

Characterization of vanadium carbide coating deposited by borax salt bath process

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Abstract. Thermal reactive diffusion coating of vanadium carbide on DIN 2714 steel substrate was performed in a molten borax bath at 950-1050°C. The coating formed on the surface of the substrate had uniform thickness (1-12 μm) all over the surface and the coating layer was hard (2430-2700 HV), dense, smooth and compact. The influence of the kinetics parameters, temperature and time, has been investigated. Vanadium carbide coating was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and X-ray diffraction analysis (XRD). The corrosion resistance of the coating was evaluated by potentiodynamic polarization in 3.5% NaCl solution. The results obtained showed that decrease of coating microhardness following increasing time and temperature is owing to the coarsening of carbides and coating grain size.

Keywords: surface treatments; thermal reactive diffusion coating; corrosion; X-ray analysis; salt bath

1. Introduction

Thermal diffusion process is one of the earliest methods to increase the life of forming dies and machining tools. Thermo-reactive deposition and diffusion (TRD) treatment is a process by which a carbide former element is deposited onto the surface of a substrate containing carbon to produce carbide layers of that element. The main characteristics of these layers are high hardness, wear resistance, low coefficient of friction. Other properties that can be mentioned are good oxidation and corrosion resistance and a metallurgical bond with the metal substrate. These advantages make the process very effective for obtaining a product with excellent tribological properties (Arai 1965, 1991, Nakanishi *et al.* 1992). Vanadium carbide coating by TRD method has been widely used in die industry.

Corrosion resistance of a coating is dependent on the thickness, microstructure and the porosity of the protective layer (Arai 1979, 1993). In other words, the presence of solution-path defect within coating lets the electrolyte to reach the substrate surface. This phenomenon accelerates the formation of a galvanic couple between the coating and the substrate that finally results in fast dissolution of the substrate (Oliveira *et al.* 2006).

Fabrication of vanadium carbide by molten borax bath or pack cementation and the effect of

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process parameters have been studied by a number of works (Fan *et al.* 2010, Liu *et al.* 2006). Concerning vanadium carbide coating process, the effect of rare earth elements in borax salt bath immersion has been investigated (Liu *et al.* 2008).

The growth kinetic of vanadium carbide coating was also assessed in other reports (Aghaie-Khafri and Fazlalipour 2008, Fan *et al.* 2010). It has been shown that the formation and the growth of different coating layers at the interface between the substrate and the top coat in the thermochemical coating treatment are mainly governed by diffusion laws. The kinetics of vanadium carbide coating by the pack method showed a parabolic relationship between the carbide layer thickness and the treatment time.

The properties of duplex surface treatment based on TRD method were also studied (Aghaie-Khafri and Fazlalipour 2008, Chicco *et al.* 1999). Duplex surface treatment which combines two surface engineering techniques involves thermo-chemically treating a steel substrate prior to the deposition of a hard surface coating. Thermo-chemical treatments, such as nitriding and carburising, inherently form a graded hardness from the surface to the substrate. This results in a gradual transition in interfacial properties and provides a tough and supportive sub-surface for the hard coating.

To the best of authors' knowledge, there have been few reports concerning the corrosion properties of vanadium carbide coating deposited by the borax salt bath process. In the present study, vanadium carbide coating was produced by borax salt bath process in different conditions. Microstructures, mechanical and electrochemical behaviors of coatings have been characterized.

2. Experimental procedure

2.1 Materials and thermal processing

DIN 2714 steel was used as substrates, the chemical composition of which is given in Table 1. Test pieces were machined to the dimensions of 20×20×5 mm and prepared by grinding with 1200 grid emery paper in the final stage. Vanadizing was performed by molten borax bath method. The bath composition was 80 wt.% Na₂B₄O₇, 17 wt.% ferro vanadium (Fe-48%V) and 3 wt.% Al. Treatments were done in an electrical resistance furnace as following. First, borax was melted in a stainless steel crucible and afterwards the ferroalloy powder and aluminum were added and dissolved. The treatments were accomplished at 900°C, 950°C, 1000°C and 1050°C for 3 and 5 h. The bath salt attached to the specimens was washed off by immersion in hot water.

