JMEPEG (2009) 18:162–167
DOI: 10.1007/s11665-008-9270-0



# Tensile Properties of Boronized N80 Steel Tube Cooled by Different Methods

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*(Submitted February 18, 2008; in revised form May 31, 2008)*

**The microstructures and tensile properties of boronized N80 steel pipes by pack boriding under four different cooling conditions were investigated. The boride layer was composed of FeB and $Fe_2B$ phases with a hardness range of 1200-1600 HV. Fan cooling and fan cooling with a graphite bar in the center of the boriding agent were employed to improve the tensile properties. As cooling velocity was increased, the thickness of boride layer and grain size of the steel substrate were consequently reduced, whereas the pearlite volume in steel substrate was increased, resulting in improvement of tensile properties. Boronized N80 steel pipe which was fan cooled with a graphite bar inside possessed the highest ultimate tensile strength and yield strength, in accordance with the mechanical properties required by API SPEC 5L. Fracture surface analysis revealed that the boronized N80 steel showed ductile fracture at room temperature.**

**Keywords** carbon/alloy steels, heat treating, mechanical testing, surface engineering

## 1. Introduction

Many thermochemical treatments have been employed to improve mechanical and tribological properties of materials. Among the available thermochemical surface treatments, boronizing is a technically well developed and widely used process in which boron diffuses into a metal surface, basically steel and cast iron in mass scale, and forms an extremely hard and wear resistant surface layer on metallic substrate (Ref 1-3). Boronizing can be made from mixtures of powders, salts, molten oxides, as well as gas mediums and pastes. The process is generally performed in a temperature range of 700-1000 °C for 1-10 h (Ref 4). The most frequently used method is pack boriding. It has some important advantages: easy handling, the possibility of changing the composition of the powder, minimal equipment, and resultant cost saving. However, it is stated that the pack boriding also has some shortcomings: the distribution of boron is not uniform and the component needs to be frequently cleaned (Ref 3). In general, the commercial boriding mixture contains $B_4C$ as a donor, $KBF_4$ as an activator, and SiC as a diluent to control the boriding potential of the medium (Ref 5). The diffusion of B into the steel results in formation of iron borides (FeB and $Fe_2B$) and the boride layer thickness is determined by the temperature and time of the treatment (Ref 6). Usually, depending on process temperature, chemical composition of substrate materials, boron potential of boronizing medium, and boriding time, single or duplex (FeB + $Fe_2B$) boride layers may be formed (Ref 7). Boronized steel consistently outperforms nitrided and carburized steels essentially in terms of hardness, wear resistance, and anticorrosion because the iron boride formed exhibits substantially higher hardness (1600-2000 HV) as compared with carburized or nitrided steels (650-900 HV). Generally, the formation of a monophase ($Fe_2B$) with sawtooth morphology is more desirable than a double phase layer with FeB and $Fe_2B$ for industrial applications, because FeB (orthorhombic) phase is more brittle than $Fe_2B$ (tetragonal) phase (Ref 7, 8). Furthermore, crack formation is often observed at the FeB/$Fe_2B$ interface due to substantial difference in coefficient of thermal expansion between the FeB and $Fe_2B$ phases (Ref 5).

N80 steel tube is relatively cheap and widely used in oilfield, but it displays unsatisfied performance under severe conditions of high corrosion and heavy wear, especially in acid environment containing $CO_2$, $H_2S$ and partial-wear of the tube and sucker rod in the oil well (Ref 9, 10). Martini (Ref 11) reported the wear behavior of the boride coating thermochemically grown on iron and medium carbon steel by pack boriding, in comparison with samples submitted to alternative surface modifications including nitriding, hard chromium, and WC-Co. The wear resistance of boride coating was intermediate between nitrided steel and WC-Co, and comparable to the hard chromium. The borided AISI H13 hot work steel presented a better corrosion resistance in $H_2SO_4$ and $H_3PO_4$ environments in the investigation conducted by Kariofillis (Ref 12). Therefore, boronizing is expected to improve effectively the corrosion and wear resistance of N80 steel tube. However, due to the problems associated with the fragility of the boride layer and the slow cooling velocity caused by the incompact powder boriding agent, for boronized workpiece are usually cooled in the furnace or in the air, tensile properties such as ultimate tensile strength and yield strength may deteriorate dramatically and fail the mechanical properties

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required by API SPEC 5L. Thus, in the present study, four different cooling methods were taken to compare the resulting tensile properties of N80 steel tube after boronizing and chose one among them which is qualified for the mechanical properties required by API SPEC 5L. The relationship between microstructures and tensile properties were also discussed. The results are considered to be useful for extending the application of boronizing into oil industry.

