INVESTIGATION OF THE ELECTROLYTE EFFECT ON VN CREATED VIA PES

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Abstract

One of the most important methods of hardening steel tools is nitriding. During this process, nitrogen diffuses into the sample surface at high temperature and reacts with the elements existing in the sample and creates hard nitrides. Another way to create hard nitrides is the simultaneous hard diffusion of two nitride-causing elements. During the plasma electrolytic saturation process, one nitride –causing element, together with nitrogen, diffuses into the surface of the sample and forms a hard nitride coating on the surface of the component. In this process, a voltage is applied between a cathode (sample with smaller surface) and an anode (sample with larger surface); the plasma is formed on the surface of the cathode which then let the given elements diffuse into the surface of the base metal. In the present study, nitrogen and vanadium have diffused into the surface of the sample, 1.2436 tool steel, and vanadium nitride has been formed. The best combination of electrolyte solution is 4g Ferro vanadium, 50±1 ml nitric acid and sodium hydroxide. The results is indicating that the formed coating layer thickness is about 2-3.5 μm. As the conductivity increases, the condition for diffusion is provided; however, with over increasing the temperature, diffusion decreases. The coating formation has observed in 7-10±0.5 A current.

Keywords: wear, Vanadium nitride, Steel 1.2436, Plasma electrolytic saturation

1 Introduction

Advances in technology and the current intense industrial competitions have forced materials and metallurgical engineers to seek and use cost efficient with maximum efficiency methods. Thus, the significant attention is drawn to the surface metallurgy methods. The surface metallurgy is a suitable method to produce engineering material with hard surface and though matrix. In the modern surface engineering, the method which can enrich requirements as fast and cheap as possible is regarded as a better one.

Hard coating is usually used in some working that surface resistant resistance wear should be very high. Vanadium nitride (VN) is one of these hard coats which is using in such cases as molds using in metallurgical processes e.g. casting, forging, extrusion etc. The main old way of VN coating was “molten salt bath method” based on setting whole a sample in a salt bath of ferro vanadium with 900 Celsius degree for 6-10 hours. This means a lot of wasted time and energy in industrial scale; besides thermal stress will be very high in the sample bulk. In the new method of VN coating called “plasma electrolysis method”, only the surface of samples are in touch with high temperature of 900 Celsius degree and also, whole of this process taking just 15 minutes. Hence, the obvious fact is using this method can present better performance and efficiency to the

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industrial nuggets. Moreover, in the molten salt bath method, ferro vanadium used as the source of vanadium is pure and in shape of ferro and oxide. Something that can be a cancer-causing and dangerous point for the living environment. The plasma electrolysis method is based on getting essential vanadium from its solution in HNO3 and is easier to manage its negative effects. Therefore, although this process includes vanadium, it can be considered as an environmentally friendly method in comparison with other ones.

Coating by plasma has been used since 19th century [1]. Nowadays, a new technique using plasma called the plasma electrolysis has been emerged [2-3]. Plasma electrolysis process is nearly the same as conventional electrolysis process [4] but much higher voltages was applied in later one [2]. Strong electric field is generated near the electrode which can form electric discharge in gas packet. Deposition in plasma electrolysis processes was classified into two main categories by Yerokhin et al. [2] in their review paper:

1. Oxidation method with the use of the Plasma Electrolyte Oxidation (PEO): in (PEO), the work piece plays the role of anode and is often used for creating the carbide coatings [1-8].
2. Deposition techniques using plasma electrolytic saturation (PES) include plasma electrolyte carburizing (PEC) [6,13], plasma electrolyte nitriding (PEN) [7], plasma electrolyte carbonitriding (PEC/N) [8], plasma electrolyte boriding (PEB) [9,11] plasma electrolyte vanadizing (PEV). Vanadizing is a thermo-chemical process in which vanadium free radicals diffuse into base metals at sub-critical temperatures. In a typical PEV process, an electrolyte containing vanadium-rich and materials such as Ferro-vanadium is used.

Different power sources were used such as (a) DC sources, (b) Unbalanced AC sources, (c) Pulsed DC sources and (d) Bipolar pulsed sources [1]. DC sources are usually used in the PES method. The effective parameters in this study are the conductivity of solution, coating time and coating current [10-17].

