

# THE DIFFUSION GROWTH OF CARBIDE LAYERS ON STEEL SURFACES

## DIFUZIJSKA RAST KARBIDNE PLASTI NA POVRŠINI JEKLA

**Božidar Matijević, Mladen Stupnišek**

Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, I. Lučića 5, 10000 Zagreb, Croatia  
bozidar.matijevic@fsb.hr

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This paper discusses the diffusion process of carbide-layer formation on steels. Applying the principles of physical chemistry, a mathematical model of the process has been set up and a computer program for calculating technological parameters has been developed. Based on the results of the experimental work and literature data, the assumption that the speed of the process is proportional to the thermodynamic activity of carbon in the austenite has been proven.

Key words: carbide layers, vanadium carbide, diffusion

V delu je opisan difuzijski proces rasti karbidne plasti na površini jekla. Upoštevajoč principe fizikalne kemije smo naredili matematični model procesa in računalniški program za izračun tehnoloških parametrov procesa. Na podlagi rezultatov eksperimentalnega dela in literarnih virov smo potrdili, da je hitrost procesa premo sorazmerna aktivnosti ogljika v avstenitu.

Ključne besede: karbidne plasti, vanadijev karbid, difuzija

### 1 INTRODUCTION

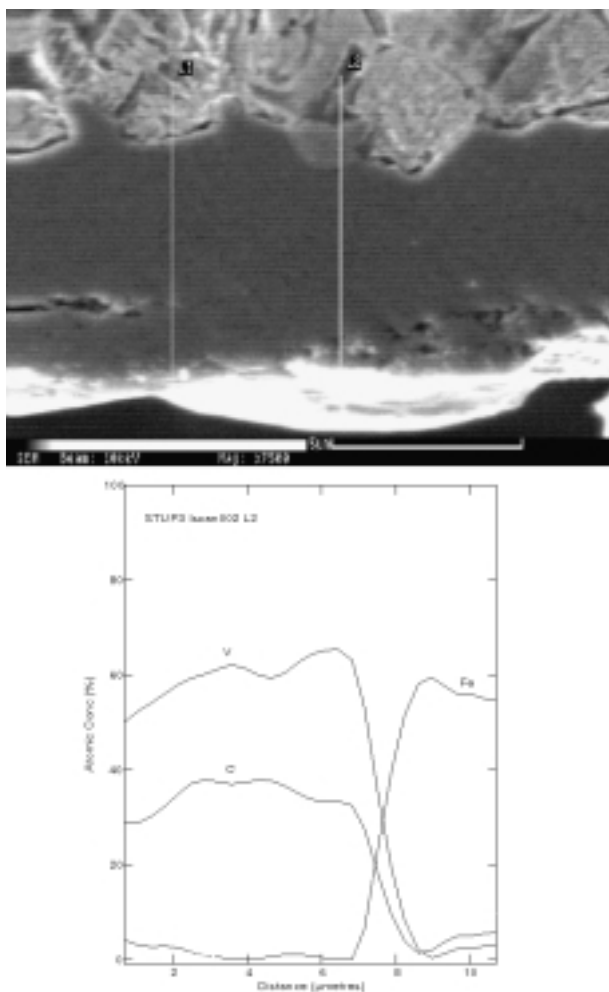
The process of forming carbide layers on steels by diffusion is of growing importance for industrial applications because of its advantages over other processes. The procedure is usually performed in a salt bath of special composition which contains the carbide-forming element vanadium, but might also contain some other elements, e.g. Cr, Nb<sup>1,2</sup>. At elevated temperatures from 900 to 1000 °C a molten bath of borax containing vanadium, either in the form of metal or an oxide, results in atomic vanadium forming on the surface of the substrate, which is usually steel. Entering the austenite lattice, the vanadium diffuses from the surface into the substrate, up to the solubility limit which depends on temperature and chemical composition of steel matrix. At this point the reaction of vanadium and carbon results in the formation of vanadium carbides. Through the formed carbide layer the carbon moves towards the newly generated surface where the process of forming carbides continues, thus increasing the thickness of the carbide layer. Carbon moves from the inner layers of the substrate towards the surface by diffusion. As carbon from the austenite is used in forming the vanadium carbide, its concentration beneath the carbide layer is substantially lower than that of the substrate<sup>3,4</sup>. As a consequence, carbon is the most important element for the formation of carbides. The carbide layer has a high hardness and a high wear resistance to abrasion, adhesion and tribocorrosion, which is particularly important for machine parts and tools. The thickness of the layer is in the range 3 to 20 µm. With the aim of better understanding the process and

improving applications, research into the metallurgical fundamentals of the process was carried out.

