Journal Homepage: http://dergipark.gov.tr/ejens

EJENS
European Journal of Engineering and Natural Sciences

DergiPark AKADEMİK

CODEN: EJENS

Generation of a Multi-Layered Diffusion Coating on an Interstitial-Free Steel

Fikri Erdem Şeşen*, Omer Serdar Özgen

Istanbul Technical University, Faculty of Chemistry-Metallurgy, Department of Metallurgical and Materials Engineering, 34469, Istanbul, Turkey

Corresponding Author email: sesen@itu.edu.tr

Publication Info

Abstract

Boronizing and titanium diffusion were applied to an interstitial-free steel substrate separately and one after another. Boronizing was carried out in a liquid environment by applying an electric current, but titanium diffusion was performed in a closed chamber containing solid chemicals. The generated single-layered and multi-layered diffusion coatings were characterised by utilising an optical microscope, a scanning electron microscope equipped with an energy dispersive spectrometer, and a Vickers microhardness tester. Phase analysis was carried out by an x rays diffractometer. Some chemical reactions were supposed to occur regarding titanium diffusion process and the standard formation enthalpies of these reactions were calculated by using a database. Microstructural investigations revealed that titanium diffusion was able to be applied after boronizing, causing the formation of a titanium based diffusion layer over the previously generated boride layer. On the other hand, when a titanium diffused substrate was boronized, the titanium based diffusion layer acted as a diffusion barrier to the introduced boron atoms, preventing the formation of a boride layer. However, if boronizing duration and the current density applied during boronizing were increased to a certain degree, boron atoms could surpass this barrier in small quantities and form small discontinuous regions. It was observed that the hardness of a phase which was formed within the titanium based diffusion layer was more than 4000 HV in some regions when titanium diffusion was applied after boronizing. The standard formation enthalpies of the six assumed chemical reactions were negative, indicating that these can occur at 1000 °C at which titanium diffusion was applied. Moreover, most of the products of these reactions were detected in x rays diffraction analyses.

Key words

Boronizing, Interstitial-free steel, Titanium diffusion

1. INTRODUCTION

Surface modification techniques in several types are applied to steels in order to improve their hardness, mechanical strength, corrosion resistivity, resistivity to high temperature, etc. A group of these surface modification techniques involves the formation of an outer protective layer while another group is applied by diffusing an element through the cross-section of the substrate in a certain depth. The increase of the thickness is negligible in treatments related to diffusion. Boronizing (boron diffusion) is a type of latter-mentioned group of techniques. Boronizing is performed by diffusing elemental boron on to the substrate surrounded by a boronizing agent (source) which can be in solid, liquid, gaseous or even plasma state. Boronizing can be applied to almost all types of steels, titanium alloys and refractory metal alloys [1], [2].

Elemental titanium can be applied on to steel surface either as a protective coating or by diffusion. Titanium diffusion is generally performed before or after another surface treatment or as an intermediate stage between two different treatments [3].

Interstitial-free steel is a special type of steel possessing very little amount of alloying elements. Interstitials (carbon and nitrogen) are removed from solid solution through precipitation hardening. It is extensively used in cases where high ductility is desired [4].

This study aimed to investigate the resultant microstructure, phases and hardness that are achieved via boronizing and titanium diffusion applied separately or one after another. Moreover, some chemical reactions were introduced related to titanium diffusion process by the help of the x rays diffraction analysis results and the standard formation enthalpies of these reactions were calculated by using a database.

2. EXPERIMENTAL PROCEDURE

2.1. Samples

An interstitial-free steel was used as the substrate material. The chemical composition of the interstitial-free steel is given in Table 1. The steel plates were obtained after cold-rolling during the intermediate stages of the production held at Eregli Iron and Steel Works Co. (ERDEMİR) in Zonguldak, Turkey. The steel plates, having a thickness of 4 mm, were cut in to 50×23 mm dimensions and their surfaces were ground in order to eliminate any undesired matter before the diffusion coating processes.