The purpose of this study is forming vanadium nitride coating. The use of Ferro vanadium and nitric acid in plasma electrolysis leads to diffusion of vanadium and nitrogen into the steel surface. Moreover, the effects of parameters such as electrolyte conductivity, time and current on the final coated steel properties are investigated.

2 Experimental materials and methods

The experimental sample in this study is steel 1.2436. The quantum analysis has been presented in **Table 1**.

Table 1 Chemical combination of steel used in the present study

Elements	%C	%Si	%Mn	%Cr	%Mo	%Fe
Atomic percent	2	0.2	0.3	11	0.75	Balance

The steel samples with 20mm diameter and 5mm height in the required quantity were cut with a cutter and then the samples were polished by the sandpapers of 80 and 400.

The elements of the electrolyte solution should contain the vanadium element and should be ionized to a positive ion of vanadium with the effect of the plasma process. The electrolyte consisted of 4±0.1g ferro vanadium (which contains 20% iron), 50±1ml nitric acid, different amounts of sodium hydroxide (NaOH) and water which was added to reach 2litters solution.

The voltage of about 150 volts, current of 7 A and coating time is 900 s (only one sample was treated in 180s) were applied for creating plasma and anode is stainless steel.

For the temperature measurement at the back of the samples, a hole has been made up to 300 μm near the surface and the thermocouple has been placed inside. For preventing the effect of the current applied to the sample during temperature measurement, thermocouple has been isolated by a ceramic pipe from the surface of the metal. **Fig. 1** shows the device and the sample being tested in this study [18].

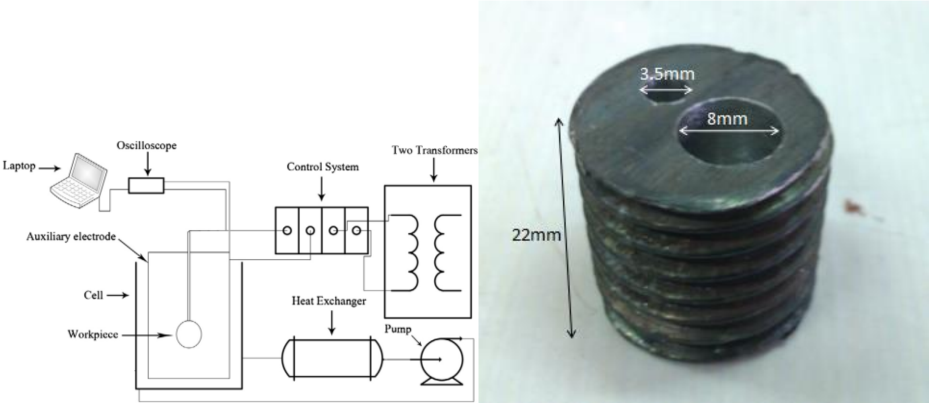


Fig. 1 The device and the sample being tested in this study

After performing the test and after metallography for the microscopic checks, the cross-sectioned sample was etched into picral solution (5ml picric acid and 95 ml ethanol). For determining the created phase XRD test, and for observing the topography of the surface and chemical map, the Scanning Electron Microscope (SEM) test has been used.

3 Results and discussion

Table 2 presents the effect of conductivity rate on the breakdown voltage as well as the temperature of the piece surface. As can be seen in the table, by increasing the amount of NaOH, electrical conductivity of the electrolyte goes up. On the other hand, the breakdown voltage decreases by rising electrical conductivity of the electrolyte. It should be noted that the diffusion coatings are formed at high temperatures. At high temperatures, due to increasing vacancies, the appropriate condition is prepared for diffusion. **Table 2** shows that in a conductivity of 34 ±3 and 45±3 mS, the temperature increases and diffusion coatings are formed; however, in conductivities higher than 65±3 mS, the temperature dose not rise further and non-diffusion coatings with low adhesion are formed. In 65±3 mS voltage, the sample was destroyed due to extensive temperature increase. In other words, as the conductivity enhances, first the temperature goes up and then it swiftly goes down.

