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Study of Current and Voltage Diagram In The Formed Vanadium Carbide Coatings Via Plasma Electrolytic Saturation Method

Fariba Momeni, Babak Ghorbanian*, Seyed Mohammad Mousavi Khoie,
Seyed Mohammad Mousavi Nazari , Mahmood Rasouli
Mining and Metallurgy Department in Amirkabir University of Technology Tehran/Iran

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**Corresponding Author. E-mail:*ghorbanian.babak@yahoo.com

Abstract

One of the most important hardening methods of tool steel is the use of carbide coatings, that during this process, vanadium atoms at the high temperature diffuses the specimen's surface and reacts with the available carbon in steel and create vanadium carbide with the high hardness. During Plasma Electrolytic Saturation Process vanadium element diffuses with the help of plasma and as the result of temperature increases up to around 980 degrees the condition for creation of vanadium carbide is provided. In this process the voltage has been established between cathode (sample) and anode, plasma has been created on the surface of cathode which penetrates vanadium to the surface of the component and the plasma itself causes an increase in the temperature to form the vanadium carbide. In this article the effects of the parameters of conductivity and current on fixed voltage will be studied and results such as formation of coatings in currents between 6 – 9 mA and also increase in the possibility of the formation of coatings in higher conductivities have been obtained. In this study X-Ray Diffraction test and Scanning Electron Microscope have also been used.

Key words: Carbon materials, Diffusion, Surfaces, Thin films

1-Introduction

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 piece plays the role of anode and is often used for creating the carbide coatings.

2- Deposition techniques using plasma electrolytic saturation (PES) include plasma electrolyte carburizing (PEC) [5,6], plasma electrolyte nitriding (PEN) [7], plasma electrolyte carbonitriding (PEC/N) [8], plasma electrolyte boriding (PEB) [9-12] 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 vanadium oxide 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 [1-2]. 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.

The purpose of this study is forming vanadium carbide coating. The use of vanadium oxide and hydrochloric aside in plasma electrolysis leads to diffusion of vanadium into the steel surface. Then vanadium reacts with carbon in base metal and creates vanadium carbide. Moreover, the effects of parameters such as electrolyte conductivity, time and current on the final coated steel properties is investigated.

2-Experiment method

This process is implemented in a few minutes. In order to provide the condition of vanadium diffusion into surface of tool steel, the sample should be kept in 980°C for 6-10 hours. The samples used in this work were DIN 1.2436 cold work tool steel with the following chemical compositions (wt.%.): Cr (11-11.5), Mo (0.75-0.8), C (2-2.1), Si (0.2-0.25), and Fe balance. Samples are in cylindrical shape with 20 mm diameter and 22 mm height. To measure the temperature of the sample surface, a hole with 8±0.01mm diameter and 21.87±0.01 mm height was created and a thermocouple has been placed inside. Another hole has 3.5±0.01mm diameter and 10±0.01 height to hold the sample. In order to prevent the influence of the applied current on the sample during the temperature measurement, the thermocouple has been isolated from the surface of the metal by a ceramic pipe. An auxiliary electrode made of stainless steel 316 with a cylindrical shape was used. The sample was placed in the center of the auxiliary electrode. Samples were polished to a mirror finish using emery paper and then degreased with analytical grade ethanol. The ratio of samples surface area to auxiliary electrode surface area was kept constant at, approximately, one to hundred. The power source used in this investigation consisted of two transformers which were connected to a control system. This control system had the capability of producing pulsed bipolar regime. The electrolyte consisted of 4±0.1g vanadium oxide, 50±1ml hydro choleric aside, different amounts of sodium hydroxide (NaOH) and water which was added to reach 2litters solution [1]. All the coating processes were performed in 900 s. Coating voltage were 170±3 v via DC source. In the current research the effect of increasing electrolyte conductivity on coating formation and increasing voltage on current in different electrolyte conductivity were investigated.

The microscopic observation was carried out by a Philips XL 30 Scanning Electron Microscope and films composition was investigated by Philips 1840 X-ray diffraction (XRD). The cross-sectioned sample was etched with picral solution ($(NO_2)_3C_6H_2OH$) 5% picric acid and 95%ethanol) for microscopic analysis.

