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BORIDE LAYER GROWTH KINETICS ON X90CrMoV-18 STEEL

KINETIKA RASTI BORIDNE PLASTI NA JEKLU VRSTE X90CrMoV-18

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Boronizing is a type of thermal diffusion with the primary goal of increasing the surface hardness, wear and corrosion resistance. The wear resistance of boronized parts depends on the type of borides that form on the steel surface and their thickness. This study investigated the properties of boride layers formed on X90CrMoV-18 martensitic stainless steel, using pack boronizing carried out in a temperature range of 850–1000 °C and in durations of (1, 3 and 5) h. Results indicate a difference in the boride layer thickness of 3–80 μm and volume share of boride phases depending on the temperature and time of boriding. From the boriding compound depth, values of the frequency factor and activation energy were determined using the Arrhenius equation. With these values, the parabolic equation for predicting the growth rate of a boride layer was formulated and validated for different times and temperatures of boriding.

Keywords: boronizing, martensitic stainless steel X90CrMoV-18, Arrhenius equation

Boriranje je vrsta toplotne obdelave oziroma difuzijskega postopka katerega primarni namen je povečati trdoto površine in s tem tudi povečati abrazijsko odpornost in korozijsko obstojnost zlitine. Odpornost proti obrabi boriranih delov je odvisna od vrste boridov, ki nastanejo na jekleni površini in njeni debelini. V tem članku avtorji opisujejo raziskavo boridne plasti, nastale na martenzitnem nerjavnem jeklu vrste X90CrMoV-18. Pri tem so uporabili 1, 3 in 5 urno paketno boriranje v temperaturnem območju med 850 °C in 1000 °C. Rezultati raziskave so pokazali, da so nastale boridne plasti debeline od 3 μm pa do 80 μm. Volumski delež boridnih faz je bil odvisen od temperature in časa boriranja. Avtorji so s pomočjo frekvenčnih faktorjev debeline nastalih plasti in Arrheniusove enačbe določili aktivacijsko energijo difuzijskega procesa. S temi vrednostmi so oblikovali parabolično enačbo za napoved hitrosti rasti boridne plasti, ki so jo nato tudi ovrednotili glede na eksperimentalne čase in temperature boriranja.

Ključne besede: boriranje, martenzitno nerjavno jeklo vrste X90CrMoV-18, Arrhenius-ova enačba

1 INTRODUCTION

In general, there are two primary methods for enhancing the surface hardness of metals. One method is metal surface modification, using heat, diffusion of atoms, or mechanical modification of a material surface. The second method is the surface deposition of material on a metal surface using heat, chemical or mechanical mechanisms for the formation of a layer. Boronizing, also known as boriding, is one of the methods of thermo-chemical surface modification that relies on the introduction of boron atoms into a metal surface, leading to the creation of an interstitial solid solution and a hard boride layer on the metal surface. This layer has the primary goal of increasing the surface hardness, wear and corrosion resistance of different types of structural and tool steel. Pack boronizing an entire surface with powder, or boronizing only a certain segment of a surface with paste, are the most commonly used methods. These processes can be carried out at different temperatures ranging from 850 °C to 1050 °C in solid, liquid or gas active media with an annealing time of 1–8 h.[1,2] Boronizing with solid media (with powder or paste) is carried out by covering the workpieces with a layer of new and previously used powder in metal containers, which are heated in electric or gas furnaces. If the sealing of a metal container is done correctly, the heating can be carried out without a protective atmosphere, although for a successful formation of a boride layer, it is recommended to use a furnace with a protective gas atmosphere.

