MECHANICAL PROPERTIES, WEAR AND CORROSION OF BORONIZED N80 TUBE STEEL

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The effect of boronizing on mechanical properties, wear and corrosion of boronized N80 tube steel is studied. A dual-phase boride layer consisting of FeB and F_2B phases was formed on the surface of steel substrate in a hardness range of 1220 to1340 HV. A set-up to use less boriding agent and accelerate the pipe's cooling process was designed. In order to meet the tensile properties of N80 steel required by API SPEC 5L, four cooling methods were employed. The fan-cooling with a graphite bar inside the boriding agent resulted in the highest mechanical properties, in accordance with the mechanical properties of API SPEC 5L. The boronized N80 steel showed a high wear resistance under dry sliding condition and excellent corrosion resistance in as-received oilfield water from Jilin oil field, Northeast China.

Keywords: *boronizing, mechanical properties, wear, corrosion.*

Boronizing is a thermochemical surface treatment by thermodiffusion followed by chemical reaction into the surface. Its use increases strongly the surface hardness (about 1200...2000 HV), wear resistance and anticorrosion properties of the boride layers [1]. Boronizing of carbon steels usually leads to the formation of two different iron boride phases: FeB at the surface and Fe_2B between the matrix and FeB [2]. Industrial boronizing can be carried out on most ferrous materials such as structural steels, cast steel, armco iron, gray and ductile iron [3–5]. Boronized steel consistently outperforms the nitrided and carburized steel essentially, because the formed iron boride exhibits substantially a higher hardness as compared to carburized or nitrided steels (650...900 HV). In particular, boronized steel exhibits the excellent resistance to a variety of tribological wear mechanisms. In addition, the resistance of boronized steel to the attack of the non-oxidizing dilute acids, alkalis and molten metals is also outstanding.

A relatively cheap material widely used for a tube in oilfield is N80 steel, but it displays unsatisfied performance under severe conditions of high corrosion and heavy wear, especially in acid environment containing CO_2, H_2S according to the investigation on degradation of the tubing metal in hydrogen-sulfide environments [6, 7]. Boronizing is expected to improve effectively the corrosion and wear resistance of N80 steel tube. However, to ensure that the boronizing of N80 tube steel shall be practical in oil industry, two problems associated with the process must be addressed. Firstly, the minimum usage of boriding agent can be performed. Secondly, an appropriate cooling manner must be chosen to ensure that the tube shall meet the mechanical properties demanded by API SPEC 5L.

We have designed a boronizing set-up to use less pack powder and chose one among the different cooling methods, which is qualified for the mechanical properties required by API SPEC 5L. The effect of boronizing on the wear and corrosion are also presented. The results can provide a useful reference for extending application of in oil industry.

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Experimental procedure. Boronizing process was carried out at 1133 K for 5 h with a powder mixture constituted by B_4C (5 wt.%), KBF_4 (5 wt.%), a reducing agent (10 wt.%) and SiC (balance) in an electrical resistance furnace. Four pieces of 160 mm long pipe were cut from a N80 steel oil pipe with 73.02 mm outer diameter and 5.51 mm wall thickness. The chemical composition of N80 steel is: 0.36 wt.% C; 0.32 Si; 1.55 Mn; 0.020 P; 0.010 S; 0.040 Cr; 0.050 Cu; 1.20 V; 0.040 wt.% Ni. Different cooling manners or interior design were used to obtain different cooling velocities. A graphite bar with a diameter of 33 mm placed in the center of boriding agent was used to reduce the usage of boriding agent and to increase the cooling velocity. Four different cooling methods were used including annealing, normalizing, fan cooling and fan cooling with a graphite bar in the center of the boriding agent.

Tensile tests were carried out using specimens having a reduced cross-section of 19.8×5.5 mm and a gauge length of 50.8 mm, which were machined from the non-boronized and boronized pipes, respectively.

