ELEKTROLİTİK KAPLAMA İLE ÜRETİLEN Ni-B ALAŞIMLARINDA TMAB KONSANTRASYONUNUN SERTLİK ÜZERİNE ETKİSİ

EFFECT OF TMAB CONCENTRATION ON HARDNESS IN ELECTRODEPOSITED Ni-B ALLOYS

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Özet

Malzeme yüzeylerinin kaplanması endüstride çok yaygındır. Nikel bazlı alaşımlar genellikle krom kaplamaya alternatif olarak geliştirilmiş ve uygulanmıştır. Bunlardan Ni-B alaşımları krom kaplamaya benzer mekanik özelliklere sahiptir. Ni-B kaplamalar yüksek sertlik ve aşınma dirençleri nedeniyle çeşitli metal yüzeylere koruyucu olarak uygulanır. Ni-B alaşımlı kaplama otomotiv, havacılık ve savunma sanayiinde uygulanmaktadır. Elektrodepozisyon, basit, yüksek üretim oranı ve uygun maliyetli olduğu için tercih edilen kaplama yöntemidir. Ni-B alaşımlı kaplamalar, TMAB bor kaynağı kullanılarak geleneksel nikel kaplama banyosunda (Watt banyosu) elektrodepozisyon yöntemiyle üretildi. Kaplama banyosunda katot olarak çelik levha, anot olarak saf nikel plaka kullanıldı. Ni-B alaşımları için kaplama banyosunda $NiSO_4.6H_2O$ (240 g/L), $NiCl_2.6H_2O$ (45 g/L), H_3BO_3 (30 g/L) ve TMAB (1, 3 ve 5 g/L) kimyasalları kullanılmıştır. Banyo sıcaklığı (50^{o}C), pH (3,5) ve karıştırma hızı (450 rpm) parametreleri kaplama banyosunda optimizasyonu elde etmek için önceden belirlenmiştir. Elektrodepozit Ni-B alaşımlı kaplamaların sertlik özellikleri, kaplama banyosuna eklenen bor miktarını önemli ölçüde etkiledi. Kaplamadaki bor miktarı arttırılarak tane büyüklüğünde önemli değişiklikler gözlenmiştir. Buna göre, bor konsantrasyonundaki değişimin Ni-B alaşımlarının sertliği üzerinde bir etkisi olmuştur. Isıl işlemden önce ve sonra Ni-B kaplamaların kristal yapısındaki değişimin sertlik üzerindeki etkisi tartışıldı. Isıl işlem öncesi amorf yapıda olan Ni-B alaşımları 400 ^{o}C'de 1 saatlik ısıl işlemden sonra, tüm kaplamaların kristalliği artmış ve tane boyutları azalmıştır. Kaplama koşullarına bağlı olarak Ni-B alaşımlarının tercih edilen yönelimi kaplama banyosundaki TMAB içeriğinin artmasıyla (111) düzlem yönünde şiddetlenmektedir. Böylece, Ni-B kaplamaların sertliği artan TMAB konsantrasyonu ile oluşan Ni_3B çökeltilerinin kristal tane büyümesini engellemesiyle artmıştır. Kaplamadaki bor içeriğinin artmasıyla artan iç gerilimler ile alaşımlardaki en yüksek sertlik 750 HV olarak elde edildi. Kaplamaların yüzey morfolojisi taramalı elektron mikroskopisi (SEM) ile incelendi. Kristal tercih edilen yönelimleri belirlemek ve kristalin tane boyutunu hesaplamak için XRD analizleri yapıldı. Tüm kaplamaların Vickers sertliği Anton Paar NHT^3 cihazı kullanılarak ölçülmüş ve kaplamaların sertlikleri karşılaştırılmıştır.

Bu çalışmada Ni-B alaşımlarının kaplama koşullarını hazırladık ve bor değişiminin sertlik üzerine etkisini tartıştık.