Table 1. Chemical composition of the interstitial-free steel substrate

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Ti	V	B
wt. %	0.0088	0.0110	0.2130	0.0136	0.0089	0.0250	0.0470	0.0010	0.0286	0.0597	0.0083	0.0004

2.2. Diffusion Coating Processes

Boronizing was performed electrothermochemically in a bath containing 100% dehydrated sodium borax which was melt in a chamotte crucible placed in a pit-type furnace which was heated to 900 °C. An electric current having a density of 0.10 or 0.40 A/cm^2 was applied during boronizing which lasted 45 or 120 minutes.

Titanium diffusion was carried out thermochemically in a one-use closed cylindrical chamber that contained micro-sized titanium particles, ammonium chloride and aluminium oxide. The chamber was heated in an electric-resistant furnace to 1000 °C and kept at this temperature for 2 hours. After that, it was left to cool down to room temperature.

2.3. Characterisation

Microstructural investigation was done by using an Olympus GX71 Optical Microscope and a Jeol JSM-7000F Field Emission Scanning Electron Microscope equipped with an energy dispersive spectrometer. The samples were metallographically prepared in a standard manner before the

examinations. They were chemically etched with Nital3 solution before the optical investigations while coated with platinum and painted with silver chloride to be prepared for scanning electron microscope work. The phase analysis was carried out by utilising a Philips Pan Analytical X'Pert Professional type x rays diffractometer supplying CuKα radiation. The scanning was performed between 20 and 90 2θ values at a rate of 1° per min. The peaks on the patterns were identified manually by matching the related d values with the ones in the relevant indexes. A Future Tech FM 500 hardness tester was used in order to evaluate the hardness of the generated diffusion layers. A 50 gF load was applied for a dwelling time of 10 seconds. The standard formation enthalpies of the chemical reactions introduced about titanium diffusion process were calculated by using database HSC Chemistry Software v 6.12.

3. EXPERIMENTAL RESULTS

3.1. Results of Microstructural Investigations

A scanning electron microscope image showing the surface of the interstitial-free steel boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2 is given in Figure 1. The stable boride phases of Fe_2B and FeB are visualised clearly in the image. Semi-quantitative chemical analysis values detected in the selected regions on the scanning electron microscope image are given in Table 2 in weight per cent.

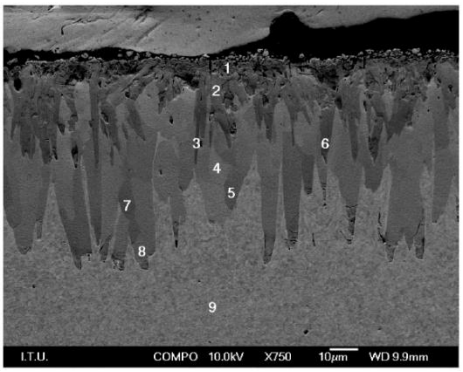


Figure 1. Scanning electron microscope image showing the surface of the interstitial-free steel boronized at 900 °C for 45 min by applying a current density of 0.10 A/cm^2

Table 2. Semi-quantitative weight per cent chemical analysis values detected in the selected regions numbered between 1 and 9

Region	1	2	3	4	5	6	7	8	9
B% wt.	17.50	18.22	18.94	11.69	9.97	18.48	10.70	9.73	-
Fe% wt.	82.50	81.78	81.06	88.31	90.03	81.52	89.30	90.27	98.95
C% wt.	-	-	-	-	-	-	-	-	1.05

Another scanning electron microscope image showing the surface of the titanium diffused interstitial-free steel is given in Figure 2. Semi-quantitative chemical analysis values detected in the selected regions on the scanning electron microscope image are given in Table 3 in weight per cent.