Wear testing was conducted on a pin-on-disc type machine under dry sliding condition at a room temperature of 298 K. Specimens of 5 mm diameter × 12 mm length were machined from the pipe wall and then boronized for wear test. The tests were carried out in a load range of 50 to150 N at a sliding speed of 0.785 ms^{-1}. The disc was 70 mm in diameter and made of high carbon chromium steel hardened to a hardness of 57 HRC.

The corrosive solution was typical of oil field water in northeast China, which was transported in glass bottles from an oil well in Jilin oilfield, China, to the authors' laboratory. It has a total mineralization of 1.8×10^4 mg/L. Composition of the oil field water is: 6.20 g/L Cl^-; 1.75 SO_4^{2-}; 1.22 HCO_3^-; 0.082 Mg^{2+}; 0.22 Ca^{2+}; 7.50 Na^+; 0.12 CO_3^{2-}; 0.040 H_2S; 0.052 CO_2. Rectangular specimens of dimensions 10.7×9.6×4.3 mm^3 were used in corrosion immersion tests.

To further evaluate the corrosion resistance and possible passivation behavior of the samples, electrochemical measurements were performed in as-received oil field water on an Electrochemical Analyzer. Linear sweep voltammetry experiments were carried out in the oil field water using a classic three-electrode cell with a platinum plate (Pt) as counter electrode and an Ag/AgCl electrode as a reference electrode with a sweeping rate of 50 mV min^{-1}at room temperature.

Experimental results and discussion. Optical microscopy cross-sectional examinations of boronized inner surfaces of N80 steel pipes cooled by different cooling methods revealed the formation of a dual-phase boride layer, the thickness of boride layer ranging from 50±5 μm to 70±5 μm in a sequence of cooling velocity from the fast to the slow, namely fan cooling with a graphite bar in the center of the boriding agent, fan cooling, normalizing (air cooling), and annealing (furnace cooling). Fig. 1 shows that a dual-phase boride layer of about 64...72 μm thickness was formed on the substrate of the annealed N80 steel pipe. The outmost zone was FeB phase with 4...8 μm thickness, next to which there was a rather thick Fe_2B phase zone of about 64 μm thickness with a saw-tooth morphology followed by the steel substrate. Thus, the removal of the F_2B saw-tooth shaped boride layer becomes very difficult by mechanical effects [4].

Microhardness profile measured on the same cross-section reveals that the hardness of the boride layer is about 1220...1340 HV, much higher than the 160 HV of the steel substrate. Because the FeB layer is so shallow this hardness is typical of Fe_2B layer. The Fe_2B is especificcially desirable for industrial applications volume and owing to the difference between the specific volume and coefficient of thermal expansion of the boride and the substrate.

The minimum values of the mechanical properties of N80 tube required by the API SPEC 5L are as follows: 1) yield strength (YS) is higher than 552 MPa; 2) ultimate tensile strength (UTS) higher than 689 MPa; 3) elongation (EL) higher than 14%, respectively.

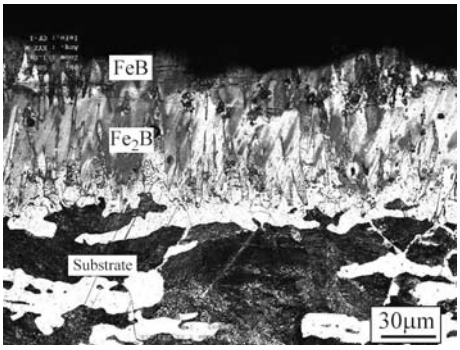

Fig. 1. Optical microscopy cross-section of N80 steel pipe boronized at 860°C for 5 h.

