# Kinetic Investigation of Boronized 34CrAlNi7 Nitriding Steel

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**Abstract:** In this study, kinetic examinations of boronized 34CrAlNi7 Nitriding Steel samples were described. Samples were boronized in indirect heated fluidized bed furnace consists of Ekabor 1™ boronizing agent at 1123, 1223 and 1323 K for 1, 2 and 4 hours. Morphologically and kinetic examinations of borides formed on the surface of steel samples were studied by optical microscope, scanning electron microscope (SEM) and X-Ray diffraction (XRD). Boride layer thicknesses formed on the steel 34CrAlNi7 ranges from 46,6 ± 3,8 to 351,8 ± 15,2 µm. The hardness of the boride layer formed on the steel 34CrAlNi7 varied between 1001 and 2896 kg/mm$^2$. Layer growth kinetics were analyzed by measuring the extent of penetration of FeB and $Fe_2B$ sublayers as a function of boronizing time and temperature. The kinetics of the reaction has been determined with K=Ko exp (-Q/RT) equation. Activation energy (Q) of boronized steel 34CrAlNi7 was determined as 169 kj/mol.

**Keywords:** Boronizing, 34CrAlNi7, Indirect Heated Fluidized Bed Furnace, Kinetics of Boron.

## 1. INTRODUCTION

Boron element in the periodic table is located next to the carbon. The boron and its compounds are in a unique position in terms of their properties in various applications [1]. In the periodic table, the boron, indicated by the symbol *B*, is a semiconductor element with an atomic weight of 10,81 and an atomic number of 5 and it is also the first and the lightest element of group 3A in the periodic table. Metallic or non-metallic elements produced from boron compounds have wide use in the industry. Under normal conditions, boron compounds have the property of non-metal compound, but pure boron, like carbon element, has electrical conductivity. In addition, the crystalline boron has similar properties to the diamond. For example, its hardness is close to diamond [2].

Boronizing, also commonly referred to as boriding, is a thermochemical surface hardening process applied to well cleaned surfaces of metallic materials at high temperatures. As a rule, Boronizing treatments are usually carried out between 1123 and 1223 K. The boride layers formed as a result of boronizing treatment have high hardness as well as wear, corrosion and high heat resistance [3]. Boronizing increases the resistance to certain acid types, partly to hydrochloric acid. It is possible that the irregularly shaped parts can be boronized evenly and have a positive effect on the tool life [4]. The formation of boride layer is diffusion controlled. As the temperature increases, the thickness of the boride layer formed on boronized iron surfaces also increases. The phase formed as a result of boriding of iron-based materials, only FeB, is the permanent tension, prone to tensile, if the phase, $Fe_2B$, is prone to compress. Because of this situation, the phases apply the tensile-compressive force in the double-phase boride layers [5,6]. The hardness depends on the type of material and FeB or $Fe_2B$ phases on the surface. FeB phase is harder and brighter than $Fe_2B$ phase [7]. The atoms of the boronizing compound used in the boronizing process are settled between the atoms of the iron-based material by diffusion. The hardness of the boride layer changes depending on the composition of the boronized material and the structure of the boride layer [8].

One of the methods used for the boronizing process is the *pack boronizing* technique. This technique is based on the principle of heating the material embedded in the boron powder mixture in a heat-resistant steel pot by the furnace [9]. There are many powder mixtures for boronizing in the literature. But the common point of all is the formation of boron source, activator and inert diluents. The Ekabor boronizing agent used in this study is also a powder mixture containing these components. It is stated that in the literature, this boronizing agent is composed of 5% $B_4C$ + 5% $KBF_4$ + 90% SiC [8,10].

As boronizing is widely used in different engineering areas and industrial sectors. Some of these sectors can be listed as follows; metallurgy and materials, mining, textile, chemical and mechanical engineering and also agriculture, food and porcelain industry [11].

Boriding can be carried out on different types of cast irons and steels such as structural steels, case hardened steels, tool steels, stainless steels, cast steels, or sintered steels. However, due to the risk of cracking between FeB and $Fe_2B$ phases in nitriding steels, a thick layer of boride is not desirable [12].