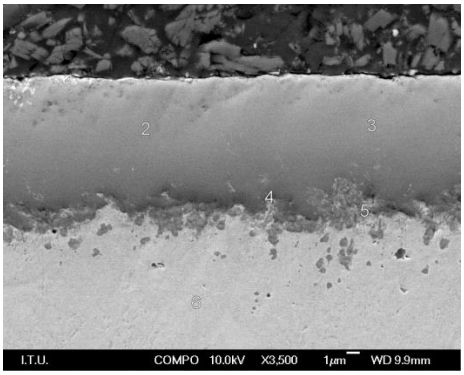


Figure 2. Scanning electron microscope image showing the surface of the interstitial-free steel titanium diffused at 1000 °C for 2 hours

Table 3. Semi-quantitative weight per cent chemical analysis values detected in the selected regions numbered between 1 and 6

Region	1	2	3	4	5	6
Al% wt.	7.08	1.30	-	2.85	2.32	-
Ti% wt.	46.88	98.70	100.00	72.03	71.53	-
Fe% wt.	46.05	-	-	25.12	26.15	100.00

The surface of the interstitial-free steel first boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2 and then titanium diffused at 1000 °C for 2 hours can be viewed in another scanning electron microscope image given in Figure 3. Semi-quantitative chemical analysis values detected in the selected regions on the scanning electron microscope image are given in Table 4 in weight per cent.

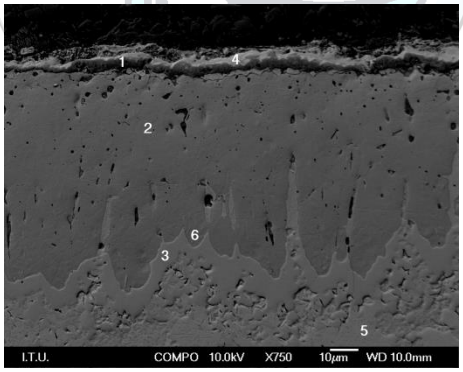


Figure 3. Scanning electron microscope image showing the surface of the interstitial-free steel first boronized at 900 °C for 45 min by applying a current density of 0.10 A/cm^2 and then titanium diffused at 1000 °C for 2 hours

Table 4. Semi-quantitative weight per cent chemical analysis values detected in the selected regions numbered between 1 and 6

Region	B% wt.	O% wt.	Al% wt.	Si% wt.	S% wt.	Ca% wt.	Ti% wt.	Mn% wt.	Fe% wt.	Ni% wt.
1	-	23.56	11.08	-	0.29	-	54.07	-	11.00	
2	6.70	-	-	-	-	-	-	2.32	90.99	
3	-	-	-	-	-	-	-	2.24	97.76	
4	-	6.19	2.44	0.92	-	1.21	72.98	-	7.45	8.80
5	-	-	-	-	-	-	-	1.92	98.08	
6	-	-	-	-	-	-	-	2.75	97.25	

The outer layer of the surface of the interstitial-free steel first boronized and then titanium diffused, by applying the above-mentioned parameters, can be visualised in more detail in the scanning electron microscope image given in Figure 4. Semi-quantitative chemical analysis values detected in the selected regions on the scanning electron microscope image are given in Table 5 in weight per cent.

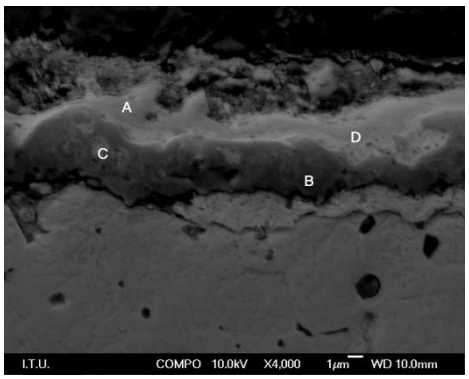


Figure 4. Scanning electron microscope image focusing on the outer surface (titanium based diffusion layer) of the interstitial-free steel first boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2 and then titanium diffused at 1000 °C for 2 hours

Table 5. Semi-quantitative weight per cent chemical analysis values detected in the selected regions named A-D

Region	B% wt.	O% wt.	Al% wt.	Si% wt.	P% wt.	Ca% wt.	Ti% wt.	Fe% wt.	Ni% wt.
A	-	10.90	5.79	0.95	-	1.94	69.69	6.83	3.89
B	23.61	-	2.98	-	-	-	59.85	13.56	-
C	-	-	-	-	22.44	-	33.52	36.44	7.44
D	-	5.59	4.13	1.05	-	0.99	65.91	10.52	11.81

Another optical micrograph presenting the microstructure of the surface of the interstitial-free steel which was first titanium diffused at the above-mentioned parameters and then boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2 is given in Figure 5. As can be seen in the micrograph, boronizing could not be accomplished after titanium diffusion.

