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The Effect of Boronizing on Metallic Alloys for Automotive Applications

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In this study the wear resistance, corrosion resistance, and oxidation resistance of boronized metallic alloys were investigated. Thermochemical treatment was performed by powder pack boronizing process at temperature 850-950 °C for 4 h. Saw-tooth morphology and smooth interface microstructures were observed with an optical microscope; microhardness was measured across the coating depth. The phases present in the boron coatings depend on the substrate material. High-temperature oxidation resistance was investigated and it was found that boron coating on ferrous alloys can resist temperatures up to 800 °C. The corrosion resistance of the boronized samples was improved and the corrosion rate was calculated for boronized and plain specimens. Wear testing was conducted by following the procedures of ASTM G99, ASTM D2526, and ASTM D4060. The obtained experimental results revealed that boronizing significantly improves the wear-resistance, corrosion-resistance, and oxidation resistance of metallic alloys.

Keywords boronizing, corrosion resistance, high-temperature oxidation, wear resistance

1. Introduction

The surface of materials plays a key role in determining the service life of construction elements used in engineering components, the most important factor being the surface's wear resistance, corrosion resistance, and oxidation resistance.

There are a number of coatings used for surface protection and a material's performance improvement. Diffusion coatings are widely used in the manufacturing industry. These coatings are produced by the surface diffusion of a metal or a nonmetal into the substrate material at elevated temperatures. As a result of the thermochemical treatment, the surface chemical composition of the material is modified and new phases are formed on the substrate. Carburizing, nitriding, chromizing, and aluminizing are some of the techniques used for surface modification (Ref 1-4).

Thermochemical treatments with boron to form iron borides typically require process temperatures of 700 and 1000 °C for 1-10 h (Ref 5-8). Boronized steel consistently outperforms nitrided and carburized steels (Ref 9-11) essentially because the iron boride formed exhibits substantially higher hardness (HV: 1600-2000) as compared to carburized or nitrided steels (HV: 650-900). In particular, boronized steel exhibits excellent resistance to a variety of tribological wear mechanisms (Ref 10, 12-14). In addition, the resistance of boronized steel to attack by nonoxidizing dilute acids, alkalis, and molten metals is also outstanding (Ref 10, 14).

Boronizing is a diffusion coating by which boron atoms are introduced into the surfaces of metallic material-forming borides. Boron has very small atomic size that allows its diffusion in a variety of metals and alloys, e.g., steel, nickel-based alloys, titanium alloys, transition metals. Typically, the thermochemical treatment is carried out at 850-1050 °C by solid-state diffusion, liquids, or gaseous atmosphere.

The boronized layer has a number of characteristic features with special advantages over conventional case-hardened layers. One basic advantage is the extremely high hardness values (between 1450 and 2100 HV). This clearly illustrates that the hardness of boronized layers produced on carbon steel is much greater than any other conventional surface treatment; it exceeds that of the hardened tool steel and hard chrome electroplate, and is equivalent to that of the tungsten carbide. The combination of high hardness and a low surface coefficient of friction of the boronized coating also makes a significant contribution in combating the main wear mechanisms: adhesion, abrasion, and surface fatigue (Ref 12, 13).

By boronizing, very hard layers are produced, allowing a better wear strength and abrasion than other thermochemical processes such as carburizing and nitriding (Ref 1, 4, 15).

The significant feature of boronizing as a surface hardening treatment is to produce multifunctional coating with high hardness, low surface coefficient of friction, sufficient corrosion, and oxidation resistance.

The aim of this work was to investigate the above-mentioned properties and analyze whether boronizing can be used as a multifunctional coating for automotive applications.