2.2 Microstructure, hardness and roughness analysis

Microstructure of samples was characterized using Vega II Scan SEM and Nikon Microphot - FXA optical microscope. Samples were mechanically polished by 120, 400, 600, 800 and 1200 grit wet SiC emery paper followed by fine polishing in the presence of fine alumina particles containing

Table 1 Chemical composition of DIN 2714 steel, in wt%

C	Cr	Mo	Ni	V	Fe
0.56	1.10	0.50	1.56	0.18	bal.

solution. Water diluted Nital solution in a 1 to 1 ratio was applied to reveal the specimen structure. The thickness of the layers was measured by means of a micrometer attached to the optical microscope. Each reported value was determined as the average of five measurements. EDX Line scan analysis across the coating/steel interface was performed. The phase analysis of the coating was determined by XRD (Philips Expert Pro with Cu cathode).

Microhardness measurement was carried out using a Shimadzu type B Vickers hardness tester at 50 g load. Surface roughness of samples was measured using a Mitutoyo surface texture measuring system. The measurement conditions were as follows: traveling length, 5 mm; cut-off length, 0.8 mm; tracing speed of stylus, 0.5 mm s⁻¹. Direct measurements of surface roughness and waviness were made from a single traverse over the surface, both being recorded on a profile graph. Other traverses parallel to the first trace were attempted to ensure the consistency and uniformity of the results. To accommodate the profile variations, the arithmetic mean value, R_a , was employed as the roughness parameter in this work.

2.3 Corrosion test

The electrochemical characterization was carried out by potentiodynamic polarization test (PGSTAT30 model) connected to a standard three electrode cell. The cell comprises a working electrode (sample) a saturated calomel reference electrode and a platinum counter electrode. The electrolyte used was a 3.5 wt.% NaCl solution. Approx. 0.72 cm² of the working electrode surface was in touch with the corrosive solution. Prior to the test, proper time of suspension was provided in order to achieve steady state condition. Then, open circuit potential was recorded at 1 mV/s as a potential scan.

Two markers on each of the anodic and cathodic branches in the curve for the anodic and cathodic Tafel lines were set and then the corrosion current was obtained. The intersection point of the anodic and cathodic Tafel lines was used to determine the corrosion current by the software employing the Stern–Geary relation (Ailor 1971)

$$I_{corr} = [b_a b_c / 2.303(b_a + b_c)] [1/R_p] \quad (1)$$

where b_a is the slope on the anodic side of the curve, b_c is the slope on the cathodic side, R_p is the polarization resistance which is determined by $R_p = (\Delta I / \Delta E)$ for $\Delta E \rightarrow 0$, ΔE is the deviation from the corrosion potential and ΔI is the resulting change in the current. The software calculated the corrosion current density (i_{corr}) based on the I_{corr} and the area which was exposed to the media and was given by the user. Afterwards, the accurate value of the corrosion current density was obtained by fitting the crossing point of the anodic and cathodic Tafel lines with E_{corr} line.

3. Results and discussion

Molten bath that was prepared by Na₂B₄O₇ consisted of Na₂O and two B₂O₃. The layer formed in the borax bath can be identified considering the free energies of carbide and oxide formation relative to the dissolved elements. The vanadium carbide layers were possibly formed on DIN 2714 steels due to the relatively large free energy of carbide formation (approx. -90 kJ/mol at 1000°C) and a relatively small free energy of oxide formation (approx. -323 kJ/mol at 1000°C) (Arai 1979, 1991).

