Boronizing in Arms Industry

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Abstract. Comparison is made between several thermochemical treatment methods, with focus on boronizing. Boronizing has the potential to become a substitute for chromium plating or nitriding (gas nitriding) in the arms industry. This experimental study explored the chemical composition, hardness, corrosion resistance, tribological properties and toughness of several surface layers and coatings. The experimental substrates were EN 32CrMoV12-10 and EN 31CrMoV9 steels. Boronizing is intended for the gas tube and piston of a specific firearm. In the boride layer, the hardness of 1900 HV 0.1 was reached. In the chromium and nitrided layers, hardness was 1100 HV0.1. In these experiments, original rifle tubes and disc samples were used. The thicknesses were as follows: the chromium layer: up to 70 µm, boride layer: 100 µm and nitride layer: 290 µm. Wear properties were compared using the Pin-on-Disc wear test. Fracture toughness according to Palmquist was the highest in the nitride case and the lowest in the chromium layer. Across all the layers, the range was from 2.5 to 9.5 MN/m 3/2. Some differences were found between the boride layer with post-process heat treatment and layers without heat treatment. As a result of the research, it was found that Boronizing of the gas tube proved a suitable substitute for hard chrome plating or nitriding.

1. Introduction
Technological way of boronizing could be different, such as molten salt boriding, gas boriding, plasma boriding, paste boriding, and pack boriding [1]. In the arms industry, chromium-molybdenum steel is commonly used for many parts where high toughness is required, for bolts, screws, crankshafts etc. Sen and colleagues, [2], Boronized EN 42CrMo4 steel in the salt bath. [3]Borided same steel using plasma-assisted and gas boriding methods, with single-phase (Fe2B) on the surface of the steel. There are other investigations have been carried out on the properties of borided steels. [4,5]

2. Materials and methodology
The materials chosen for this study were EN 32CrMoV12-10 “gun-barrel steel” and medium-alloy hardening chromium-molybdenum-vanadium EN 31CrMoV9 grade. Specimens were prepared from these two steels.

The EN 32CrMoV12-10 steel is used for making components for CZ BREN 2 assault rifle, including the gas tube and piston. The nitriding grade EN 31CrMoV9 was chosen because of its similar composition, mechanical properties, better availability and, above all, lower price. If it delivers equivalent or better performance, it may be recommended as a substitute material for relevant
components. Coatings were created on specimens which were then examined and measured using the following tests. Hardness testing of the surface layer was performed using the Vickers indenter. Fracture toughness testing of the surface layer by forcing a diamond right pyramid indenter with an apex angle of 136° into the surface and measuring the resistance to crack initiation and propagation through the coating. Pin-on-Disc wear test. Test was carried out using 10N load and Al₂O₃ ball as a counterpart. This wear test simulates the action of the piston in the gas tube. After the gun is fired, the pressure of combustion gasses from the burnt composition causes linear reciprocating movement of the piston which involves friction between the piston and the gas tube. Finally, a corrosion test was designed and carried out to simulate the weather conditions in regions with high humidity. Corrosion test was Carried out in a ClimaCORR CC 1000-TL FR (40/80) cyclic corrosion chamber. The test parameters: Demi water/40°C/96hours. For dimensional changes measurement, passameter were used.

The chemical composition of the materials in weight per cent is given in Table 1. These steels are normally supplied in the hardened condition. 32CrMoV12-10 were Austenitized at 920°C/40min/ quenched in oil. Tempering temperature was 590°C/90min/air. 31CrMoV9 were Austenitized at 860°C/40min/ quenched in oil. Tempering temperature was 590°C/90min/air. The materials were therefore hardened to the following hardness levels: 459HV (32CrMoV12-10) and 371HV (31CrMoV9).

| Table 1. Steel compositions in wt. % |
|-------------------------------------|
| C | Si | Mn | Cr | Ni | Mo | V | P | S |
|---|----|----|----|----|----|---|---|---|
| 32CrMoV12-10| 0.31 | 0.25 | 0.46 | 3.13 | 0.19 | 0.81 | 0.26 | 0.02 | 0.02 |
| 31CrMoV9 | 0.32 | 0.25 | 0.59 | 2.68 | 0.05 | 0.18 | 0.12 | 0.017 | 0.017 |

Deposition parameters and coating characteristics are given in the following sections.

**Hard Chrome Plating**

The chromium coating was deposited by hard chrome plating in a bath with Heef25 catalyst. [6, 7, 8]The chromium coating contained distinct pores across its entire thickness. On 32CrMoV12-10 specimens, the chromium coating thickness was 60 μm. The chromium coating thickness on the 31CrMoV9 specimens was 70 μm. The increase in the specimen and part dimensions fully matched the coating thickness (0.06 mm and 0.07 mm, respectively). The chromium coating had a hardness of 1067±28 HV0.1 on 32CrMoV12-10 steel. On the 31CrMoV9 grade, it was 1088±61 HV0.1.