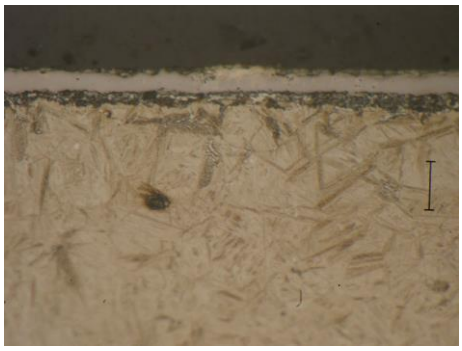


Figure 5. Optical micrograph showing the surface of the interstitial-free steel first titanium diffused at 1000 °C for 2 hours and then boronized at 900 °C for 45 min by applying a current density of 0.10 A/cm^2 (Scale length: 10 µm)

The inhibiting effect of titanium based diffusion layer is visualised more clearly in Figure 6 where an optical migrograph showing two different surfaces of the interstitial-free steel which was first titanium diffused, then one surface cropped and finally boronized is given.

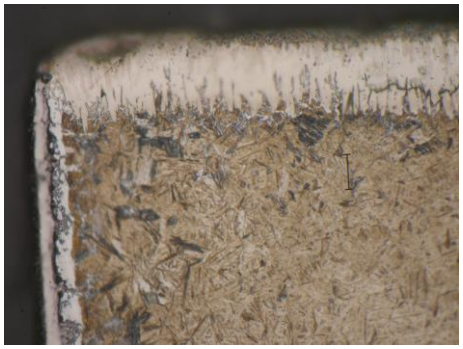


Figure 6. Optical micrograph of the interstitial-free steel showing the horizontal surface which was only boronized and the vertical surface which was first titanium diffused and then boronized (Scale length: 20 µm)

When the boronizing duration and the current density applied during boronizing carried out after titanium diffusion were increased to a certain degree, boron atoms were able to surpass the already generated titanium based diffusion layer. This phenomenon is visualised in an optical micrograph given in Figure 7 and a scanning electron microscope image given in Figure 8. Semi-quantitative chemical analysis values detected in the selected regions on the scanning electron microscope image are given in Table 6 in weight per cent.

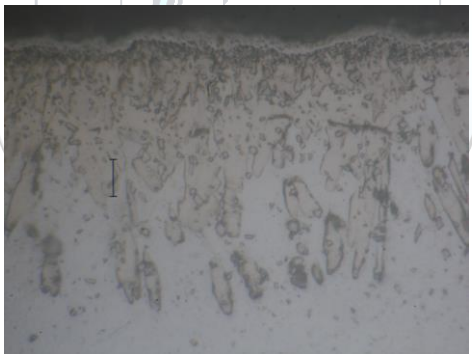


Figure 7. Optical micrograph of the surface of the interstitial-free steel titanium diffused at 1000 °C for 2 hours and then boronized at 900 °C for 120 min by applying a current density of 0.40 A/cm^2 (Scale length: 10 µm)

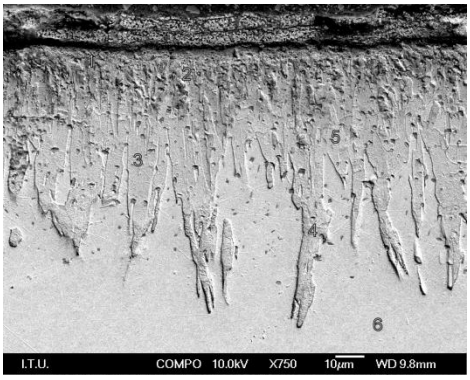


Figure 8. Scanning electron microscope image of the surface of the interstitial-free steel first titanium diffused at 1000 °C for 2 hours and then boronized at 900 °C for 120 min by applying a current density of 0.40 A/cm^2

