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STUDY ON VANADIUM CARBIDE COATING FORMATION ON AISI L2 STEEL BY THERMO-REACTIVE DEPOSITION TECHNIQUE

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Abstract: *The possibility of vanadium carbide coating formation on AISI L2 steel was studied in molten salt bath containing 33 wt% NaCl- 67 wt% CaCl2. In this research, the effects of time, temperature and bath composition on growing layer thickness were studied. The vanadium carbide coating treatment was performed in the NaCl-CaCl2 bath at 1173, 1273 and 1373 K temperatures for 3, 6, 9 hours and in bath containing 5, 10, 15, 25 wt% ferrovanadium. The presence of VC formed on the surface of the steel substrate was confirmed by optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction analysis. The layer thickness of vanadium carbide and surface hardness ranged between 4.8 to 25.7 µm and 2645 to 3600 HV, respectively. The kinetics of layer growth was analyzed by measuring the depth of vanadium carbide layer as a function of time and temperature. The mean activation energy for the process is estimated to be 133 kJ/ mol.*

Keywords: *Vanadium carbide, TRD, Layer thickness, Kinetics, AISI L2*

1. INTRODUCTION

Hard coating with nitride, carbide or carbonitride of transition metals is a common method for improving resistance to wear, seizure and corrosion. These types of coatings are required to enhance the life of mechanical components such as forming and machining tools [1-3]. Various methods have been used to produce thin hard coatings which are classified as chemical vapor deposition (CVD), physical vapor deposition (PVD) and thermo reactive deposition /diffusion [4-6].

The TRD process is unlike conventional case-hardening methods, where the specific elements (carbon and nitrogen) in a treating agent diffuse into the substrate. In this process, carbon and nitrogen in the substrate diffuse into a deposited layer and react with a carbide-forming element and nitride-forming element such as vanadium, niobium, tantalum, chromium, molybdenum or tungsten [5, 7]. These TRD coatings have applications similar to those of coatings produced by CVD or PVD. The thickness of typical CVD coatings (usually less than 25 µm) has about the same range as TRD coatings [8]. The salt bath immersion process in ambient atmosphere has two advantages over the CVD. It is much easier to coat specimens within a very short immersion time if the specimens are sufficiently small to rapidly reach the bath temperature. The other advantage is the capacity of rapid cooling from the coating temperature to quench the growth pattern [9]. The high temperature salt bath TRD process is performed in a molten salt (usually borax) at 850 to 1250 °C. Immersion time ranges from 0.5 to 10 h to obtain an optimum layer thickness [1,7]. The TRD process is applied to steel containing more than 0.3 wt. % carbon to form carbide layer [8, 10]. The distinct boundary line between coating and substrate is attributable to the difference in physical and chemical properties between the carbide and the steel [5]. There are many reports about TRD coatings. Arai et al. [8, 9] studied the nucleation and growth behavior of vanadium, niobium and chromium carbide coating using a borax bath. Kinetics of growth of niobium carbide, chromium carbide and titanium nitride coating were studied by Saduman and Ugur Sen [2, 6, 11]. Khoee et al.

[12] examined the formation of VC and NbC in borax bath. Aghaie-Khafri et al. [13] examined the formation of VC coating by pack method. Oliveria et al. [7] and Sen et al. [5] studied the wear properties of vanadium carbide and niobium carbide.

The aim of this study was to produce vanadium carbide thin layer on AISI L2 substrate by the TRD method in chloride bath instead of borax and to investigate the effects of treatment time and temperature and bath composition on surface hardness and layer thickness and also layer growth kinetics. The probable reactions during coating treatment were determined as well.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and treatments