In this study, the activation energy (Q) value required for boronizing of 34CrAlNi7 nitriding steel and the growth rate constant of boride layer were investigated. Arrhenius equation was used to determine the relationship between growth rate constant and activation energy [13].

## 2. MATERIAL AND METHOD

In this study, 34CrAlNi7 nitriding steel material was boronized. The results of the chemical analysis performed with optical emission spectrometry prior to the experimental procedures are shown in Table 1. below.

**Table 1.** The chemical composition of 34CrAlNi7

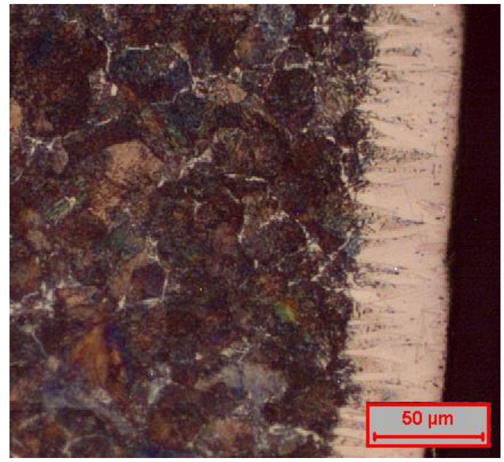
| **Boronized Material** | **Alloying Elements (wt.-%)** | | | | |
|---|---|---|---|---|---|
| | **C** | **Mn** | **Si** | **Cr** | **Ni** |
| **34CrAlNi7 Nitriding Steel** | 0,38 | 0,72 | 0,23 | 1,66 | 0,80 |
| | **Alloying Elements (wt.-%)** | | | | |
| | **Mo** | **V** | **W** | **Al** | |
| | 0,17 | 0,03 | 0,04 | 0,98 | |

The pack-boronizing method was used for the boronizing heat treatment. In this method, commercial name is Ekabor 1™ powder mixture was used. Samples embedded in Ekabor 1™ powder in AISI 304 stainless steel pot were heated in fluidized bed furnace at 1123, 1223 and 1323 K as three process temperatures and for 1h, 2h and 4h as three different treatment times. Then the boronized samples were cooled in air. After this processes, boronized samples were sanded with 120 to 1000 numbered emery paper, then polished with diamond paste. The free from scratches samples were etched by Nital 4 (4% $HNO_3$ + 96% ethyl alcohol) etcher. An optical microscope and an integrated image analyzer were used to measure the thickness of the boron layer formed on the surface of the samples. In order to obtain a more detailed view of the two-phase boride layer, a SEM image of the sample was taken with the help of the back scattered electrons. The microstructural studies were carried out on boronized samples. Vickers hardness tester was used for hardness measurements. The hardness measurements were performed from surface to matrix, by 4 different points and using with 100 g. weight.

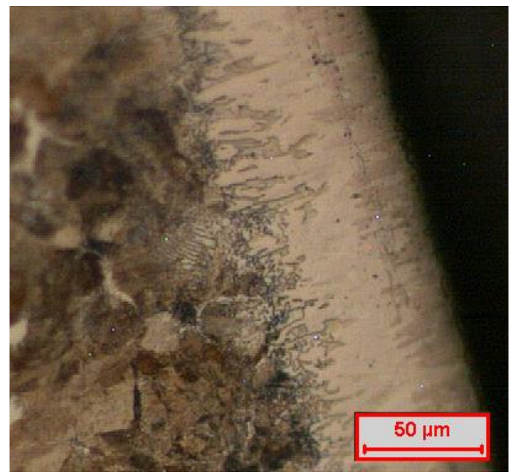
## 3 RESULT AND DISCUSSION

### 3.1. Microstructure and Hardness Analyses

It has been revealed in many studies [8, 10, 13] that the boron layer formed on stainless steels has a columnar morphology. On the contrary, in this study, the shape of the boron layer formed by the saw-tooth morphology also shown in Figures 1, 2 and 3. In addition to the binary phase structure forming the boride layer and the matrix microstructures are also shown in Figure 4.