2. Experimental Procedure

In the present work, the powder pack boronizing of low-carbon steel (AISI 1018), high-strength alloy steel

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(AISI 4340), austenitic stainless steel (AISI 304), nickel-chromium-molybdenum alloy (Inconel 625), precipitation-hardenable nickel-chromium alloy (Inconel 718), titanium alloy (Ti-6Al-4V) was studied. These substrates were chosen for a wide variety of potential applications in the automotive industry: steel gears, valves, plungers, discs, rollers, screw cases, extruder screws, bushings, bolts, nozzles, gear drives, pump shafts, tool dies, press tools. The alloy specimens were cut in the dimension of $10 \times 10 \times 3$ mm^3, ground on 180, 320, and 600 grit SiC sandpaper; and finally cleaned with acetone to remove grease and dirt. The finished specimens were packed in a crucible with a powder mixture of boron carbide (B_4C), and potassium tetraborofluorate (KBF_4). Boronized heat treatment was performed under an argon atmosphere in furnace at 850 °C 4 h for low-carbon steel, high-strength alloy steel, and austenitic stainless steel; at 900 °C; 4 h for titanium alloy and at 950 °C 4 h for nickel-based alloys.

After boronizing, the cross-sectional specimens were embedded in the resin; ground on 180, 320, and 600 grit SiC sandpaper; and polished on 6 μm lapping, 3 and 1 μm diamond paste, and 0.05 μm silica suspension for studying microstructures and microhardness. Microstructures and coating thicknesses of boronized steels and alloys were observed using an optical microscope. Phases present on the boronized steel and alloys specimens were identified by XRD. The microhardness of boronized steel and alloy specimens was measured with a microhardness tester with 10 gf load with an average of 10 indentations for each point. Wear testing was conducted by following the procedures of ASTM G99, ASTM D2526, and ASTM D4060. Finally, corrosion resistance (per ASTM G5) and high-temperature oxidation resistance were investigated.

3. Results and Discussion

3.1 Microstructure

The experimental results (Fig. 1a-f) show two types of microstructures: saw-tooth morphology and smooth interface. For ferrous specimens, the saw-tooth morphology is formed on low-carbon steel (AISI 1018) and high-strength alloy steel (AISI 4340), while austenitic stainless steel (AISI 304) shows the smooth interface layer.The smooth structure is demonstrated in nickel-based alloys (Inconel 625 and Inconel 718) as well as in titanium alloy (Ti-6Al-4V).

The morphologies of boron coating on steel and alloys are an effect of alloying elements in specimen chemical composition. In the case of ferrous specimens, high alloying elements of nickel (8%) and chromium (18%) in austenitic stainless steel (AISI 304) suppress the diffusion of boron atoms and cause to the formation of the smooth structure with high boron contents of FeB; on the other hand, no alloying elements in low-carbon steel (AISI 1018) and lower alloying elements in high-strength alloy steel (AISI 4340) can help in the occurrence of the saw-tooth structure of Fe_2B due to the preferred diffusion direction.

On the surface of boronized ferrous alloys, a compound layer (or boride layer) is normally composed of two sublayers: the outermost and the innermost are rich in FeB and Fe_2B, respectively (Ref 15).

Similar to austenitic stainless steel, nickel-based alloys with a high amount of chromium (21.5%) and molybdenum (9%) in Inconel 625 and chromium (19.1%) in Inconel 718 flatten the microstructure and form a smooth multilayer structure. For the titanium alloy (Ti-6Al-4V), titanium plays a significant role to retard the rate of boron growth that causes the smooth interface layer.

3.2 Coating Thickness

The alloying elements not only have an effect on the different morphologies of coatings, but also cause decreasing coating thicknesses. The boron coating thickness decreases when the alloying elements increase. Compared to the ferrous specimens, low-carbon steel, having no alloying elements, shows a saw-tooth structural coating of about 75-80 μm, while high-strength steel alloy with a higher amount of alloying elements demonstrates a thinner saw-tooth morphology coating of about 50-55 μm. In the case of stainless steel, large amounts of alloying elements (especially, Cr and Ni) reduce the coating thickness to 21-23 μm as well as smoothen the coating.

In the case of nickel-based alloys, Inconel 625 shows a multilayer coating of 70-76 μm, while Inconel 718 demonstrates the same structure with a coating thickness of about 66-72 μm. A thin smooth layer coating of about 3-5 μm is observed on the titanium alloy (Ti-6Al-4V). However, the coating thickness can be increased by raising the operating temperature and the time of the boronizing process.