## 2. Experimental Procedure

The substrate material was an N80 steel with chemical composition as listed in Table 1.The testing pipes of 160 mm in length were cut from an N80 steel oil pipe with 73.02 mm outer diameter and 5.51 mm wall thickness. The schematics of the boronized pipes are shown in Fig. 1. 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 increase the cooling velocity, for graphite has lower specific heat than incompact boriding agent. Boronizing process was performed in a solid medium, which had a nominal composition of 80% SiC, 5% $B_4C$, 5% $KBF_4$, and 10% reducing agent, at 860 °C for 5 h in an electrical resistance furnace under atmospheric pressure, followed by four different cooling methods including annealing, normalizing, fan cooling, and fan cooling with a graphite bar in the center of the boriding agent. The choice of boriding temperature and time is to ensure that the thickness of the boride layer is thicker than 40 μm, which can meet the requirement of wear and corrosion resistance and make the tube to be less deformed during boronizing process.

The phases present on the surfaces of the boronized steel samples were identified by a Rigaku X-ray diffractometer (XRD). Boronized samples for microstructure observation were sectioned, mounted, polished, and etched using standard metallographic technique, and then examined using a laser optical microscopy. On the same sectioned surfaces, the microhardness profiles as a function of the distance from the top surface were also evaluated using a Vickers hardness tester at a testing load of 25 g and an applied time of 15 s.

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 as required by API SPEC 5L, as shown in Fig. 2, which were machined from the non-borided and borided pipes. Fracture surface was examined by a JSM-5310 scanning electron microscopy (SEM).

## 3. Results and Discussion

### 3.1 Microstructures of Boride Layers and Steel Substrates

X-ray diffraction analysis, as illustrated in Fig. 3, revealed that boride layer on the surface of N80 steel substrate was composed of FeB and $Fe_2B$ phases. The minimum values of tensile properties of tube required by the API SPEC 5L are as follows:

1. yield strength is higher than 552 MPa,
2. ultimate tensile strength higher than 689 MPa,
3. elongation higher than 14%, respectively.

To meet the tensile properties of API SPEC 5L, four different cooling methods were conducted to obtain different

**Table 1 Chemical composition of the material used**

| | Chemical composition, wt.% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Material | C | Si | Mn | P | S | Cr | Cu | V | Ni |
| N80 steel | 0.36 | 0.32 | 1.55 | 0.020 | 0.010 | 0.040 | 0.050 | 1.20 | 0.040 |