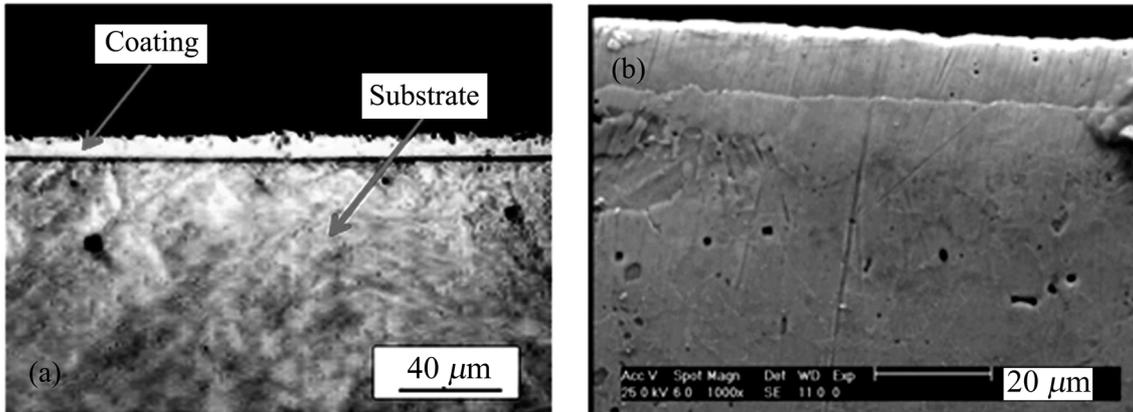


Fig. 1 (a) Optical and (b) SEM micrograph of cross-section of vanadium carbide – coated steel at 1050°C/3 h

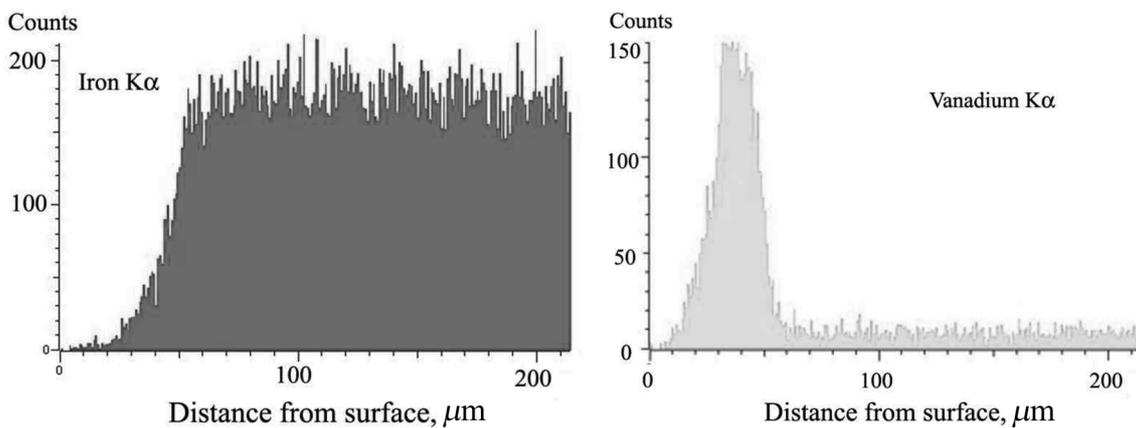


Fig. 2 Iron and vanadium EDX line analysis of vanadized sample

3.1 Characterization of the vanadium carbide coating

Optical and SEM micrographs of the vanadized layer formed on the DIN 2714 steel are shown in Fig. 1. It is clear that a distinct layer has been formed on the surface of the vanadized steel. SEM micrograph revealed that the coating formed on the surface of the substrate had uniform thickness all over the surface. Moreover, the coating layer was dense, smooth and compact. However, it can be observed that the surface roughness of the sample is not uniform. The average surface roughness for 1050°C/3 h sample is $R_a = 0.47 \mu\text{m}$. It is worth noting that the surface roughness of different samples varied between 0.42 to 0.63 μm .

Elemental distribution of the vanadized layer (V and Fe) detected by SEM-EDX analysis from surface to interior is shown in Fig. 2. It is obvious that the coating is rich in vanadium, but scarce of iron.

