Investigation of corrosion properties of box boring din 20MnCr5 steel bars

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Abstract. In this study, boriding process was carried out on Ø11 mm diameter DIN 20MnCr5 quality steel bars, used in chain elements such as links and rings, and fasteners such as bolts, at 950°C boronizing temperature, boriding times of 2.5 and 7.5 hours. In this study, the formation and growth of the boride layer and the metallographic structure, the coating thickness and corrosion properties of the boronized steels were investigated depending on the boriding conditions. In the box boriding process, Ekabor-II powder mixture, with its commercial name, was used as boriding powder. According to the optical microstructure results made as a result of box boriding, the coating thickness was 371.5 µm in the Ø11 mm diameter boronized DIN 20MnCr5 steel bar for 7.5 hours boriding times while it was 195.6 µm in that steel bar for 2.5 hours boriding times. Corrosion experiments were carried out in solutions prepared by adding 3.5% NaCl to distilled water. According to the results of the immersion test, the lowest corrosion rate in mdd was measured as 112 mg/(dm^2 x day) in the Ø11 mm diameter, 7.5 hour boronized sample, and the highest corrosion rate in mdd was 1456.75 mg/(dm^2 x day) in the untreated Ø11mm diameter sample. In the potentiodynamic polarization test, parallel results were obtained for immersion corrosion. Corrosion rate values (i_{cor}) were measured at the highest value of 209 x 10^{-6} A/cm^2 in the untreated Ø11 diameter sample, while the lowest icor value was 0.0039 x 10^{-6} A/cm^2 in the Ø11 mm diameter sample borided for 7.5 hours.

1 Introduction

In a study by Ergun Y. et al. [1], by applying box boriding process with a different steel quality (AISI 420), the affinity of the boron element against oxygen was used and the effect of the protective thin oxide layer formed on the surface was investigated. In addition, hardness values were also compared. Liszewski, M. et al. [2]applied box boriding, box cementation, box chroming and vacuum chroming processes to DIN 20MnCr5 steel and they carried out that the working hardness tests were limited to tribological analyzes performed on a pin-on disc type wear device that makes it possible to determine the wear

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density. Krumes D. et al. [3] performed duplex surface hardening of DIN 20MnCr5 steel. First, box boriding (900°C and 4 hours) was carried out, and in the second stage after boriding, plasma nitriding (520oC and 40 minutes) was performed using a commercial (pn-mono 5) unit. Box boriding surface treatment on DIN 20MnCr5 steel was limited to the specified studies. However, today, many metals are subject to corrosion as a result of electrochemical reactions with their environment due to the environment and environmental factors they are exposed to, and therefore, their service life ends before the expected time. Considering this situation, the investigation of the corrosion properties of DIN 20MnCr5 steel bars used in chain elements such as links and rings, and fasteners such as bolts, has been incomplete

In can boriding studies for DIN 20MnCr5 steel; boronizing process is a thermochemical surface treatment in which a hard boride layer is obtained on the surface by spreading the boron element on the metal surface in the range of 700-1000 °C, in boriding times of 1-12 hours [4-7]. Boron-coated materials have a wide range of industrial use due to their superior properties. Therefore, boronizing is a surface treatment that has advantages among the surface treatments applied for these purposes [8-10].

In boriding process, boron atoms diffuse rapidly to ferrous alloys at high temperature (700–1000°C) and settle in the matrix of ferrous alloys with thermal energy, forming FeB and Fe2B type intermetallic compounds thanks to their small atomic diameters and strong mobility [5,11]. Iron borides (Fe2B, FeB) formed on the surfaces as a result of boriding have high hardness, high wear resistance and high corrosion resistance, as well as low friction coefficient of the boride layer, high thermal and electrical conductivity [12-14].

Depending on the duration and temperature of the boriding process, a single-layered boride layer containing only Fe2B from these single-phase or double-phase intermetallic compounds or a two-layered boride layer containing the FeB intermetallic compound together with this layer is formed on the boronized surface [15-18]. Contrary to the Fe2B + FeB dual phase structure, the development of Fe2B as a single phase is preferred because it is much more advantageous for industrial applications. Because the outermost FeB phase is a much more brittle phase and has a higher coefficient of thermal expansion. Due to the different thermal expansion rates of the Fe2B and FeB phases formed in the two-phase system, surface cracks occur. Therefore, the occurrence of these cracks can be prevented by reducing the ratio of the FeB phase or preventing the formation of the FeB phase [19-22].

Within the scope of the study, the formation of the boride layer was to accomplish by applying the box boriding method to DIN 20MnCr5 steel bars with Ø11 mm diameters at a constant boriding temperature of 950 ºC and at two different boriding times of 2.5 and 7.5 hours. And also the aim of this study is to investigate the microstructure and corrosion properties of the coated DIN 20MnCr5 steel bars. The corrosion resistance of the investigated steel bars performed with Potentiodynamic Polarization and immersion corrosion tests.