**1h.**

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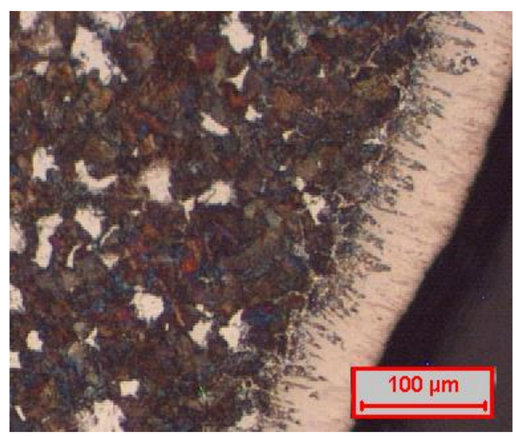


**3h.**

**Figure 1.** Boride layers formed on 34CrAlNi7 at 1123 K

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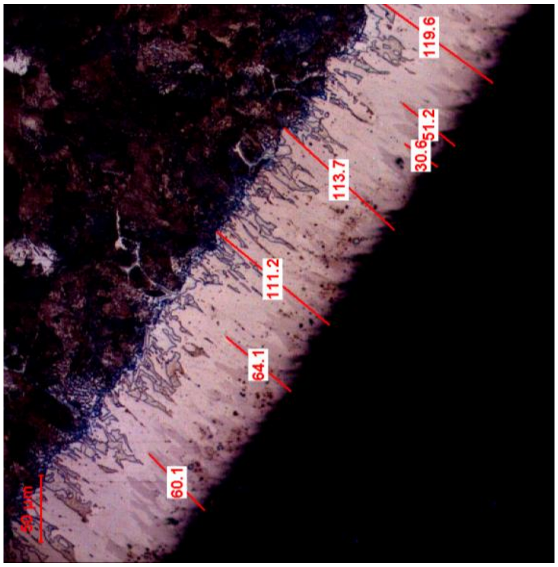


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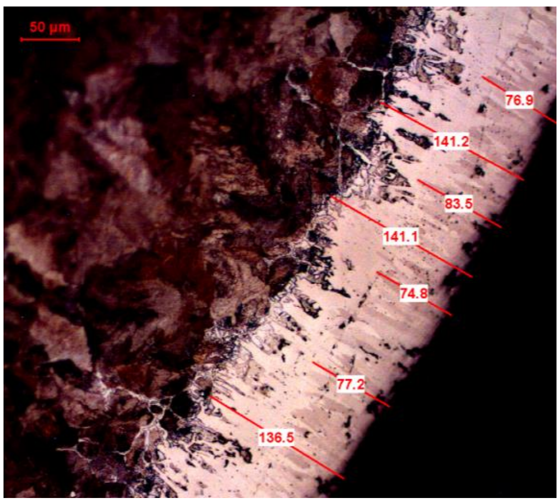


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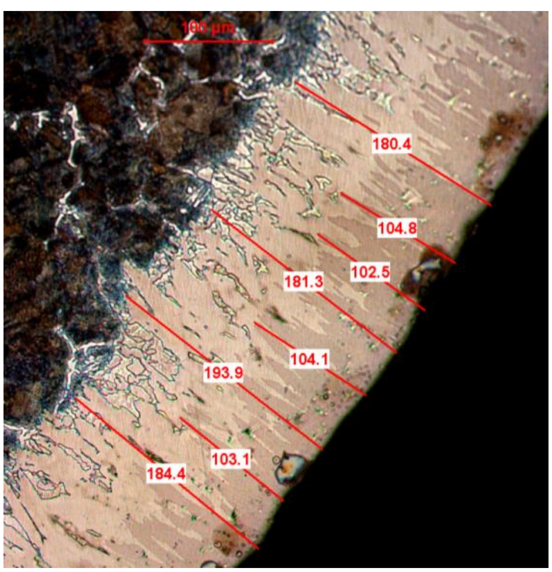