XRD analysis was done to detect formed chemical composition. **Fig. 2** shows the X-ray diffraction pattern for a sample that is kept for 180s in 900°C. The first peak belongs to iron which exists in base metal. As mentioned in experimental method, the base metal was free of vanadium but the second peak confirmed vanadium existence that shows it diffuses to surface through PES. Owing to temperature increase to 900°C, thermodynamic condition was created to form vanadium nitride. Since base metal has 12% chrome and 2% carbon, rising in temperature resulted in appearing the chromium carbide peak along with the peak of iron and vanadium nitride in the diffraction pattern. Roughness of surface and non uniformity of coating are the main reasons for appearing many undesirable peaks in diffraction pattern that are the characteristic of plasma electrolysis.

Table 2 Effect of changes in NaOH coating formation on solution conductivity and discharge voltage

COATING TYPE	SURFACE TEMPERATURE (^{O}C)	BREAKDOWN VOLTAGE±3 (FINAL VOLTAGE±5)	NAOH RATE G PER 2LITER SOLUTION (CONDUCTIVITY MS±3)
Diffusion coating	870	(150) 90	**(34) 50**
Diffusion coating	900	(150) 79	**(45) 100**
-	Sample destruction	(150) 65	**(65) 150**
Non- Diffusion coating	150	(150) 52	**(85) 200**
Non- Diffusion coating	120	(150) 43	**(115) 250**

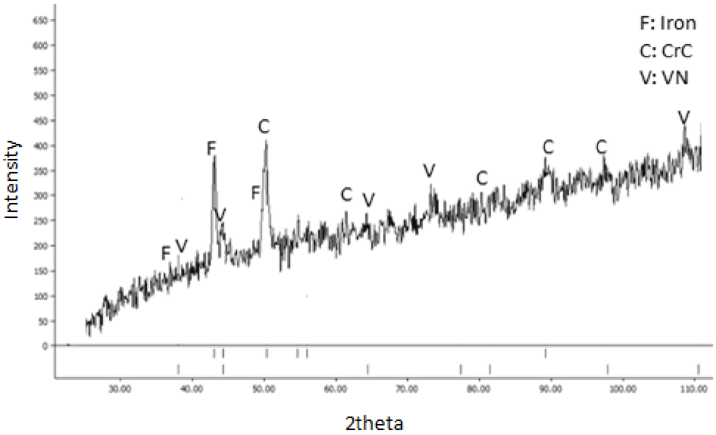
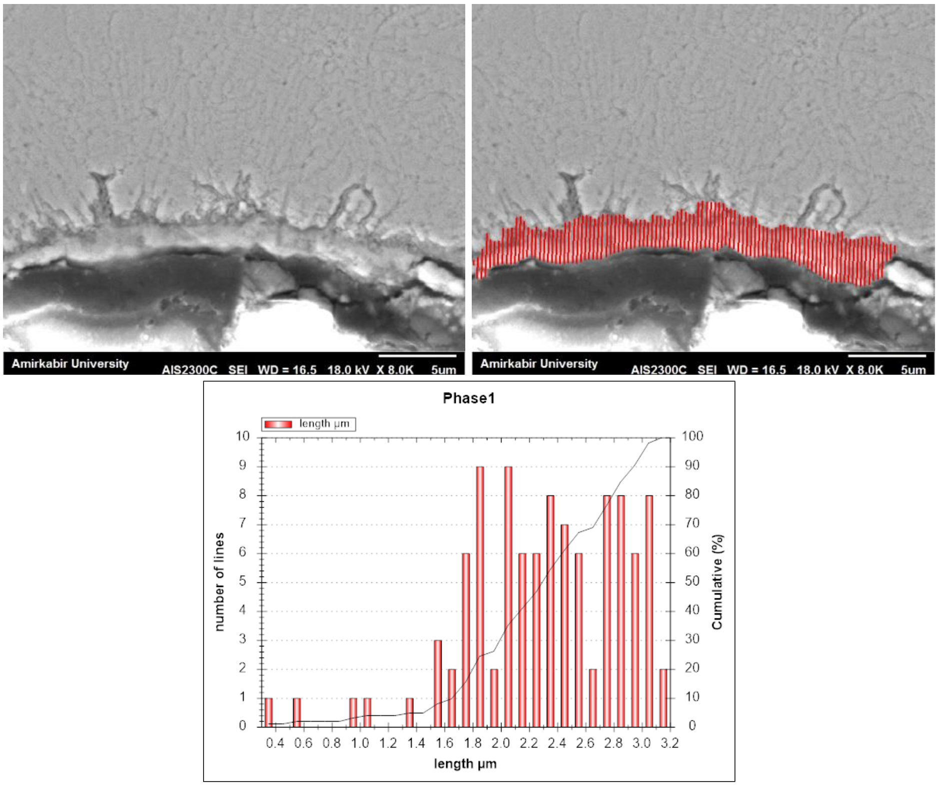