Anahtar Kelimeler: Elektrolitik Kaplama, Ni-B Alaşım, Sertlik, Kristal Yapı, Isıl İşlem

Abstract

Coating of material surfaces is very common in the industry. Nickel-based alloys have generally been developed and applied as an alternative to chrome plating. Of these, Ni-B alloys have mechanical properties similar to chrome plating. Ni-B coatings are applied to various metal surfaces as protective because of their high hardness and abrasion resistance. Ni-B alloy coating applied in automotive, aerospace and defense industries. Electrodeposition is the preferred coating method because it is simple, high production rate and cost effective. Ni-B alloy coatings were produced by electrodeposition method in conventional nickel plating bath (Watts bath) using TMAB boron source. Steel plate was used as cathode and pure nickel plate was used as anode in the coating bath. For Ni-B alloys, $NiSO_4.6H_2O$ (240 g/L), $NiCl_2.6H_2O$ (45 g/L), H_3BO_3 (30 g/L) and TMAB (1, 3 ve 5 g/L) chemicals were used in the coating bath. Bath temperature (50^{o}C), pH (3.5) and stirring speed (450 rpm) parameters were predetermined to achieve optimization in the coating bath. The hardness properties of electrodeposited Ni-B alloy coatings significantly affected the amount of boron added to the coating bath. Significant changes in grain size were observed by increasing the amount of boron in the coating. Accordingly, the change in boron concentration had an effect on the hardness of Ni-B alloys. The effect of the change in the crystal structure of Ni-B coatings before and after heat treatment on hardness was discussed. Amorphous Ni-B alloys before heat treatment, after 1 hour of heat treatment at 400 ^{o}C, the crystallinity of all coatings increased and grain sizes decreased. Depending on the coating conditions, the preferred orientation of the Ni-B alloys intensifying in the plane direction (111) with increasing TMAB content in the coating bath. Thus, the hardness of the Ni-B coatings was increased by increasing the concentration of TMAB, resulting in the inhibition of crystal grain growth by Ni_3B precipitates. The highest hardness was obtained as 750 HV with increasing internal strain due to the B content in the coating. The surface morphology of the coatings was examined by scanning electron microscopy (SEM). XRD analyzes were performed to determine crystal preferred orientations and to calculate the grain size of the crystal. The Vickers hardness of all coatings was measured and compared using Anton Paa NHT^3 apparatus. In this study, we prepared the coating conditions of Ni-B alloys and discussed the effect of boron change on hardness.

Keywords: Electrodeposition, Ni-B alloy, Hardness, Crystalline structure, Heat treatment

1. Inroduction

Most industrial metallic components require operating conditions that require improved surface properties such as high hardness, wear and corrosion resistance. Surface engineering techniques continue to be used to produce coatings with improved surface properties. The application of protective coatings is an effective method for producing coatings with high hardness, abrasion and corrosion resistance (Mirak, 2018). Hard chrome coatings are widely used in aviation, automotive, mold, hydraulic applications due to their high hardness, high wear and corrosion resistance. However, electrolytic baths containing Cr^{6+} (hexavalent chromium) in hard chrome coatings are known to be toxic and carcinogenic. Therefore, chrome coatings were made using Cr^{3+} (trivalent chromium) baths (Bagchi, 2002). However, many attempts have been made recently to produce environmentally safe new coatings instead of hard chrome coatings as thick Cr coatings are not easy to accumulate successfully (Monteiro, 2015). It is aimed to replace hard chrome plating by making many double, triple and quaternary alloy coatings (Mulukutla, 2012). However, most of the coatings show experimental difficulty and low hardness (Capel, 2003). Among the dual alloy coatings, Ni-B coatings can be preferred due to their high hardness, wear and corrosion resistance (Ogihara, 2012). Experimental studies of electroless and electrodeposition of Ni-B coatings are carried out. Electrodeposition of Ni-B coatings have many advantages such as low cost, high production rate, control of chemical composition (Srinivasan, 2010). Electrolytically produced Ni-B coatings are made in different Sulfamate and Watts baths (Peeters, 2001). During electrodeposition, parameters such as current density, temperature, mixing speed and pH are controlled and Ni reduction rate is kept constant (Ogihara, 2012). The amount of B in Ni-B coatings has important effects on the structure and hardness of the coating. It is stated that Ni-B coatings that are not heat treated have an amorphous structure, but after the heat treatment, Ni_3B phases dispersed in the alloy matrix turn into a crystal structure and thus increase their hardness (Lee, 2005). The increase in coating hardness is related to the applied heat treatment temperature. Researchers consider 300 or 400°C as the proper annealing temperature for precipitation of Ni_3B phases (Ogihara, 2012). In this study, we prepared Ni-B films produced with different boron quantities and discussed their effects on crystal structures and film hardness.

2. Experimental

Electrodeposited Ni-B coatings were produced using a conventional Ni coating bath (Watt type bath). The chemicals used in the coating bath are shown in the Table 1.