The boriding process consists of two thermal-chemical reactions: boride nucleation and boride layer growth. The first reaction occurs between the boron-rich active medium and the metal surface through the chemical interaction between the diffused atoms and the base metal. The rate of boride nucleation on the surface depends on the duration and temperature of boridation. The second reaction is controlled by boron diffusion into the surface layer of the metal and it determines the achieved thickness of the boride layer. Depending on the temperature, time and type of steel, different boride layers form on the steel surface. A surface layer obtained by boriding exhibits a distinctive saw-toothed morphology and can be composed of either a single-phase Fe_2B or a double-phase layer consisting of an outer phase of FeB and an inner phase of Fe_2B. While the FeB layer has a higher hardness of 1600–2100 HV compared to Fe_2B

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(1400–1600 HV), it is generally regarded as undesirable due to its brittleness. Additionally, because FeB and Fe_2B borides have distinct coefficients of thermal expansion, the interface between FeB and Fe_2B often experiences crack formation.[3] Along with the type of boride layer, the thickness of the achieved layer is also very important. Understanding the growth of a boride layer is important for predicting the part wear and scheduling maintenance. As with other thermally activated processes, the growth rate of a boride layer can be predicted by applying the Arrhenius equation, in which the activation energy and the diffusion frequency factor for the specific chemical composition of a borated steel should be experimentally determined. For some types of steel like C45, the boride layer growth rate and layer thickness depending on the time and temperature of the boronizing process are calculated and well presented in the literature.[1,4]

X90CrMoV-18 is a stainless martensitic steel that can be hardened and strengthened by heat treatment while retaining very good corrosion and wear resistance. Austenitization of this steel is carried out in a temperature range of 1000–1050 °C, which partially overlaps with the boronizing temperature range. Cooling after the austenitization can be carried out in oil, air or inert gas. These options for choosing heat treatment parameters make it suitable for the simultaneous application of surface boronizing and hardening of the entire volume. This work aims to investigate the kinetics of boronization of X90CrMoV-18 martensitic stainless steel. Powder boronization experiments, a microstructure analysis of the surface layer and hardness tests are conducted while the rate of growth of the layer and the activation energy of boron diffusion in X90CrMoV-18 steel are determined.

2 EXPERIMENTAL PART

In the presented study, X90CrMoV-18 steel was boronized in the Durborid 3 solid agent using a chamber furnace without an inert atmosphere at temperatures of 850–1000 °C for durations of (1, 3 and 5) h. To achieve a uniform temperature, samples were heated from room temperature inside the furnace. After the furnace achieved the boronizing temperature, one hour was added to the boronizing time to achieve the exact temperature on a sample surface due to the heat isolating properties of the boronizing agent. Then the samples were moved to a different furnace, with a temperature of 300 °C, to achieve a perlite carbide microstructure in the core of the samples. Due to the 18 % chromium present in X90CrMoV-18 steel, a martensite microstructure would have formed if the samples were cooled in air rather than in furnace. After boronizing, all samples were longitudinally cut in cross-section and prepared for metallographic examinations (ground using up to 2000-grit emery paper, alumina polished and etched with 3 % Nital). After metallographic preparation, the thickness of the boride layers was measured using light microscopy. Cross-section hardness was measured using a Vickers hardness tester. From the boriding compound depth, the values of frequency factor (d) and activation energy were determined using the Arrhenius equation. From the frequency factor and activation energy, the equation predicting the growth of the boride layer was determined. Results indicate the differences in the boride layer thickness and volume share of boride phases depending on the temperature and time of boriding.

3 RESULTS

3.1 Boriding

The boride layer formed on X90CrMoV-18 steel is compact, consisting of a dual layer of Fe_2B and FeB borides due to the high chromium content which accelerates the formation of dual boride layers compared to medium or low alloy steel. Due to the high chromium content, the boride layer does not exhibit saw-tooth morphology characteristics on low alloy steel. Although the boride layer thickens increases with an increase in the boronizing duration and temperature, the growth rate slows down with the increase in the duration, which corresponds with earlier studies.[5–7] To measure the thickness of boride layers and carry out other experimental measurements, 36 samples were boronized at temperatures of (850, 900, 950 and 1000) °C for (1, 3 and 5) h.

3.2 Hardness measurements and light microscopy

Table 1 shows different boride layer thicknesses (μm) achieved at different durations and temperatures of boronizing. Standard deviation (σ) is also included to indicate the degree to which the boride layer thickness varies from one temperature and duration to another.