The presence of carbide phases in the vanadized samples in the present study was confirmed by the XRD results, as is shown in Fig. 3. Excluding the sample vanadized at 900°C/3 h, VC phase was

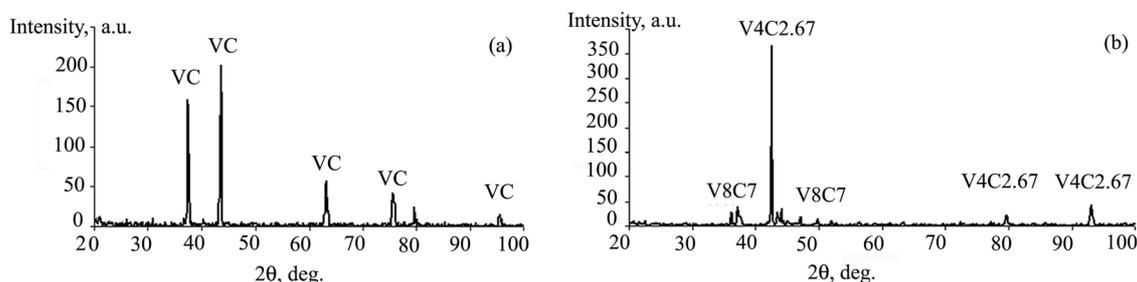


Fig. 3 XRD profile of coating layer formed on the steel substrate (a) at 1050°C/3 h and (b) 900°C/3 h

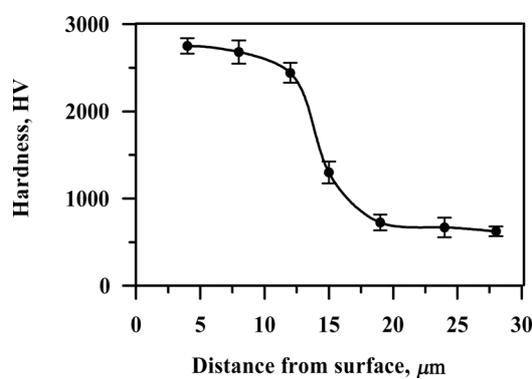


Fig. 4 Variation of the microhardness versus distance from the surface of the specimen coated at 1050°C/5 h

revealed. However, V_8C_7 and $V_4C_{2.67}$ phases were observed in the sample vanadized at 900°C/3 h (Fig. 3b). Formation of V_8C_7 phase is attributed to the vacancy of some C sites (Oliveira *et al.* 2006, Lipatnikov *et al.* 1997). VC phase with a lattice parameter of $a=0.412\text{--}0.416$ nm, is characterized as NaCl-type face centered cubic (fcc), with octahedron gaps all taken by carbon atoms (Zhimei *et al.* 2010, Liujie *et al.* 2006). However, these octahedron gaps are not often fully taken by carbon atoms thus vacant positions form. If these vacant positions are arranged in an ordered sequence then a superlattice structure such as V_6C_5 and V_8C_7 will form. A simple cubic superlattice of V_8C_7 , with a lattice parameter of $a' = 0.833$ nm will form when the ratio of C to V is approximately 0.875.

Fig. 4 shows the microhardness versus distance from the surface of the transversal section of the sample vanadized at 1050°C/5 h. It is clear that the hardness profile is fairly correlated with the distribution of V from the surface of the specimen. The hardness decreased with decreasing of the vanadium concentration. Furthermore, it can be observed that the microhardness at the vicinity of the interface of the coating layer and the substrate abruptly decreased and then reached a constant value in the substrate. The phenomenon observed is due to carbon being removed from the substrate to form the carbide coating (Aghaie-Khafri and Fazlalipour 2008, Chicco *et al.* 1999).