**Boronizing**

**Boronizing without post-process heat treatment**

The specimens to be boronized were placed in a container and buried in Durborid boronizing compound. To prevent the ingress of air during the diffusion-based process, the container lid was sealed using a special sealant. At 900°C, boronizing in argon took 12 hours. The container then cooled in the furnace to 700°C. After that, it was removed from the furnace and cooled in still air.

The 32CrMoV12-10 specimens developed a Fe₃B boride layer with a wedge-like morphology and a mean thickness of 75 μm (Figure 1a). On the 31CrMoV9 steel grade, FeB boride layer had an approximate thickness of 7 μm and transitioned to a Fe₂B layer with a wedge-like structure and a mean thickness of 90 μm (Figure 2). [9]
Measurement of dimensional changes revealed that the increment is equal to approximately 33% of the layer thickness on 32CrMoV12-10 and 20% of the layer thickness on 31CrMoV9 grade. The impact of the higher chromium level in 32CrMoV12-10 on the thickness and morphology of the boride layer is apparent. A higher level of chromium leads to a thinner coating. It also compromises the anchorage of the boride layer because it loses its wedge-like morphology.

![Figure 1. Boride layer on 32CrMoV12-10 steel without post-process heat treatment (left: magnification 500×, right: magnification 1000×)](image1)

Molybdenum has similar effects on the formation of the layer (0.8% in 32CrMoV12-10, and 0.2% in 31CrMoV9). The hardness of these layers exceeded 1500 HV0.1 by a large margin (32CrMoV12-10=1913 HV0.1 and 31CrMoV9=1710 HV0.1).

**Boronzing and post-process heat treatment**

The boronizing parameters were identical to those in the previous case. However, there was an additional post-process heat treatment (HT) whose role was to achieve the normal strength in the core of the part.

HT parameters:
- Quenching temperature 920°C, soaking time 40 minutes, quenching in oil bath, no bath circulation.
- Tempering temperature 620°C, holding time 90 minutes, cooling in still air.

**Nitriding**

Nitriding was carried out in ammonia/nitrogen atmosphere at 495°C for 20 hours. It was followed by gradual cooling in the furnace atmosphere to 100°C. Then the specimens were removed and left to cool in ambient air.

The layers had a thickness of 0.26 mm (31CrMoV9) and 0.29 mm (32CrMoV12-10). The corresponding dimensional changes were 0.008 mm and 0.01 mm (32CrMoV12-10). In both nitride layers, the nitrides in the matrix were embedded in tempered martensite. No continuous nitride network was formed. The white layer thickness has not exceeded 10 μm in
any location. The microstructure at the core remained virtually intact upon nitriding. It comprised tempered martensite with the visible orientation of fresh martensite structures, particularly in the 31CrMoV9 grade. The layer on the 32CrMoV12-10 steel exhibits higher hardness. As with boronizing, this is due to its higher chromium level which contributes to hardness.

3. Results and discussion

3.1 Wear testing

In this test, the volume loss from the specimen due to a ball being forced into the surface is measured. The specimen is affixed to a revolving plate.

The circular wear track was measured according to ASTM 99 standard. The ball was made from Al₂O₃.

![Figure 3. Wear volume loss for the surface treatment techniques](image)

The boride layer with no post-process heat treatment showed the best wear resistance. The lowest resistance was found in the nitride layer (Figure 3). The wear resistance is related to the hardness of the layer and its resistance to delamination. Poor adhesion may lead to a sudden increase in wear, as seen in the data for the test on 31CrMoV9 chromium coating.

3.2 Fracture toughness

Fracture toughness testing was carried out using a diamond right pyramid with a 136-degree apex which was forced into the surface layer at a load of 50 kg and produced cracks whose lengths were measured.

The chromium coating and the boride layer without post-process heat treatment suffered delamination. These hard layers had poor adhesion to the substrate. The causes are given by the very deposition process. The cracks induced by indentation were shallow (Palmqvist cracks). Fracture toughness was calculated using Palmqvist equation according to ISO 28079. The measured and calculated values were plotted in the graph shown in Fig. 4.

![Figure 4. Palmqvist fracture toughness](image)

As the results show, the chemical composition of the steel is not the primary factor here. The chromium coating has the lowest fracture toughness. The values are in agreement with the wear test.
data. The toughness of the nitride layer is almost four times that of the chromium coating. Heat treatment after boronizing led to a slightly higher toughness of the layer.