Table 1: Boride layer thickness (μm) after different boriding times and temperatures

Temperature	t = 1 h	σ_{1h} (μm)	t = 3 h	σ_{3h} (μm)	t = 5 h	σ_{5h} (μm)
850 °C	3.10	± 1.61	7.40	± 1.31	11.40	± 2.04
900 °C	3.87	± 0.165	12.34	± 1.38	16.40	± 1.77
950 °C	4.61	± 0.860	24.33	± 3.42	42.28	± 1.78
1000 °C	11.20	± 1.14	48.24	± 2.17	80.50	± 1.18

Since the formation of boron layers does not use carbon, regions rich in carbon are present below the boride layer (carbon barrier). According to the metallographic examination and difference in the nital etching of FeB-Fe_2B layers (color difference), accumulation of carbon in the diffusion zone slows down the growth of the boride layer. Boride layers that form in 3 h or more appear to be dual layers consisting of FeB-Fe_2B (**Figure 1**). The pictures of the surface-layer microstructures were captured using an Olympus GX51 light microscope with a 200:1 magnification.

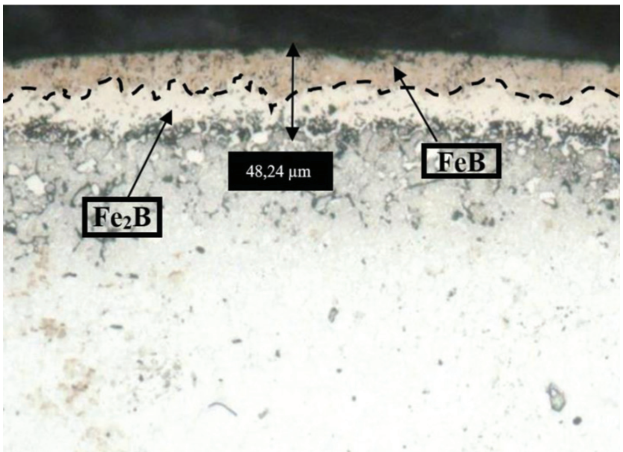

Figure 1: Color difference in the FeB-Fe_2B layer after etching in 3 % Nital (sample boronized at 1000 °C for 3h)

Figure 2 shows the morphologies of the boride layers achieved after 5 h of boronizing at temperatures of 850 °C (**Figure 2a**) and 1000 °C (**Figure 2b**). The thickness of the boride layer after 5 h at 850 °C is 11.40 µm. The thickness of the boride layer after 5 h at 1000 °C is 80.5 µm, consisting of Fe_2B, FeB and other alloying elements and boron compounds. Following the metallographic examination, cross-sectional microhardness was assessed at every 20 µm using the Vickers method (HV0.1), starting from the surface and extending to the sample's core. The boronizing hardness depth (BHD) was calculated as the distance from a sample's surface to the average depth of peaks and troughs of the Fe_2B compound. All samples exhibit a robust outer layer with its hardness exceeding 1300 HV0.1, while the core remains unchanged after boronizing. The hardness of the base material within the diffusion zone, between the teeth and boron layer, is higher than that of the core of samples. This phenomenon arises due to the elevated carbon content, a result of its suppression beneath the border layer.