2 Objects and methods of research

In this study, the chemical composition of the examined DIN 20MnCr5 steel bars with Ø11 mm diameters is given in Table 1.

Table 1. Chemical composition of DIN 20MnCr5 steel bars

Quality Code	Diameter (mm)	Chemical Composition					
		%C	%Mn	%Si	%S	% P	% Cr
20MNCR5	Ø11	0.199	0.68	0.217	0.016	0.017	1.003

The boriding process was carried out by annealing at 950 oC at different boriding times of 2.5 and 7.5 hours using a powder mixture known as Ekabor-II in 3-6 micron sizes into a cast iron box in a furnace under atmospheric conditions (Fig. 1). Copper flakes were used as deoxidant material in boriding process.

Fig. 1. Box boriding process stages

Examination of the morphology of the boride layer and the coating thicknesses was carried out under a Carl Zeiss optical microscope. For microstructural studies, the samples were subjected to traditional microstructural preparation processes and then etched in an etching agent prepared with 3.5 ml HNO_3 and 100 ml Ethyl alcohol (3.5% Nital) for 50 seconds. Corrosion test was done by potentiodynamic polarization test and immersion test. After being wrapped with copper wire for the potentiodynamic polarization test, the samples to be examined were embedded in epoxy resin perpendicular to the hardened surface, leaving an area of 254 mm2 exposed from the front. Potentiodynamic polarization tests were performed at room temperature, in 3.5% NaCl solution, with a computer-controlled DC105 corrosion analysis Gamry model PC4/300 mA potentiostat/galvanostat. Graphite rod was used as counter electrode, saturated calomel electrode (SCE) as reference electrode and classical three-electrode cell with sample surface as working electrode. Polarization curves were generated by scanning in the range of -0.25 V (vs. Open circuit potential, Eoc) to +0.25 V (vs. Eoc) at a scanning rate of 1 $mV.s^{-1}$. Three potentiodynamic polarization tests were performed for each parameter and the average of the results was taken.

For the immersion corrosion test, 6 different samples of DIN 20MnCr5 steel bar quality, boronized and unbored in Ø11x15 mm dimensions, were first calculated on their surface areas and weighed with a precision balance. Then, the solution prepared by the addition of 3.5% NaCl in pure water in a glass jar at ambient temperature was placed in a polymer net and immersed. The samples, which were immersed in the solution, were removed from the solution-filled jars at intervals of two at 0-8 hours, four at intervals of 8-24 hours, and eight hours at intervals of 24-48 hours. After cleaning, drying process was applied and weighed with a precision balance of 0,1 mg. Immediately after the weighing result was recorded, the samples were dipped into the jars in the same way and this process was repeated at the specified time intervals. After the test, it was calculated as mdd (mg/(dm^2*day)). Here; mg: The measured weight loss of the sample removed from the corrosion environment at certain periods, dm^2: the surface area of the sample before the test, day: The time was exposed to the corrosion environment.

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3 Results and their discussion

As seen in Fig. 2, the boride layer and the matrix region are clearly separated by color in all microstructures. The interface between the main matrix and the boride coating changed from a flat interface to a discontinuous wavy interface morphology with increasing coating layer thickness. As the boriding time of DIN 20MnCr5 steel with Ø11 mm diameter increased, the boride coating thickness increased as % 90 (Figure 2). Since the grain boundaries are more reactive, they are the nucleation starting points of the boride layer formation. At these points, Fe2B nuclei are formed and developed. For this reason, when the layer thicknesses given in Table 2 are examined, the boride layer thicknesses are higher in Ø11 mm diameter steel bars because the boriding time increased.

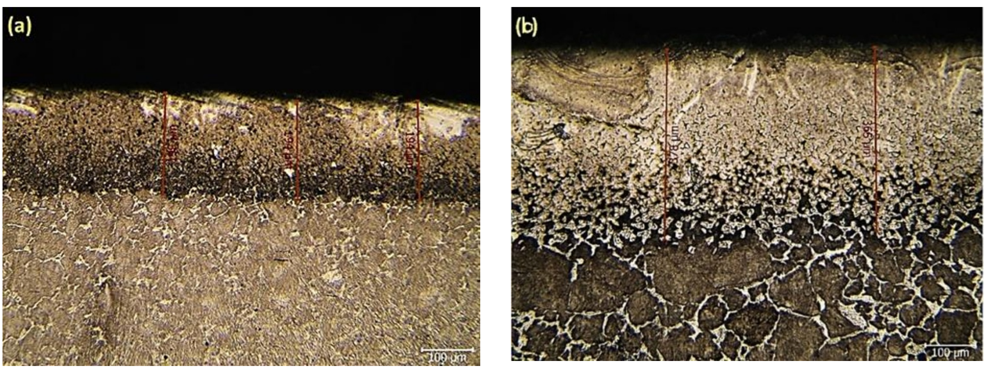

Fig. 2. Optical microstructure and layer thicknesses of DIN 20MnCr5 steel rods boronized at 950 °C a) Ø11 mm diameter – 2.5 hours and b) Ø11 mm diameter – 7.5 hours