Table 6. Semi-quantitative weight per cent chemical analysis values detected in the selected regions numbered between 1 and 6

Region	1	2	3	4	5	6
B% wt.	31.22	2.11	-	-	-	-
Al% wt.	0.51	-	-	0.29	0.38	-
Ti% wt.	48.13	0.34	0.20	0.56	0.37	-
Fe% wt.	20.15	97.55	99.80	99.16	99.25	100.00

3.2. Results of X Rays Diffraction Analyses

The pattern of the x rays diffraction analysis, obtained by scanning the diffusion layer formed on the surface of the interstitial-free steel that was boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2, is shown in Figure 9. Stable boride phases of Fe_2B and FeB were detected on the scan as well as a metastable boride phase of Fe_3B. The pattern of the x rays diffraction analysis, obtained by scanning the diffusion layer formed on the surface of the interstitial-free steel that was titanium diffused at 1000 °C for 2 hours, is given in Figure 10. Phases of titanium iron, iron nitride and titanium nitride were detected in the scan in different stoichiometric ratios. The pattern of the x rays diffraction analysis, obtained by scanning the diffusion layer formed on the surface of the interstitial-free steel that was first boronized at 900 °C for 45 minutes by applying a current density of 0.10 A/cm^2 and then titanium diffused at 1000 °C for 2 hours, is presented in Figure 11. Stable boride phases of Fe_2B and FeB, iron nitride, titanium iron, titanium nitride and boron nitride were detected in the scan. Finally, the pattern of the x rays diffraction analysis, obtained by scanning the diffusion layer formed on the surface of the interstitial-free steel that was first titanium diffused at 1000 °C for 2 hours and then boronized at 900 °C for 120 minutes by applying a current density of 0.40 A/cm^2, is given in Figure 12. Stable boride phases of Fe_2B and FeB, metastable boride phase of Fe_3B, boron nitride, titanium diboride, titanium nitride and iron nitride in three different stoichiometric ratios were detected in the scan.

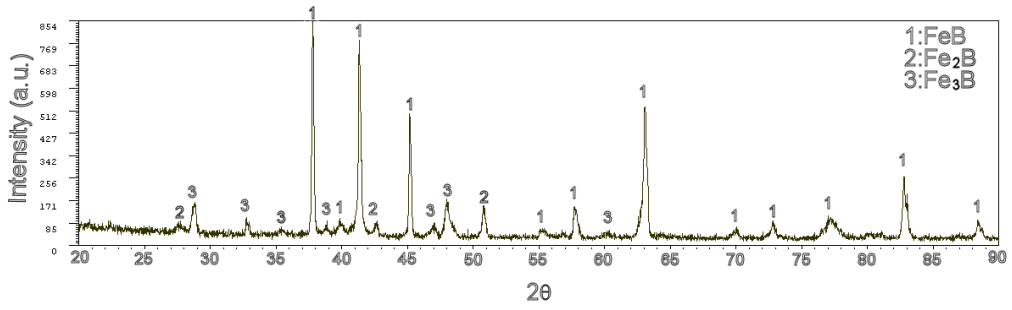


Figure 9. X rays diffraction pattern of the surface of the interstitial-free steel boronized at 900 °C for 45 min by applying a current density of 0.10 A/cm^2