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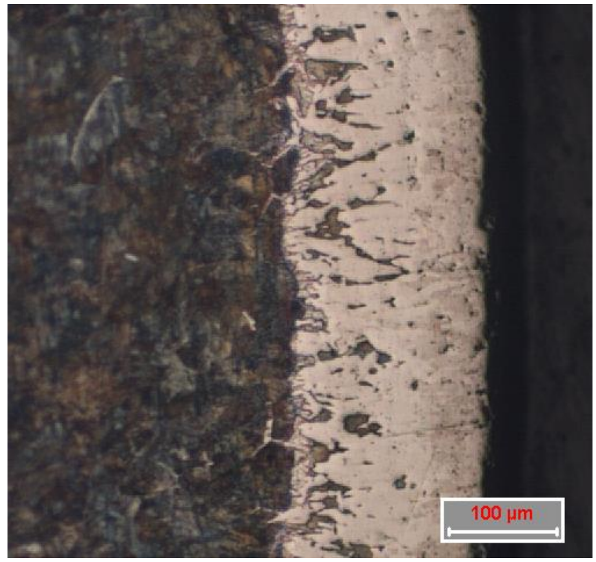
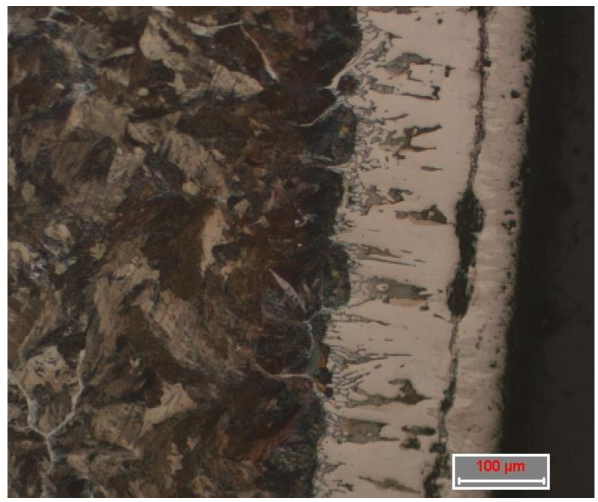
**Figure 2.** Boride layers formed on 34CrAlNi7 at 1223 K




**1h.**

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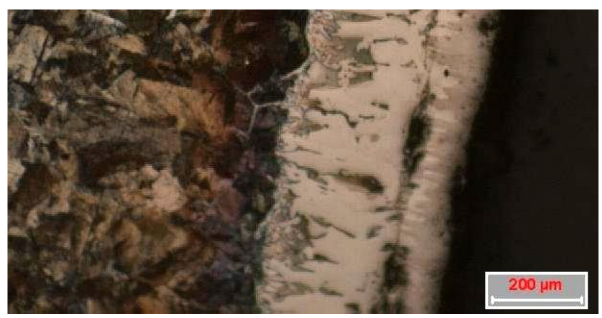


**3h.**

**Figure 3.** Boride layers formed on 34CrAlNi7 at 1323 K

According to the microstructure investigations, boride layer formed on the surface of the boronized 34CrAlNi7 nitriding steel was found to consist of FeB and $Fe_2B$ phases. As can be seen from the SEM (BEI) image, the outermost dark gray phase is FeB and the adjacent light gray color phase is $Fe_2B$.

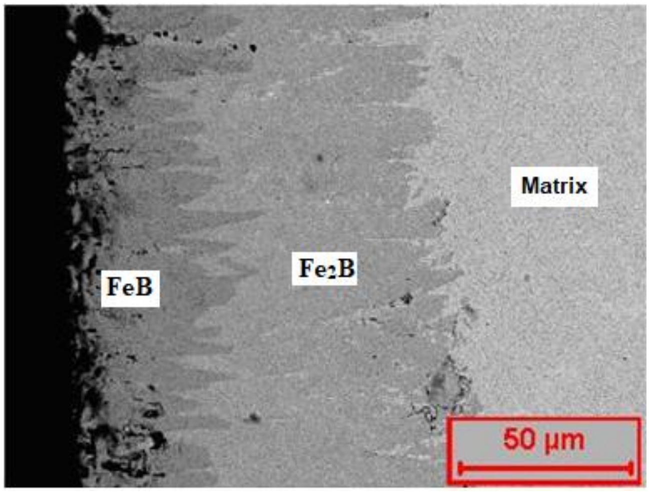


**Figure 4.** SEM (BE) image of boronized 34CrAlNi7

In the present investigation, the boride layer thicknesses of the boronized samples at three different temperatures and times range from 42,8 to 367µm. Measurement results of the layer thicknesses can be seen from Figure 3. as well as Table 2.

