A Model of Vanadium Carbide Growth on Steel Surfaces Obtained by Thermo Reactive Deposition

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In this article, the mathematical model of vanadium carbide growth was established on the basis of principles of physical chemistry. 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. An analysis of the relationship between the thickness of the vanadium carbide layer and the salt bath temperature, immersion time, and chemical composition of the substrate was conducted. A comparison of the model-calculated values and the results obtained by the experiment indicates that the model has been properly founded.

INTRODUCTION

Some of the various methods used by researchers to increase the life of forming dies and machining tools are the thin film hard coatings and the thermal diffusion processes. The thin film hard coatings are nitride, carbide, or carbonitride layers with a thickness of 3–10 μm. They are conventionally applied by chemical vapor deposition (CVD) and physical vapor deposition (PVD). CVD can lead to a heavy distortion of the treated parts, and PVD requires expensive and complicated equipment. The process of forming carbide layers on steels by the thermal diffusion (TD) process, which is also referred to as the thermoreactive deposition/diffusion (TRD, Springfield, OH) process and the Toyota diffusion process is of growing importance for industrial applications because of its advantages over other processes. The procedure is usually performed by immersing parts in a fused salt bath of special composition that contains the carbide-forming element vanadium but might also contain some other elements, e.g., Cr, Ti, Ta, and Nb,[1,2] for 1–10 h, whose temperature may be selected to correspond to the steel austenitizing temperature, permitting the steel to be quenched directly after cooling.[3] At elevated temperatures from 900°C to 1100°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 or other carbon-containing materials such as nickel and cobalt alloys, cemented carbides, and steelbonded carbides.[4] Entering the austenite lattice, the vanadium diffuses from the surface into the substrate, up to the solubility limit, which depends on the temperature and chemical composition of the 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 toward 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 toward the surface by diffusion. As carbon from the austenite is used in forming the vanadium carbide (VC), its concentration beneath the carbide layer is substantially lower than that of the substrate.[5,6] As a consequence, carbon is the most important element for the formation of carbides. As one of the hardest transition metal carbides,[7,8] VC coating obtained by the TRD process is commonly used in tribological applications. The performance of coatings is rather sensitive to the microstructures. For instance, columnar grains are anisotropic and the grain boundaries become the sites for crack initiation, resulting in premature failure of coatings, whereas the fine equiaxed grains throughout the coating are randomly oriented and can improve its tribological performance.[9] The different microstructures of a VC coating may be induced by the significant composition difference among substrates with a carbon content of 0.3 wt% or higher.[10] In fact, both columnar and equiaxed grains were observed in the VC coatings obtained by the TRD process.[11]
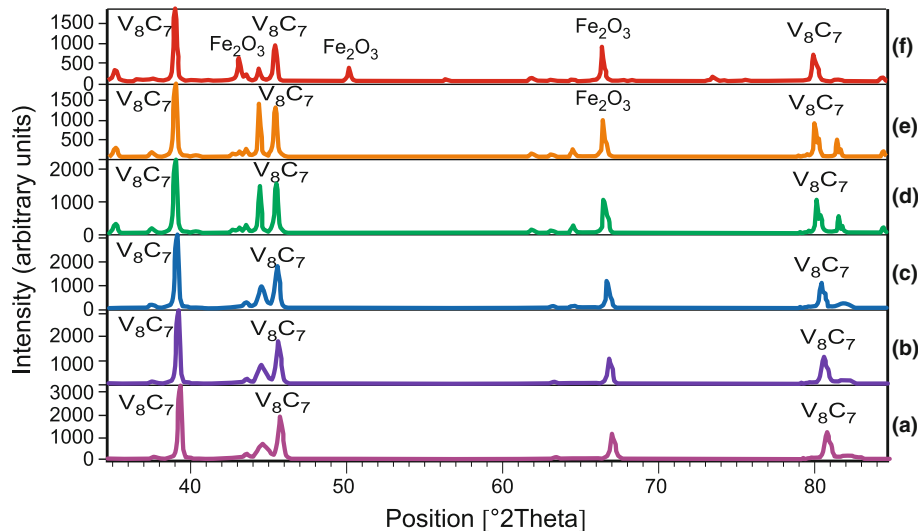
Fig. 1. X-ray diffraction patterns of the carbide layer taken from a different examination temperature: (a) 20°C, (b) 250°C, (c) 400°C, (d) 620°C, (e) 780°C, and (f) 870°C.[16]