Fig. 2 Exemplary XRD pattern of the sample (Ta-ANO-0.5-400 sample) that was coated at 150 V in a NaOH solution of 100g in solution and coating time is 180s.

The electron microscope image of the coating is shown in **Fig. 3** The sample is kept for 3 min in 900±10 ºC. As it is seen in the **Fig. 3**, the maximum thickness of the formed coating is 3.18±0.01 µm and the minimum thickness is 0.33±0.01 µm. Thus, the average thickness is about 2-2.5±0.01 µm. The reason for this thin thickness is the short period of coating time. Also, simultaneous diffusion of nitrogen and vanadium to the steel surface is another reason. Considering **Fig. 3**, the direction of the diffusion of the two elements in the base metal is clearly seen. The difference between maximum and minimum thickness is due to non uniformity of coating. **Fig.4** is the schematic view of PES method that justifies Roughness of surface and non uniformity of coating.



Count	Min	Max	Average	Std
103	0.33	3.18	2.31	0.55

Fig. 3 Scanning Electron Microscope picture of the formed diffusion coating in coating time of 3 minutes

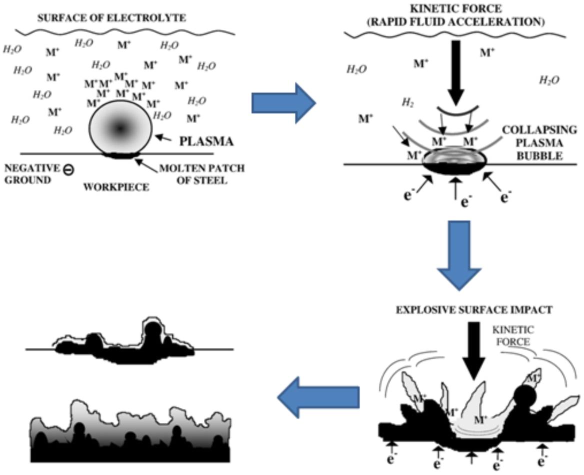


Fig. 4 Schematic view of PES method [2]

The interface coating and the base metal chemical map of nitrogen and vanadium elements have been presented in **Fig. 5** and **Fig. 6** respectively. In order to detect the situation of vanadium nitride coating and distribution of vanadium and nitrogen on surface backscattered electron micrograph was done. As **Fig. 5** and **Fig. 6** show, the aggregation of vanadium and nitrogen is high and reduces as approaching to the base metal. In distance above 3 μm the concentration of vanadium and nitrogen sharply decrease to about zero. Indeed, **Fig. 5** displays the created coatings on the surface including nitrogen and vanadium. In fact, it is another indication on the formation of vanadium nitride coating on the surface of the steel sample.

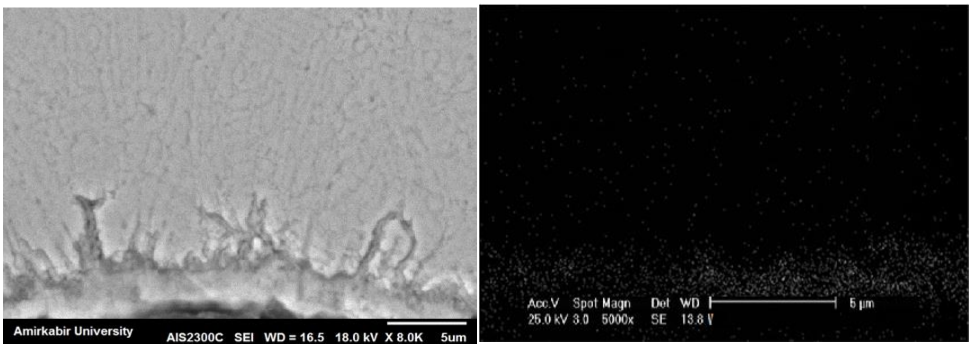


Fig. 5 The resulted chemical map from Scanning Electron Microscope for Vanadium element