Microhardness values of the coatings for different samples are listed in Table 2. It is interesting to note that the sample vanadized at 900°C/3 h shows the lowest hardness. Mechanical properties of vanadium carbide coatings are sensitive to the C/V atomic ratio and microstructures. It has been shown that the increasing of C/V atomic ratio and the ordering of structural vacancies in vanadium carbides are accompanied by an increase in the microhardness (Lipatnikov *et al.* 1997, Rafaja *et al.*

Table 2 Microhardness of different samples

Sample	Temperature °C	Time (h)	Microhardness (HV)
1	900	3	2430
2	900	5	2900
3	1050	3	2850
4	1050	5	2700

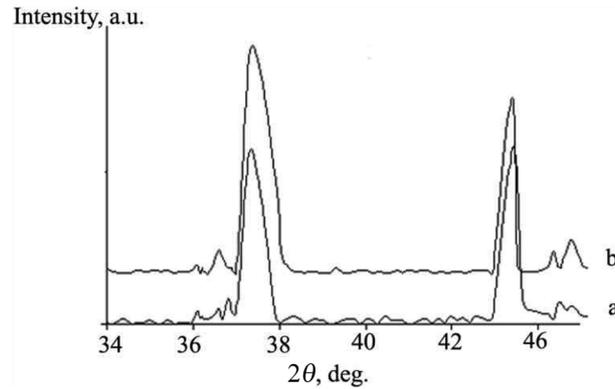


Fig. 5 XRD profile of vanadium carbide layer formed on the steel substrate (a) at 1050°C/5 h and (b) at 900°C/5 h

1998). Consequently, the low value of the microhardness in the sample vanadized at 900°C/3 h is due to the low value of C/V ratio in the carbide phase.

It is worth noting that microhardness of coatings in other samples decreases with increasing time and temperature. Hollox (Hollox 1968) showed that at low temperatures, the carbides are hard and brittle, but become relatively soft and ductile at higher temperatures. Besides, it has been proved that microhardness usually increases with decreasing grain size in accordance with a Hall-Petch relationship, wherein hardness varies with the inverse square root of grain size (Quinn 2000).

Concerning XRD profile of vanadized samples, significant peaks with highest intensity have been located at the angle of $2\theta = 34^\circ$ and 46° . The crystallite size is determined using Scherrer formula (Klug and Alexander 1962)

$$L = \frac{0.9\lambda}{B \cos \theta} \quad (2)$$

where 0.9 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity in radians and θ is the Bragg angle and L is the mean size of the crystalline domains. It has been shown that the peak width (B) is inversely proportional to the crystallite size (L) (Klug and Alexander 1962). The peak width of the sample vanadized at 900°C/5 h is broader than the sample vanadized at 1050°C/5 h, shown in Fig. 5. Consequently, the sample vanadized at 900°C/5 h has smaller grain size than the sample vanadized at 1050°C/5 h. Finally, the decrease of the coating microhardness with increasing time and temperature is owing to the roughening of carbides and coating grain size.

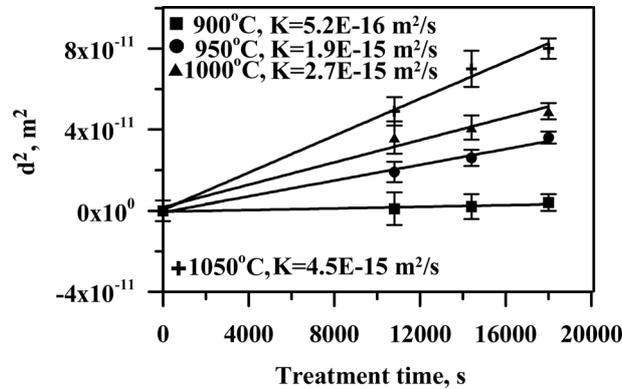


Fig. 6 Square of the layer thickness versus the treating time at different temperatures

3.2 Kinetics

It has been proved that the carbide layer grows at the surface front through reaction between carbide forming elements and carbon atoms successively supplied from the substrate (Arai 1979). In the present study, the 900°C/3 h vanadized sample undergoes the lowest imposed temperature and time. This results in inadequate carbon supply. As it is reported in other studies (Liu *et al.* 2006, Fan *et al.* 2010), the coating thickness increases with increasing treatment time and temperature.