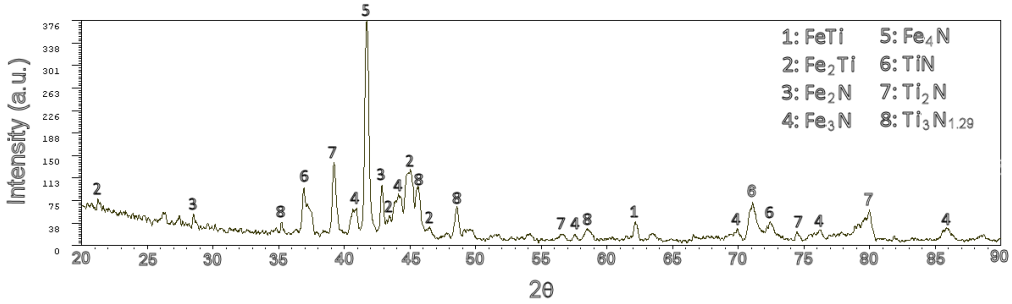


Figure 10. X rays diffraction pattern of the surface of the interstitial-free steel titanium diffused at 1000 °C for 2 hours

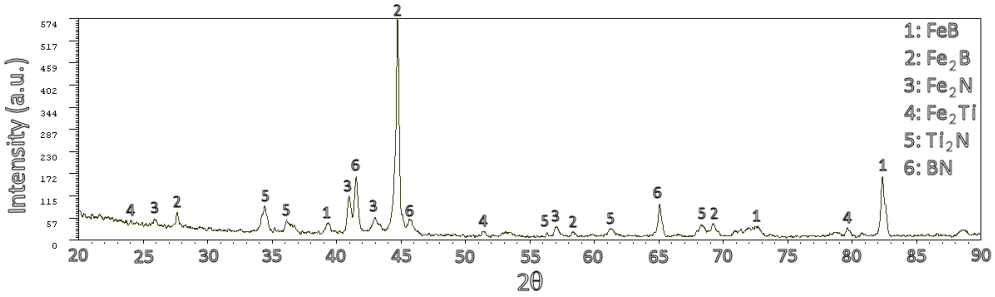


Figure 11. X rays diffraction pattern of the surface of the interstitial-free steel first boronized at 900 °C for 45 min by applying a current density of 0.10 A/cm^2 and then titanium diffused at 1000 °C for 2 hours

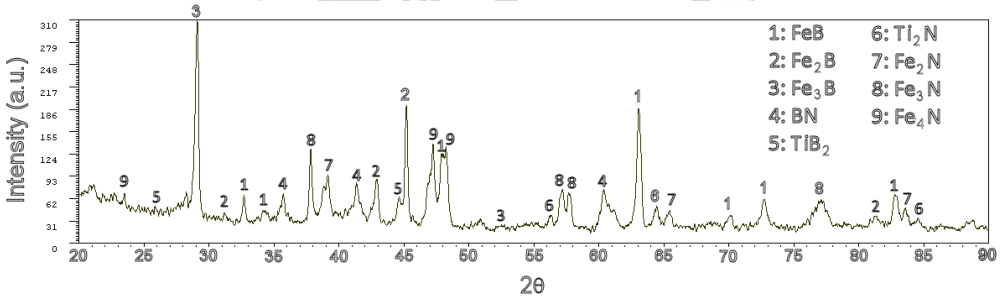


Figure 12. X rays diffraction pattern of the surface of the interstitial-free steel first titanium diffused at 1000 °C for 2 hours and then boronized at 900 °C for 120 min by applying a current density of 0.40 A/cm^2

3.3. Results of Hardness Measurements

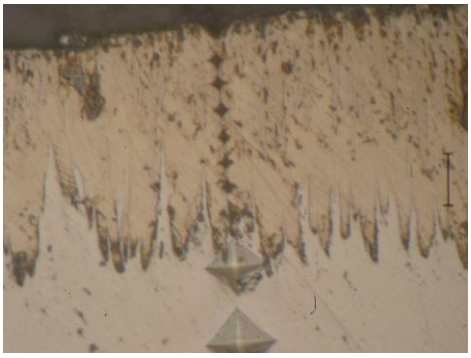


Figure 13. Optical micrograph presenting the difference of hardness between the substrate and the boride layer generated as a result of boronizing (Scale length: 20 µm)

An optical micrograph showing the boride layer generated as a result of boronizing after which Vickers hardness testing was applied is given in Figure 13 in order to present the hardness difference between the boride layer and the substrate considering the size of the indentation traces. The diagram shown in Figure 14 presents the change of hardness with respect to the distance from surface and the applied current density. Two other optical micrographs showing the outer layer of the diffusion coating on the surface of the sample which was first boronized and then titanium diffused are given in Figures 15 (a) and 15 (b). The size of the indentation traces indicates the extremely high hardness of a phase within the titanium based diffusion layer, which was formed as a result of titanium diffusion carried out after boronizing. Hardness values over 4000 HV were detected in this phase.