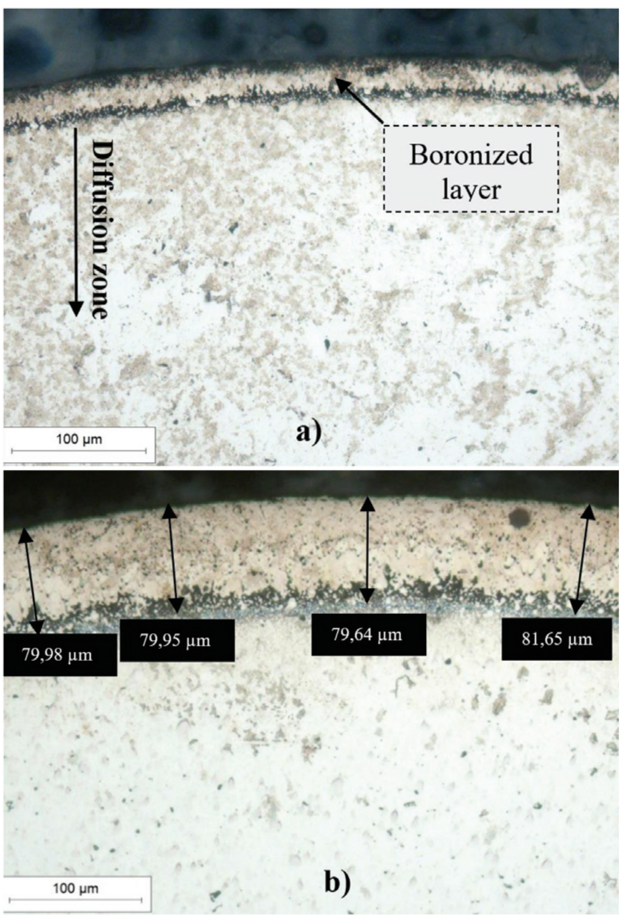

Figure 2: Microstructures of the boride layers after etching in 3 % Nital: a) boronizing for 5 h at 850 °C, b) boronizing for 5 h at 1000 °C

The hardness distribution across boronized samples, measured with a Tukon 2100B micro-Vickers testing instrument, is illustrated in **Figure 3**. The blue curve represents the hardness distribution of the sample boronized for 1 h at 1000 °C, the red curve refers to the hardness distribution on the sample boronized for 3 h at 1000 °C and the grey curve refers to the sample boronized for 5 h at 1000 °C. The thickness and morphology of the boride layers were influenced by the composition of the substrate material which contained alloying elements: chrome (Cr), molybdenum (Mo) and vanadium (V). These alloying elements present in X90CrMoV-18 enter the iron boride lattice, leading to modifications in the boron diffusivity. For instance, in the case of martensitic stainless steel, which has a high chromium (Cr) content, the boride layer contained less chromium compared to the substrate due to its limited solubility.[8,9] Consequently, the low solubility of the Cr element had a detrimental impact on the boriding process, slowing down the boride layer growth. Similar diffusion-limiting effects were observed with other elements such as nickel (Ni), aluminum (Al), copper (Cu), and so on.[10–12]

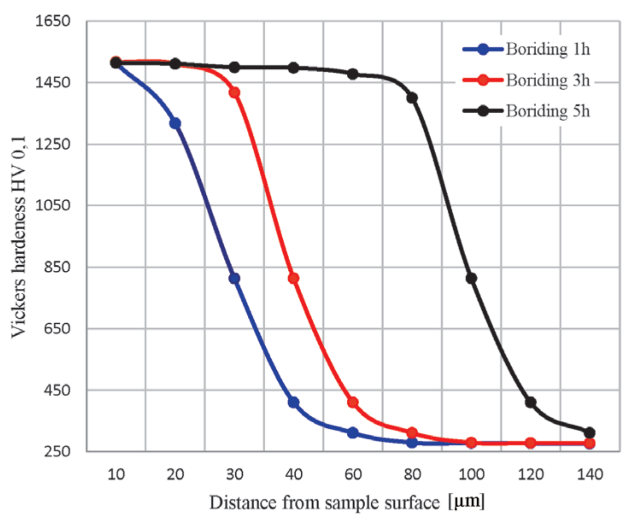

Figure 3: Hardness distribution for the samples boronized at 1000 °C for 1, 3 and 5 h