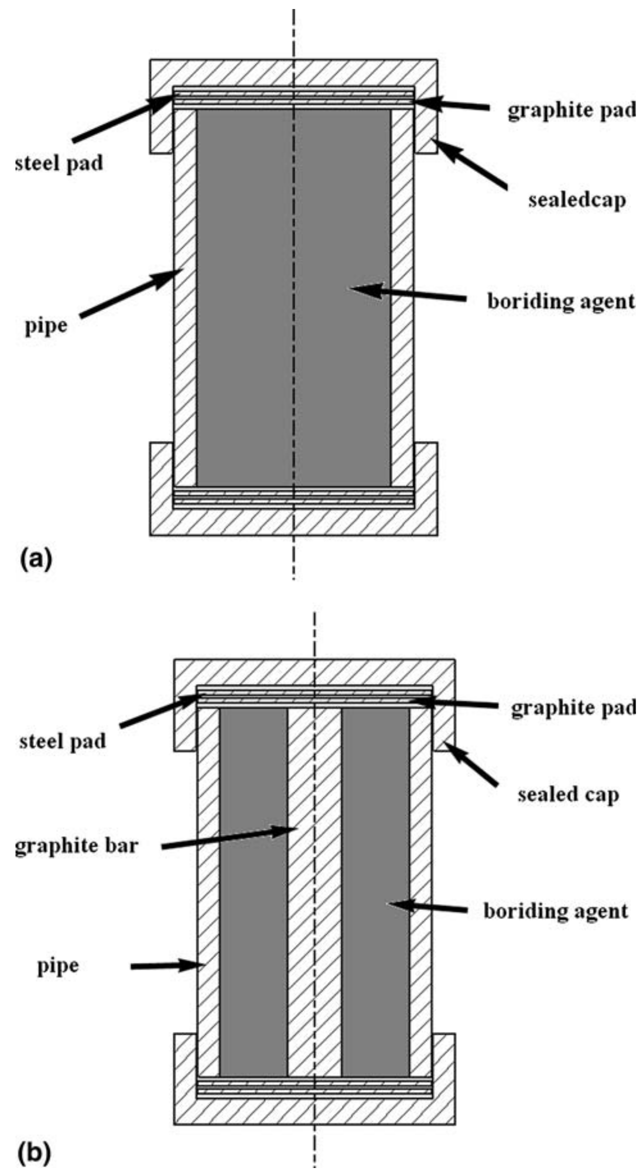


**Fig. 1** Schematic representation of the setup used to boronize pipes: (a) without graphite bar and (b) with a graphite bar inside boriding agent

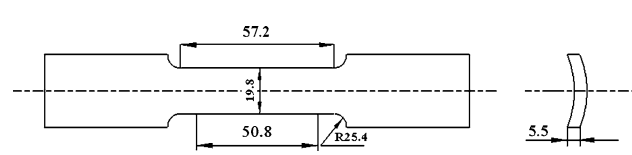


**Fig. 2** Schematic of tensile specimen

cooling velocities in a sequence of from the slow to the fast, namely annealing (furnace cooling), normalizing (air cooling); fan cooling, and fan cooling with a graphite bar in the center of the boriding agent. The microstructures of the boride layers on the steel substrates cooled by different methods are shown in Fig. 4. It notes that boride layers formed on the substrates have saw-tooth morphology, which is required for good adhesion between the layer and the substrate. The thicknesses of boride layers were 85 ± 5 μm, 55 ± 5 μm, 60 ± 5 μm, and 50 ± 5 μm for annealing, normalizing, fan cooling, and fan cooling with a graphite bar in the center of the boriding agent, respectively.

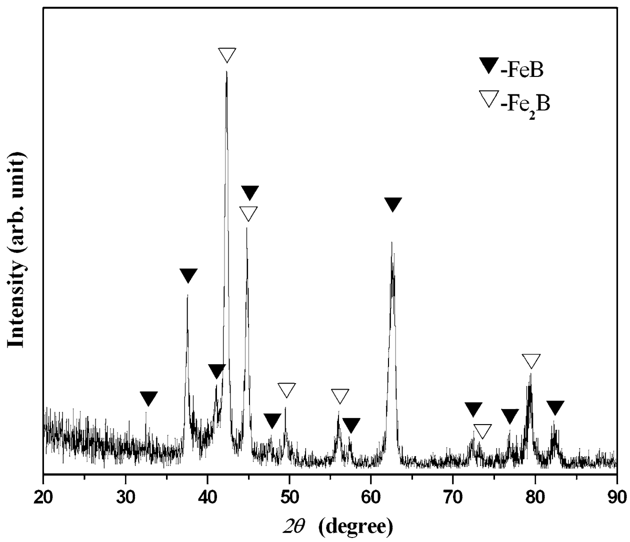


**Fig. 3** X-ray diffraction patterns of boronized N80 steel

The greatest thickness of boride layer obtained for the annealing steel is due to the slowest cooling velocity during cooling process in furnace, promoting a longest period of diffusion of B element into substrate and the growth of the boride layer. In contrast to this, owing to the fastest cooling rate and comparatively less boronizing mixture within it, the pipe, fan-cooled with a graphite bar inside, has the thinnest boride layer. A C-rich layer was formed beneath the boride layer with evident grain coarsening due to C atom being squeezed into steel substrate by smaller B atom. The thickness of C-rich layer was varied from 106 to 177 μm in four cases, and it is considered to be helpful for the tensile strength because of high C composition.

The boride layer is so thin as compared with the steel substrate that the tensile properties of boronized N80 steel pipe, to a great extent, are reliant on the properties of steel substrates from different cooling methods. The comparison of microstructures of steel substrates under different cooling conditions is given in Fig. 5. It can be seen that microstructures of steel substrates equally consist of proeutectoid ferrite and pearlite in four cases, but the differences in volume fraction and the grain size for both ferrite and pearlite are rather distinct. As the cooling velocity was increased from annealing to fan cooling with a graphite bar inside, the volume of pearlite consequently increased from 45.5 to 66.1%, whereas the volume of ferrite was accordingly decreased, and the grain size of ferrite decreased from 9 to 4 μm as listed in Table 2.