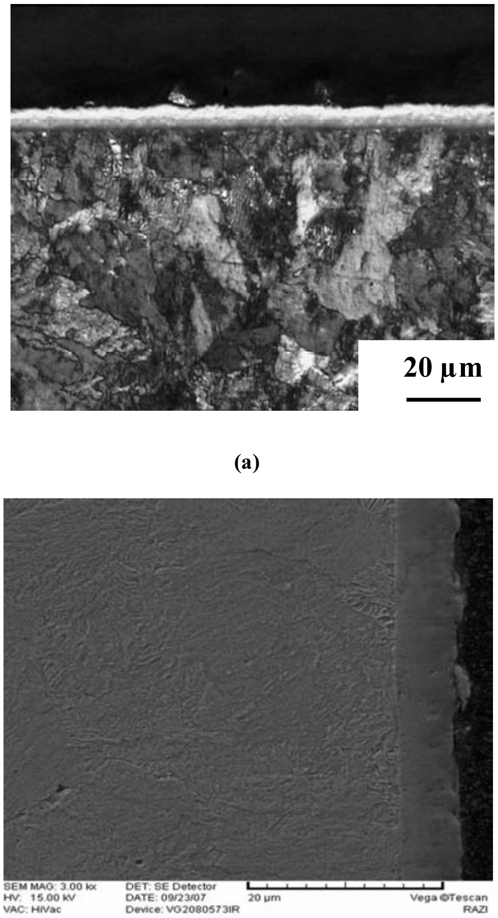
Chemical composition of AISI L2 steel is given in Table 1. The specimens were sectioned from a round bar and machined to the dimension of θ 10 mm × 12 mm. They were then ground up to 600 mesh emery paper. Based on the NaCl-CaCl2 phase diagram [14], eutectic composition (33 wt% NaCl- 67 wt% $CaCl_2$) was selected as salt bath composition. Borax adheres to the surface of samples but chloride salt is wiped out easily and also ferrovanadium is dissolved in NaCl-$CaCl_2$ salt. So in this research chloride salt was used. The bath containing 5, 10, 15, 25 wt% ferrovanadium (40 wt% V) was used. The bath was kept at temperatures of 1173, 1273 and 1373 K in an ambient atmosphere for 3, 6 and 9 hours. The left NaCl and $CaCl_2$ at over the surface of the samples was removed by cold water. In order to study on probable reactions during treatment, two samples were prepared in the beginning and at the end of coating process from the bath containing 10 wt% Fe-V kept at 1373 K, for 6 h to be analyzed by XRD.

Table. 1. Chemical composition of AISI L2 steel, in wt.

Fe	V	Mo	C	Si	Mn	Cr
Bal.	0.059	0.08	1.105	0.12	0.451	0.567

2.2. *Characterization*

The samples were cross sectioned, polished and etched with Nital 2% reagent for microscopical investigation. Vanadium carbide layer morphology was investigated by optical microscopy (NEOPHOT32) and scanning electron microscopy – secondary electron image (TESCAN, VEGAIIXMU). The layer thickness was measured by means of a micrometer attached to the optical microscope and its values were determined as the average of ten measurements. Micro-hardness measurements were carried out at the surface by a Micro MET BUEHLER micro-hardness tester under the load of 100 g.



(a)

(b)

Fig. 1. (a) Optical micrograph of cross-section of vanadium carbide coated AISI L2 steel at 1173 K for 9 h in bath containing 5 wt% . **(b)** Secondary electron image.

The XRD analysis of the vanadium carbide layer and also molten bath was performed by JOEL-JDX-8030, with 2θ varying from 5° to 80°, using CuKα radiation.

3. RESULTS AND DISCUSSION

3.1. Layer formation

In Fig. 1(a) and (b) the cross section of the coated sample treated for 9 hours at 1173 K in salt bath containing 5 wt% Fe-V is shown. As can be seen, the coating thickness is uniform and there is a flat interface between the formed layer and substrate.

On the cross-section of the samples, there are two distinct regions namely: (i) a surface layer consisting of vanadium carbide. (ii) steel matrix. Line scan of vanadium, iron and carbon is shown in Fig. 2. It is indicated that the vanadium content in the coating was high and decreased drastically in substrate-carbide interface. The iron content was high in the substrate and decreased drastically in the coating.

In this study, the XRD pattern shown in Fig.3 indicated that the coating consisted of VC with some iron present. The peak of iron most probably is affected by the iron content of the substrate. Formation of VC was observed in all process conditions.