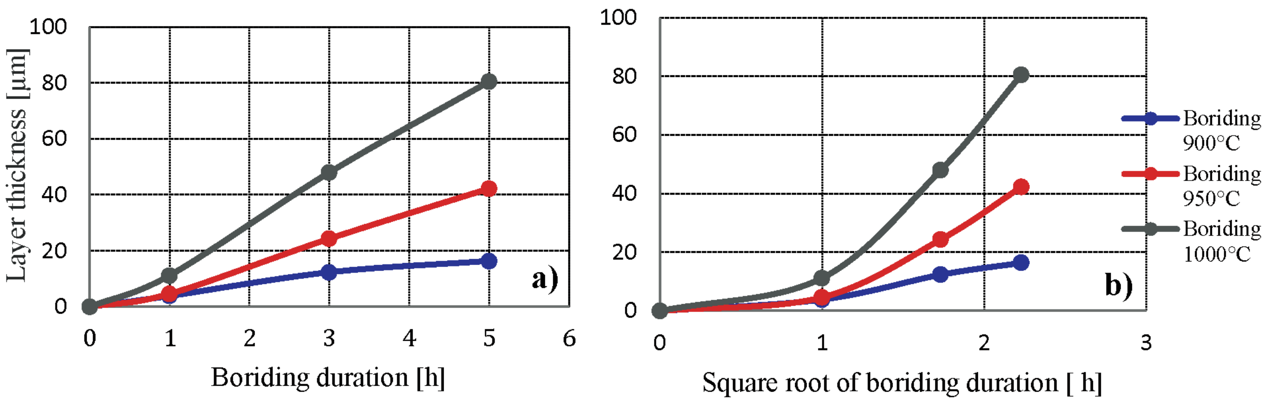

Figure 4: Boride layer thickness as a function of: a) time and b) square root of boronizing time

3.3 Kinetic studies

In this paper, boride layer growth kinetics is analyzed with the classical kinetic method based on the Arrhenius equation.[13–15] Most of diffusion process obeys the parabolic law described by:

$$d^2 = D\, t \tag{1}$$

where:
d: diffusion layer thickness, m
D: boride layer growth rate constant, m/s
t: diffusion time, s

The thickness of diffusion layer linearly increases with the square root of time as follows:

$$d = \sqrt{D}\sqrt{t} \tag{2}$$

Figure 4 shows a graphical representation of the variation in the boride layer depth with respect to the time and temperature of boriding. It was observed that the depth of the boride layer increased from 3.1 µm to 80.5 µm as the temperature increased from 850 °C to 1000 °C and the time from 1 h to 5 h.

Figure 4 confirms the diffusion nature of boronizing described with the parabolic rule. The graph in **Figure 4b** reveals that the thickness of the diffusion layer linearly increases with the square root of duration. Growth rate constant D depends on the diffusion temperature and this relationship is expressed by an Arrhenius Equation (3):[16]

$$D = D_0 e^{-\frac{Q}{RT}} \tag{3}$$

where:
T: temperature, K
D_0: frequency factor, m²/s
Q: activation energy, kJ/kmol
R: universal gas constant, kJ/(kmol·K)

Taking the natural logarithm of Equation (3), it follows that

$$\ln D = \ln D_0 - \left(\frac{Q}{R}\right)\left(\frac{1}{T}\right) \tag{4}$$

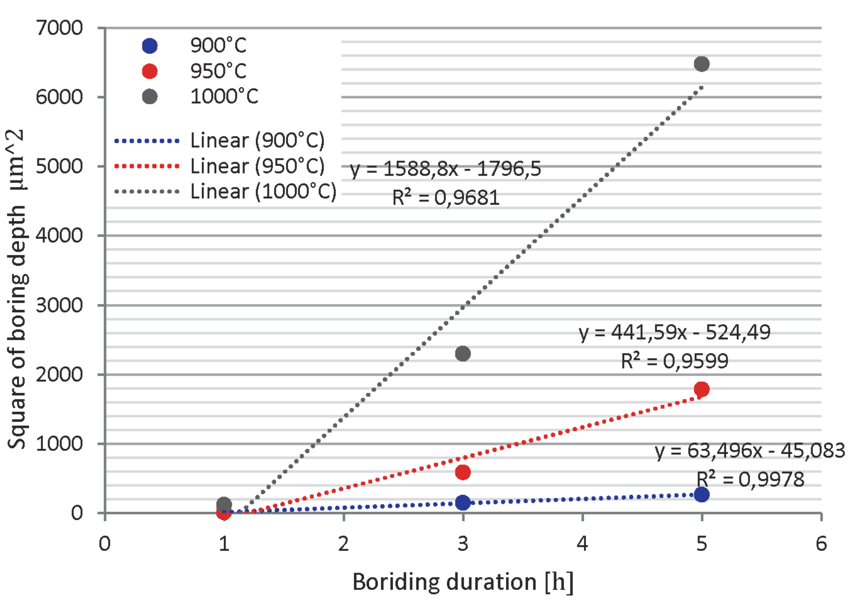

Figure 5: Growth rate constants in relation to the duration of boronizing

Using linear regression, functions for the square of boriding depth as a function of time were calculated for temperatures of (900, 950 and 1000) °C.