### 2 A MODEL FOR CARBIDE-LAYER FORMATION

By dipping the part of steel into the molten bath the carbide layer is formed on the steel surface. The diffusion processes that take place during the formation of the carbide layer on the surface are very complex. The formation of the vanadium-carbide layer VC0.88 on the steel surface is explained using the example of vanadizing, where vanadium is added to a molten bath as a metal or as an oxide. At the steel surface vanadium is combined with carbon dissolved in the austenite at the processing temperature. Through the formed carbide layer, the carbon diffuses to the newly formed surface, where it is combined with vanadium, thus increasing the layer thickness. At the same time, vanadium diffuses to the surface layer of the steel through the carbide layer. The rate of vanadium diffusion is lower than that of carbon through the carbide layer. As a result, the thickening of the carbide layer is not from the surface towards the center, like in the other diffusion processes (carburizing, nitriding, boriding, ...), but happens due to the growth of the carbide layer on the steel surface. **Figure 1** shows an SEM image of the vanadium-carbide layer with the marked analysing line (L2) and the AES spectrum of iron, carbon and vanadium in, and below, the vanadium-carbide layer.

The kinetics of the process of carbide-layer formation and the thickness of the formed layer depend on the temperature and the duration of the process and on the



**Figure 1:** (a) SEM image of vanadium-carbide layer; (b) AES spectrum Fe, C and V measured along the line L2. IMT Report 22/99  
**Slika 1:** (a) SEM-slika plasti vanadijevega karbida, (b) AES-spekter Fe, C in V na črti L2. Poročilo IMT 22/99

content of carbon and alloying elements in the steel. Previous research suggests that the carbide layer thickness is linearly proportional to the carbon concentration in the steel<sup>5</sup>. However, in order to analyse the influence of the chemical composition of the steel on the process it is necessary to consider the quantity of carbon in the austenite at the processing temperature, not the total content of carbon in the steel. This is of particular importance for high-carbon high-alloyed steels, which have one part of the carbon combined in the carbides at the processing temperature. These carbides in steel are mostly stable carbides of chromium, tungsten and other carbide-forming elements. It is necessary to determine how much of the total carbon is in solid solution in the austenite, because only atomic carbon participates in the process. Isothermic diagrams provide a quantitative presentation and enable identification of the carbon distribution and the distribution of other elements in the austenite and carbide. According to the principles of physical chemistry, the gradient of the

chemical potential of the diffusing elements is the driving force of the diffusion processes. The concept, which states that thermodynamic activity of carbon in austenite controls the process of diffusion of carbon, has been confirmed in the carburizing process<sup>6</sup>. At constant temperature, instead of the chemical potentials, thermodynamic activities of the diffusing elements may be used. Numerous authors have investigated both the two-component Fe-C system and multi-component systems for the thermodynamic activity of carbon within austenite. The Thermodynamic activity of carbon depends on the chemical composition of the steel and the processing temperature. There are empirical equations for the quantitative influences<sup>7,8,9</sup>.

$$\log a_c = \frac{2300}{T} - 2.21 + 0.15 \cdot \%C + \log \%C \quad (1)$$

$$\frac{\log a_c^{alloy}}{\log a_c^{Fe-C}} =$$

$$0.055 \cdot \%Si - 0.013 \cdot \%Mn - 0.04 \cdot \%Cr + 0.014 \cdot \%Ni - 0.013 \cdot \%Mo - 0.102 \cdot \%V - 0.014 \cdot \%Al - 0.006 \cdot \%Cu + 0.22 \cdot \%N \quad (2)$$

The thickness of the diffusion layer for most diffusion processes increases in proportion to the square root of the processing time and can be calculated using the equation:

$$d^2 = k \cdot t \quad (3)$$

where  $d$  is the thickness of the layer in m;  $k$  is the layer growth-rate constant in  $m^2/s$  and  $t$  is processing time in s.

The layer growth-rate constant depends on the processing temperature, since for heat-activated processes the exponential relationship of growth rate according to the Arrhenius equation is valid:

$$k = k_0 \cdot e^{-\frac{Q}{R \cdot T}} \quad (4)$$

where  $k_0$  is the frequency factor in  $m^2/s$ ;  $Q$  is the activation energy of the process in J/mol;  $R$  is the gas constant in J/mol K and  $T$  is the absolute temperature measured in K.