3- Results and analysis

Table 1 shows conductivity rate on ignition voltage as well as the temperature of the component surface. As it can be seen from Table 1 with increasing NaOH rate conductivity increases and with increasing conductivity the ignition voltage decrease which is followed in turn with an increase in the temperature of the specimen surface. As you may know, in higher temperatures due to the increase in empty space the required conditions for diffusion exists, in other words, diffusion coatings are formed in high temperatures. In low conductivities, due to low temperature the required conditions for diffusion are not provided or in other words diffusion coating doesn't form or in case of formation it doesn't have a good adhesion. However, with an increase in conductivity temperature increases and the required conditions for diffusion are provided and then a diffusion coating is formed, until due to the high conductivity, surface of the specimen or component is melted or destructed.

Table 1 The effect of conductivity rate on the formed coating (final voltage of 170 volts and times are 12min)

Specimen No.	Conductivity (ms)	NaOH (gr)	Ignition voltage (v)	Surface temperature (°C)	Coating type
1	28	30	110	100	-
2	30	40	79	120	Non-diffusion
3	35	50	65	970	Diffusion
4	42	75	52	1010	Diffusion
5	69	100	43	-	Specimen destruction

XRD analysis was done to detect formed chemical composition. Fig.1 shows the X-ray diffraction pattern for a sample that is kept for 900s in 980^{o}C. The first peak belongs to iron oxide (Fe_3O_4) which is formed on surface during process. 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 980^{o}C, thermodynamic condition was created to form vanadium carbide. 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.

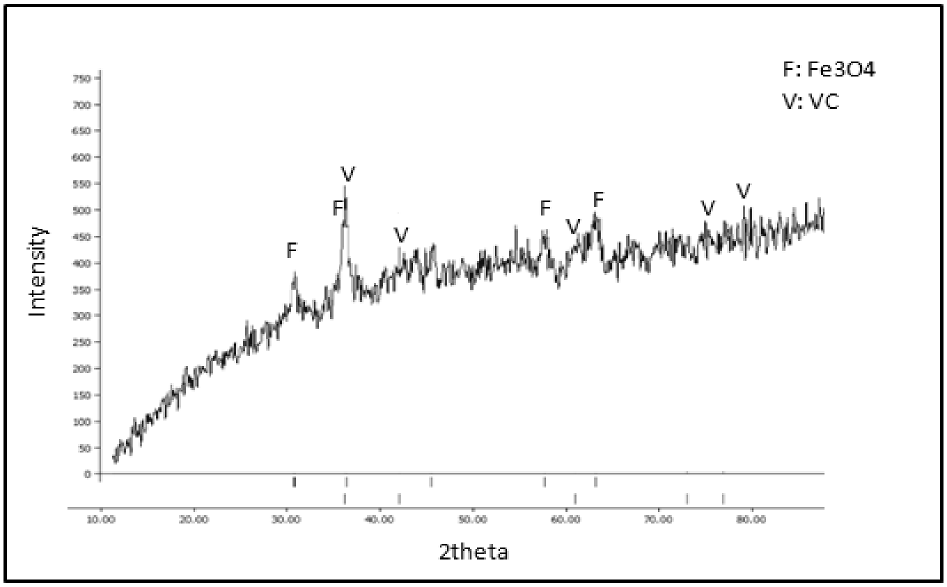


Fig. 1. X-ray diffraction pattern of the sample

The formed gaseous envelope around the gas sample oxygen exists that this gas is generated as per the following reaction [10]:

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

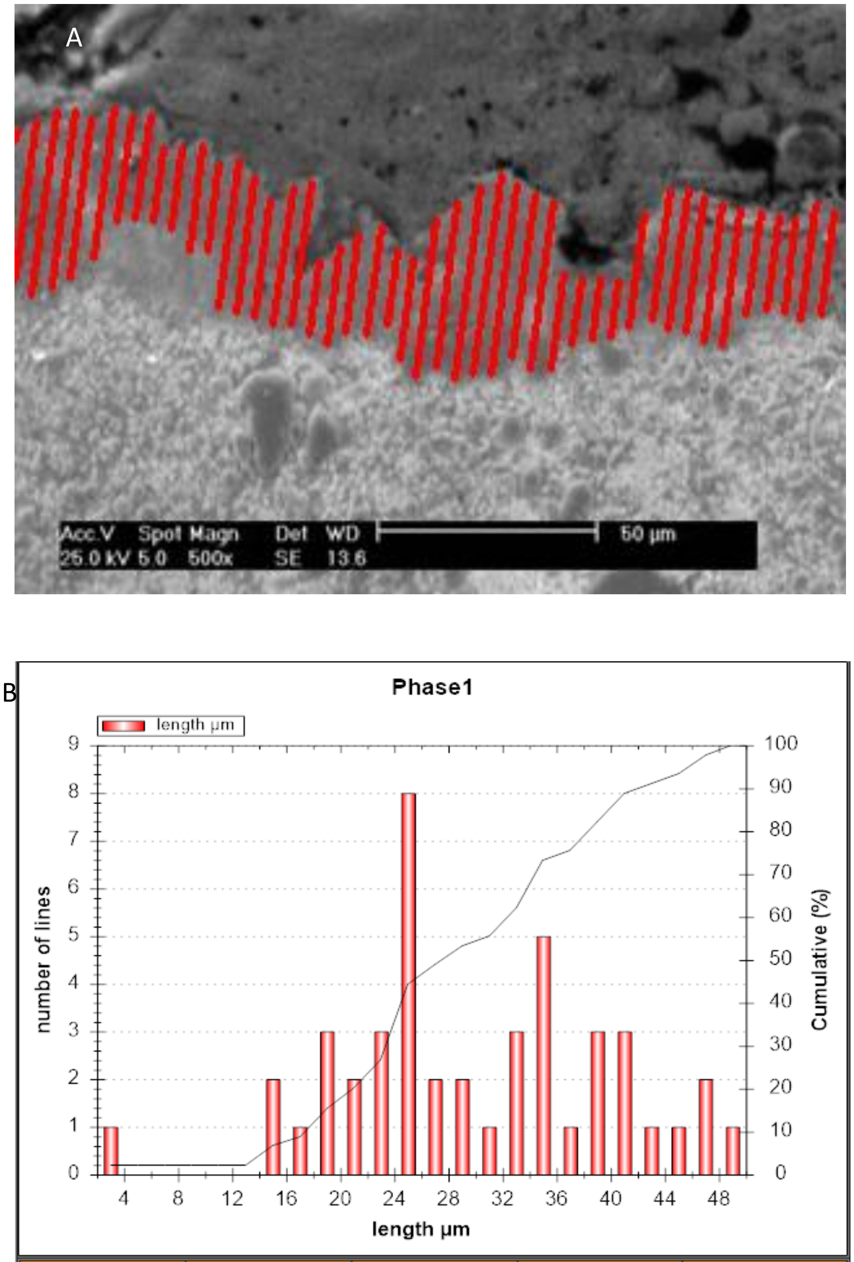
According to this process due to the creation of layer of gas in addition to vanadium Oxygen atom both ionized and penetrates the surface of the component due to high magnetic field and also reacts with iron due to temperature higher than 400 degrees and forms Iron oxide.

The electron microscope image of the coating is shown in Fig. 2. The sample is kept for 15 min in 980±10 ºC. As it is seen in the Fig. 2. , the maximum thickness of the formed coating is 48.82±0.01 µm and the minimum thickness is 2.94±0.01 µm. Thus, the average thickness is 2.76±0.01 µm. The difference between maximum and minimum thickness is due to non uniformity of coating

Fig. 3.(A) 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 coating is diffusion coating.

The voltage-current diagram of specimen no. 3 is presented in Fig.3.(B) 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. 3.(C) 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.