$$y_{900} = 63.496x - 45.083\ ;\ \ R^2 = 0.9978 \qquad (5)$$
$$y_{950} = 441.59x - 524.49\ ;\ \ R^2 = 0.9599 \qquad (6)$$
$$y_{1000} = 1588.8x - 1796.6\ ;\ \ R^2 = 0.9681 \qquad (7)$$

The growth rate constants, calculated from the gradients of the linear relationship (**Figure 5**), are provided in **Table 2** for each temperature.

Table 2: Growth rate constants for X90CrMoV-18 steel

Temperature (°C)	Growth rate constant *D*, m^2/s
900	$1.763\ 10^{-14}$
950	$1.226\ 10^{-14}$
1000	$4.413\ 10^{-13}$

The results (**Table 2**) show that the growth rate constant increases with the boronizing temperature for each temperature relationship between the natural logarithm of growth rate constants and reciprocal values of the boronizing temperatures for the boron diffusion for X90CrMoV-18 steel given in **Figure 6**.

The plots (**Figure 6**) reveal linear dependence and confirm that boronizing follows the Arrhenius equation. The activation energy was determined from the slope of the straight line and the frequency factor from the intercept of the extrapolated straight lines and ordinate axis. The frequency factor is 16342 m^2/s, and the activation energy is 402777 kJ/kmol. If considering the used equations and determined data, the expression for boronizing X90CrMoV-18 steel in the observed temperature range and duration is derived as follows:

$$d = \sqrt{16342 \cdot t \cdot e^{-\frac{402777}{RT}}} \qquad (8)$$

where:
d: thickness of the boronized layer, m
t: boriding duration, s
R: universal gas constant, 8.314472 kJ/kmol
T: temperature, K

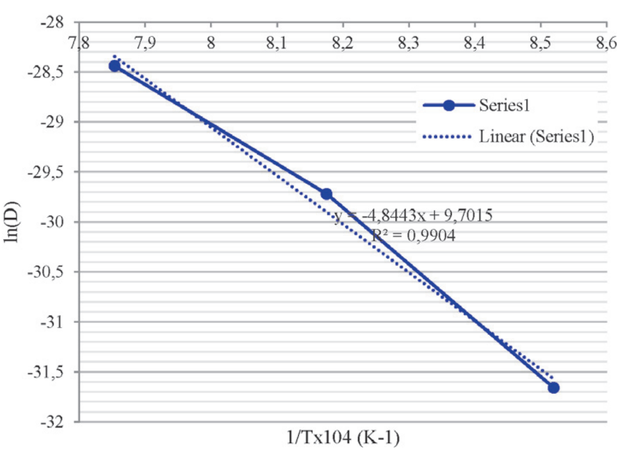

Figure 6: Natural logarithm of growth rate constant as a function of reciprocal boronizing temperature for X90CrMoV-18 steel

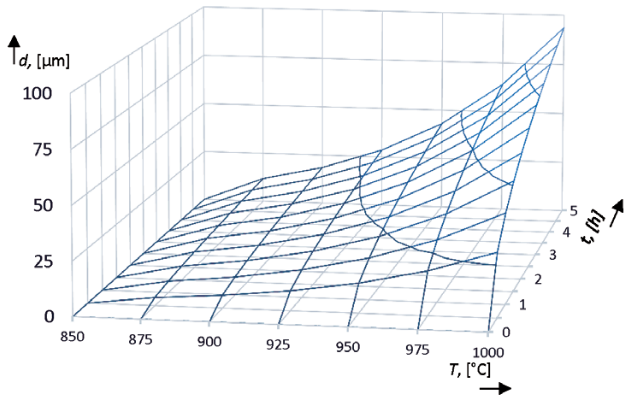

Figure 7: Layer depth as a function of time and duration of boriding

3.4 Data representation

Expression 8 can be verified by comparing it to the values measured on real samples. The results show errors in the expression ranging from 0.26 % to 6.96 % for different temperatures and times of boronizing. Using the derived mathematical model, a 3D graph showing the boride layer depth as a function of time and temperature of boriding can be constructed (**Figure 7**).