Several authors have studied the growth kinetics of coating on different steels as DIN 1.2367, AISI 1040, and AISI D2.[12–15] With the aim of better understanding the process and improving applications, research into the metallurgical fundamentals of the process, the mathematical model of kinetics of the carbide coating growth by TRD process, is established on the basis of the unsteady diffusion theory and compared with the experiment results to prove the mathematical model. The analysis of the relationship between the thickness of the vanadium carbide layer and the immersion time, salt bath temperature, and type of substrate was carried out. The carbide layer has a high hardness and a high wear resistance to abrasion, adhesion, and tribo-corrosion, which is particularly important for machine parts and tools. The thickness of the layer is in the range 1–15 μm. The vanadium carbide layer has high thermal stability, more than 800°C, as is shown in Fig. 1.

A MODEL OF 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 complex. The vanadium carbide coatings obtained by TRD process consisted of single-phase VC.[17,18] However, the crystallographic structure of vanadium carbide is rather complex because vanadium carbide is one kind of nonstoichiometric transition metal carbide and has a wide region of homogeneity ($VC_{0.65}$–$VC_{0.90}$).[19,20]

The formation of the vanadium carbide layer type $VC_{0.88}$ 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. The TRD

process is different from the conventional case-hardening techniques, in which the specific elements (C and/or N) diffuse into the substrate for hardening.[21] The TRD process results in the outward growth of the coating on the substrate surface.[18] At the steel surface, vanadium combines 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. Figure 2a shows the typical microstructure of the cross section of the vanadium carbide layer, in which both the vanadium carbide layer and the steel substrate can be clearly observed. Figure 2b shows the Auger electron spectroscopy (AES) spectrum of iron, carbon, and vanadium in, and below, the vanadium carbide layer.