Count	Min	Max	Average	Std
45	2.94	48.82	29.76	9.84

Fig. 2. Scanning Electron Microscope picture of the formed diffusion coating

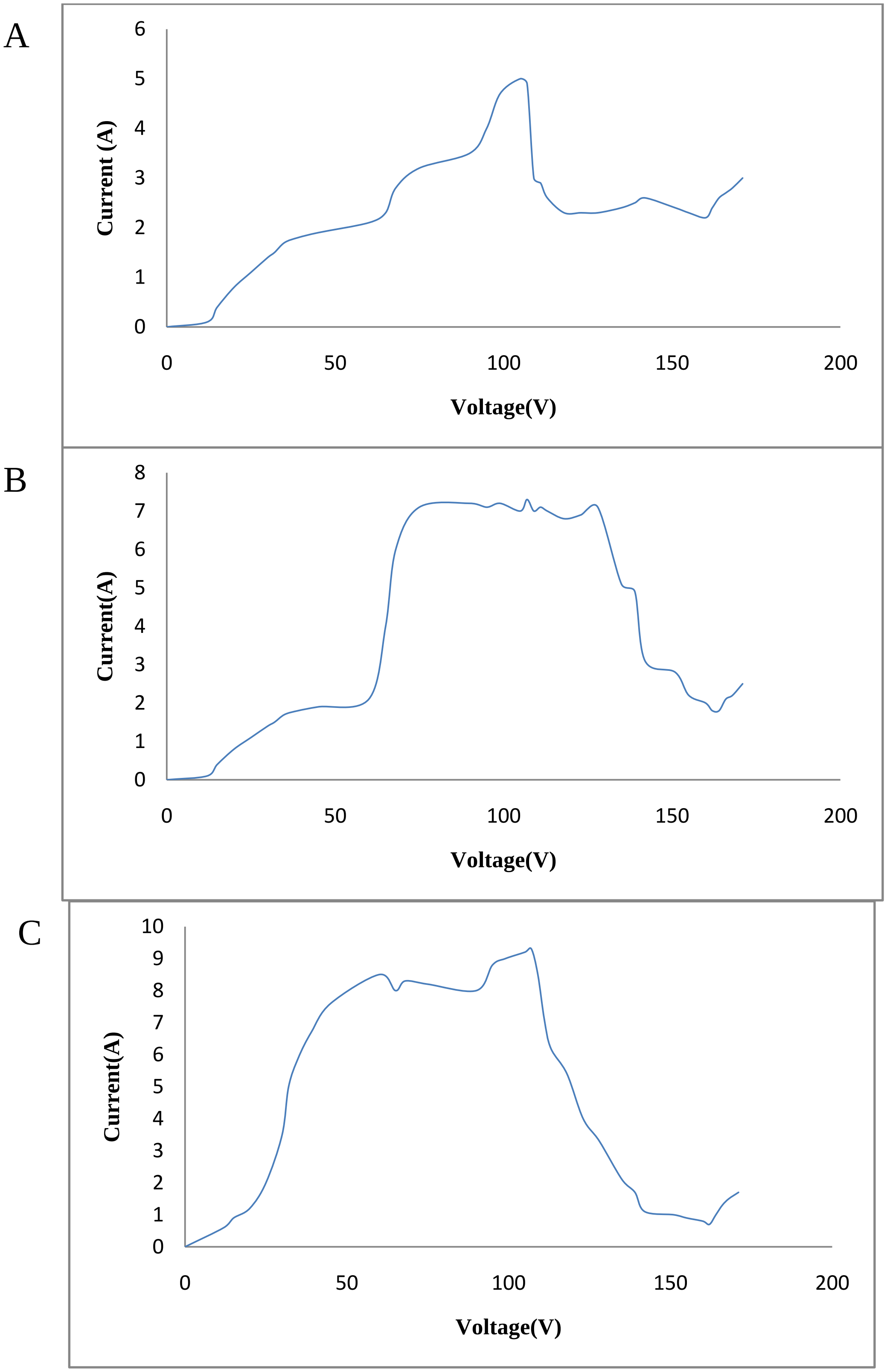


Fig.3. Current – voltage diagram of A)specimen no. 2 (100g NaOH), B) specimen no. 3(150g NaOH), C) specimen no. 4(200g NaOH)

Conclusion

With increasing the Sodium hydroxide rate conductivity increases which reduces ignition voltage and is followed by an increase in temperature; however an over increase in conductivity increases turbulence of the solution which instead of the component's temperature increases the solution's temperature.

In all the current – voltage diagrams first current increases and then suddenly it decreases, in currents in the range of 6-9 A coatings are formed and in higher currents the specimen are destructed.

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