Using Equation (8), a contour diagram can be constructed, which is much more practical for easy and fast calculation of the boride layer thickness in relation to the time and temperature. These types of diagrams are widely used in the nitriding, nitrocarburizing and carburizing processes. **Figure 8** shows a contour diagram of the boride layer thickness in relation to the time and temperature of boriding.

4 DISCUSSION

Taking into consideration all the results of this study, the following conclusions can be established: The boride layers formed on X90CrMoV-18 steel are compact and they consist of a dual layer of Fe_2B and FeB boride due to a high chromium content. For future research, the presence of FeB-Fe_2B and the exact shares of different phases and elements should be confirmed using EDS or

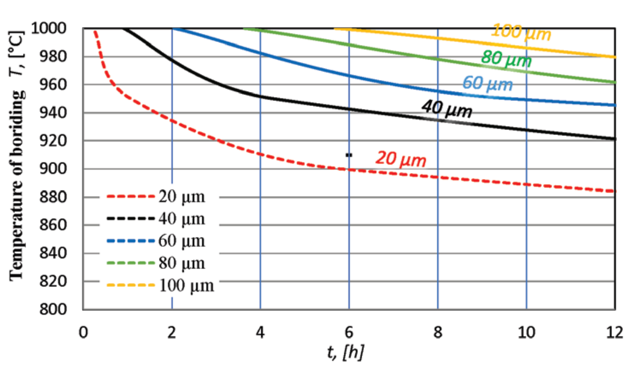

Figure 8: Contour diagram of the boride layer thickness in relation to the time and temperature of boriding

XRD. The boride layer does not exhibit saw-tooth morphology characteristics for low alloy steel. All the samples exhibit a robust outer layer with a hardness exceeding 1000 HV0.1, while the core remains unchanged after boronizing. The hardness of the base material within the diffusion zone, between the teeth and boron layer, exhibits a higher hardness than the core of the samples. The frequency factor is 16342 m2/s and the activation energy is 402777 kJ/kmol. Using previous data and the Arrhenius equation, the expression for boronizing X90CrMoV-18 steel in the observed temperature range and duration is derived. This expression can be verified by comparing it to the values measured on real samples. The results show errors in the expression of less than 7 % for different temperatures and times. The contour diagram derived in this study provides practical, easy and fast calculations of the boride layer thickness in relation to time and temperature.

5 CONCLUSIONS

Boronizing is a heat treatment that shows good potential in future steel surface hardening treatment. A better understanding of the boride-layer growth on different types of steel is important for optimizing the heat treatment and predicting the thickness of boride layers. In the presented study, it is shown that X90CrMoV-18 martensitic stainless steel can be successfully boronized. The practical temperatures of boriding are higher compared to those of low alloy steels because of the difference in the position of the austenite region of martensitic stainless steels, ranging from 900 up to 1050 °C. For longer boriding durations, the boride layer appears to consist of a Fe_2B-FeB dual phase due to a high chromium content. From the experimental results and the Arrhenius equation, a mathematical model for predicting the boride layer thickness as a function of the treatment time and temperature was constructed. From this expression, 3D graphs and contour diagrams were constructed for practical use in heat-treatment facilities for an easy and fast calculation of the boride layer thickness in relation to the time and temperature of boriding X90CrMoV-18 martensitic stainless steel.