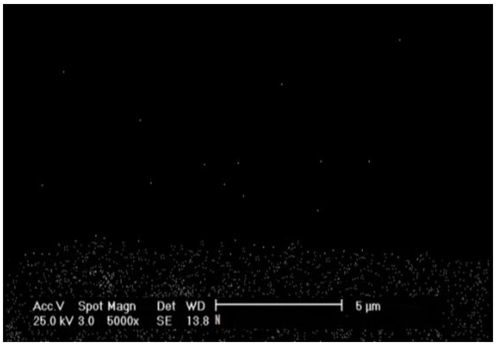


Fig. 6 The resulted chemical map from Scanning Electron Microscope for Vanadium element

Fig. 7 shows the X-ray diffraction pattern for a sample that is kept for 900s in 900±10°C. As shown in **Fig. 6**, in addition to iron and vanadium nitride, iron oxide layer exists in the surface specimen. Because of high thickness of iron oxide, chromium carbide peak was not appeared.

The reason for creating iron oxide is:

Oxygen exists in gas packet which is formed around the surface of specimen. Gas is generated as the following reaction [16]:

$$H_2O=H^o+OH^o$$
$$H^o+H^o=H_2$$
$$OH^o+OH^o=H_2O+1/2O_2$$

According to this process, due to the creation of a layer of gas, the vanadium and oxygen atoms ionize and diffuse into the surface of the component. Since the magnetic field is high, the gaseous layer also reacts with the iron. Consequently, iron oxide (Fe_2O_3) is formed when temperature is higher than 400±10°C. **Fig. 8** represents the sample which is kept for 15 min in 900ºC. As it is seen, the maximum thickness of the formed coating is 5.36 µm whereas minimum thickness is 0.04 µm. Thus, the average thickness is about 3-3.5±0.01 µm. considering **Fig. 3** and **Fig. 8** The difference between maximum and minimum thickness rises by passing time.

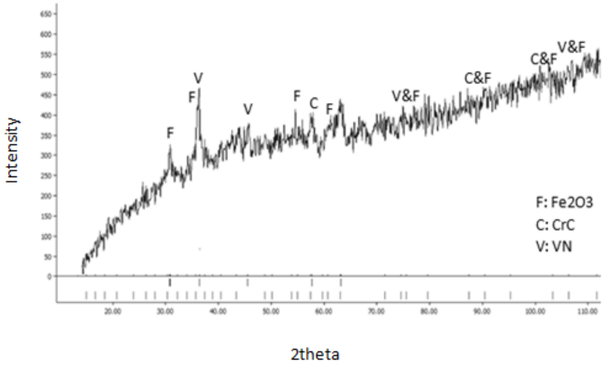
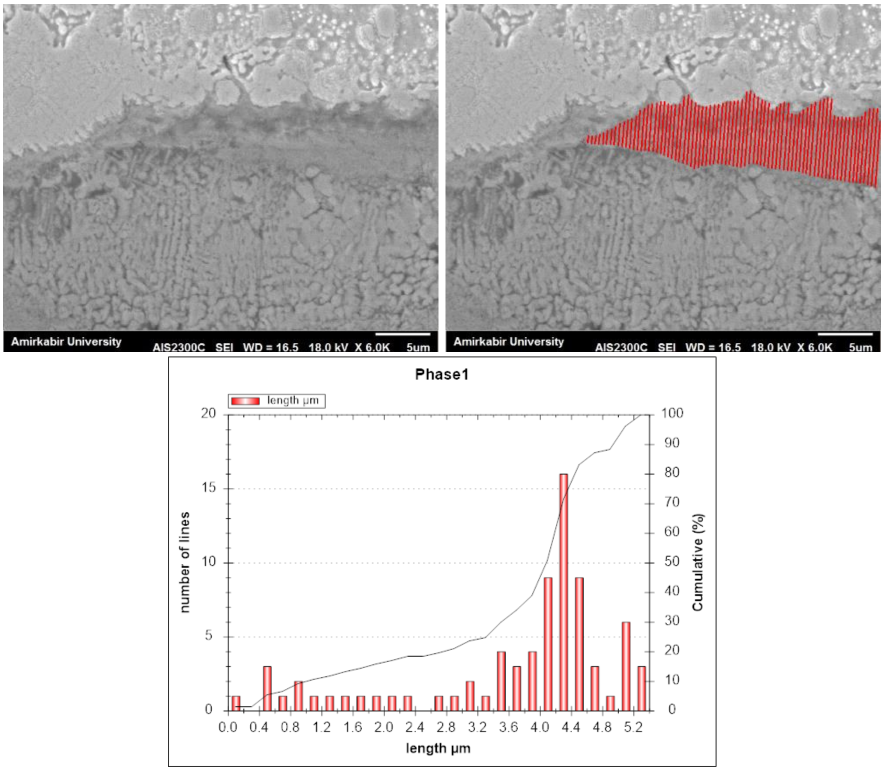