Table 1. Chemical composition of the plating bath and the operating conditions

Chemicals/parameters	
$NiSO_4.6H_2O$	240 g/L
$NiCl_2.6H_2O$	45 g/L
H_3BO_3	30 g/L
TMAB	1, 3 and 5 g/L
Current density	0,6 A/dm^2
pH	3,5
Temperature	50°C
Stirring rate	450rpm

Substrates were prepared from steel plate by cutting 40 × 30 × 1.5 mm^3. A pure nickel plate (50 x 40 x 15 mm^3) was used as the anode placed parallel to the cathode. After the substrates were abraded using 400, 600, 800, 1200 and 2000 sandpaper, ultrasonic cleaning was done in acetone and ethanol baths for 10 minutes and washed with distilled water. Before electrodeposition, the substrates were activated in 30% HCl for 60 seconds, and then rinsed with distilled water. After coating, the samples were heat treated at 400°C for 1 hour. The heat treatment of Ni-B coatings was performed to investigate the effect of the intermetallic compound on hardness.

Structural changes of nanocrystalline coatings X-ray diffraction (XRD). The surface morphologies and cross-sectional images of the coatings were characterized by scanning electron microscopy (SEM). Vickers' micro hardness was obtained using a micro hardness tester under 50 g of indent load at five different locations of a sample.

3. Results and Discussion

XRD patterns of Ni-B coatings with different TMAB concentrations before heat treatment are shown in Figure 1. It is seen that the Ni-B coatings produced in different TMAB concentrations have peak expansion in diffraction models. It can be said that the degree of crystallinity of the coatings is low due to wide diffraction peaks. It is seen that with increasing boron content (111), the reflection intensity increases (200) and (220) reflections decreasing. The fact that the XRD peak in the orientation (111) is enlarged clarifies that the structure is nanocrystalline. Also, it appears that the Ni_3B or Ni_2B intermetallic phases are not formed or the volume fractions are too low to be detected by XRD.

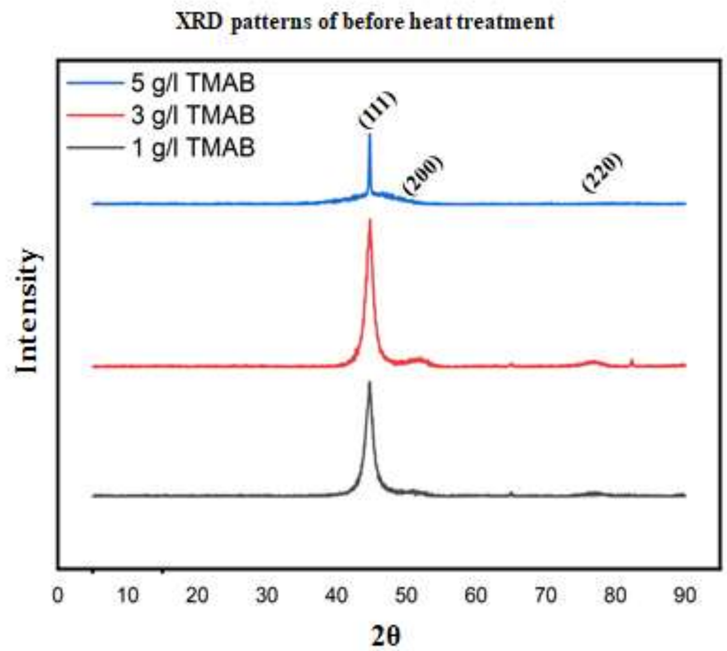

Figure 1. XRD patterns of the as-deposited coatings containing: 1 g/L, 3 g/L and 5 g/L boron.

XRD patterns of heat treated coatings that were subjected to isothermal annealing at 400°C for 1 hour are shown in Figure 2. The XRD pattern of annealed nickel coatings represents diffraction peaks with higher densities and narrower widths than as-deposited coatings. Concentrated diffraction peaks indicate a higher degree of crystallinity, since grain growth after annealing is limited for these coatings. After annealing at 400°C for 1 hour, the diffraction peaks of Ni_3B hard intermetallic phases are seen in coatings containing 3 g/L and 5 g/L boron. For samples that have been heat treated at 400°C, the Ni_3B phase is in the form of very fine precipitates dispersed throughout the coating microstructure. Also, it is seen that the orientation of (111) after heat treatment is the highest in the coating with a boron concentration of 3 g/L (Lee, 2005).