The XRD patterns shown in Fig. 4 (a) and (b) are the analysis of molten salt in the beginning and at the end of process for the sample treated at 1373 K for 6 h. NaCl, $CaCl_2$, V_2O_3, VCl_3, VCl_2, $AlCl_3$, Al_2O_3, Fe, Fe_2O_3 are detected in the beginning and NaCl, $CaCl_2$, V_2O_3, V_4O_9, VCl_3, VCl_2, $AlCl_3$, Al_2O_3, Fe and Fe_2O_3 are detected after 6 h. On the basis of XRD analysis and also the thermodynamic analysis of the probable reactions, vanadium reacts with chlorine and forms VCl_2, VCl_3 and gaseous VCl_4. The chlorides of V presumably react with the steel (Fe) according to the following reactions:

$$VCl_4(gas) + 2Fe = V + 2FeCl_2(gas) \qquad (1)$$

$$VCl_3 + \tfrac{3}{2}Fe = V + \tfrac{3}{2}FeCl_2(gas) \qquad (2)$$

The released active V reacts with carbon in the substrate to form vanadium carbide layer. Also, vanadium may react with oxygen in the system and forms V_2O_3 and V_4O_9, as detected in the XRD pattern. The thermodynamic analysis shows that oxides of V can be reduced by Fe. On the basis of detection of AlCl3 in the XRD patterns and the probability of entrance of Al from Al_2O_3 of crucible, oxides and chlorides of V can also release V by reaction with Al.

3.2. Hardness and layer thickness

3.2.1. *The effect of time and temperature*

Depending on different conditions, the layer thickness measured was between 4.8- 25.7 µm and the surface hardness of coated samples was between 2645- 3600 HV. The hardness of AISI L2 steel was only 245 HV.

The graphical representations in Fig.5 show the effect of treatment time and temperature on

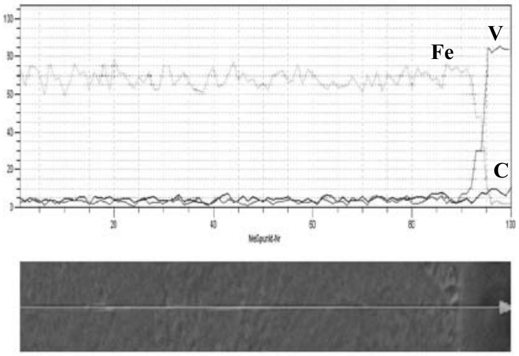


Fig.2. Line scan of vanadium, iron and carbon in the cross-section of the coated sample shown in Fig.1.

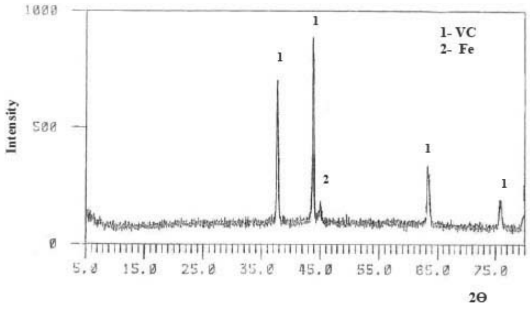


Fig.3. X-ray diffraction patterns of the coated sample shown in Fig.1.

layer thickness.

As in many diffusion treatments, the effect of time on coating thickness is expressed by the following Equation: [1]

$$d^2 = Kt \qquad (3)$$

where d is the thickness of the diffusion layer (m), t is the treatment time (s) and K is the growth rate constant (m^2 s^{-1}). The plot of the square of the vanadium carbide layer thickness versus treatment time is shown in Fig. 6. The experimental results are found to be in reasonable agreement with Eq. (3). The linear relationship between and t has been observed in the experiments done by Aghaie-Khafri et al. [13], Arai et al. [9] and Liu et al. [15] in production of vanadium carbide coating. It implies that the coating growth was achieved by the diffusion controlled reaction. According to Liu et al. [15] the growth of coating is controlled by the diffusion of carbon in the carbide coating.