3.3 Microhardness

The microhardness of boron coatings is varied by the phase presence on the specimens, corresponding to the amount of boron atoms diffused into the specimens. By increasing the depth of the coating, the microhardness is decreased as shown in Fig. 2. The boron coatings (FeB and Fe_2B) of ferrous specimens provide a microhardness of about 2000-2300 HK. The boron coatings of nickel-based alloys consisting Ni_2B, Ni_3B, and Ni_4B_3 give a microhardness of about 2400-1700 HK, while the microhardness of the boron coating on the titanium alloy is about 700 HK.

3.4 Phases Present

The coating phases of steel and alloy specimens detected by XRD are shown in Table 1. The ferrous specimens provide the coating phases of Fe_2B and FeB on low-carbon steel and high-strength alloy steel; however, austenitic stainless steel exhibits only the smooth FeB phase due to the high amount of alloying elements present in the specimen. In the case of nickel-based alloys, the phases of Ni_2B, Ni_3B, and Ni_4B_3 are found as a boronized multilayer coating on both Inconel 625 and Inconel 718. For the titanium alloy, a single boron-rich phase of TiB is identified.

3.5 Corrosion Resistance

The experiments followed ASTM G5—Potentiostatic and Potentiodynamic Anodic Polarization Measurement. The ASTM G5 requires 1 N H_2SO_4 to perform testing. All the specimens were tested in 1 N H_2SO_4 using a potentiostat; the Tafel plots were plotted and calculated for the corrosion rate (mpy). The results have shown that the corrosion resistance of the boronized specimens is improved, compared with the unboronized specimens as shown in Table 2, in which the