It is well-known that at a given temperature the dependence of the thickness of a diffusion reaction layer on time can be described by (Aghaie-Khafri and Fazlalipour 2008)

$$d = Kt^n \quad (3)$$

where d is the thickness of the diffusion layer, K the growth rate constant, t the treatment time and n is the kinetics exponent. If n in the equation above is near 0.5, this indicates that the growth of the diffusion reaction layer is diffusion-controlled. However, n values of nearly 1 imply that the growth is interface-reaction-controlled (Christian 1975). In the present study, all the calculated n values were ranged between 0.410-0.505.

On the basis of the assumptions above and the classical kinetic theory, the squared thickness of the chromium boride layer (d^2) as a function of treatment time (t) can be described by

$$d^2 = Kt \quad (4)$$

where K is the growth rate constant which can be evaluated if the diffusion coefficients are known for the phases in the coating. Fig. 6 shows the square of the layer thickness versus the treating time at different temperatures. It is clear that the square of the layer thickness changes linearly with time. Consequently, the growth rate constant, K , can be calculated from the slope of d^2 versus t . The relationship between the growth rate constant, K , activation energy, Q and the temperature in Kelvin, T , can be expressed as

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

where K_0 is the pre-exponential constant and R is the gas constant. Q and K_0 can be calculated

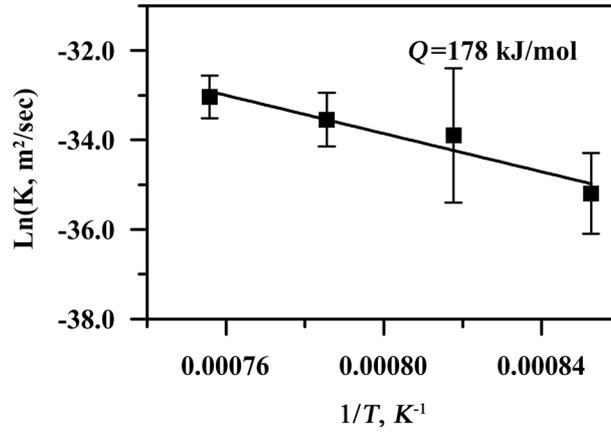


Fig. 7 A plot of $\ln(K)$ versus $1/T$

from a plot of $\ln(K)$ versus $1/T$, shown in Fig. 7. The mean activation energy in the case of the chromo-boronizing coating was calculated as 178 kJ/mol which is greater than the activation energies for the diffusion of carbon in steel (123 kJ/mol, Castle and Gabe 1999). Inserting the calculated values of Q and K_0 in Eq. (5)

$$K = 5.59 \times 10^{-8} \exp\left(-\frac{21420}{T}\right) \quad (6)$$

Combining Eq. (6) and Eq. (4) results in

$$d = 2.36 \times 10^{-4} \sqrt{t \exp\left(-\frac{21420}{T}\right)} \quad (7)$$

Eq. (7) can be used for predicting the coating thickness at different process temperatures and time.

3.3 Corrosion properties

Potentiodynamic results obtained from the polarization studies of the untreated sample, samples vanadized at 900°C/3 h and 1050°C/5 h in 3.5% sodium chloride solutions are shown in Fig. 8. The electrochemical corrosion parameters obtained by Tafel polarization curves are listed in Table 3. It is clear that the corrosion resistance of the vanadized samples increased compared to the untreated specimen. The surface of the vanadized samples have been covered by carbide phases. Carbides are noble phases and are positive with respect to steel in electrochemical series, provide mechanical protection while remain intact (Fontana 1986).

Corrosion resistance increased by increasing the vanadizing temperature and time. The changes of corrosion potential with treatment temperature can be explained by the effect of temperature on the type of carbide formed and formation of cracks in the coated layer. There are some cracks on the substrate of the sample vanadized at 900°C/3 h, shown in Fig. 9. Cracks were formed in the vanadized sample due to the existence of different phases that exhibit substantially different coefficients of thermal expansion (Carbucicchi and Palombarini 1987, Bindal and Erdemir 1966). Surface defects such as cracks affect the corrosion resistance of the coating layer (Ahn *et al.* 2002).