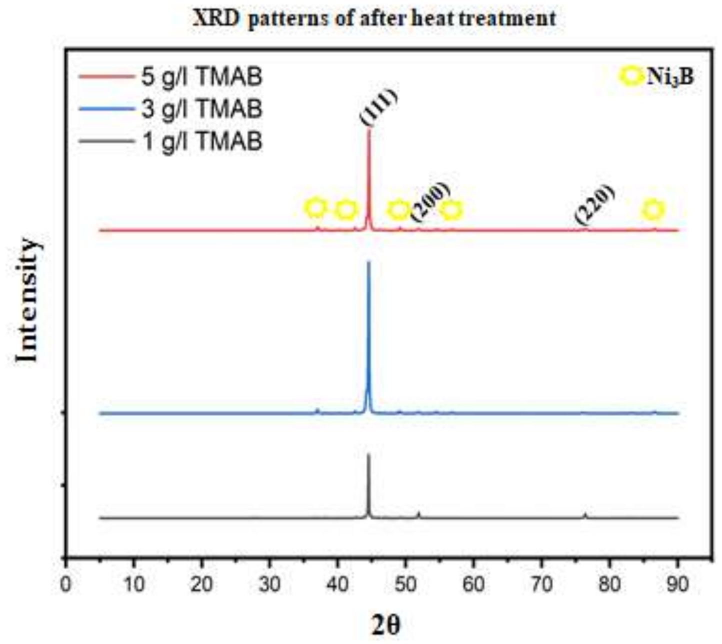

Figure 2. XRD patterns of heat treated coatings containing: 1 g/L, 3 g/L and 5 g/L boron.

Changes in the crystallite size as the different TMAB concentration of the heat treated coatings are shown in Figure 3. The lowest crystallite size of the precipitated coatings was calculated as 27 nm. The addition of boron atoms to the Ni coating results in a reduction in particle size. The reduction of grain size with the addition of boron can be explained by the fact that boron atoms support new nucleation areas by preventing grain growth. Ni_3B deposits formed at the grain boundaries of Ni-B coatings prevent growth mechanisms and strongly change the character of these boundaries (Hentschel, 2000).

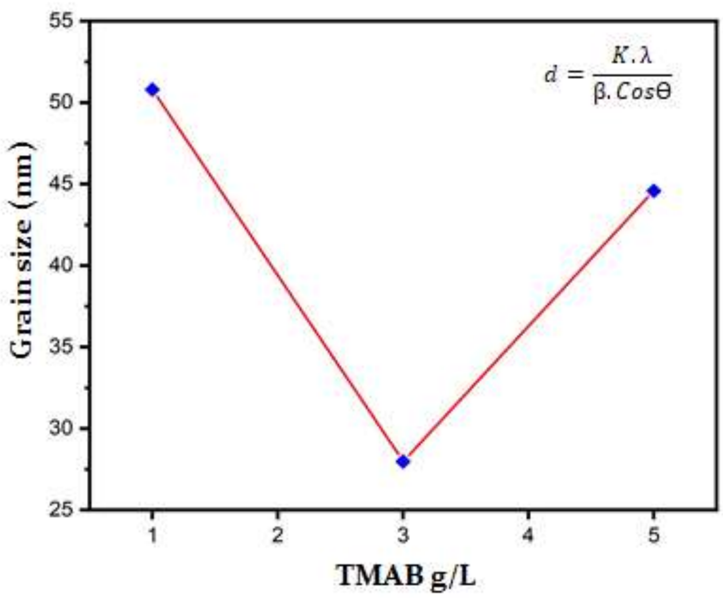

Figure 3. Changes in the crystalline size of heat treated coatings as a function of the amount of TMAB.

SEM images of the surface morphology of the precipitated coatings containing different amounts of B are shown in Figure 4. It is seen that all Ni-B coatings have cauliflower morphology. When the TMAB concentration in the coating bath is increased to 3 g/L, the Ni-B coating has a smooth and shiny surface morphology. When the amount of TMAB is more, the number density of spherical nodules increases.