Taking the logarithm of the Arrhenius equation the following expression is obtained:

$$\ln k = \ln k_0 - \left(\frac{Q}{R}\right) \cdot \left(\frac{1}{T}\right) \quad (5)$$

It provides the possibility to graphically determine the activation energy of the process for the formation of vanadium carbide ( $Q$ ) and the frequency factor ( $k_0$ ) using a " $\ln k - 1/T$ " diagram. The intersection of " $\ln k$ " in the " $\ln k - 1/T$ " diagram determines the value of the frequency factor ( $\ln k_0$ ) and the slope of the  $Q/R$  line determines the activation energy of the process ( $Q$ ).

### 3 EXPERIMENTAL DETAILS

Since data relating to values of the activation energy of the process ( $Q$ ) and the frequency factor ( $k_0$ ) for the vanadizing process are not available in the literature, three different carbon steels of grades DIN: Ck 45, Ck 60 and C 105 W1 have been investigated. The chemical composition of the steels was determined by bulk spectroscopic analysis using glow discharge. The results are shown in **Table 1**.

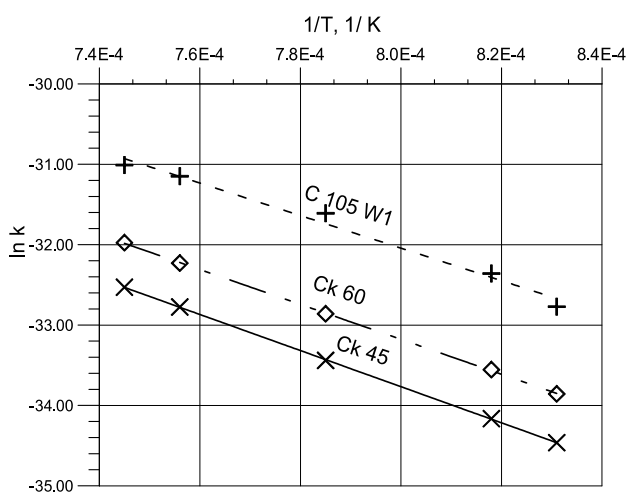
**Table 1:** Chemical analysis of the tested steels

**Tabela 1:** Kemična analiza preizkušanih jekel

Steels grade	C %	Si %	Mn %	S %	P %
Ck 45	0.49	0.33	0.69	0.027	0.013
Ck 60	0.68	0.27	0.87	0.025	0.014
C 105 W1	0.98	0.15	0.25	0.024	0.013

The temperature and duration of the vanadizing process were determined according to the model for a central composite experiment, which has certain advantages in planning experimental work for heat-activated processes<sup>10</sup>. In accordance with the experimental plan, the following temperatures were selected: 930, 950, 1000, 1050 and 1070 °C, and times: 60, 110, 240, 370 and 420 minutes. Vanadizing is performed in a salt bath for forming the carbide layer, which was developed in the course of previous studies<sup>4</sup>. After vanadizing process, the samples were cut in a direction perpendicular to the carbide layer and prepared for micrographic testing. The depth of the vanadium-carbide layer on the metallographically prepared samples was measured with a LECO 2001 image analyser.

From the measured thicknesses of the vanadium carbide, values for the carbide-layer growth-rate constant ( $k$ ) at the temperatures 930, 950, 1000, 1050 and 1070



**Figure 2:** Relationship between the carbide-layer growth-rate constant and the absolute temperature for the tested steels

**Slika 2:** Zveza med konstanto rasti karbidne plasti in absolutno temperaturo za preizkušena jekla

°C were calculated for different processing times, in accordance with the parabolic equation (3).

The results of the average calculated values of the carbide-layer growth-rate constant i.e. the relationship between the constant of the carbide-layer growth rate ( $\ln k$ ) and the reciprocal values of the absolute temperature ( $1/T$ ) is graphically presented for the three tested steels in **Figure 2**.

From the equations of the lines in **Figure 2**, the values of activation energy ( $Q$ ) and the frequency factor ( $k_0$ ) were calculated for the tested steels. The obtained values are shown in **Table 2**.