To meet these mechanical properties, four cooling methods were used to obtain different cooling velocities in a sequence from the slow to the fast, namely annealing, normalizing, fan-cooling and fan-cooling with a graphite bar in the center of the boriding agent. Two points can be drawn from the tensile properties of boronized as well non-boronized N80 steels as given in Table 1: firstly, the boride layer, to a certain extent, deteriorates the tensile properties of the N80 steel tube since the tensile properties of boronized pipes are lower than the original one except elongation. Secondly, the cooling velocity can considerably influence the mechanical properties, especially YS and UTS. The deterioration of tensile properties is due to the forepart fracture of boride layer since a common phenomenon was observed for all boronized samples during tensile testing at about a stress of 479 MPa, the boride layer cracked due to its fragile nature, consequently a saw-like plateau occurred on the curve. SEM examination of the cracks on the sample surface reveals the cracks penetrating through the boride layer, which may cause stress concentration and tensile properties hence are deteriorated. However, the negative influence of boride layer cracks is limited because no evidence of brittle fracture like cleavage plane but ductile fracture of dimples is observed nearby the boride layer. It is noticeable that there is not much difference in the fracture mode for N80 steel pipes cooled by different ways, all specimens failed in ductile manner with numerous dimples over the fracture surface.

Table 1. Tensile properties of boronized N80 steel obtained by different cooling methods

Cooling method	σ	σ_u	δ, %
	MPa		
Annealing	562	606	23
Normalizing	623	667	24
Fan-cooling	625	687	26
Fan-cooling with graphite bar	643	722	25
Non-boronized	648	701	20

As the cooling velocity is increased, the tensile strengths including yield strength and ultimate strength are remarkably improved. Since the boride layer is not differentiated from each other very much in terms of hardness and thickness under four given cooling conditions, and it is so thin as compared with the wall thickness of steel substrate the tensile properties of boronized N80 steel pipes, to a great extent, are reliant on the properties of steel substrates from different cooling methods. The comparison of microstructures of steel substrates under two different cooling conditions is given in Fig. 2. It can be seen that microstructures of steel substrates equally consist of light ferrite and dark pearlite, and it is well known that the latter has much higher strength than the former. However, the differences in volume fraction for both ferrite and pearlite are rather distinct. On the basis of the microstructure constituent law of the mixture theory, the yield strength (σ_y) of a mixture of ferrite and pearlite can be expressed in terms of volume fraction of ferrite (V_f) and pearlite (V_p) and yield strength of ferrite (σ_f) and pearlite (σ_p) as follows:

$$\sigma_y = V_f \sigma_f + V_p \sigma_p .$$

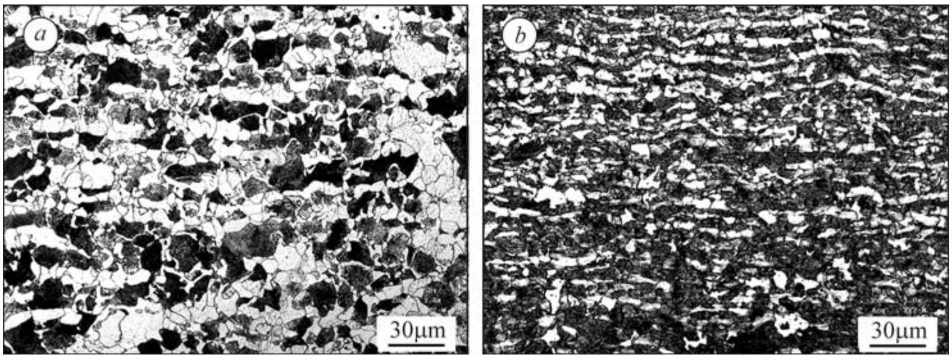

Fig. 2. Microstructures of N80 steel substrate treated with different methods: *a* – annealing; *b* – fan-cooling with a graphite bar inside the boriding agent.

As the cooling velocity increased from the annealing to fan cooling with a graphite bar inside, the pearlite consequently increased from 45.5 vol.% to 66.1 vol.%, whereas the volume of ferrite accordingly decreased, consequently leading to an increase in YS and UTS. In the case of YS, three kinds of pipes exceeded 552 MPa of API SPEC 5L except the annealing one, whereas only the fan-cooling tube surpassed 689 MPa of UTS required by API SPEC 5L. The four kinds of tube exhibited good elongation higher than 20%. Therefore the fan-cooling with a graphite bar is the best choice suitable for boronizing N80 tube.