The diffusion coefficient (growth rate constant), K, was determined from the slope of the lines in Fig. 6.

As in many diffusion treatments, the relationship between growth rate constant (K), activation energy (Q) and process temperature is expressed by the following Equation:

$$K = K_O \exp(\frac{-Q}{RT}) \qquad (4)$$

where K_o is a constant (m^2 s^{-1}), Q is the activation energy (kJ mol^{-1}), R is the gas constant and T is the temperature (K). As shown in Fig. 5, the thickness of carbide layer increases with increasing the treatment time and temperature. As can be seen in Fig. 5 and Fig. 6, the higher the treatment temperature, the higher the growth rate constant (m^2s^{-1}), resulting a the thicker the carbide layer. The increase in temperature increases the diffusion rate of carbon in the

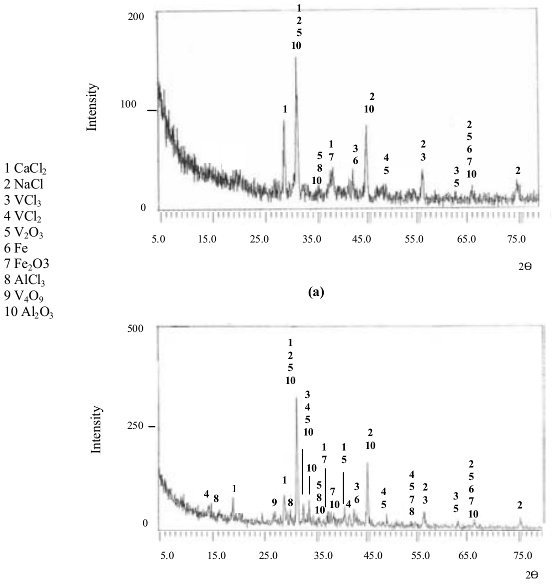


Fig.4. X-ray diffraction patterns of molten salt (a) in the beginning of the process (b) at the end of process.

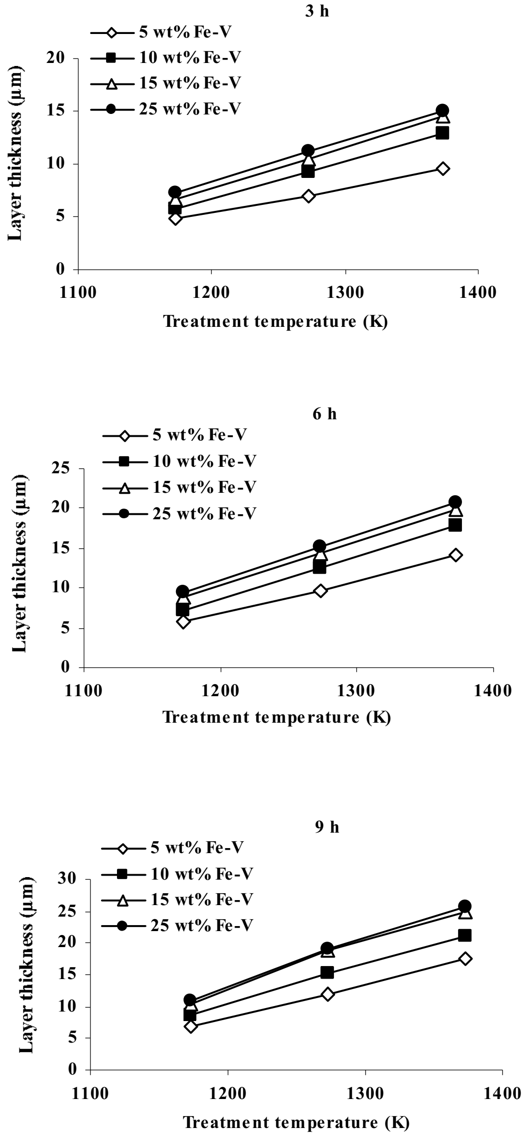


Fig.5. The effect of time and temperature on layer thickness.