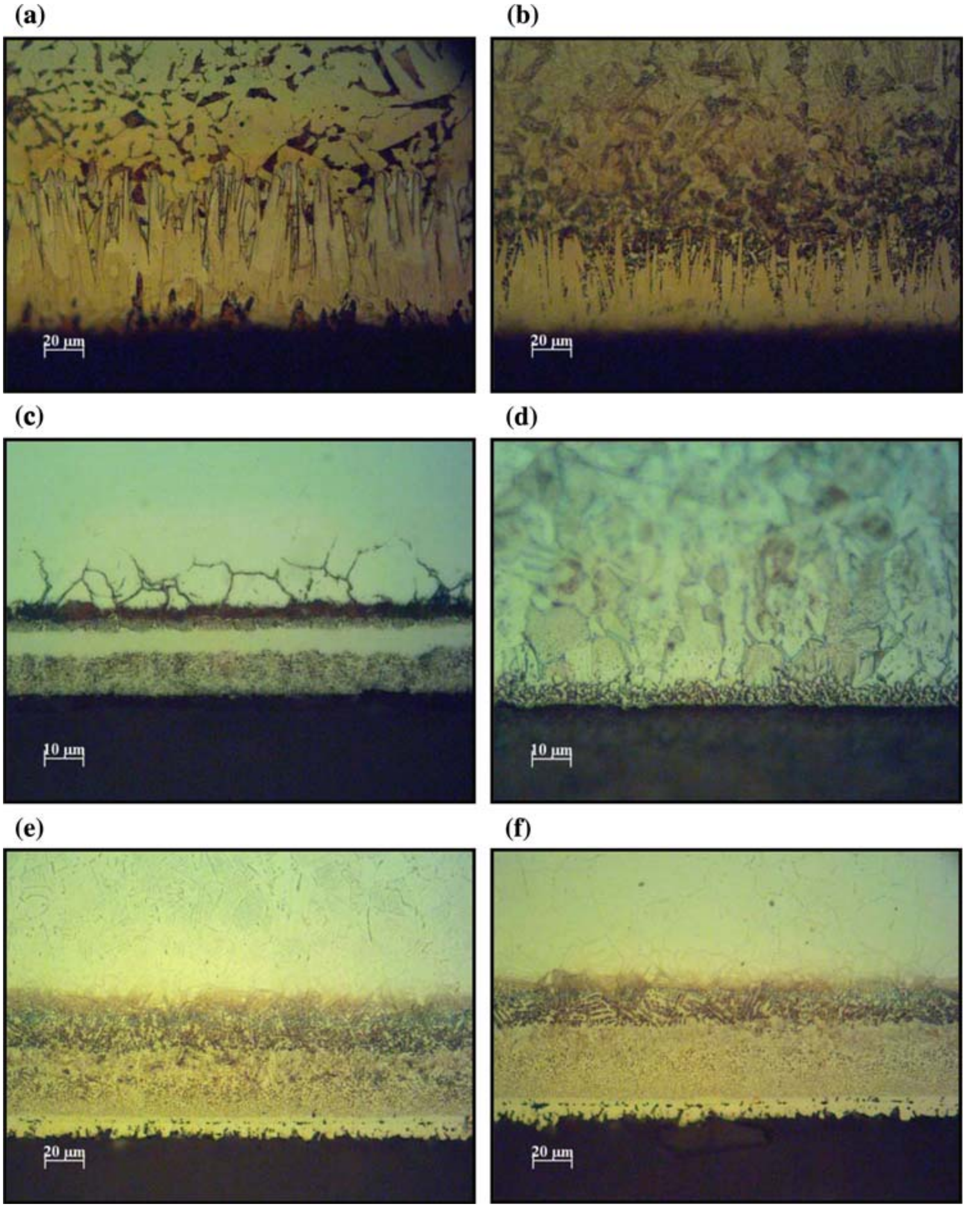

Fig. 1 Optical microstructure images of (a) low-carbon steel (AISI 1018), (b) high-strength alloy steel (AISI 4340), (c) austenitic stainless steel (AISI 304), (d) titanium alloy (Ti-6Al-4V), (e) nickel-based alloy (Inconel 625), and (f) nickel-based alloy (Inconel 718)

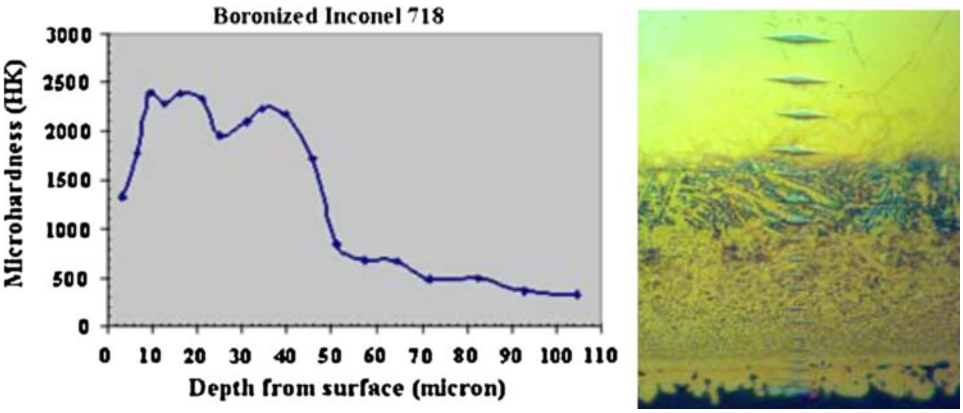

Fig. 2 Microhardness versus coating depth and microhardness indentation images

Table 1 Coating thickness, phases present, and microhardness of boronized specimens

Substrate	Coating thickness, µm	Phase present	Microhardness, HK (Coating/Substrate)
Low-carbon steel, AISI 1018	75-80	FeB, Fe_2B	2250/158
High-strength alloy steel, AISI 4340	50-55	FeB, Fe_2B	2000/520
Austenitic stainless steel, AISI 304	21-23	FeB	2100/275
Nickel-based alloy, Inconel 625	70-76	Ni_4B_3, Ni_3B, Ni_2B	2400/373
Nickel-based alloy, Inconel 718	66-72	Ni_4B_3, Ni_3B, Ni_2B	2400/625
Titanium alloy, Ti-6Al-4V	3-5	TiB	700/363