The forepart cracking of the boride layer can cause the protection against wear and corrosion lost, but this does not mean that the borided tube has great limitation in practical application for the stress level of 479 MPa and can bear a total weight of 43.2 tons of oil pipes, which can reach a 4000 m depth and is enough for the conventional oil well.

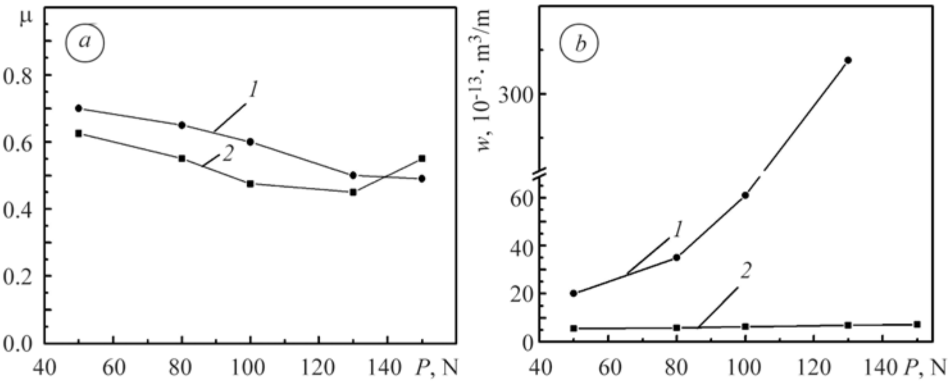

Fig. 3. Variation in coefficient of friction (*a*) and wear rate (*b*): *1* – non-boronized N80 steel; *2* – boronized N80 steel.

The coefficient of friction and wear rate as a function of applied load are shown in Fig. 3. The coefficient of friction for both materials decreases with increasing the applied load, and boronized steel exhibits the lower value than the non-boronized one. Friction coefficient ranges from 0.45 to 0.63 for boronized, and from 0.49 to 0.70 for non-boronized N80 steels, respectively. It is evident that the friction coefficient depends systematically on surface hardness. However, as the load increased to 150 N, the sudden rise in friction coefficient for the boronized N80 steel is due to localized spalling of the bride layer on a worn surface. The boronized samples exhibited the effective wear resistance as compared with the untreated ones. The wear rate of non-boronized steel dramatically went up as the applied load was over 100 N because of surface softening caused by substantial friction heat whereas the boronized steel can maintain a low and steady wear process under given conditions due to presence of boride layer. It was observed that after sliding a distance of 754.56 m, as the load was lower than 150 N, the boride layer remained uninjured except of a few grooves on the worn surface. Thus, an abrasive wear mechanism was effective. Previous studies by Hungar and Trute have shown that the boronized steels are extremely resistant to abrasion and adhesion on account of their great hardness [8]. The boride layers have a low welding tendency. This property is of the great consequence for adhesive wear and explains why boronized samples show higher wear resistance.

The corrosion resistance of the boride layer was investigated by immersion tests and polarization curves. Fig. 4*a* shows the weight loss curves for both the boronized and non-boronized specimens immersed in oil field water. As indicated, the weight loss curve as a function of immersion time for boronized steel slightly increases linearly in a very low slope with increasing immersion time, indicating the effective anticorrosion property of the boride layer in the studied corrosion solution.

