COMPARISON THE VANADIUM CARBIDE COATING CREATED VIA PLASMA ELECTROLYTIC SATURATION AND TERMO REACTIVE DIFFUSION

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Abstract

One of the most important hardening methods of tool steel is the use of carbide coatings, in which during this process, vanadium diffuses to the specimen's surface and reacts with carbon. During the Plasma Electrolytic Saturation (PES) Process, the vanadium element diffuses with the help of plasma and increases up to around 1000°C as a result of the temperature, providing conditions for the creation of vanadium carbide. On the other hand, the thermo reactive diffusion (TRD) method during which the specimen is placed inside a salt bath containing the vanadium for a long period of time and the vanadium carbide coating is formed. In this paper, an attempt is made to study the formed coating with the method of plasma electrolytic saturation in addition to comparing the coatings formed by these two methods and obtain some vanadium carbide that created with TRD is purer than PES but that is thinner than plasma method, hardness of coating that created with TRD is about 2500 HV but in TRD is 1100 HV finally. In some PES samples the temperature increase slowly and the maximum temperature is about 120°C, in this condition, the coating is non- diffusion. The hardness of PES coating is about 1100 HV so we can use that in industrial molds.

Keywords: Wear, Vanadium carbide, Plasma electrolytic saturation, Thermo reactive diffusion

1 Introduction

Due to the advances in technology and the current intense industrial competitions, materials and metallurgical engineers and professionals are seeking the methods including the minimum cost and the maximum efficiency, and this is one of the most significant reasons for the importance of the surface metallurgy methods.

In fact, surface metallurgy can be explained as being a branch of materials engineering in which engineering components with better mechanical and physical properties can be produced without changing the material but at low cost. That is, producing the components which have higher resistance to wear, corrosion and oxidation [1].

Due to such good physical and mechanical properties of the carbide layers and improvement in their abrasion resistance and high hardness, these layers have had great significance in the industry during recent years and are often used for increasing the life of molds such as in hot and cold forging, extrusion, molding, wiring and tube molds, powder metallurgical molds, plastic and rubber molds, cutting tools and in general, all the tools which are exposed to the abrasion forces [2].

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Although the discharge phenomena in the process of electrolysis have been discovered more than a century in recent years, this field experienced a great spur in research and after that, this technique was improved and became common under the name of micro-arc-coatings [3-10]. Consequently, the effects of surface heat discharge on the liquid electrolyte used for heat treatments of metals. This technique is known as heating in the plasma electrolyte [8]. The diffusion process at the time of heating in the plasma electrolyte environment was also studied. New conditions and situations for an industrial application of the technique, known as saturation in plasma electrolyte, were developed[10] However, further development of these processes requires a better understanding of the physical and chemical principles of the plasma phenomena on the electrode during the electrolysis [11-17].

The method of plasma electrolyte is comparatively new and suitable method. This method is used for creating coatings that improve the mechanical properties of the surface [1-4]. This method is often used for coating aluminium and steel [5-8]. Plasma electrolyte is performed in two ways:

1. Oxidation method with the use of Plasma Electrolyte Oxidation (PEO): this method, the piece plays the role of anode and is used for creating the carbide coatings.
2. Plasma electrolyte saturation (PES): in this method, the piece is used as a cathode and used for the non-oxide coatings [9].

One of the most important and effective existing coatings in tool steels is the formation of carbide coatings. These coatings will create hardness and resistance against high abrasion in cold worked tool steels and will increase the life of the mold up to a few times. These days, there are so many technologies for creating carbide coating; however, more focus has been given to the formation of vanadium carbide on steels containing vanadium [10]. In the present study, we have focused on creating and assessing vanadium carbide coatings on tool steels via plasma electrolytic saturation and thermo-reactive diffusion method (TRD).

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 20 mm 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 is selected from the dissolution of 4gr vanadium oxide in 50 ml hydrochloride acid that has brought its volume to 2 liters and then for creating the different conductivities, different amounts of sodium hydroxide (NaOH) were added to the electrolyte solution.

For the creating a coating with the use of the plasma electrolytic method, an electrolytic solution with a composition, presented in **Table 2**, has been used. The conductivity of the generated solution is about 35 ms.