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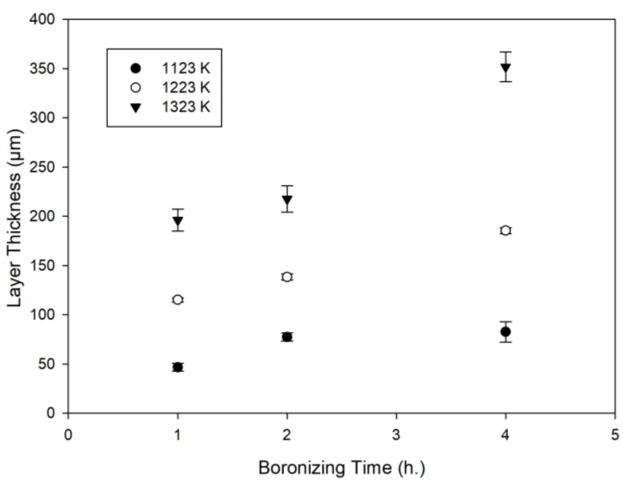



**Figure 5.** Thicknesses of boride layer on 34CrAlNi7

**Table 2.** Boride layer thicknesses on 34CrAlNi7

| Boronized Material | Boronizing Temperature (K) | Boronizing Time (hour) | Boron Phase Layer Thickness (µm) |
|---|---|---|---|
| **34CrAlNi7** | **1123** | 1 | 46,6±3,8 |
| | | 2 | 77,3±4,1 |
| | | 4 | 82,6±10,4 |
| | **1223** | 1 | 115,2±2,1 |
| | | 2 | 138,4±3,1 |
| | | 4 | 185,5±2,1 |
| | **1323** | 1 | 196,3±11,2 |
| | | 2 | 217,6±13,3 |
| | | 4 | 351,8±15,2 |

The hardness values measured from the surface to the matrix by the Vickers method at a distance of 20 µm to 220 µm and the changes in these values can be seen at Table 3.

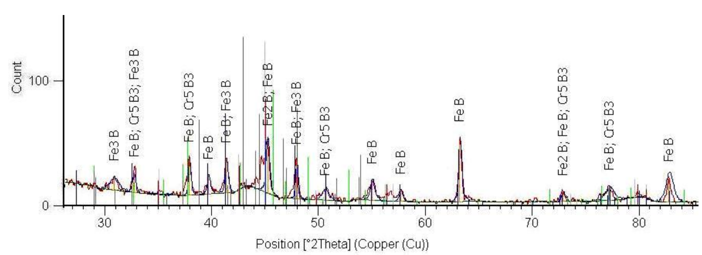
**Table 3.** Microhardness measurements of the boronized 34CrAlNi7

| Boronizing Temp. (K) | Boronizing Time (h.) | Microhardness Measurement ($kg/mm^2$) Distances From Surface to Center | | | |
|---|---|---|---|---|---|
| | | **20µm** | **40µm** | **100µm** | **220µm** |
| **1123** | **4** | 2216 | 1961 | 426 | 381 |
| | **2** | 2106 | 1899 | 389 | 317 |
| | **1** | 1869 | 971 | 361 | 321 |
| **1223** | **4** | 2857 | 2446 | 2016 | 392 |
| | **2** | 2814 | 2167 | 1896 | 321 |
| | **1** | 2321 | 2002 | 1772 | 383 |
| **1323** | **4** | 2896 | 2521 | 2111 | 1997 |
| | **2** | 2881 | 2186 | 1989 | 1808 |
| | **1** | 2403 | 1999 | 1921 | 1001 |