It is obvious that the coating is rich in vanadium and carbon but scarce in iron. At the coating/substrate interface, a sharp decrease of both vanadium and carbon contents along with a dramatic increase in iron content is observed, which indicates that no obvious interdiffusion of V and Fe atoms occurred. The absence of substantial interdiffusion is probably the reason for the formation of the distinct and flat interface without transition zone. Similar flat interfaces were also observed in the research on NbC,[23] TiN,[24] VC,[18,25,26] and V(C, N)[27] coatings. The kinetics of the process of carbide-layer formation and the thickness of the formed layer depend on the temperature and the immersion time and on the content of carbon and alloying elements in the steel. Previous research suggests that the carbide layer
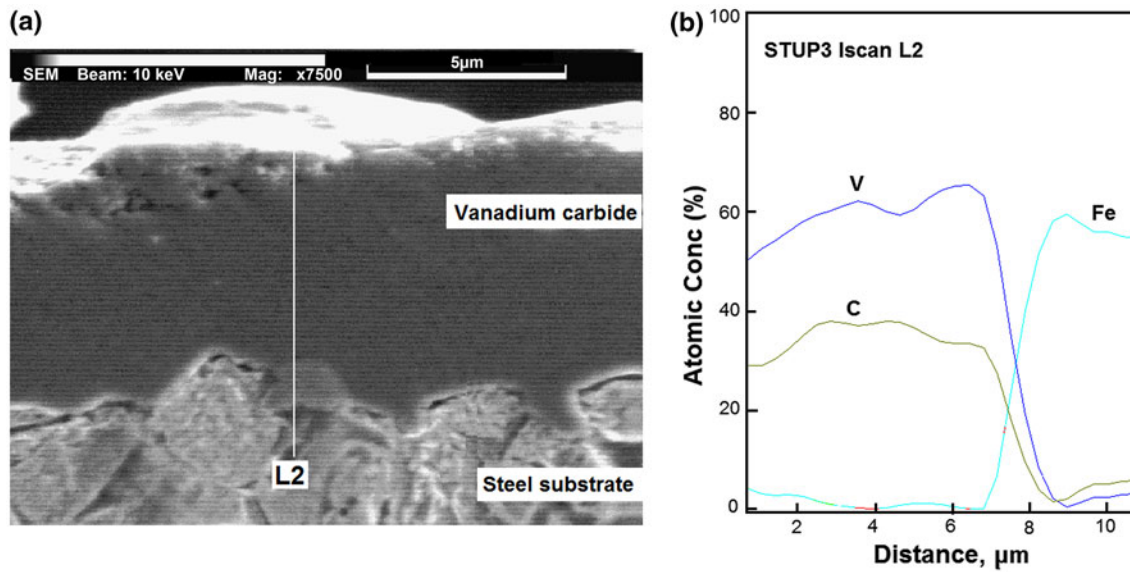
Fig. 2. (a) Scanning electron micrograph of a cross section and (b) the results of the AES spectrum line of Fe, C, and V measured along line L1 of AISI D2 steel vanadized at 1000°C for 4 h.[22]
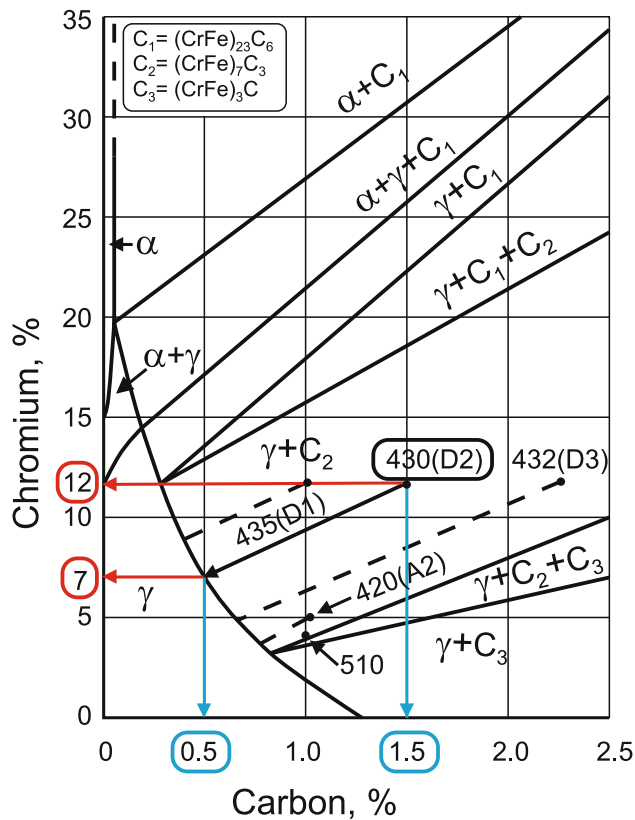

Fig. 3. Isothermal cross section of Fe-C-Cr system at 1000°C.[28]

steel. This is of particular importance for high-carbon, high-alloyed steels, which have one part of the carbon 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 (i.e., interstitially dissolved) carbon participates in the process. Isothermal diagrams provide a quantitative presentation and enable identification of the carbon distribution and the distribution of other elements in the austenite and carbide. Carbon is effective in the process only in this form, i.e., interstitially dissolved in the austenite. A quantitative presentation and a possibility of determining carbon distribution (and the distribution of other elements) are provided by the isothermal phase diagrams. By an example of isothermal cross section in the system Fe-C-Cr in Fig. 3, it is demonstrated how the concentration of carbon and chromium dissolved in the austenite can be determined in the phase diagram for a given composition of steel at the temperature of 1000°C. This case demonstrates that in the case of the ledeburitic tool steel of D2 grade (1.5% C, 12% Cr), only 0.5% of carbon is contained in the austenite during vanadizing at the temperature of 1000°C, whereas the balance of carbon is combined into the M_7C_3 carbide. Moreover, it should be noted that only 7% of chromium is dissolved in the austenite, which according to principles of physical chemistry affects the thermodynamic activity of carbon in austenite.