### 3.2 Tensile Properties

Figure 6 shows microhardness profile measured on the same cross-sections as in Fig. 4. The hardness of the boride layers is in a range of about 1220-1600 HV, much higher than the

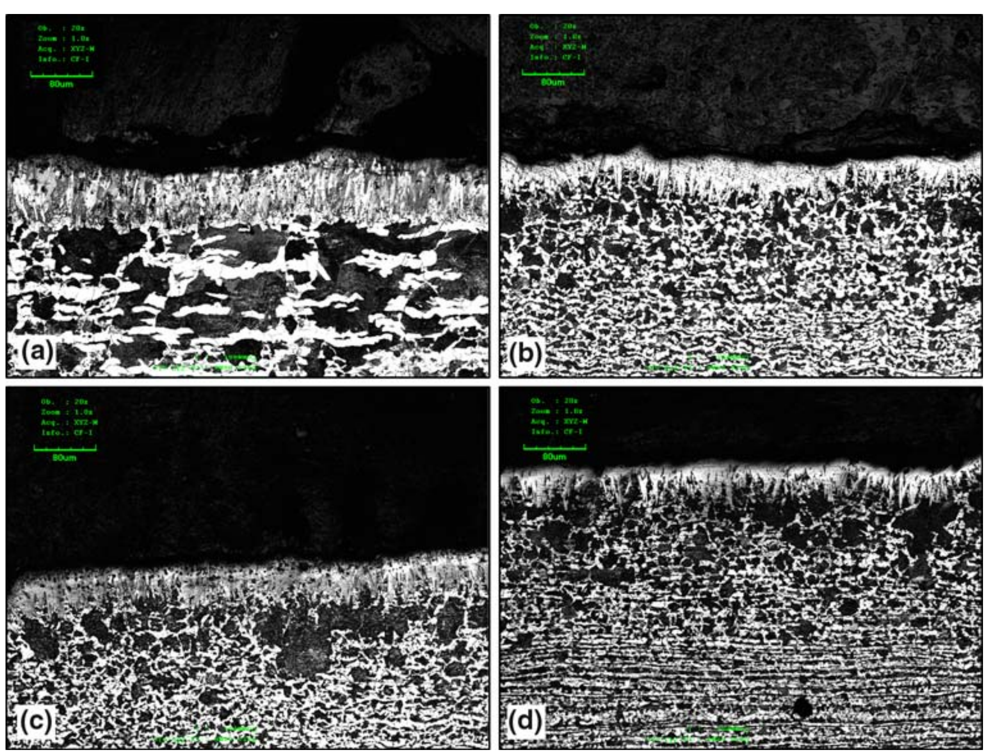


**Fig. 4** Laser optical microstructures of boride layers on steel substrates formed by different cooling methods: (a) annealing, (b) normalizing, (c) fan cooling, and (d) fan-cooling with graphite bar inside boriding agent