Fig. 7 X-ray diffraction pattern of the formed diffusion coating in coating time of 15 minutes



Count	Min	Max	Average	Std
77	0.04	5.36	3.68	1.34

Fig. 8 Scanning electron microscope image of the formed diffusion coating in coating time of 15 minutes at 5 µm scale

As previously mentioned, at high temperatures, conductivity does not increase and no diffusion occurs. In fact, a non-diffusion coating with low adhesion is formed instead of a diffusion coating. Images taken by the scanning electron microscope of these samples show that on the surface of these samples, cauliflower particles are formed. **Fig. 9** reveals that the average distance between these particles is about 4-8±0.01 μm. Also, the chemical map of vanadium in non-diffusion coating can be seen in **Fig. 10** This figure shows that vanadium does exist in coating, but it could not diffuse because of low temperature.

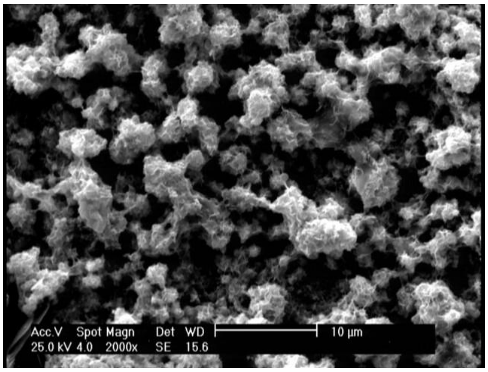


Fig. 9 Scanning Electron Microscope image from the surface of the formed non- diffusion coating at the scale of 10 μm

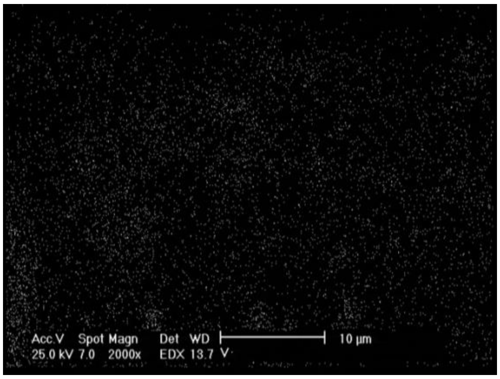


Fig. 10 Scanning Electron Microscope image from the surface of the formed non- diffusion coating at the scale of 10 μm

According to Ohm's law, with increasing current, voltage goes up. This trend will continue until bobbles appear on the cathode surface and elements in solution are ionized. This phenomenon is created in the highest current. Finally, due to plasma discharge the current decrease sharply and the condition gets ability for diffusion and coating formation. After that, rising in voltage, which is followed by increasing current leads to elevating the temperature of sample to 900±10 ^{o}C.

In this section, voltage and current of bobble formation, discharging plasma and coating formation will be estimated by voltage-current diagram. These data have been extracted from the oscilloscope.

Fig. 11 is the current diagram according to the voltage of specimen no. 2 in which no coating has been formed as a result of the application of the voltage. As voltage increases, the current rises and this trend continues to about 5±0.5 A at 100volts and bobbles were appeared. Then, current dramatically drops and this reduction goes on to about 2.1 A and discharge happened as well. But, because of low current of bobble forming, the created coatinsssg is diffusion coating.