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 thermo-

thickness is linearly proportional to the carbon concentration in the steel.[18] However, to analyze 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

dynamic activity of carbon in austenite controls the process of diffusion of carbon, has been confirmed in the carburizing process.[29] 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 multicomponent systems for the thermodynamic activity of carbon in austenite. The thermodynamic activity of carbon depends on the chemical composition of the steel and processing temperature. There are empirical equations (Eqs. 1 and 2) for the quantitative influences:[30–32]

$$\log a_C = \frac{2300}{T} 2.21 + 0.15 \cdot \%C + \log \%C \qquad (1)$$

$$\frac{\log a_C^{alloy}}{\log a_C^{Fe-C}} = 0.055 \cdot \%Si - 0.013 \cdot \%Mn - 0.04 \cdot \%Cr$$

$$+ 0.014 \cdot \%Ni - 0.013 \cdot \%Mo$$

$$- 0.012 \cdot \%V - 0.014 \cdot \%Al$$

$$- 0.006 \cdot \%Cu + 0.22 \cdot \%N \qquad (2)$$

The thickness of the diffusion layer, as in many diffusion treatments, increases in proportion to the square root of the processing time and can be expressed by the equation:

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

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

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

$$k = k_0 \cdot e^{-\frac{Q}{RT}} \qquad (4)$$

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:

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

It provides the possibility to determine graphically 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).

EXPERIMENTAL

As the 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 I.

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.[33] In accordance with the experimental plan, the following temperatures were selected: 930°C, 950°C, 1000°C, 1050°C, and 1070°C, and times: 1.0, 1.8, 4.0, 6.2, and 7.0 h (Fig. 4). Vanadizing is performed in a salt bath for forming the carbide layer, which was developed in the course of previous studies.[6]

After the 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 (St. Joseph, MI) image analyzer. From the measured thicknesses of the vanadium carbide layer,

Table I. Chemical analysis of the tested steels

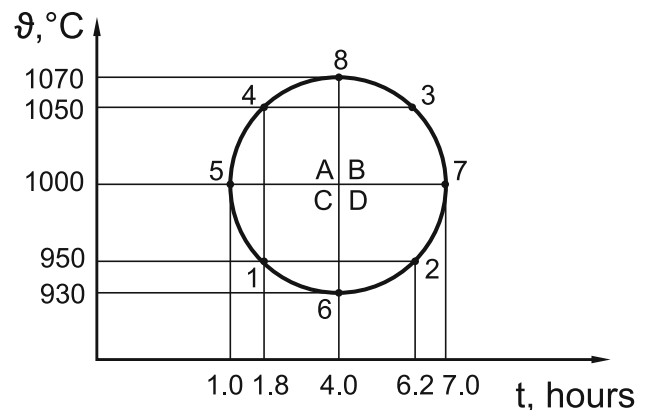| Steels grade	%C	%Si	%Mn	%S	%P
Ck 45	0.49	0.33	0.69	0.027	0.013
Ck 60	0.68	0.27	0.87	0.025	0.014
C 105 W1	0.98	0.15	0.25	0.024	0.013

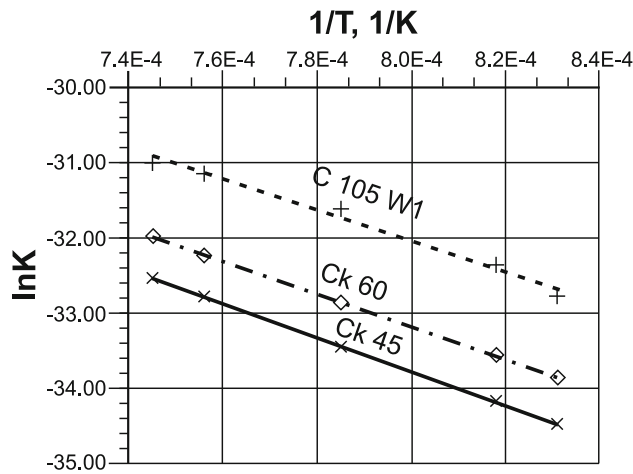Fig. 4. The central composite design of experiments.

1/T, 1/K

Fig. 5. Relationship between the carbide layer growth-rate constant and the absolute temperature for the tested steels.

Table II. Frequency factor (k_0) and activation energy (Q) for the vanadium-carbide forming process

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

Table III. Relationship between thermodynamic activity of carbon and the temperature of the process for the three tested steels

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

values for the carbide layer growth-rate constant (k) at the temperatures 930°C, 950°C, 1000°C, 1050°C, and 1070°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 Fig. 5.