Table 2 Calculated equations for growth rate constant and layer thickness.

wt% Fe-V	K (m^2/s)	d (μ)
5	$K = 9.81\times10^{-9}\exp(\frac{-18836}{T})$	$d = 9.9\times10^{-5}\sqrt{\exp(\frac{-18836}{T})t}$
10	$K = 1.91\times10^{-10}\exp(\frac{-13314}{T})$	$d = 1.38\times10^{-5}\sqrt{\exp(\frac{-13314}{T})t}$
15	$K = 1.96\times10^{-9}\exp(\frac{-15658}{T})$	$d = 4.43\times10^{-5}\sqrt{\exp(\frac{-15658}{T})t}$
25	$K = 1.98\times10^{-9}\exp(\frac{-15658}{T})$	$d = 4.45\times10^{-5}\sqrt{\exp(\frac{-15658}{T})t}$

carbide layer and results in an increase in the growth rate constant and the coating thickness. Increase of growth rate constant with temperature is in agreement with the Eq. (4).

3.2.2. *The effect of bath composition*

Fig. 7 shows the effect of the vanadium content of bath on the coating thickness. As can be seen, the layer thickness increases with increasing the amount of ferrovanadium in salt bath. However, using higher amounts of ferrovanadium beyond 15 wt% does not change considerably the thickness. In fact by using a bath containing more than 15 wt% ferrovanadium, the viscosity of the molten bath is increased and results in the increased amount of undissolved ferrovanadium.

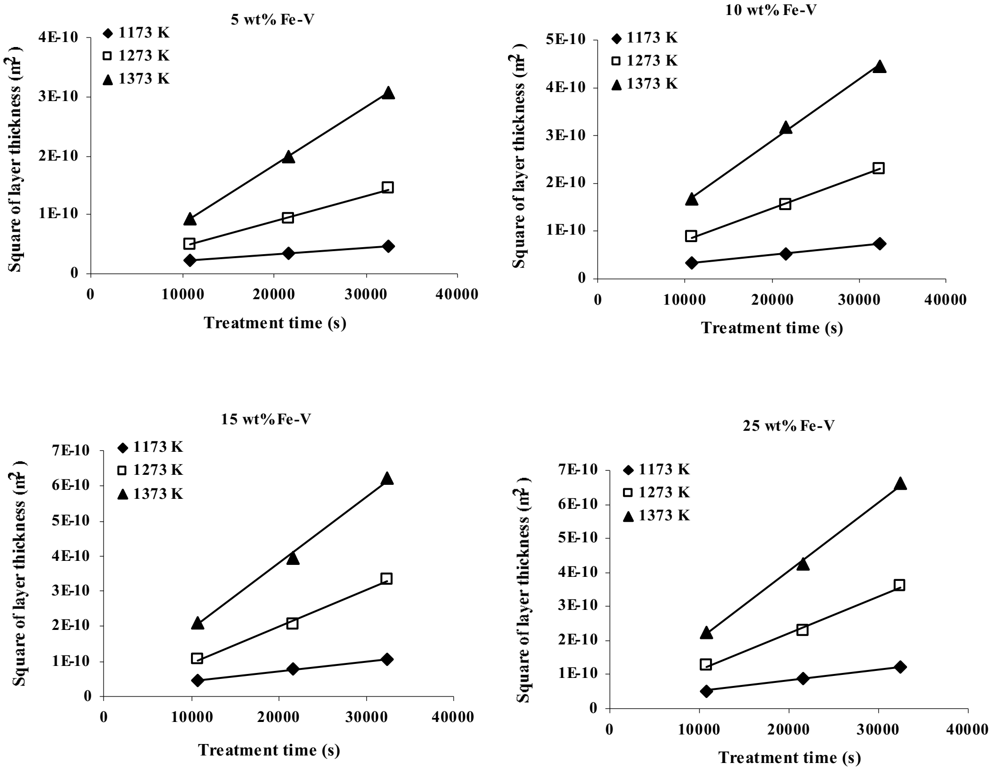


Fig.6. Square of the layer thickness, d2, versus treatment time.