The voltage-current diagram of specimen no. 3 is presented in **Fig. 12**. There is a rise in current as the voltage goes up. This trend continues until about 7±0.5A and 70±3 Volts. Where the voltage-current diagram reaches to 120±5volts, the current has almost remained constant. The current has almost stayed constant while the voltage reaches to 120±5 volts and bobbles were appeared. After that, the current sharply falls to about 2.2 A. In this section temperature increases steeply and sample was destructed.

Fig. 13 is the current diagram according to the voltage of specimen no. 4 in which coating has been formed as a consequence of the application of voltage. As the diagram reveals, with the increase of voltage, the current experiences a rise to about 9±0.5 A while voltage meets 50 volts.

Voltage goes up to about 120±5 volts and bobble was formed. Then, the current and voltage goes down steeply to about 0.9 A at 150±5 volts, which is followed by a slight increase in the current. Since the final discharge current reduces from 2 to 1 and turbulent current was created in electrolyte, the resulted coating is non diffusion.

From the **Table. 2** it can be concluded that the coating is created when formed bobbles current is between 5-7±0.5 A and final current is about 2A. In other condition coating is non diffusion.

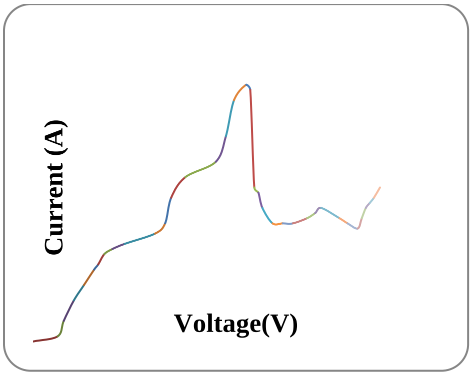


Fig. 11 Current – voltage diagram of specimen no. 2 (100g NaOH)

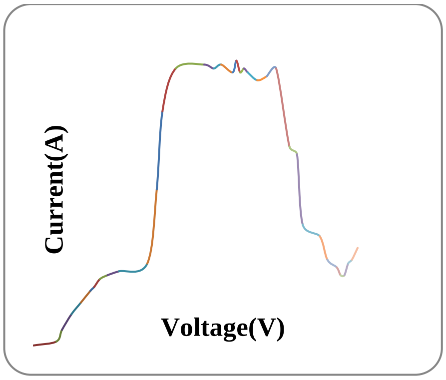


Fig. 12 Current – voltage diagram of A)specimen no. 3 (150g NaOH)

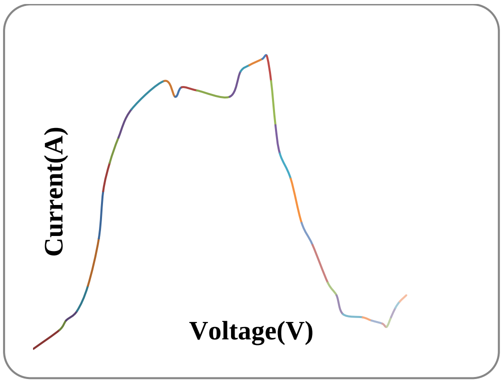


Fig. 13 Current – voltage diagram of A)specimen no. 4 (200g NaOH)

Table 3 Condition of current and voltage for forming coating.

SAMPLE	WEIGHT OF NAOH(G)	BOBBLES VOLTAGE (V)±5	BOBBLES CURRENT (A)±0.5	FINAL CURRENT (A)
No. 2	100	100	5	2.1
No. 3	150	120	7	2.2
No. 4	200	120	9	0.9

Conclusions

1) The thickness values of vanadium nitride layers vary from 2±0.05 to 3.5±0.05µm under different concentration of sodium hydroxide. With increasing the sodium hydroxide

concentration, solution conductivity increases continuously. The coatings are formed in the range of 34-45 ms. When the concentration of sodium hydroxide reached up to 100 g in solution, surface temperature is decreased sharply and the coating is non diffusion. When the coating time is 180s the thickness is about 2.3±0.05μm. As the coating time goes up, the thickness increases until reaches to 3.8±0.05 μm in 900s.