Table 2. Boride layer thickness of DIN 20MnCr5 steel after box boriding

Steel Quality	Layer Thickness (µm)	
	Ø11 mm diameter - 2.5hour	Ø11 mm diameter - 7.5hour
DIN 20MnCr5	Avg: 195.6	Avg : 371.5

The tafel curves including the anodic and cathodic regions of the potentiodynamic polarization experiment are given in Fig. 3.

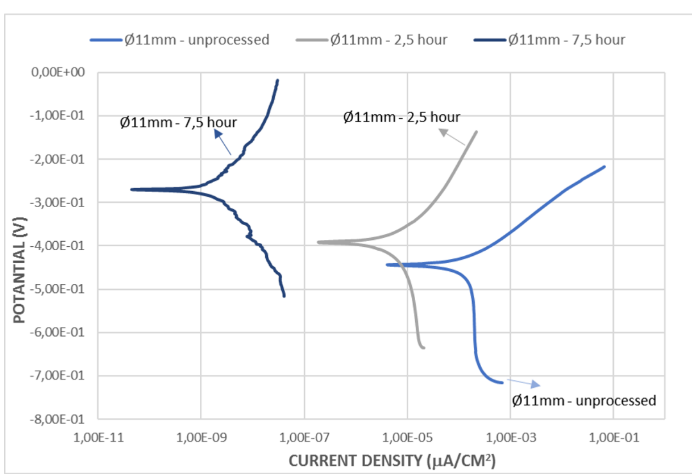

Fig. 3. Potentiodynamic polarization test plots.

In the graph given in Figure 3, untreated samples show close potential values according to the potential values in the anodic region. It is seen that the steel with Ø11 mm diameters boronized for 2.5 and 7.5 hours have a higher equilibrium potential (Ecor) than untreated steels, that is, they are in a more passive area and have a lower corrosion tendency. Thus, the corrosion tendency of DIN 20MnCr5 steels decreases as a result of boriding. When looking at the Ø11 mm diameter samples boronized for 2.5 hours and 7.5 hours, the potential values (Ecor) of Ø11 mm diameter steels boronized for 7.5 hours are higher than that of the Ø11 mm diameter steels boronized for 2.5 hours.

The Icor (µA/cm^2) values on the x-axis of the graph give the corrosion rate. Corrosion rate (icor (µA/cm^2)) and potential (Ecor (V)) values of DIN 20MnCr5 steel bar samples are given in Table 3. The untreated steels bar with Ø11 mm diameter has a higher corrosion rate than that steels with Ø11 mm diameters boronized for 2.5 and 7.5 hours. When looking at Ø11 mm diameter steels boronized for 2.5 and 7.5 hours, corrosion rate decreases with increasing boriding time.

Table 3. I_{cor} and E_{cor} values of DIN 20MnCr5 steel samples with Ø11 mm diameter

	Unprocessed Sample	2.5 hours Boring	7.5 hours Boring
E_{cor} (mV)	-445	-391	-271
I_{cor} (A/cm^2)	209 x 10^{-6}	19 x 10^{-6}	0.004 x 10^{-6}

The weight loss-time curves at the end of the immersion corrosion test are given in Fig. 4 and the steady-state corrosion rates of the samples in the form of a bar graph in Fig. 5.