Table 2 The amount used in 2 liters of electrolyte solution

Water	Sodium hydroxide	hydrochloride acid	Vanadium oxide	Substance type
The rest	**50 g**	**50 ml**	**5 g**	**Amount**

The voltage of about 170 volts and a current of 7 mA 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.

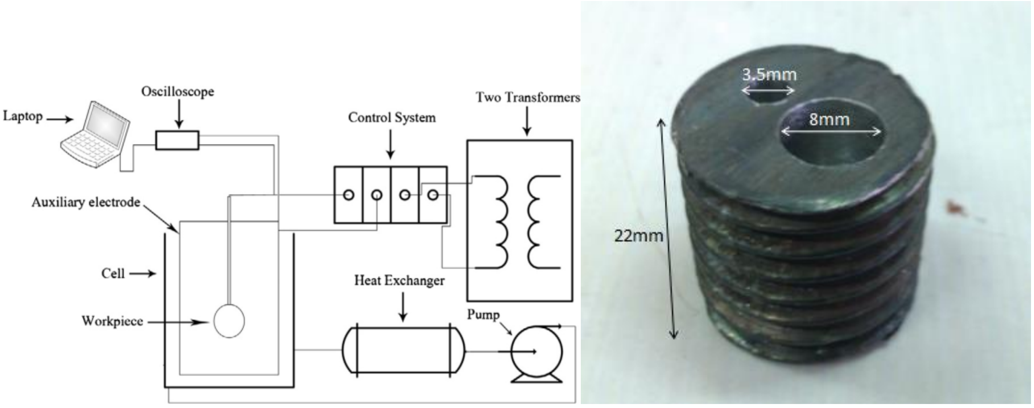

Fig. 7 The device and the sample being tested in this study

The anode is stainless steel 404, and its cross section is about 150 times the cathode surface (sample) and covered all around the sample. After hanging sample in electrolyte applied high voltage (about 170 V) between anode and cathode next created gas packet on cathode (has low area) and vanadium ionized in gas packet. If the temperature rises, vanadium diffuses and reacts with carbon (exist in steel) and created vanadium carbide.

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

3.1 Coatings created with the use of the plasma electrolytic method

Fig. 2 and **Fig. 3** show, changes in the temperature as the effect of voltage in two similar experiments. As **Fig. 2** shows, during this experiment, the temperature of the component surface increases slowly and reaches 120 – 140°C eventually. In this process, the no diffusion coating has been formed, because the requirement of the diffusion is a high temperature. What is very important in this experiment is that the temperature of the electrolyte solution has increased to such an extent that the solution starts to boil, but in a similar experiment in which **Fig. 3** shows the diagram of temperature changes due to the voltage effect, we can see, in beginning, the temperature is low and then it increases suddenly. In this experiment, the formed coating and the electrolyte temperature don't have changed significantly. The reason for the creation of this phenomenon is the solution viscosity. In cases in which the viscosity of electrolyte is high, the level of the turbulence is high; it affects the gaseous envelope around the specimen. Thus, the generated heat from plasma is used for heating the solution. This is while, in case of the low viscosity, this phenomenon does not occur and the heat resulting from the plasma is used for the diffusion of the vanadium atom to the component's surface and formation of vanadium coatings (**Fig. 2**).

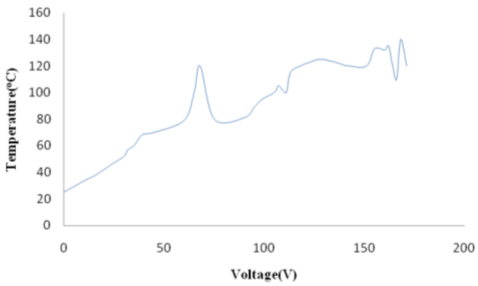

Fig. 2 Temperature - voltage (non-diffusion coating has been formed)

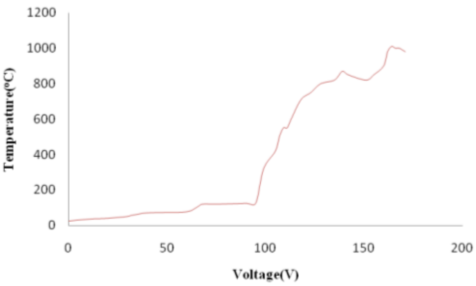

Fig. 3 Temperature - voltage (diffusion coating has been formed)

3.2 XRD results of the formed coating

Fig. 4 shows the X-ray diffraction pattern for a sample with diffusion. In the diffraction pattern, in addition to the peak of Fe_3O_4 and vanadium carbide, the diffraction pattern shows that the formed diffusion coating is made vanadium carbide material.