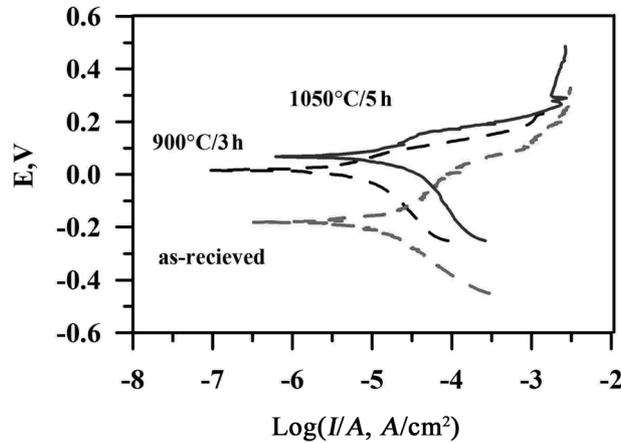


Fig. 8 Potentiodynamic polarization curves for untreated sample, sample vanadized at 900°C/3 h and sample vanadized at 1050°C/5 h

Table 3 Corrosion parameters of different samples in 3.5 wt%. NaCl

Sample	I_{corr} (A/cm^2)	E_{corr} (v)
Untreated sample	6.51×10^{-6}	-0.172
Vanadized at 900°C/3 h	6.04×10^{-6}	-0.088
Vanadized at 1050°C/5 h	5.73×10^{-6}	0.64

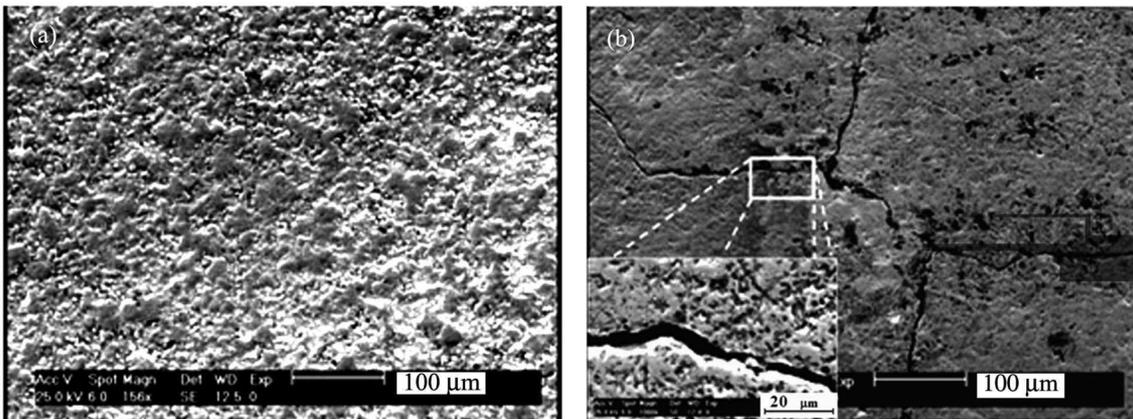


Fig. 9 Surface morphology of (a) sample vanadized at 1050°C/5 h and (b) sample vanadized at 900°C/3 h

Local defects formed during vanadizing act as channels which cause a direct path between the corrosive environment and substrate, leading to rapid local galvanic attacks and pitting corrosion of the base materials (Fontana 1986). It has been shown that the rate of deposition increases at high temperatures. Consequently, a dense carbide layer formed at high temperature that exhibits a superior protection.

4. Conclusions

- TRD process in molten borax bath produces hard and uniform vanadium carbide coatings on DIN 2714 steel. The surface roughness of the coated samples varies between 0.42 to 0.63 μm .
- Different vanadium carbide phases including VC , V_8C_7 and V_4C_2 in coating layers were identified by the XRD method.
- Microhardness of coatings is mainly dependent on C/V atomic ratio of vanadium carbides and temperature and time of treatment.
- Corrosion tests revealed that the vanadium carbide coated steel exhibits higher resistance than that of the uncoated steel. However, the presence of surface defect like cracks affects the protective quality of the coating.

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