**Table 2:** Frequency factor ( $k_0$ ) and activation energy ( $Q$ ) for the vanadium-carbide forming process

**Tabela 2:** Faktor frekvenc ( $k_0$ ) in aktivacijska energija ( $Q$ ) procesa nastajanja vanadijeva karbida

Steels grade	$k_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )
	930 do 1070 °C	930 do 1070 °C
Ck 45	$1.3011 \cdot 10^{-7}$	186.670
Ck 60	$1.3299 \cdot 10^{-7}$	180.090
C 105 W1	$1.6278 \cdot 10^{-7}$	169.982

The starting point for setting up the mathematical model is the assumption that the driving force for the process of formation of the vanadium-carbide layer is the gradient of the chemical potential of carbon ( $\mu_c$ ), as has been confirmed in other diffusion processes, for example in carburizing process. Thus, the thermodynamic activity of carbon ( $a_c$ ) in austenite has the most significant influence on the kinetics of formation for the vanadium-carbide layer. Using such an approach, a mathematical model for the vanadizing of steels is developed, providing the possibility to determine the thickness of a layer or the required processing time for a given composition of steel and a particular processing temperature<sup>11</sup>. The model is based on solving Arrhenius' equation and the parabolic relationship between the layer thickness and the processing time. For solving Arrhenius' equation, i.e. calculating the layer growth-rate constant, the relationship between the activation energy of the process and the thermodynamic activity of carbon, as well as the relationship between the frequency factor and the thermodynamic activity of the carbon have been established. **Table 3** shows the variation of the thermodynamic activity of carbon depending on the temperature for the three tested steels.

**Table 3:** Relationship between thermodynamic activity of carbon and the temperature of the process for the three tested steels

**Tabela 3:** Razmerje med aktivnostjo ogljika in temperaturo za tri preizkušena jekla

Steels grade	thermodynamic activity of carbon, $a_c$				
	930 °C	950 °C	1000 °C	1050 °C	1070 °C
Ck 45	0.292	0.272	0.229	0.196	0.185
Ck 60	0.433	0.303	0.340	0.290	0.273
C 105 W1	0.692	0.644	0.543	0.464	0.437

Applying the above mentioned expressions, an algorithm and flow chart have been designed for calculating the time required for the vanadizing process to produce a layer of certain thickness, or the thickness of the layer for a certain processing time. Using the flow chart and the MATCAD THE software package, a computer program has been developed, providing an easy method for calculating the mentioned values, depending on the chemical composition of steel and the temperature of the process. The second version of the program offers the possibility to determine the required processing time for obtaining a predefined depth of carbide layer for a particular processing temperature.

Since the reported mathematical model for the formation of the vanadium-carbide layer is based on the thermodynamic activity of carbon, the mathematical model is also applicable to the low-alloyed steels. To test the model, vanadizing of samples of steel grades Ck 60 (0.68 %C, 0.27 %Si, 0.87 %Mn) and 55 Si 7 (0.54 %C, 1.56 %Si, 0.71 %Mn) at 1000 °C has been performed. The steels were selected because they have approximately the same thermodynamic activity of carbon at 1000 °C. The chemical composition of the steels is determined by the spectroscopic method based on glow discharge. After 4 hours at 1000 °C, the samples were metallographically prepared. The thickness of the carbide layers was measured using a LECO 2001 image analyser. The carbide-layer thickness results, calculated using the mathematical model and measured on metallographic samples, are presented in **Table 4**.

**Table 4:** Comparison of calculated and experimentally determined carbide-layer thickness

**Tabela 4:** Primerjava izračunanih in eksperimentalno dobljenih vrednosti debelin karbidne plasti

Steel grade	Ck 60	55 Si 7
Chemical composition	0.68 %C, 0.27 %Si, 0.87 %Mn	0.54 %C, 1.56 %Si, 0.71 %Mn
$a_c$ at 1000 °C	0.341	0.334
Thickness of layer, Experimental (µm)	8.9	8.8
Thickness of layer, Calculated (µm)	9.0	8.8

The obtained results for the layer thickness indicate that the model is also applicable for some alloyed steels and confirms the starting point of the model, that the driving force of the process is the chemical potential of

the carbon in the steel and not the content of carbon. Although they have different chemical compositions, but similar thermodynamic activities of carbon at 1000 °C ( $a_c = 0,341$  of Ck 60 and 0, 334 of 55 Si 7), the thickness of the layer for the same temperature and processing time was approximately the same.

#### 4 CONCLUSION

The Speed of carbide-layer growth depends on the composition of the bath, the temperature and the length of the process, but it also depends on the chemical composition of the treated steel. The Thermodynamic activity of the carbon in the austenite at the particular temperature is the most important factor. Based on the principles of physical chemistry, a mathematical model was developed, incorporating the effects of the chemical composition of the steel, temperatures and the time of the diffusion-formation process used to produce carbide layers. The model has been developed using vanadizing as an example. A Comparison of computer-calculated values and results obtained by experiment indicates that the model has been properly founded. It is valid for low-alloyed steels and steels having a monophase austenitic structure at the processing temperatures. This model is not applicable for high-carbon and high-alloyed steels which still have undissolved carbides in the austenite at the temperature of carbide-layer formation.

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