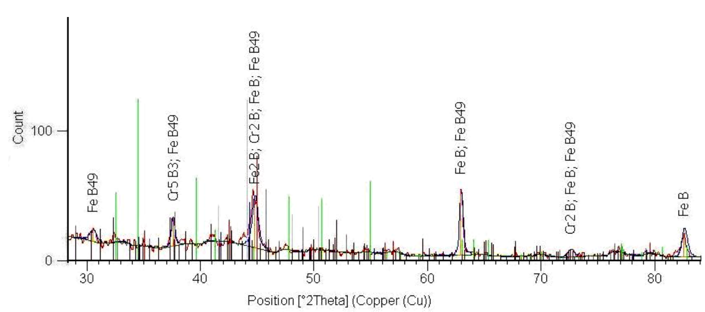
### 3.2 XRD Analyses

XRD analyses were carried out on the sample that had been boronized for 1123K, 1223K and 1323K for 1 h. For analysis, Philips Panalytical X-Pert Pro Brand X-Ray Diffractometer is used. Cu(Kα) having the wavelength 1.5406 Å which matches the interatomic distance of crystalline solid materials as well as the intensity of Cu(Kα) is higher than other which is sufficient for the diffraction of solid material so Cu(Kα) is used for analysis. The peaks obtained after the analysis are shown in Figure 3.

As in all steel types, boride layer formed on 34CrAlNi7 has a double-phase structure occure with FeB and $Fe_2B$. However, due to the alloying elements in this type steel, small amounts of $Fe_3B$, $FeB_{49}$, $Cr_2B$ and $Cr_5B_3$ phases were found.




**(a)**




**(b)**

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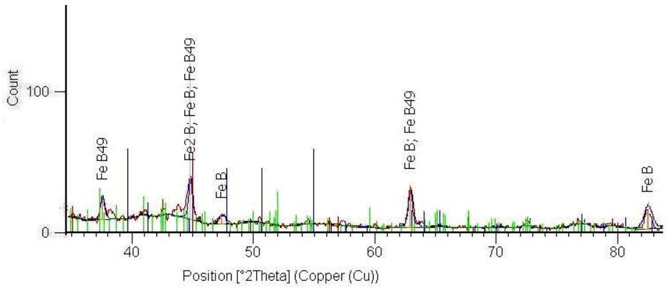


**(c)**

**Figure 5.** X-ray diffraction patterns of boronized 34CrAlNi7 (1h.) at different temperatures, a)1123K, b)1223K, c)1323K

### 3.3 Kinetic Examinations

The equation that determines the thickness of boride layer changes parabolically over time is given below [8,13].

$$\mathbf{x = \sqrt{Kt}} \tag{1}$$

According to this equation; *x* indicates the boride layer thickness in cm, *t* indicates the boronizing time in s., and *K* indicates the growth rate constant in $cm^2\ s^{-1}$. If the growth kinetics of the boride layer is desired; As can be seen from Figure 4, the square of the boride layer thickness changes linearly over time.

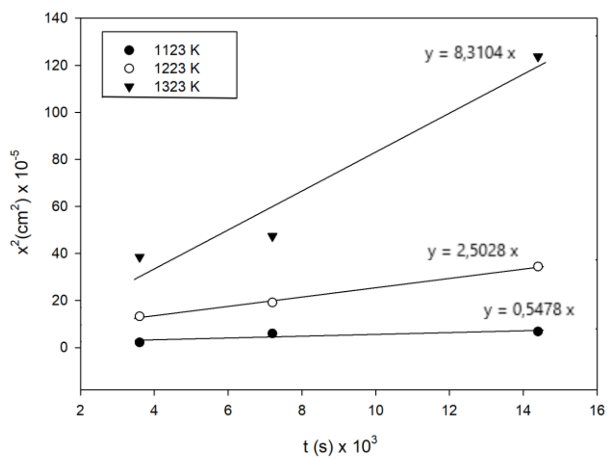


**Figure 6**. Square of the boride layer thicknesses on boronized steel 34CrAlNi7over treatment time.

Boron diffusion is the primary factor affecting layer growth. The relationship between growth rate constant and activation energy is explained by the Arrhenius equation is given below [13,14].