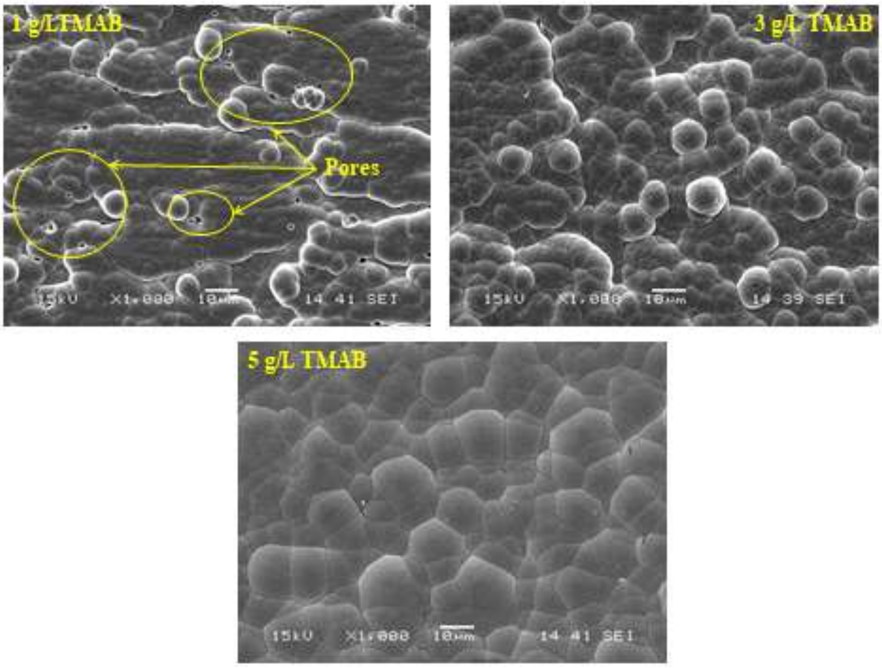

Figure 4. SEM micrographs of surface morphology of Ni-B coatings: 1 g/L, 3g/L and 5 g/L, respectively.

Cross-sectional SEM images of coatings are shown in Figure 5. The formation of island-shaped grains shows that the columnar structure was formed. Columnar growth is associated with directional surface morphology to minimize surface energy. The formation of columns in Ni-B coatings proceeds with the nucleation of grains and the placement of boron into grain boundaries (Vitry, 2012). In the coating produced with 1 g/L TMAB concentration, it is seen that the adhesion is weak due to the low energy of coating/substrate interface and thus cracks are formed. The coating produced with a concentration of 3 g/L TMAB appears to be intact and well adhered at the coating/substrate interface. It also exhibits a compact and defect-free microstructure, suggesting a suitable bond between them. Cracks appear on the coating surface produced at a higher concentration (5 g/L). It is caused by cracks in cauliflower structure and high internal tensions in pores.

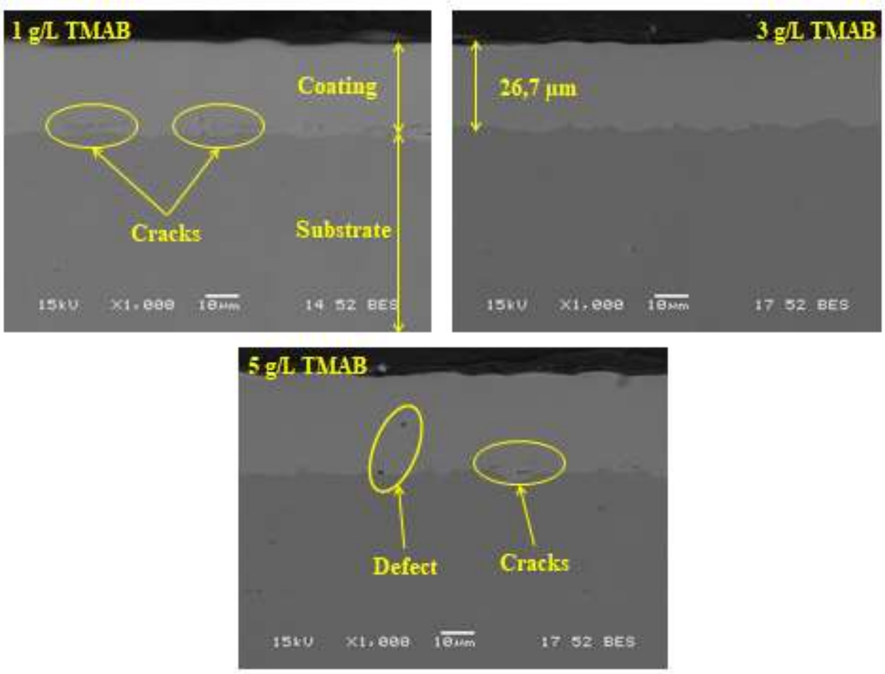

Figure 5. Cross-sectional SEM images of coatings.