From the equations of the lines in Fig. 5, 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 II.

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 (μ_c), as has been confirmed in other diffusion processes, for example, in the 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.[34] The model is based on solving the Arrhenius equation and the parabolic relationship between the layer thickness and the treating time. For solving the 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, has been established. Table III shows the variation of the thermodynamic activity of carbon depending on the temperature for the three tested steels.

Applying the previously mentioned expressions, an algorithm and flowchart have been designed for calculating the time required for the vanadizing process to produce a layer of certain thickness (Fig. 6). Using the flowchart and the MATLAB (Natick, MA) 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.

As 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 ware 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 h at 1000°C, the samples were metallographically prepared. The thickness of the carbide layers was measured using a LECO image analyzer, and the results are shown in Fig. 7a and b. The carbide layer thickness results, calculated using the mathematical model and measured on metallographic samples, are presented in Table IV. Figure 8a and b shows the optical microscope image of tested steels.
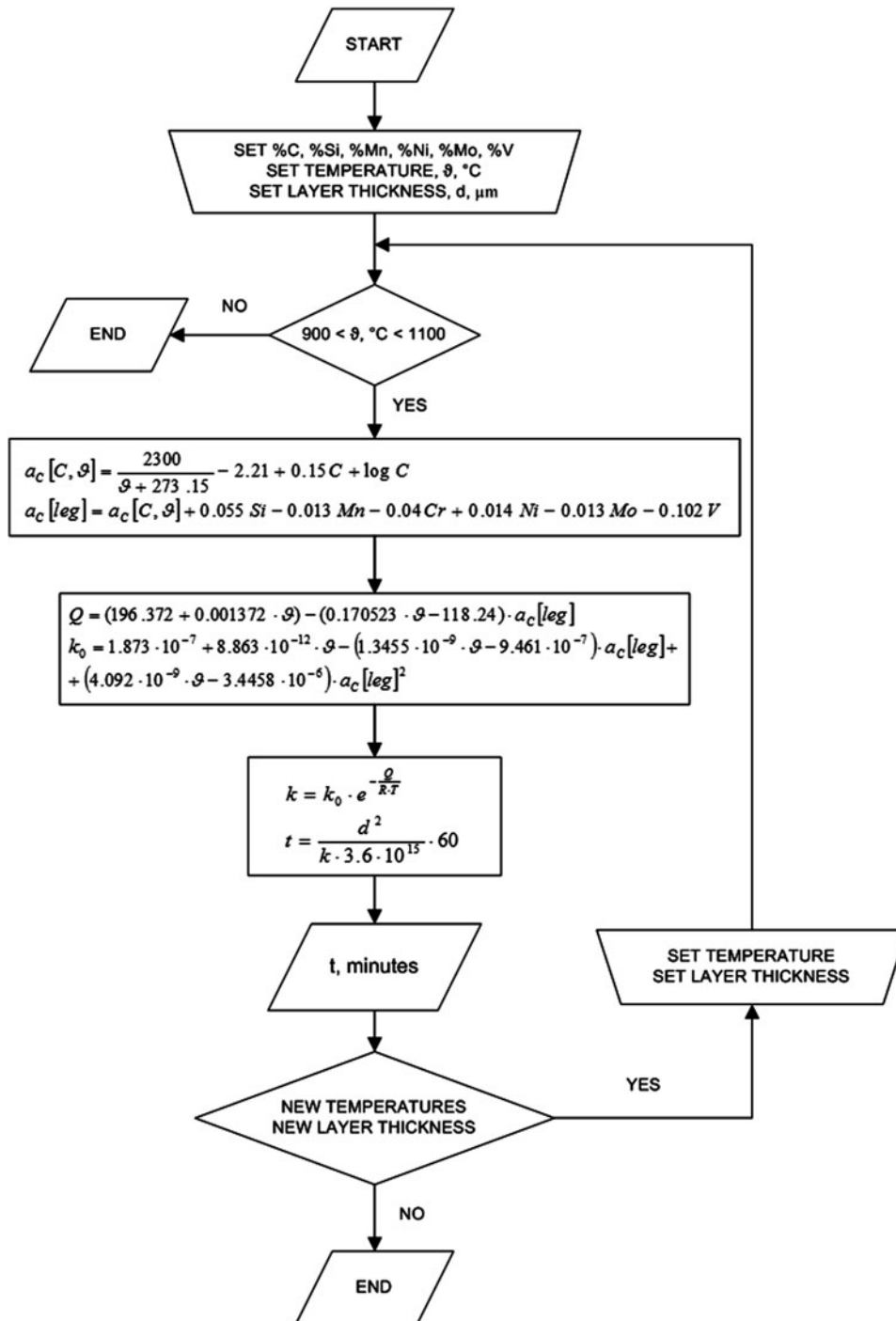
Fig. 6. The flowchart for calculation of the time required for the vanadizing process to produce a layer of certain thickness.