3.3. Kinetics of Vanadium carbide layer growth

Equations (3) and (4) show the effect of treatment time and temperature on the layer thickness, respectively. Taking the natural logarithm of Eq. (4) results in the following Equation:

$$LnK = LnK_O - \frac{Q}{RT} \qquad (5)$$

K was determined from the slope of line in Fig. 6. Mean activation energy (Q) in the case of vanadium carbide coating determined from the slope of the plot of Ln K versus reciprocal temperature was to be 133 kJ/mol.

It is possible to predict the vanadium carbide layer thickness formed at different processing time and temperature. By using of these equations, the thickness of the VC coatings formed at different times and temperatures by using different ferrovanadium concentrations can be calculated. The resultant equations for calculating the values of K and d are shown in Table 2.

CONCLUSIONS

1. Vanadium carbide coating (VC) can be formed on AISI L2 steel by salt bath immersion method.
2. Using NaCl-$CaCl_2$ eutectoid composition as the bath composition facilitates cleaning of residual salt from the surface of samples.
3. Coating layer presents a flat interface with the substrate and with a uniform thickness.
4. The XRD analysis of the outer layer formed after TRD confirmed that the layer consists of the VC phase. The surface hardness of coatings varies between 2650 to 3600 HV.
5. The longer the treatment time, the higher the treatment temperature, the thicker the vanadium carbide layer became. The thickness of carbide layer varies between 4.8-25-7 µm.
6. The higher amounts of ferrovanadium in molten bath, the thicker the vanadium carbide layer became. Higher amounts of ferrovanadium beyond 15 wt% do not change considerably the thickness.
7. The mean activation energy of vanadium carbide coating formation by salt bath immersion method is estimated to be 133 kJ/mol. The growth rate constant and layer thickness equations are calculated for vanadium carbide coating.

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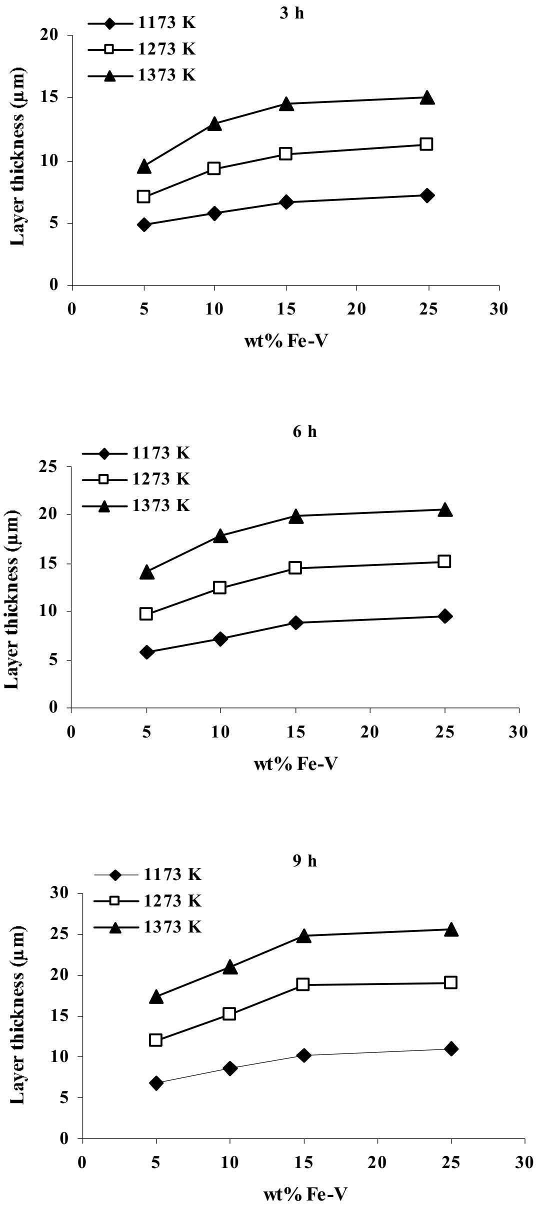

Fig.7. The effect of bath composition on layer thickness.

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