particles formed on their surfaces. The wear resistance increased between 36% and 40% with the formation of the Ni3B phase. There was an increase in the wear width of the sample treated at 400°C in an argon atmosphere compared to the sample treated at 350°C. There was also a significant increase in the wear width and wear volume of the sample heat-treated at 400°C in an open atmosphere compared to the sample heat-treated at 400°C in an argon atmosphere. This was attributed to the oxidation of the steel interface due to the presence of oxygen on the surface, which prevented the diffusion of nickel into the steel. In surface roughness measurements, the surface roughness of the amorphous sample heating process at 250°C in argon atmosphere was higher than all other samples. The best surface roughness value was observed at 350°C in argon atmosphere.
- When all the data supporting each other are brought together, the best results of the findings obtained as a result of the analysis and test were obtained in the heat treatment experiment performed at 350°C in argon atmosphere. Instead of high temperature heat treatment after nickel-boron (Ni-B) plating on an industrial scale, the most suitable heat treatment temperature was determined to be 350°C in an argon atmosphere. It is thought that performing the process under these conditions will save energy costs.

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