The hardness of Ni-B coatings prepared in different TMAB concentrations before and after heat treatment is shown in Figure 6. The hardness of the coatings before heat treatment is lower than the coating hardness after heat treatment. Ni_3B formed in the structure after the heat treatment settles in the grain boundaries in the matrix, preventing the growth of the grains, thus increasing the coating hardness. Initially, low coating hardness can be explained by high internal stress. The hardness of the Ni-B coating produced with a concentration of 3 g/L TMAB has reached the maximum value (750 HV) due to the formation of intermetallic Ni_3B deposits by heat treatment (Lee, 2005).

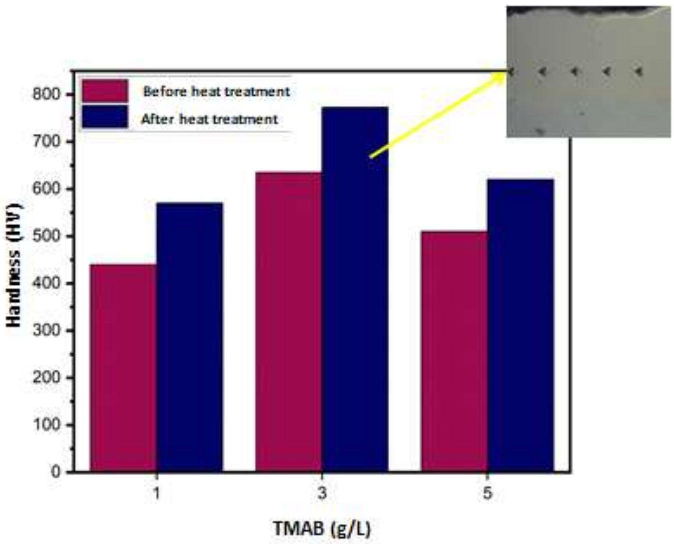

Figure 6. Hardness change of Ni-B coatings as a function of pre-heat and post-heat treatment temperature.

Elastic modulus (E) of the coatings was measured using the nano-indent technique. Figure 7 shows the load displacement curve for different TMAB concentrations. The coating produced with the amount of 3 g/L TMAB has higher hardness due to the lower indentation depth compared to the others. Thus, it confirms that the coating has high surface strength (hardness and elastic modulus).

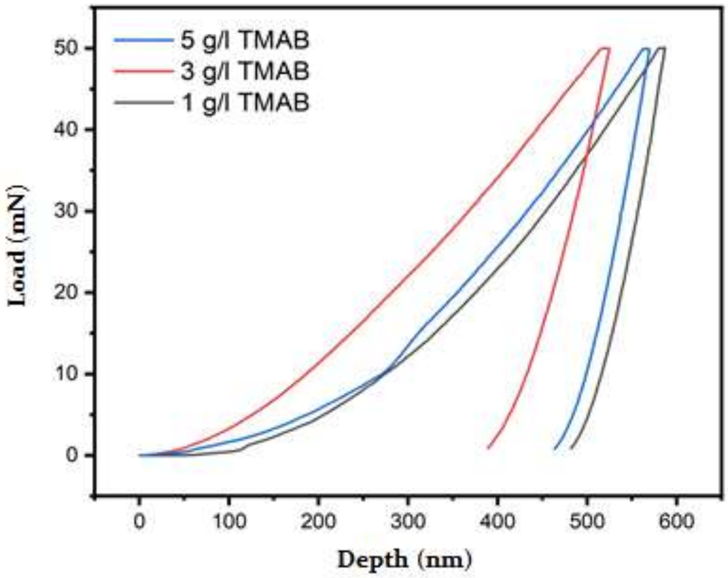

Figure 7. Load-depth curves for 1 g/L, 3 g/L and 5 g/L.

4. Conclusions

In this study, an alternative application to chrome plating was attempted. The properties of electrodeposited Ni-B coatings (crystalline structure, morphology and hardness) are significantly influenced by the concentration of boron sources in the coating bath. For Ni-B coatings, the coating hardness increased linearly with the boron content up to a concentration of 3 g/L TMAB. Coating hardness decreased as the amount of TMAB increased more. Crystalline Ni-B coatings tend to show higher hardness than amorphous structure. With the Ni_3B precipitation between metals by heat treatment, the hardness of Ni-B coatings has increased significantly. Although the amount of Ni-B alloy (Ni_3B) is too small to be detected by XRD pattern measurements, it increases the coating hardness of the alloy. The highest hardness value was measured as 750 HV. When the TMAB concentration in the coating bath was increased to 3 g/L, 27 nm diameter grains were calculated. It can be made by adding ceramic particles into the matrix to further improve the hardness properties of the coating.

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