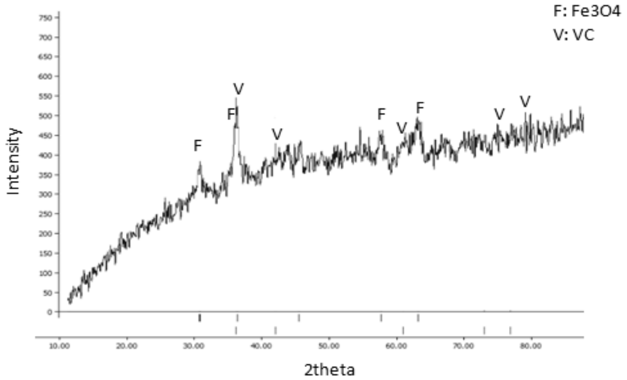

Fig. 4 X-ray diffraction pattern of the sample

3.3 Non- diffusion coatings

As it was mentioned in low conductivities, the temperature does not increase and no diffusion occurs and instead of a diffusion coating, a non- diffusion coating with low cohesion is formed.

The images taken with a scanning electron microscope method from the surface of these samples show that on the surface of these samples, cauliflower particles have been formed. **Fig. 5** shows, the average distance between these particles is about 17 – 20 µm and in **Fig. 6** it is observed that the maximum size of the formed particles is about 9 µm. This coating will create the diffusion coats.

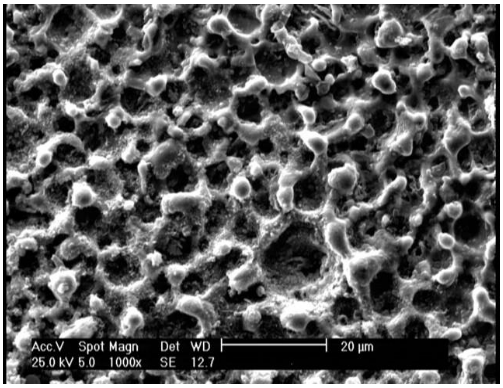

Fig. 5 SEM image the surface of the non- diffusion coating (20 µm)

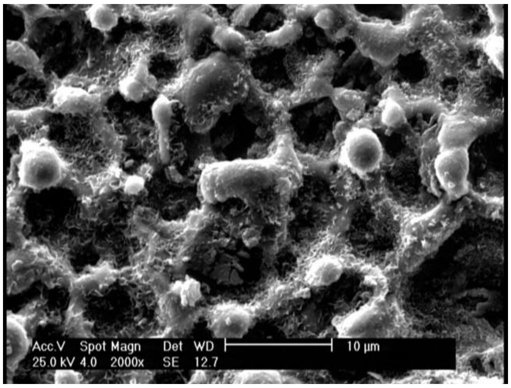

Fig. 6 SEM image the surface of the non- diffusion coating (10 µm)

3.4 Comparison of the coating formed by PES and TRD

In order, to ensure the formed coating, a chemical map was prepared from the cross section of the coating for iron, chromium, carbon and vanadium elements. **Fig. 7**, **Fig. 8**, **Fig. 9**, **Fig. 10**, **Fig. 11** are the chemical maps of the four elements of vanadium, carbon, iron and chromium, respectively that have been prepared from the images of **Fig. 7** The chemical maps show, the formed coating contains the carbon and the vanadium and also some amounts of the iron impurities are seen in PES sampels and the amounts of the vanadium is less in the coating. It is predicted that the reason for this might be the small duration of the coating which shows that the existing dark particles are associated with the chromium carbides. As **Fig. 7** indicates, the formed coating is about 11 microns.