### 3.3 Corrosion test
The corrosion test of parts of 32CrMoV12-10 and 31CrMoV9 steels was carried out in ClimaCORR CC 1000-TL FR (40/80) cyclic corrosion test chamber. The specimens were examined and appearance rating (RA) based on the corrosion deterioration area A was assigned and listed in Table 2.

| Treatment             | Steel       | Surface Area Effect [%] | Degree [RA] |
|-----------------------|-------------|-------------------------|-------------|
| No treatment          | 32CrMoV12-10| 2.5 < A ≤ 5             | 4           |
|                       | 31CrMoV9    | 25 < A ≤ 50             | 1           |
| Chromium plating      | 32CrMoV12-10| Bez vad                 | 10          |
|                       | 31CrMoV9    | 2.5 < A ≤ 5             | 4           |
| Boronizing and no HT  | 32CrMoV12-10| A > 50                  | 0           |
|                       | 31CrMoV9    | A > 50                  | 0           |
| Boronizing and HT     | 32CrMoV12-10| 10 < A ≤ 25             | 2           |
|                       | 31CrMoV9    | 25 < A ≤ 50             | 1           |
| Nitriding             | 32CrMoV12-10| 0 < A ≤ 0.1             | 9           |
|                       | 31CrMoV9    | 0 < A ≤ 0.1             | 9           |

The highest corrosion resistance on 32CrMoV12-10 is with the chromium coating and the nitride layer. On 31CrMoV9 steel, the highest resistance is found in the nitride layer followed by the chromium coating. On 32CrMoV12-10 and 31CrMoV9 steels, boride layers perform poorly, as the almost entire surface was attacked by corrosion.

### 3.4 Discussion
Thermochemical treatment and surface treatments explored in this experiment led to the enlargement of the parts. Understandably, this must be taken into account at the product design stage. Where chromium plating is to be substituted with boronizing, the initial dimensions prior to thermochemical treatment must be corrected by 0.04 mm. In terms of manufacturability, this substitution is seamless. The alternative without post-process heat treatment is more convenient, as heat treatment may cause distortion.

In the chromium-plated specimens, there is a step-change in hardness between the surface and the core. The hardness of the surface layer is 1027–1091 HV0.1. The reason for the step change is that electrochemical deposition causes chromium to attach to the surface without any substantial diffusion layer being formed. Clearly, this poses a risk of delamination under load. The hardness of boride layers on these steels is approx. 1900 HV0.1. With these layers, there is a steep hardness gradient as well, where hardness decreases towards the core. After boronizing, the anchorage of the layer to the substrate greatly depends on the chemical composition of the latter. Metallographic examination revealed that in these steels, the anchorage is strong thanks to a transition zone of several dozen micrometres, as opposed to high-alloy tool steels where anchorage is virtually non-existent. Since the present steels are essentially nitriding steels, the nitriding process can produce hardnesses over 1000 HV0.1. The characteristic properties are attained thanks to hard nitrides embedded in a hardened matrix, which delivers high toughness, the main benefit of this thermochemical treatment method. From the perspective of wear resistance, the boride layer is the best choice. It is due to the combination of surface hardness and adhesion. However, once delamination occurs in a chromium or boride layer, the wear rate soars. Provided that proper adhesion of the Fe2B intermetallic is achieved, the boride layer is certain to deliver the best wear resistance. In fracture toughness tests,
an indentation of the surface layer produced cracks and caused delamination. The impact of chemical composition was minimal between the steels chosen for this experiment. The post-process quenching and tempering did not impair the adhesive-cohesive behaviour of the boride layer. Corrosion testing highlighted the clear benefits of chromium plating and nitriding as these surfaces were virtually intact after the test – in contrast to the boride layer.

4 Conclusion

Boronizing of the gas tube proved a suitable substitute for hard chrome plating or nitriding. The acceptable substrate material is 31CrMoV9+QT steel. Sound layers formed on both steels in the experiment but chemical composition makes 31CrMoV9 a better candidate than 32CrMoV12-10. Lower chromium and molybdenum levels help adhesion. The chemistry of the steel affects not only the morphology and composition of the surface layer but the composition and microstructure of the transition zone as well.

Process planning will require changes, as the dimensions related to the gas tube diameter need to be corrected by almost 0.1 mm on production drawings. From the wear resistance viewpoint, the outcome of the comparison between the layers is dictated by the occurrence of delamination of the hard chromium coating. In the wear tests, the boride layer clearly dominated. It is because of its high hardness and good adhesion.

On the other hand, its weakness lies in its poor corrosion resistance. It can be eliminated by using the borochromizing process. This is an essentially boronizing process where a chromium coating is created on the final surface. The materials for pack boronizing is ferrochromium.

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