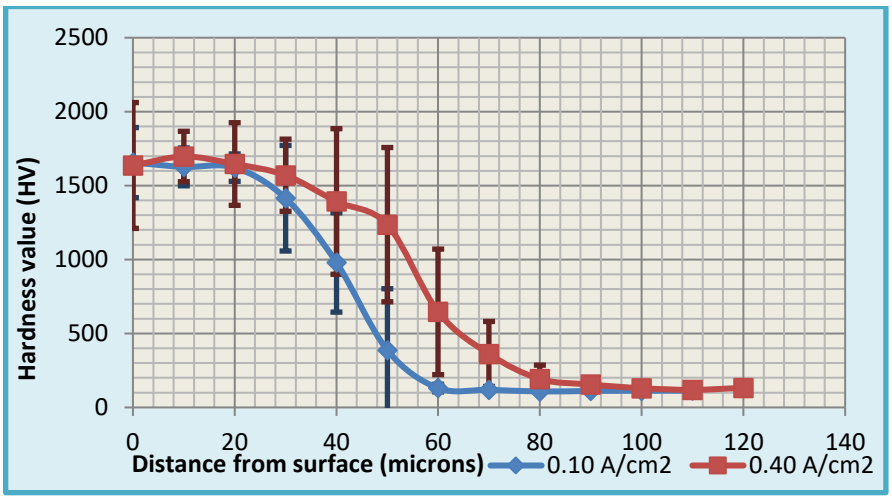
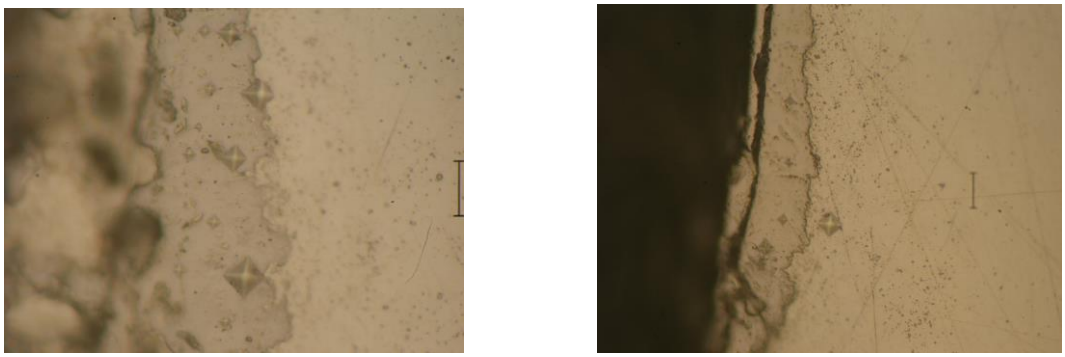


Figure 14. Change of hardness with respect to the distance from surface and the applied current density in case of merely boronizing at 900 °C for 45 min



(a) (b)

Figure 15. (a) and (b) The outer layer of the diffusion coating generated as a result of first boronizing and then titanium diffusion. The size of the indentation traces indicates the existence of a very hard phase within the titanium based diffusion layer (Scale length: 20 µm)

3.4. Results of Thermodynamic Calculations

Six chemical reactions were supposed to occur related to titanium diffusion process. They are written on the right side of Figure 16 and the standard formation enthalpies of five of them with respect to temperature are presented in a diagram on the left side of Figure 16. It is already known that the standard formation enthalpy of the first chemical reaction is negative over approximately 380 °C indicating that ammonium chloride decomposes into ammonia and hydrochloric acid [5]. It is concluded that, at normal atmospheric pressure, all of these six chemical reactions can occur at 1000 °C at which titanium diffusion was performed.