$$\mathbf{K = K_0 \times \exp\left(-\frac{Q}{RT}\right)} \tag{2}$$

According to equation; *K* indicates the growth rate constant in $m^2\ s^{-1}$, *Q* indicates the activation energy in j $mol^{-1}$, $K_0$ indicates the pre-exponential constant in $m^2\ s^{-1}$ and *R* indicates the gas constant in j $mol^{-1}\ K^{-1}$. Equation 3 is natural logarithm of Equation 2.

$$\mathbf{\ln(K) = \ln(K_0) - \left(\frac{Q}{RT}\right)} \tag{3}$$

In order to find the activation energy value, ln K - 1 / T graph should be plot first. The slope of this graph gives the activation energy value and this can be seen in Figure 7.

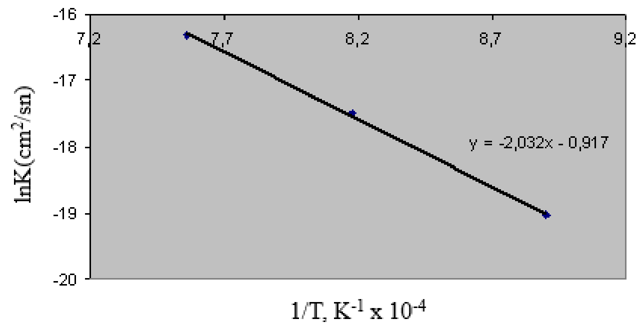


**Figure 7.** Growth rate constant vs. temperature of boronized 34CrAlNi7

The activation energy and pre-exponential constant values were obtained from the relationship of the slope of the straight line obtained at 1 / T = 0 with the abscissa as origin; the results are listed in Table 4.

**Table 4.** Activation energy, frequency factor, and diffusion depth of boronized 34CrAlNi7

<table>
<tr><th>Boronized Material</th><th>Q<br>(kj/mol)</th><th>$K_0$</th></tr>
<tr><td rowspan="3">34CrAlNi7</td><td>169</td><td>$40{*}10^{-2}$</td></tr>
<tr><td colspan="2">x<br>(cm)</td></tr>
<tr><td colspan="2">$\sqrt{\ 40{*}10^{-2}\ \exp(20320/T) * t}$</td></tr>
</table>

### 3.4 Discussion

Based on these experimental results, boride layer can be formed on the 34CrAlNi7 nitriding steel surface without oxidation with fluidized bed furnace by pack boronizing treatment. At the same time, it is an efficient way to obtain high surface hardness. Increasing treatment time and temperature, increases layer thickness.

The microstructures showed that two distinct regions were identified on the surface of the specimens; the boride layer formed from FeB and $Fe_2B$ phases, and matrix. Unlike the stainless steels, the boride layer formed on 34CrAlNi7 has a saw-tooth morphology.

From the micro hardness measurements, a decrease in hardness values from the surface to the matrix was found. This is because, the amount of boron in the $Fe_2B$ phase is less than in that FeB phase.

According to the XRD results, boride layer formed on 34CrAlNi7, has a double-phase structure occure with FeB and $Fe_2B$. However, due to the other alloying elements in this type of steel, $Fe_3B$, $FeB_{49}$, $Cr_2B$ and $Cr_5B_3$ phases were also found. The Arrhenius equation was used to calculate the growth kinetics of the boride layer. As a result of calculations, activation energy of boronized 34CrAlNi7 nitriding steel has been determined as 169 kJ/mol. and this value is consistent with the other studies in the literature. This comparison can be seen in Table 5.

**Table 5.** The comparison of activation energy for diffusion of boron with respect to the different studies

| Type of steel | Range of Temp. (K) | Boronizing Process | Activation Energy (kj/mol) | Ref. |
|---|---|---|---|---|
| 34CrAlNi7 | 1123-1223 | Powder pack | 270 | [15] |
| | 1123-1323 | Powder pack | 169 | This study |
| X5CrNi 18-10 | 1123-1323 | Powder pack | 244 | [16] |
| X5CrNi 18-10 | 1123-1223 | Powder pack | 234 | [17] |

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