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. The obtained results also agree compared with the mathematical model developed by Xiujuan et al.[35]
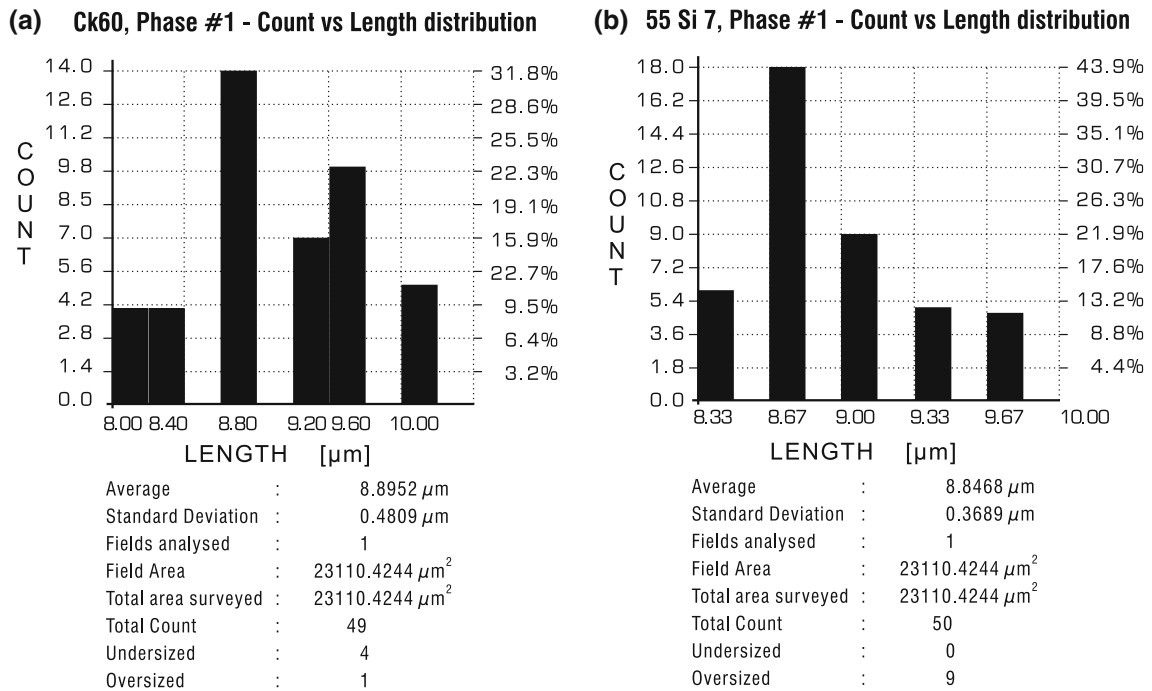
(a)   Ck60, Phase #1 - Count vs Length distribution

Average	:	8.8952 μm
Standard Deviation	:	0.4809 μm
Fields analysed	:	1
Field Area	:	23110.4244 μm^2
Total area surveyed	:	23110.4244 μm^2
Total Count	:	49
Undersized	:	4
Oversized	:	1

(b)   55 Si 7, Phase #1 - Count vs Length distribution

Average	:	8.8468 μm
Standard Deviation	:	0.3689 μm
Fields analysed	:	1
Field Area	:	23110.4244 μm^2
Total area surveyed	:	23110.4244 μm^2
Total Count	:	50
Undersized	:	0
Oversized	:	9

Fig. 7. The thickness of carbide layers on (a) Ck 60 and (b) 55 Si7 steel measured using a LECO image analyzer.