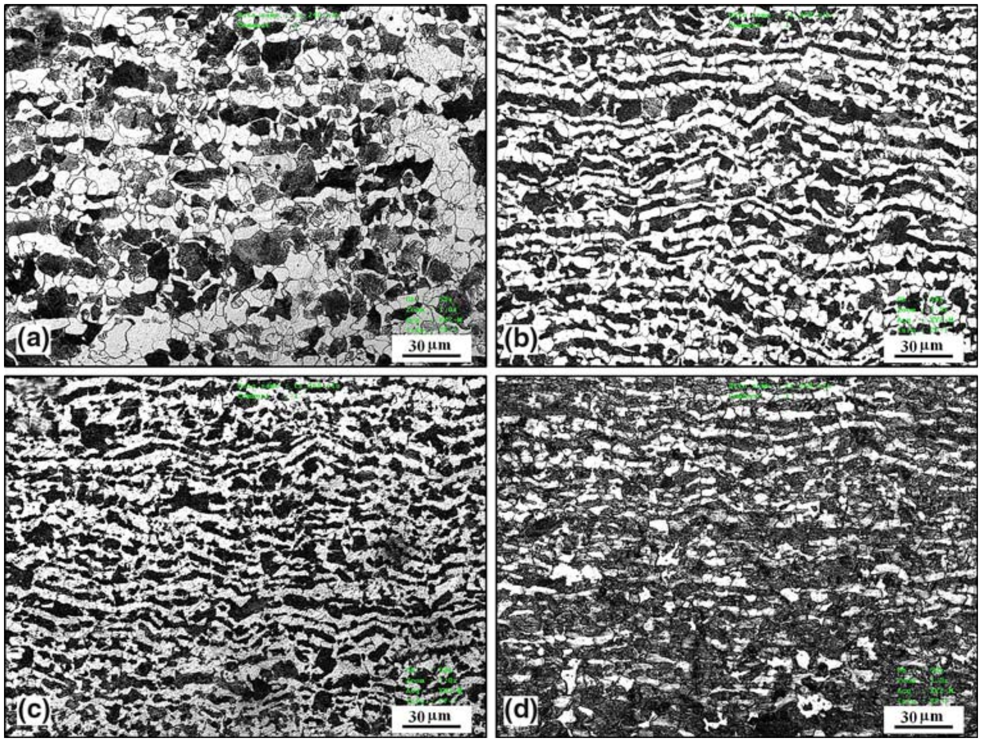


**Fig. 5** Laser optical microstructures of the substrates by different cooling methods: (a) annealing, (b) normalizing, (c) fan cooling, and (d) fan cooling with a graphite bar inside boriding agent

**Table 2 Microconstituent and yield strength for boronized steels cooled by different methods**

| Cooled method | Pearlite volume, % | Pearlite size, µm | Ferrite volume, % | Ferrite size, µm | Theoretical yield strength, MPa | Measured yield strength, MPa |
|---|---|---|---|---|---|---|
| Annealing | 45.5 | 10.9 | 54.5 | 9.3 | 547 | 562 |
| Normalizing | 48.8 | 7.3 | 51.2 | 6.8 | 596 | 619 |
| Fan cooling | 53.1 | 5.6 | 46.9 | 5.5 | 618 | 626 |
| Fan cooling with a graphite bar | 66.1 | 5.0 | 33.9 | 4.2 | 676 | 644 |

160 HV of the substrate. Because the FeB layer is so shallow that this hardness is typical of $Fe_2B$ layer. The $Fe_2B$ is especially desirable for industrial applications owing to the specific volume and coefficient of thermal expansion of the boride and the substrate (Ref 3, 13).

The tensile properties including yield strength, ultimate tensile strength, and elongation of boronized steels are shown in Fig. 7. It can be seen that the tensile properties of boronized pipes are lower than the original one except elongation. The forepart cracking of boride layer may be one of the reasons. The boride layer was brittle and began to crack as the tensile stress reached a stress level of ~479 MPa, consequently a saw-like plateau occurred in the tensile testing curve. The cracking of the boride layer may cause stress concentration and consequently weaken the tensile properties to a certain extent, and it can also cause the protection against wear and corrosion lost. However, this does not mean that the boronized tube has great limitation in practical application, because the stress level of 479 MPa can bear a total weight of 43.2 tons oil pipes, which can reach a 4000 m depth and is enough for the conventional oil well.

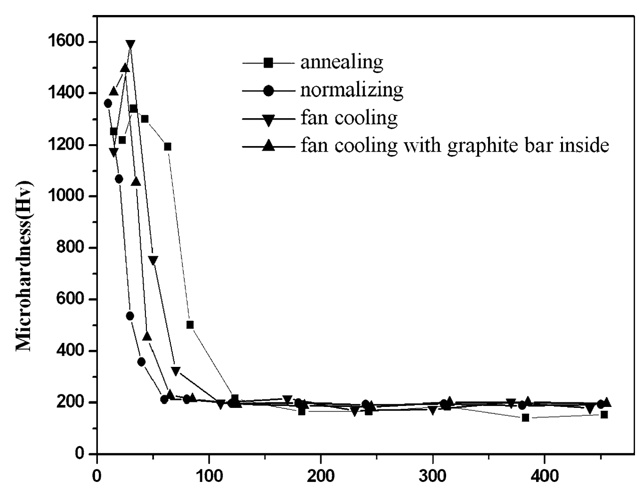


**Fig. 6** Hardness profiles of borided N80 steel under different cooling conditions

The cooling velocity displayed significant effect on the mechanical properties, especially yield strength and ultimate tensile strength. As the cooling velocity was increased, the tensile strengths including yield strength and ultimate strength were remarkably improved. This may be ascribed to two main factors. Firstly, the grain refining effect of both proeutectoid