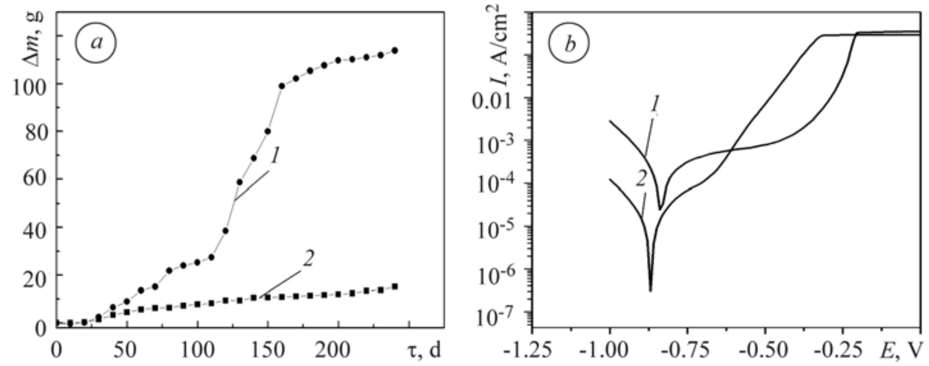

Fig. 4. Weight loss of immersion tests in oilfield water (*a*) and Potentiodynamic polarization curves (*b*): *1* – non-boronised N80 steel; *2* – boronized N80 steel.

Table 2. Values of E_{corr} and I_{corr} calculated from Tafel extrapolation method

Sample	E_{corr}, mV	I_{corr}, μA/cm^2
Boronized	–868.4	1.62
Non-boronized	–838.6	54.27

Fig. 4*b* shows the electrochemical polarization curves for the plain and boronized N80 steels in as-received oil field solution at room temperature. The corrosion potentials and corrosion currents for the respective materials, obtained from the intersection of cathodic and anodic Tafel plots, are given in Table 2. There is no much difference in corrosion potential for both non-boronized and boronized steels exposed to oilfield water, however, the boride layer can significantly reduce the corrosion current. The corrosion current density of the boronized sample is 1.62 μA cm^{-2} in oil field water, only 2.98% of the untreated N80 steel in the same corrosion solution. As the corrosion current density is related to the corrosion rate of materials, the higher corrosion current density indicates a more severe corrosion. Therefore, the polarization curves imply that the corrosion resistance of the boride layer is superior to the non-boronized steel, which is in good agreement with the immersion tests.

CONCLUSIONS

Duplex boride layers with a total thickness of 50±5 μm to 70±5 μm were obtained on N80 steel substrate at 860°C for 5 h by pack boriding, which consisted of a thin outer layer of FeB phase and a rather thick layer of Fe_2B phase with a saw-tooth morphology and a hardness range of 1220...1340 HV.

The inner structure design of the boronizing set-up to and different cooling methods can significantly influence both the microstructure and mechanical properties of borided N80 steel pipes, the finest microstructure consisting of the ferrite and pearlite has been obtained by fan-cooling with a graphite bar in the center of the boriding agent, and its mechanical properties are in accordance with API SPEC 5L.

The boride layer provides the excellent wear resistance in a load range of 50...130 N at a sliding speed of 0.785 ms^{-1} and improves the corrosion resistance of N80 steel in as-received oil field water from Jilin oilfield, Northeast China.

РЕЗЮМЕ. Вивчено вплив борування на механічні властивості, зношування та корозію трубної сталі N80. На поверхні сталевої підкладки сформовано двофазний боридний шар на основі FeB і F_2B з твердістю 1220...1340 HV. Розроблено способи для зменшення кількості компонента для борування та пришвидшення охолодження. Для забезпечення високих механічних характеристик за розтягу згідно зі специфікацією API SPEC 5L використано чотири методи охолодження. Вентиляторне охолодження з графітовим бруском всередині борувального реагента призвело до найвищих механічних характеристик. Борована сталь виявила високі зносотривкість за сухого тертя та корозійну міцність у воді з нафтового родовища в Китаї у провінції Джулін.

РЕЗЮМЕ. Изучено влияние борирования на механические свойства, изнашивание и коррозию трубной стали N80. На поверхности стальной подкладки сформирован двухфазный боридный слой на основе FeB и F_2B с твердостью 1220...1340 HV. Разработаны способы для уменьшения количества компонента для борирования и ускорения охлаждения. Для обеспечения высоких механических характеристик при растяжении согласно спецификации API SPEC 5L использованы четыре метода охлаждения. Вентиляторное охлаждение с графитовым бруском внутри борированного реагента обусловило наиболее высокие механические характеристики. Борированная сталь выявила высокие износостойкость в условиях сухого трения и коррозийную прочность в воде нефтяного промысла в Китае в провинции Джулин.

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