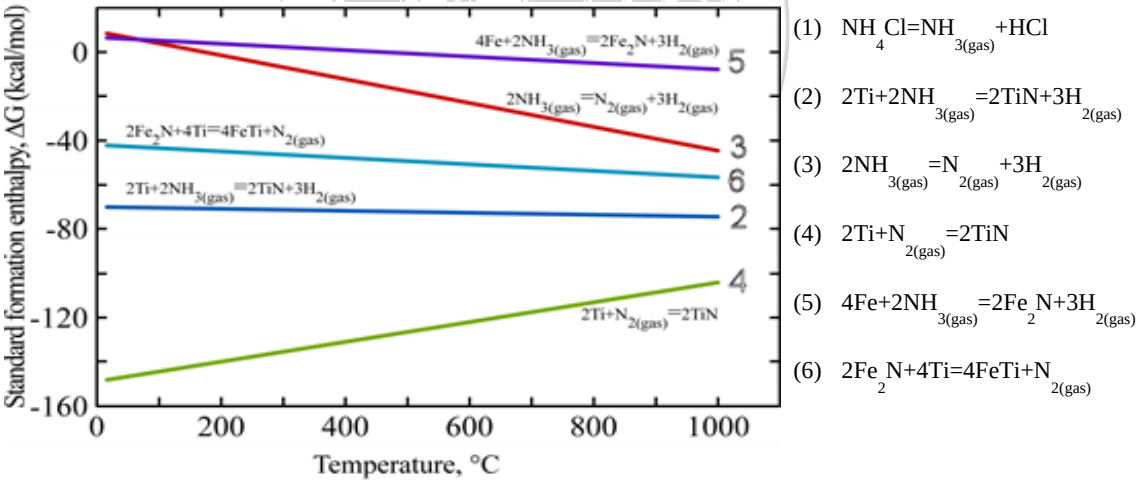


Figure 16. Six chemical reactions assumed to occur during titanium diffusion process and the standard formation enthalpies of five of them with respect to temperature

4. CONCLUSION

In this study, multi-layered diffusion coatings were generated via diffusion of boron and titanium on an interstitial-free steel and the mechanism of titanium diffusion was tried to be revealed by introducing six chemical reactions. Titanium was easily diffused over the already generated boride layer in case of first boronizing and then titanium diffusion, but boron atoms could surpass the already formed titanium based diffusion layer in small quantities only if boronizing duration and the current density applied during boronizing were increased. A metastable phase of Fe_3B was detected in the boride layer, as well as the stable phases of Fe_2B and FeB. Abundance of a very hard phase with a hardness degree of over 4000 HV was determined within the titanium based diffusion layer that was generated over the boride layer.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Ereğli Iron and Steel Works Co. (ERDEMİR) for providing the interstitial-free steel plates and the Office of Scientific Research Projects in Istanbul Technical University for financial support with the project number 34558.

REFERENCES

[1] A. K. Sinha, *Heat Treating: Boriding (Boronizing) of Steels*, ser. ASM Materials Handbook. Materials Park, OH, USA: ASM Int., vol. 4, pp. 978-997, 1995.
[2] J. R. Davis, *Surface Hardening of Steel: Understanding the Basics*: Boriding. Materials Park, OH, USA: ASM Int., pp. 213-226, 2002.
[3] N. Gidikova, "Thermodiffusion Treatment of Steel with Ti Thermodynamics and Phase Composition," *Mater. Sci. & Eng. A*, vol. 222, pp. 84-90, 1997.
[4] K. Dutta and K. K. Ray, "Ratcheting Strain in Interstitial Free Steel," *Mater. Sci. & Eng. A*, vol. 575, pp. 127-135, 2013.
[5] "ID: C1-103 Material Safety Data Sheet: Ammonium Chloride," Chem. One, Houston, TX, USA, 2010.