Table 2 Corrosion rate of boronized and unboronized specimens

Specimens	Corrosion rate, mpy
Unboronized low-carbon steel, AISI 1018	598.8
Boronized low-carbon steel, AISI 1018	6.357
Unboronized high-strength alloy steel, AISI 4340	154.7
Boronized high-strength alloy steel, AISI 4340	58.17
Unboronized austenitic stainless steel, AISI 304	6.092
Boronized austenitic stainless steel, AISI 304	0.758

corrosion resistance increases about 100 times for low-carbon steel, 2.5 times for high-strength alloy steel, and 10 times for austenitic stainless steel. To protect the specimens from environmental corrosion, boron on the coating forms boron oxide film to retard the electrochemical reaction resulting in the decrease of corrosion for iron in ferrous specimens.

3.6 High-Temperature Oxidation

To study the high-temperature oxidation, thermal gravimetric analysis (TGA) was used. The weight gain of low-carbon steel versus time at 800 °C was measured and plotted as illustrated in Fig. 3. Boron produces boron oxide glass phase and retards the diffusion of oxygen through the interior layer at low temperatures. At about 550 °C, iron borate compounds ($Fe_2B_4O_7$, FeB_2O_4, and $FeBO_3$) are formed in place of Fe_2O_3. At temperatures above 800 °C, only $FeBO_3$ is formed and finally dissociated to B_2O_3 (liquid) and Fe_20_3. The experiments also show that the boron coating on ferrous specimens is completely deteriorated at 900 °C.

3.7 Wear Resistance

Three different types of testing are performed by following ASTM G99—Standard Test Method for Wear Testing on a Pin-on-Disk Apparatus, ASTM D2625—Endurance Life of Solid

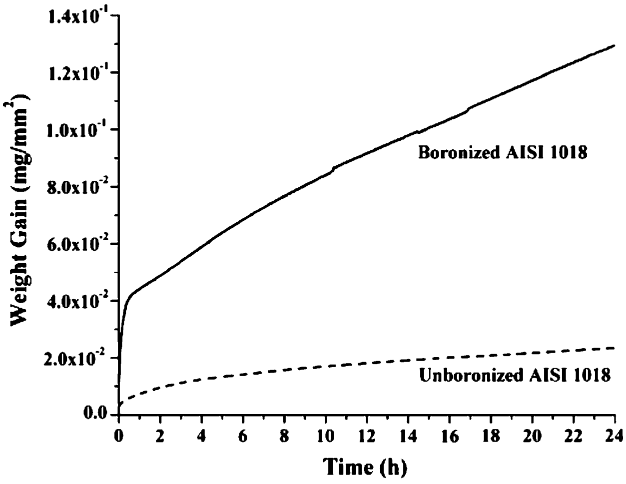

Fig. 3 Plot of weight gain versus time of boronized and unboronized low-carbon steel (AISI 1018) at 800 °C

Film Lubricants, and ASTM D4060—Abrasion Resistance on Organic Coatings. In these experiments, the specific size and shape specimens were requested.

For ASTM G99, the boronized pin-and-disk specimens were tested at 500 g loading and 70 rpm speeding for 1 h. The coefficient of friction of boronized AISI 4140 is about 0.2-0.4 as shown in Fig. 4. By calculation, the average pin scar is about 5.68×10^{-1} mm and the pin volume loss is about 6.8×10^{-4} mm^3.

For ASTM D2625, the experiment was performed by a Falex pin-and-vee block test machine, and the boronized pin-and-vee specimens were used. The average time at 200 lb (90.72 kg) loads until failure and the average load-carrying capacity were detected as a plot of load, torque, and temperature versus time as shown in Figs. 5 and 6. With a machine speed of 290 (±10) rpm, the average time at 200 lb (90.72 kg) loads until failure for boronized AISI 4140 is about 240 min and for boronized AISI 1018 about 97 min; the load-carrying capacity until failure for boronized AISI 4140 is 650 lb (294.84 kg) and for boronized AISI 1018 about 500 lb (226.80 kg).