6 REFERENCES

[1] A. Milinović, V. Marušić, I. Samardžić, Research into boride layers growth kinetics on C45 carbon steel, Metalurgija, 55 (**2016**) 4, 671–674

[2] I. E. Campos-Silva, G. A. Rodríguez-Castro, Boriding to improve the mechanical properties and corrosion resistance of steels, Thermochemical Surface Engineering of Steels, (**2015**), 651–702, doi:10.1533/9780857096524.5.651

[3] A. Motallebzadeh, E. Dilektasli, M. Baydogan, E. Atar, H. Cimenoglu, Evaluation of the effect of boride layer structure on the high temperature wear behavior of borided steels, Wear, 328–329 (**2015**), 110–114, doi:10.1016/j.wear.2015.01.029

[4] T. Polat, A. Tuna, A. Özlem, Kinetic Investigation of Boronized 34CrAlNi7 Nitriding Steel, International Journal of Engineering and Natural Sciences, 2 (**2019**) 1, 17–22

[5] S. T. de Mendonça Ferreira, A. L. Bacco, E. M. do Nascimento, C. M. Lepienski, Mechanical Characterization and Micro-Wear of FeB-Fe₂B Layers on Boriding AISI D2 and AISI 4340 Steels, Materials Sciences and Applications, 12 (**2021**) 330–344, doi:10.4236/msa.2021.127022

[6] E. Hernández-Sánchez, Y. M. Domínguez-Galicia, C. Orozco-Álvarez, R. Carrera-Espinoza, H. Herrera-Hernández, J. C. Velázquez, A study on the effect of the boron potential on the mechanical properties of the borided layers obtained by boron diffusion at the surface of AISI 316L Steel, Advances in Materials Science and Engineering, (**2014**) 1–9, doi:10.1155/2014/249174

[7] A. P. Krelling, J. C. Milan, C. E. da Costa, Tribological behaviour of borided H13 steel with different boriding agents, Surface Engineering, 31 (**2015**) 581–587, doi:10.1179/1743294414y.0000000423

[8] R. Carrera-Espinoza, U. Figueroa-López, J. Martínez-Trinidad, I. Campos-Silva, E. Hernández-Sánchez, A. Motallebzadeh, Tribological behavior of borided AISI 1018 steel under linear reciprocating sliding conditions, Wear, 362–363 (**2016**), 1–7, doi:10.1016/j.wear.2016.05.003

[9] I. Campos-Silva, M. Flores-Jiménez, D. Bravo-Bárcenas, H. Balmori-Ramírez, J. Andraca-Adame, J. Martínez-Trinidad, et al., Evolution of boride layers during a diffusion annealing process, Surface and Coatings Technology, 309 (**2017**), 155–163, doi:10.1016/j.surfcoat.2016.11.054

[10] B. Matijević, Evaluation of boride layer growth on carbon steel surfaces, Metal Science and Heat Treatment, 56 (**2014**), 269–273, doi:10.1007/s11041-014-9744-7

[11] G. Ibrahim, Y. İsmail, Rate of growth of boride layers on stainless steels, Oxidation Communications, 38 (**2015**), 2189–2198

[12] I. Campos-Silva, M. Ortiz-Domínguez, C. Tapia-Quintero, G. Rodríguez-Castro, M. Y. Jiménez-Reyes, E. Chávez-Gutiérrez, Kinetics and boron diffusion in the FeB/Fe_2B layers formed at the surface of borided high-alloy steel, Journal of Materials Engineering and Performance, 21 (**2011**), 1714–1723, doi:10.1007/s11665-011-0088-9

[13] A. Milinović, D. Krumes, I. Kladarić, Research of boride layers growth kinetics on C15 carbon steel, International Journal of Microstructure and Materials Properties, 9 (**2014**) 38, doi:10.1504/ijmmp.2014.061051

[14] C. Li, B. Shen, G. Li, C. Yang, Effect of boronizing temperature and time on microstructure and abrasion wear resistance of Cr12Mn2V2 high chromium cast iron, Surface and Coatings Technology, 202 (**2008**), 5882–5886, doi:10.1016/j.surfcoat.2008.06.170

[15] F. E. Şeşen, S. Özgen, M. K. Şeşen, Effect of process parameters on the formation of boron-titanium and titanium-boron multi-layered diffusion coatings on interstitial-free steel, Surface Engineering and Applied Electrochemistry, 53 (**2017**), 167–178, doi:10.3103/s1068375517020107

[16] G. Sundararajan, Boronizing of 42CrMo4 Steel: Microstructure, Hardness, and Wear Behaviour, Journal of Thermal Spray Technology, 27 (**2018**) 8, 1327–1339