2) The chemical map of cross-section shows that the layer has vanadium and nitrogen. In high temperature coating, iron oxide was created on vanadium nitride layer. The reason for this phenomenon is the existence of oxygen and high temperature.
3) Roughness of surface and non uniformity of coating are the characteristics of plasma electrolysis that causes appearing many undesirable peaks in disffraction pattern. The coating is created when forming bobbles current is between 5-7±0.5 A and final current is about 2A. In other condition coating is non diffusion.

References

[1] H. Tavakoli, S. M. Mousavi Khoie, S. P. H. Marashi, S. A. Hosseini Mogadam: Journal of Alloys and Compounds, Vol. 583, 2014, p. 382–389, doi:10.1016/j.jallcom.2013.08.068

[2] A. L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S. J. Dowey: Plasma electrolytic in engineering, Surf. Coat. Technol, Vol. 122, 1999, p. 73–93, doi:10.1016/S0257-8972(99)00441-7

[3] P. C. Rath, L. Besra, B. P. Singh, S. Bhattacharjee: Ceramics International, Vol. 38, 2012, p. 3209–3216, doi:10.1016/j.ceramint.2011.12.026

[4] D. J. Blackwood, K. H. W. Seah: Materials Science and Engineering C, Vol. 29, 2009, p. 1233–1238, doi:10.1016/j.msec.2008.10.015

[5] W. Simka, M. Kaczmarek, A. Baron-Wieche´c, G. Nawrat, J. Marciniak, J. Zak: Electrochimical Acta, Vol. 55, 2010, p. 2437–2441, doi:10.1016/j.electacta.2009.11.097

[6] C.S. Lin, M.T. Chen, J.H. Liu: Journal of Biomedical Materials Research Part A, Vol. 85A, 2008, p. 378-387, doi: 10.1002/jbm.a.31510

[7] H.J. Song, S.H. Park, S.H. Jeong, Y.J. Park: Journal of Materials Processing Technology, Vol. 209, 2009, p. 864–870, doi:10.1016/j.jmatprotec.2008.02.055

[8] M. Long, H.J. Rack, Titanium alloys in total joint replacement a materials science perspective, Biomaterials, Vol. 19 , 1998, p. 1621–1639, doi:10.1016/S0142-9612(97)00146-4

[9] A. Krz˛akała, et al.: Electrochimica Acta, Vol. 104, 2013, p. 425–438, doi:10.1016/j.electacta.2012.12.081

[10] M. Geetha, A. K. Singh, R. Asokamani, A.K. Gogia: Progress in Materials Science, Vol. 54, 2009, p. 397–425, doi:10.1016/j.pmatsci.2008.06.004

[11] M.F. López, A. Gutiérrez, J.A. Jiménez: Electro chimica Acta, Vol. 47, 2002, p. 1359–1364, doi:10.1016/S0013-4686(01)00860-X

[12] S. Nag, R. Banerjee, H.L. Fraser: Materials Science and Engineering C, Vol. 25, 2005, p. 357–362, doi:10.1016/j.msec.2004.12.013

[13] W. Simka, M. Sowa, R.P. Socha, A. Maciej, J. Michalska: Electrochimica Acta, Vol. 104, 2013, p. 518–525, doi:10.1016/j.electacta.2012.10.130

[14] W. Simka, R.P. Socha, G. Dercz, J. Michalska, A. Maciej, A. Krz˛akała: Applied Surface Science, Vol. 279, 2013, p. 317–323, doi:10.1016/j.apsusc.2013.04.091

[15] Y.L. Zhou, M. Niinomi, T. Akahori: Materials Science and Engineering A, Vol. 371, 2004, p. 283–290, doi:10.1016/j.msea.2003.12.011

[16] Y. Tsutsumi, M. Niinomi, M. Nakai, H. Tsutsumi, H. Doi, N. Nomura, T. Hanawa: Applied Surface Science, Vol. 262, 2012, p 34–38, doi:10.1016/j.apsusc.2012.01.024
[17] Y.L. Zhou, M. Niinomi, T. Akahori, H. Fukui, H. Toda: Materials Science and Engineering A, Vol. 398, 2005, p. 28–36, doi:10.1016/j.msea.2005.03.032
[18] B. Ghorbanian, and S.M.M Khoie: Acta Metallurgica Slovaca, Vol. 22, 2016, No. 2, p. 111-119, doi: 10.12776/ams.v22i2.659