The measured coefficient of friction of boronized high alloy steel AISI 4140 in our experiments is 0.2-0.4, which is lower as compared with the coefficient of friction of 0.50-0.60 for boronized and unboronized AISI 4140 measured by Sen et al. (Ref 16).

For ASTM D4060, a Tabor abraser was used with the testing conditions of 72 cpm speed and 1.0×10^4 cycles at 1.0×10^3 g test load. The average weight loss of AISI 4140 is about 1.01×10^{-2} g and of AISI 1018 about 1.37×10^{-2} g.

4. Conclusions

1. *Corrosion resistance*: the results have shown that the corrosion resistance of boronized samples increases about 100 times for low-carbon steel, 2.5 times for high-strength alloy steel, and 10 times for austenitic stainless steel as compared with the unboronized specimens.

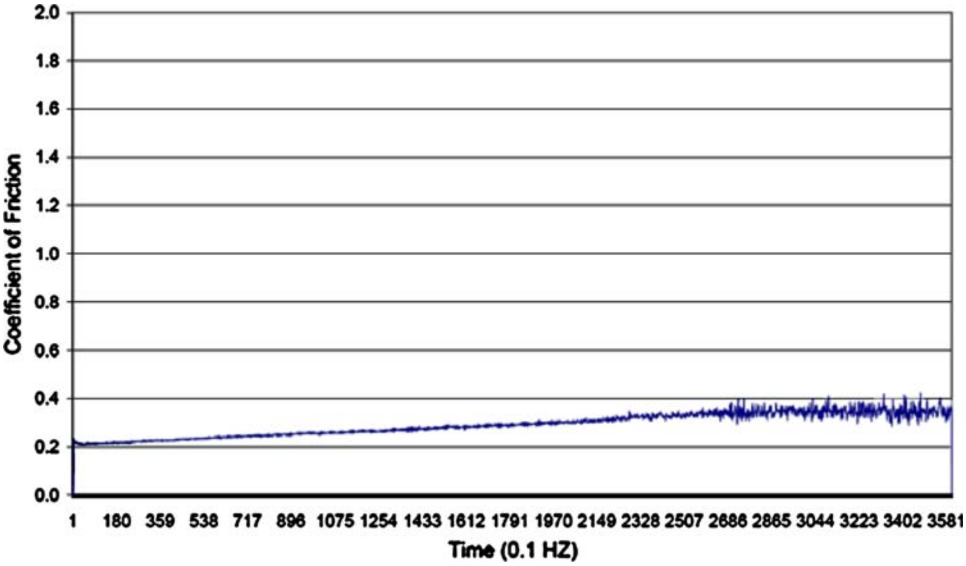

Fig. 4 Plot of coefficient of friction and time for boronized AISI 4140

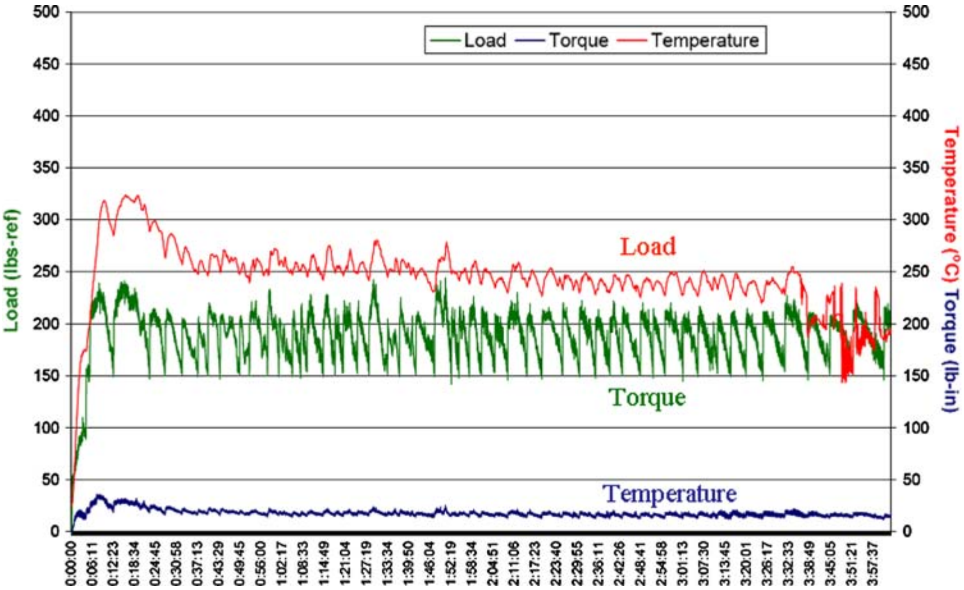

Fig. 5 Plot of load, torque, and temperature versus time at constant 200 lb (90.72 kg) load for boronized AISI 4140

2. *Wear resistance*:

   (a) the coefficient of friction of boronized AISI 4140 is about 0.2-0.4. By calculation, the average pin scar is about 0.568 mm and the pin volume loss is about 6.8×10^{-4} mm^3