Table IV. Comparison of calculated and experimentally determined carbide layer thickness

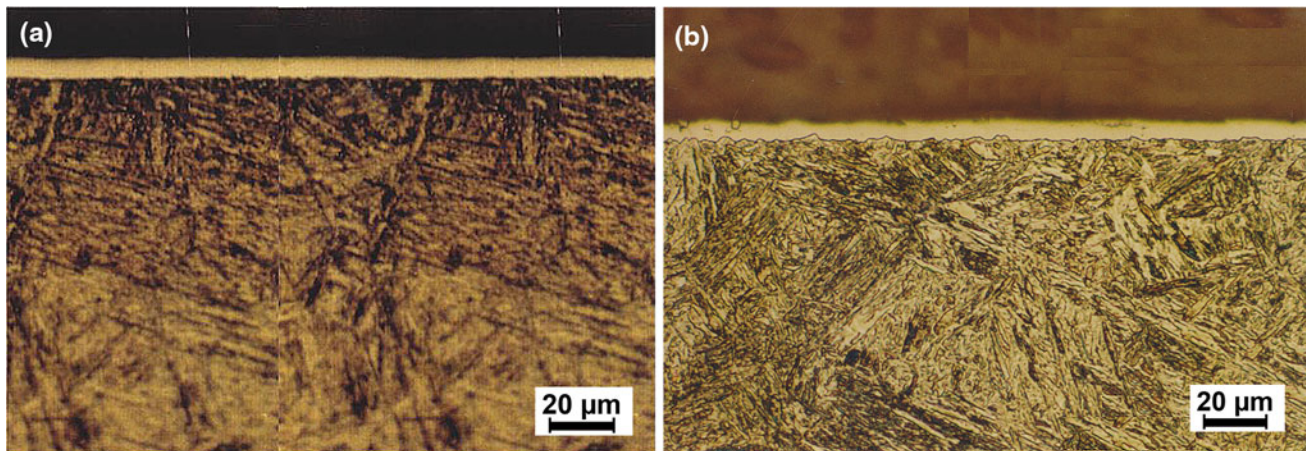| Steel grade	Ck 60	55 Si 7
Chemical composition	0.68%C, 0.27%Si, 0.87%Mn	0.54%C, 1.56%Si, 0.71%Mn
a_C at 1000°C	0.341	0.334
Thickness of layer, experimental (μm)	8.9	8.8
Thickness of layer, calculated, (μm)	9.0	8.8

Fig. 8. The optical cross-sectional micrographs of (a) Ck 60 and (b) 55 Si 7, vanadized 4 h at 1000°C, etched in NITAL.

CONCLUSION

The kinetics of carbide layer growth depends on the composition of the bath, the temperature, and the duration of the process, but it also depends on the chemical composition of the treated steel. A complex effect of the content of carbon and alloying elements on the thermodynamic activity of the

carbon in austenite and on the temperatures of the process plays a major role in the determination of technological parameters to enable the forming of required carbide layer thickness. Based on the principles of physical chemistry, a mathematical model was developed, incorporating the effects of the chemical composition of the steel, temperatures, and time of the diffusion-formation process used to produce carbide layers. The model has been developed using the vanadizing process 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 that still have undissolved carbides in the austenite at the temperature of carbide layer formation.