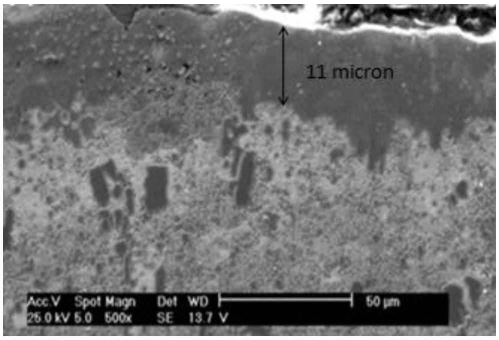

Fig. 8 The formed diffusion coating from specimen

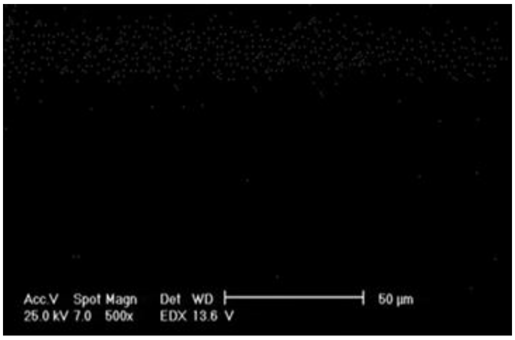

Fig. 7 The obtained chemical map from the coating from vanadium element

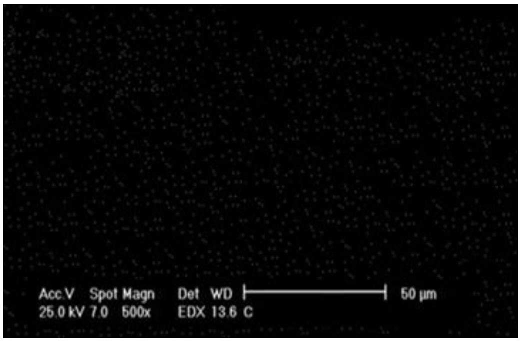

Fig. 10 The obtained chemical map from the coating from carbon element

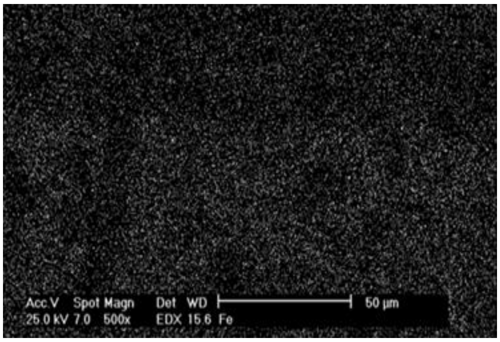

Fig. 9 The obtained chemical map from the coating from iron element

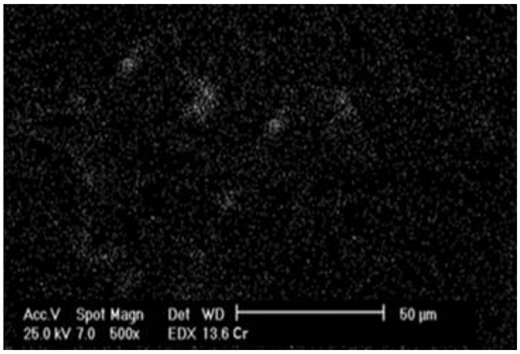

Fig. 11 The obtained chemical map from the coating from chromium element

During the TRD process, the non-diffusion coating which has been formed as a result of the lack of increase in the temperature is placed in a salt bath containing 85% of $BaCl_2$ and 15% sodium chloride with 1000°C temperature for 3 hours. Then the chemical map, for the four elements including vanadium, carbon, iron and chromium were prepared, and the results are presented in **Fig. 12** untile **Fig. 16**.

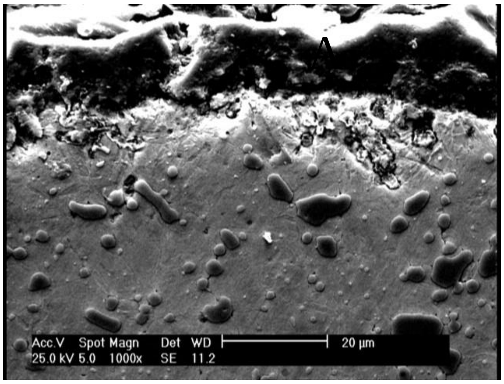

Fig. 12 Specimen No. 7 which has been placed in the bath salt.