   (b) with a machine speed of 290 (±10) rpm, the average time at 200 lb load until failure for boronized AISI 4140 is about 240 min and for boronized AISI 1018 about 97 min; the load-carrying capacity until failure for boronized AISI 4140 is 650 lb (294.84 kg) and for boronized AISI 1018 about 500 lb (226.80 kg)
   (c) the average weight loss of AISI 4140 is about 1.01×10^{-2} g and about 1.37×10^{-2} g for AISI 1018
   (d) the boronized steel samples exhibited high wear resistance, which is due to the hard borides formed on the surface
   (e) the wear resistance of boronized steel depends on the microhardness, microstructure of the coating, and its friction characteristics

3. *Oxidation resistance*: the high-temperature oxidation resistance testing revealed that the boron coating on ferrous alloys can resist temperatures up to 800 °C.

Boron coating has shown significant improvement of the wear-resistance, corrosion-resistance, and oxidation resistances of metallic alloys. Therefore, it can be used as a

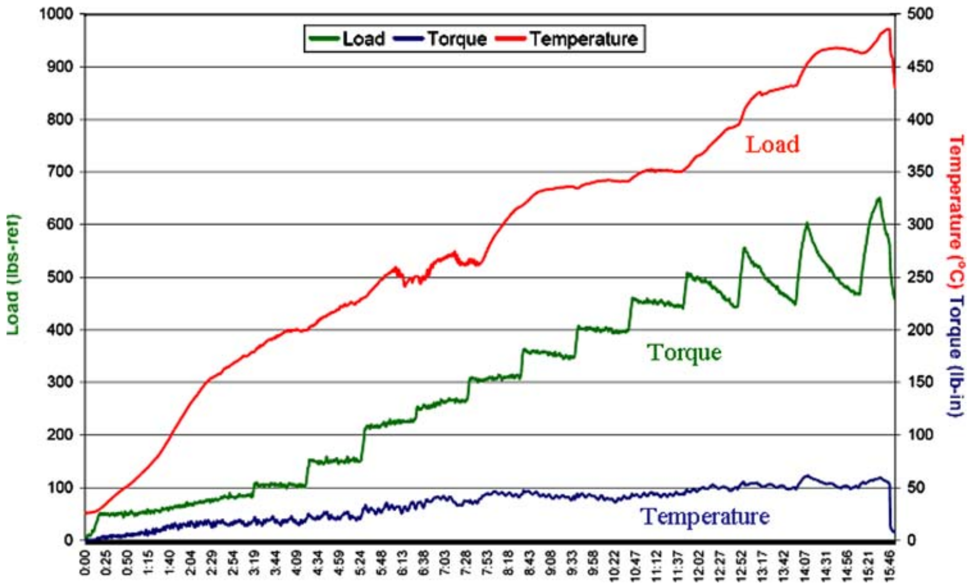

Fig. 6 Plot of load, torque, and temperature versus time with 50 lb (22.68 kg) load increment for boronized AISI 4140

multifunctional coating in automotive applications such as steel gears, valves, plungers, discs, rollers, screw cases, extruder screws, bushings, bolts, nozzles, gear drives, pump shafts, tool dies, press tools.

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