ACKNOWLEDGEMENTS

REFERENCES

1. H. Fujita and T. Arai, *Proc. 4th Int. Congress of IFHT* (Berlin, Germany, 3–7 June 1985), pp. 1109–1124.
2. S.B. Fazluddin, A. Koursaris. C. Ringas, and K. Cowie, *Miner. Met. Mater. Soc.* 45 (1993).
3. T. Arai and N. Komatsu, *Proceedings of the 18th International Machine Tool Design and Research Conference*, London, U.K., Sept. 14–16, 1977, p. 225.
4. T. Arai and H.M. Glaser, *Proc. Conf. Manufacturing Strategies*, vol. 6 (Cleveland, OH: Precision Metalforming Association, 1996), p. 549.
5. M. Stupnišek and B. Štefotič, *Proceedings of YUSTOM '86*, Plitvička jezera, May 20–23, 1986, pp. 323–330.
6. B. Štefotič, J. Vižintin, F. Grobelšek, and M. Stupnišek, *Proceedings "Tribologija v teoriji in praksi"*, Ljubljana, 1996, pp. 233–241.
7. H.L. Liu, J.C. Zhu, Y. Liu, and Z.H. Lai, *Mater. Lett.* 62, 3084 (2008).
8. J.H. Ma, M.N. Wu, Y.H. Du, S.Q. Chen, J. Ye, and L.L. Jin, *Mater. Lett.* 63, 905 (2009).
9. Y.H. Chen, K.W. Lee, W.A. Chiou, Y.W. Chung, and L.M. Keer, *Surf. Coat. Technol.* 146–147, 209 (2001).
10. C.K.N. Oliveira, C.L. Benassi, and L.C. Casteletti, *Surf. Coat. Technol.* 201, 1880 (2006).
11. T. Arai and S. Moriyana, *Thin Solid Films* 249, 54 (1994).
12. S. Sen, *Vacuum* 79, 63 (2005).
13. F.S. Chen and K.L. Wang, *Surf. Coat. Technol.* 115, 239 (1999).
14. M. Aghaie-Khafri and F. Fazlalipour, *Surf. Coat. Technol.* 202, 4107 (2008).
15. X.J. Liu, H.C. Wang, D.W. Li, and Y.X. Wu, *Surf. Coat. Technol.* 201, 2414 (2006).
16. B. Matijević and M. Stupnišek, *Surf. Eng.* 23, 1 (2007).
17. M. Aghaie-Khafri, F. Fazlalipour, and J. Phys, *Chem. Solids* 69, 2465 (2008).
18. T. Arai, *J. Heat. Treat.* 1, 15 (1979).
19. X.G. Lu, M. Selleby, and B. Sundman, *Acta Mater.* 55, 1215 (2007).
20. V.N. Lipatnikov, W. Lengauer, P. Ettmayer, E. Keil, G. Groboth, and E. Kny, *J. Alloys Compd.* 261, 192 (1997).
21. U. Sen, *Mater. Chem. Phys.* 86, 189 (2004).
22. B. Matijević and M. Stupnišek, *Mater. Tehnol.* 34, 237 (2000).
23. A. Bendavid, P.J. Martin, T.J. Kinder, and E.W. Preston, *Surf. Coat. Technol.* 163–164, 347 (2003).
24. U. Sen, *Vacuum* 75, 339 (2004).
25. M. Aghaie-Khafri and F. Fazlalipour, *J. Phys. Chem. Solids* 69, 2465 (2008).
26. X.S. Fan, Z.G. Yang, C. Zhang, Y.D. Zhang, and H.Q. Che, *Surf. Coat. Tehnol.* 205, 641 (2010).
27. B. Chicco, W.E. Borbidge, and E. Summerville, *Mater. Sci. Eng. A* 266, 62 (1999).
28. G.A. Roberts, J.C. Hamaker, and A.R. Johnson, *Tool Steels* (Materials Park: ASM, 1961).
29. M. Stupnišek, B. Koroušić, and B. Dobovišek, *Proc. 3rd Int. Congress of IFHT*, vol. 7, Shanghai, Nov. 7–11, 1983, pp. 23–28.
30. B. Koroušić, *Rudarsko-Metalurški Zbornik* 40, 5 (1989).
31. F. Neuman and B. Person, *Härterei-Technische Mitteilungen* 23, 296 (1966).
32. S. Gunnarson, *Härterei-Technische Mitteilungen* 22, 293 (1967).
33. W.G. Cohran and G.M. Cox, *Experimental Designs* (New York, NY: Wiley, 1957).
34. B. Matijević (Ph.D. Dissertation, University of Zagreb, Zagreb, Croatia, 1997).
35. L. Xiujuan, W. Huachang, L. Dongwei, and W. Yanxi, *Surf. Coat. Tehnol.* 201, 2414 (2006).