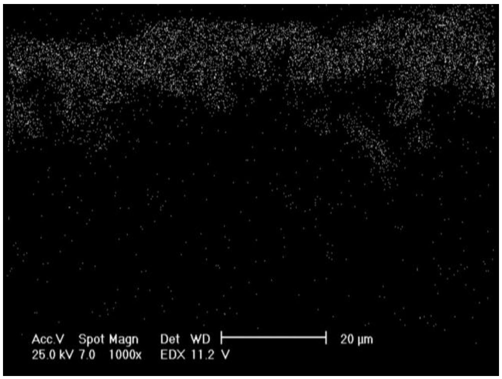

Fig. 13 The obtained chemical map from the coating from vanadium element

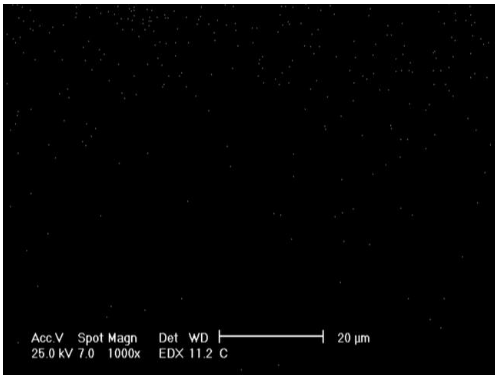

Fig. 14 The obtained chemical map from the coating from vanadium element

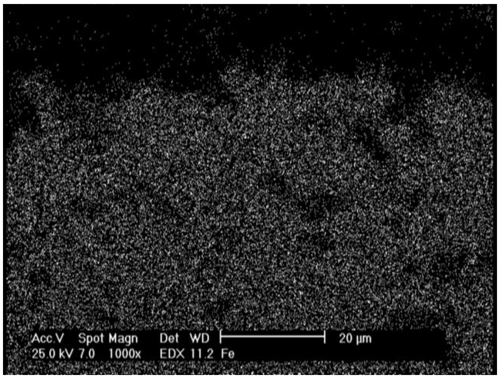

Fig. 15 The obtained chemical map from the coating from vanadium element

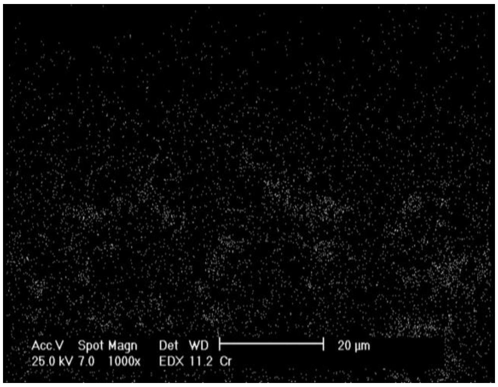

Fig. 16 The obtained chemical map from the coating from vanadium element

Comparison between the formed vanadium carbide coating by the plasma, with the formed coating by placing the non-diffusion specimen in the bath salt it can be concluded that the formed coating with the use of plasma method in addition to have the vanadium and the carbon impurities has iron impurity as well, the amount of which is very high. This is while the amount of the vanadium impurity is more in the formed coating with the use of the bath salt and its amount of the iron impurity is less. In addition to this, by performing the hardness tests on the coatings, it is seen that the coating formed with the use of the plasma method has a hardness of about 1100 HV while the hardness of the coating formed via TRD is about 2500 HV.

Table 3 Comparison of the coatings obtained from plasma and salt bath

Salt bath coatings	**Plasma coatings**	**Properties**
Maximum 7	**11-13**	**Thickness (micron)**
Low impurity	**High iron impurity**	**Purity**
2100 – 2500	**Maximum 1000**	**Hardness (HV)**
-	**There is Iron oxide on the coating**	**Remarks**

In the meantime the coating has a thickness of about 7 microns which is the thinner compared to the thickness of the coating formed in the plasma. **Table 3** shows the difference between the two formed coatings.

4 Conclusions

In the two similar solutions, sometimes the temperature does not increase that this lack of temperature increase is due to the effect of viscosity and the high turbulence in the solution that causes the formation of the non-diffusion coating on the component's surface. This non-diffusion coating has a cauliflower-like morphology and the size of each of its grains is about 7 microns, and the distance between every two grains are about 11 microns.

By placing, the specimen with the non-diffusion coating in the salt bath with 1000°C temperature, a carbide coating is formed that has a thickness of about 7 microns.

The formed coating has a lower hardness compared to the coating with the use of the plasma method, and its thickness is more and has less purity compared to the coating formed in the salt bath.

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