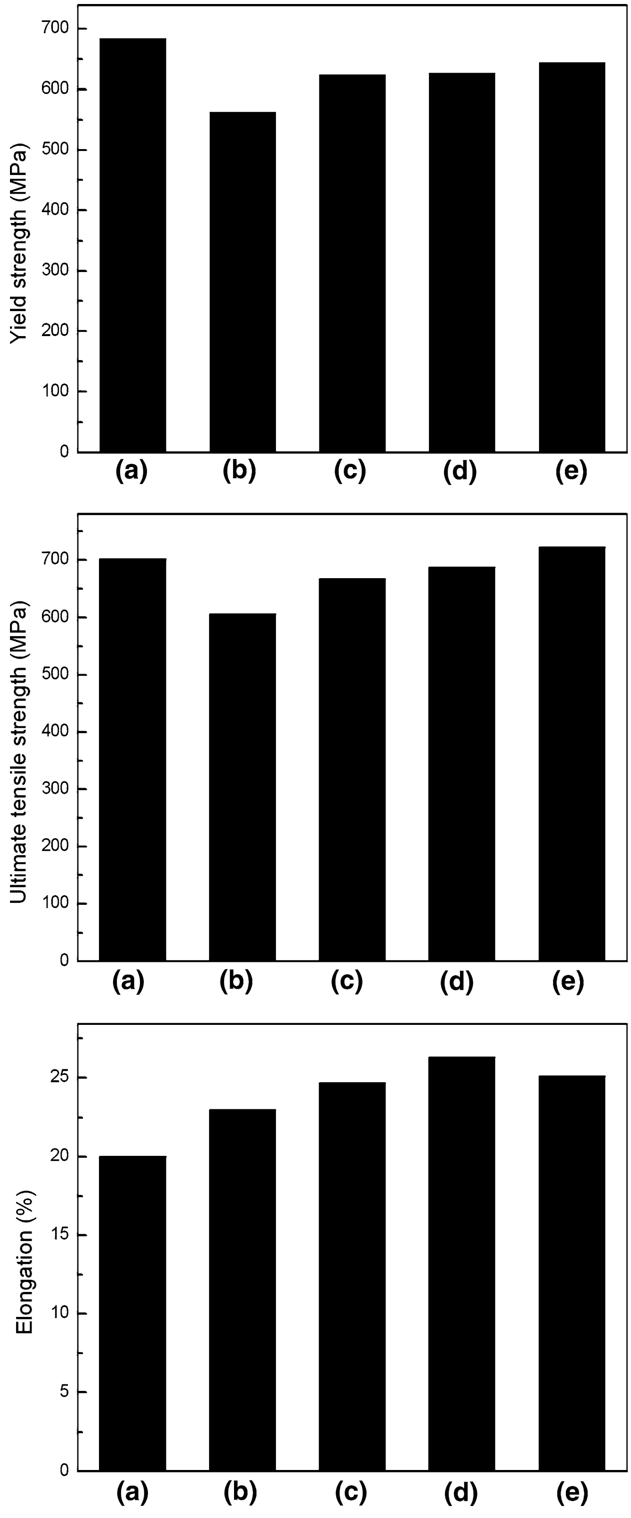


**Fig. 7** Tensile properties of non-borided and borided N80 steel pipes: (a) original state, (b) annealing, (c) normalizing, (d) fan cooling, and (e) fan cooling with graphite bar inside boriding agent

ferrite and pearlite. The substrate microstructure was refined with increasing cooling velocity, as shown in Fig. 5. The influence of grain size on yield strength can be estimated using the standard Hall-Patch equation:

$$\Delta\sigma_{cs} = Kd^{-1/2} \quad \text{(Eq 1)}$$

where $\Delta\sigma_{cs}$ is the increase in yield strength on account of grain refinement, $K$ is a constant, and $d$ is the grain size. According to the Hall-Patch equation, grain refinement plays an important role in determining strength. Secondly, substantially high volume of pearlite occurrence. According to the microstructure constituent law of mixture theory, the yield strength ($\sigma_y$) 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 ($\sigma_f$) and pearlite ($\sigma_p$) as follows:

$$\sigma_y = V_f\sigma_f + V_p\sigma_p \quad \text{(Eq 2)}$$

The pearlite has much higher strength than the ferrite; therefore, increasing the volume of pearlite greatly enhances the tensile strength. Because there was not very much difference in the grain size with increasing cooling velocity, as listed in Table 2, the grain refining effect on the tensile strength was considered to be less than the effect of increase in pearlite volume. The theoretical yield strength calculated by Eq 2 was compared with the measured ones in Table 2, the yield strength for ferrite containing 2% Mn and pearlite used in Eq 2 was 260 and 890 MPa, respectively. It is found that the effect of variation in pearlite volume on tensile yield strength with cooling velocity is well explained, even though there are large deviations between the calculated and measured results. In the case of yield strength, all four kinds of pipes exceeded 552 MPa of API SPEC 5L, whereas only the fan-cooling tube surpassed 689 MPa of ultimate tensile strength required by API SPEC 5L. The four kinds of tube all exhibited good elongation higher than 20%. Therefore the fan cooling with a graphite bar inside is the choice suitable for the boronized tube.

Figure 8 shows the fracture surface morphologies of the tensile specimens of N80 steel pipes cooled by different ways. 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 and some carbide particles can be clearly observed in the larger dimples, suggesting no change in fracture mode caused by the boride layer.

## 4. Conclusion

The tensile properties of boronized N80 steel pipes by pack boriding at 860 °C for 5 h have been studied under various cooling conditions. The following conclusions are drawn from this investigation:

1. The boride layers of boronized N80 steel pipes were composed of FeB and $Fe_2B$ phases. Borides formed on the steel substrates had saw-tooth morphology with a hardness range of 1220-1600 HV.
2. When the cooling velocity was increased, the grain sizes of both proeutectoid ferrite and pearlite in steel substrate were decreased, whereas the volume of pearlite was increased. The finest microstructure and the highest volume of pearlite have been obtained by fan cooling with a graphite bar in the center of boriding agent.

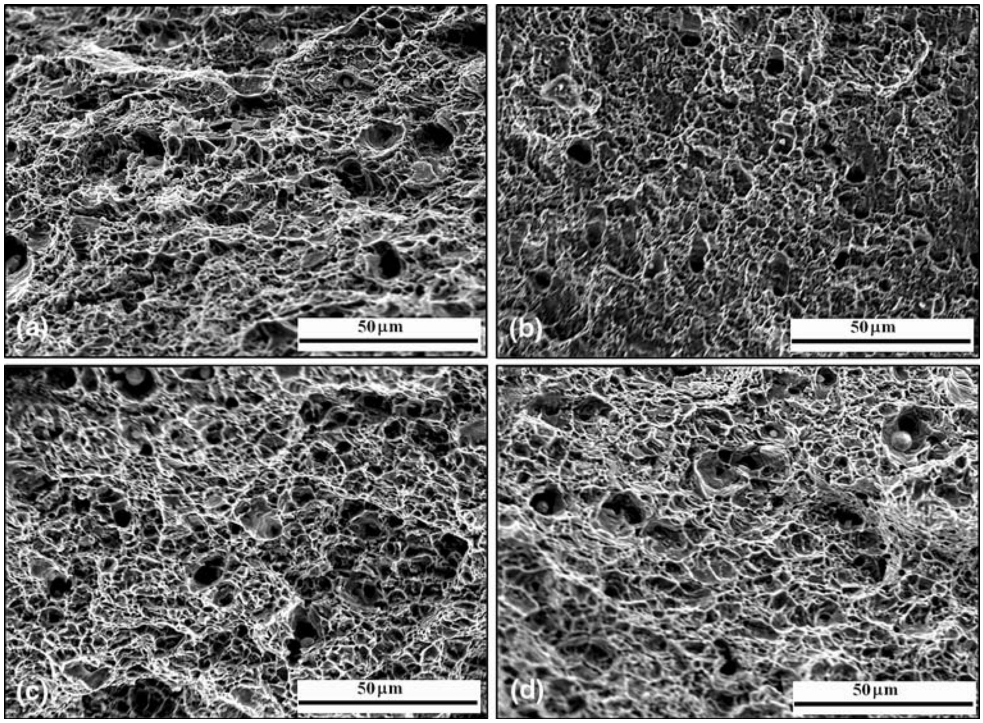


**Fig. 8** Fractured surfaces of tested samples: (a) annealing, (b) normalizing, (c) fan cooling, and (d) fan cooling with a graphite bar inside boriding agent

3. Boronized N80 steel pipe by fan cooling with a graphite bar in the center of boriding agent had the highest ultimate tensile strength and yield strength in accordance with API SPEC 5L.


## Acknowledgment

The authors thank the Project 985-automotive engineering of Jilin University.


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