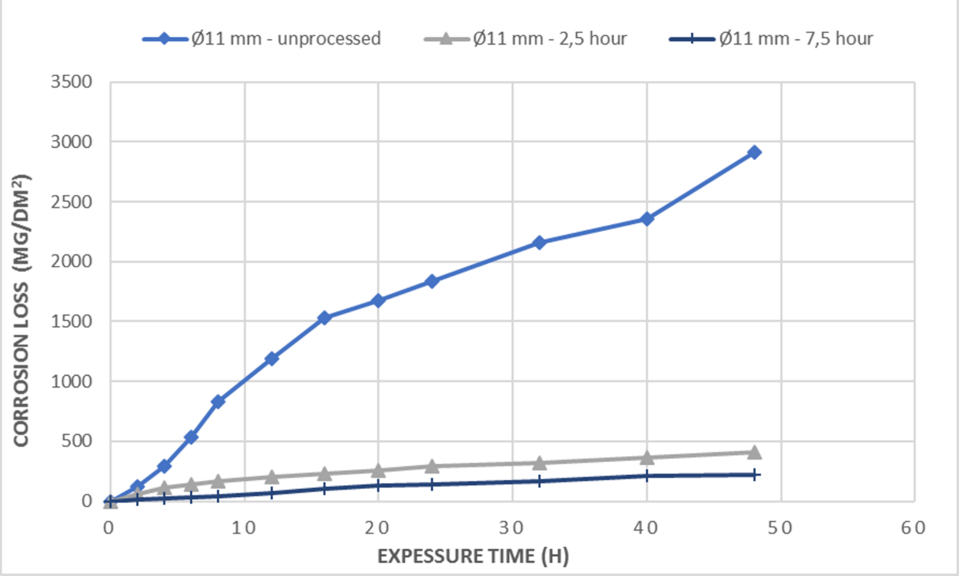

Fig. 4. Weight loss – time curves of Ø11 mm diameter DIN 20MnCr5 steel bar samples as a result of immersion corrosion

As seen in Fig. 4, the corrosion loss in the Ø11 mm untreated sample showed a higher increase over time compared to the other boronized samples. It was observed that the corrosion loss of the sample borided at 950 oC for 2.5 hours was higher than the corrosion loss of the Ø11mm diameter sample borided for 7.5 hours.

According to Fig. 5, the corrosion rate of the untreated Ø11mm diameter sample was higher than the Ø11mm diameter samples boronized at 950 °C for 2.5 and 7.5 hours. However, the corrosion rate of the sample boronized at 950 °C for 2.5 hours was higher than the corrosion rate of the Ø11mm diameter sample boronized for 7.5 hours.

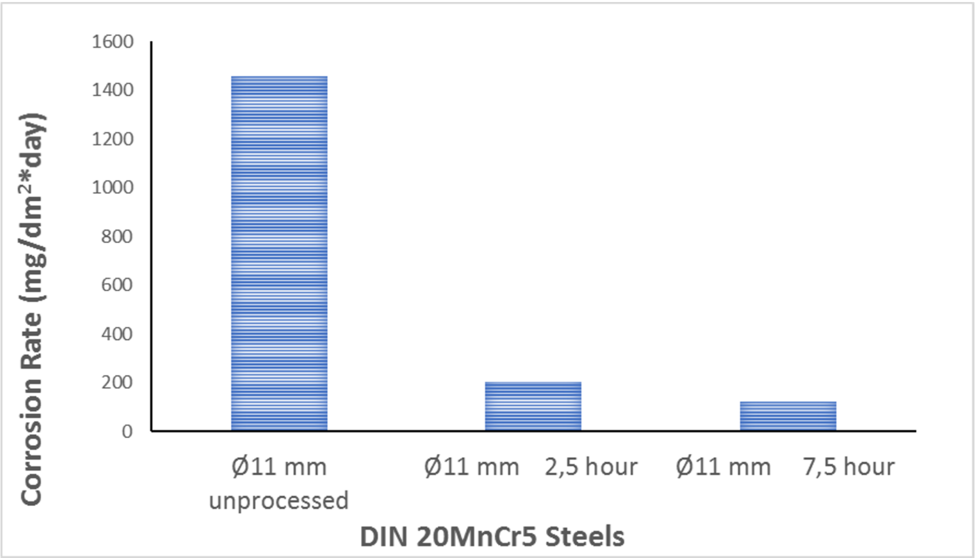

Fig. 5. Variation of steady-state corrosion rates of the investigated samples

4 Conclusions

The effect of two different boriding heat treatment times on the corrosion behavior of 11 mm diameter DIN 20MnCr5 steel bars was investigated. From the experimental results, the following results were obtained;

1. According to the optical microstructure images, the boride coating thickness of the Ø11 mm diameter sample boronized at 950°C for 2.5 hours was 195.6 µm, and the boride coating thickness of the Ø11 mm diameter sample boronized at 950°C for 7.5 hours was 371.5 µm.

2. The interface between the main matrix and the boride coating changed from a flat interface to a discontinuous wavy interface morphology with increasing coating layer thickness.

3. According to the results of immersion corrosion, the corrosion rate in mdd of the untreated Ø11 mm sample was 1456.75 mg/(dm^2 x day), the sample boronized at 950°C for 2.5 hours 205 mg/(dm^2 x day), and the sample boronized at 950°C for 7.5 hours, the corrosion rate was 112 mg/(dm^2 x day).

4. Potentiodynamic polarization tests show parallel results with immersion corrosion. Corrosion rate values (Icor) were found as 209 x 10^{-6} A/cm^2 in the untreated Ø11 mm diameter sample, 19 x 10^{-6} A/cm^2 in the Ø11 mm diameter sample boronized at 950°C for 2.5 hours and 0.0039 x 10^{-6} A/cm^2 in the Ø11 mm diameter sample boronized at 950°C for 7.5 hours.

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