

Enhancement of the RE-boronizing process through the use of La, Nd, Sm, and Gd compounds

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Abstract

Rare-earth elements have been used in the thermochemical treatment of boronizing to enhance boron diffusion. In order to further investigate the effect of these elements on the process, neodymium-, samarium-, and gadolinium were utilized for the treatment of AISI 1045 samples carried out at the temperature of 1173 K for 4 h. The resulting boride layers formed were characterized through optical microscopy, microhardness test, and X-ray diffraction (XRD). The comparison of the layers showed that the addition of neodymium increased the depth by 48%, with samarium by 54%, and with gadolinium by 76%.

Key words: boriding, boronizing, rare earth, diffusion

1. INTRODUCTION

The surface of materials is responsible, in many cases, for determining the service life of numerous engineering components. Among the properties requested, depending on the factors to which materials for industrial use are normally exposed, wear resistance, corrosion resistance and oxidation resistance stand out [1].

There are a large number of coatings used to protect the metallic surface that aim at the best service performance of these materials. The modification of the surface by compounds formed from the diffusion of chemical elements that react with metal is widely used in industry. Superficial layers are obtained typically from the diffusion of carbon, nitrogen, boron and sulfur, alone or together with other metallic elements and is carried out by thermal activation of the metal substrate. As a result, the chemical composition of the material's surface is modified and new phases are formed, with particular distinct mechanical and chemical properties. Carburizing, nitriding and boronizing are some of the surface modification techniques that can be cited [2].

Boronizing, in particular, is the thermochemical process for surface modification that features the most comprehensive range of metals to be applied, including almost all metallic elements on the periodic table, with the exception of aluminum, copper, and magnesium [2]. In steels, boronizing results in hardness values much higher than those obtained at carburizing and nitriding processes, due to the formation of high hardness iron borides on the surface. These borides constitute a continuous and compact phase, chemically more stable than the steel substrate and with a low friction coefficient, thus contributing greatly to reducing the wear [3].

In critical industrial applications, such as oil well casing tubes, abrasive wear is so severe and replacement costs so high that the use of top-performing surface hardening processes is of great interest. For these tubes, the boronizing process has been used for increasing their service life [4]. Other critical components, as for example, rolling bearings of wind energy generators, find reference for an advantageous replacement of the carburizing process by the boronizing [5].

Boronizing is a relatively unexplored thermochemical treatment when compared to other solid-state diffusion hardening processes, such as carburizing and nitriding. One of the reasons for this is the fact

that it is performed at relatively elevated temperatures (1223 K) for long periods, from 4 to 6 hours, which results in significant changes in the microstructure of the steels, such as grain growth and reduction of mechanical properties [6].

Obtaining boride layers with an adequate thickness for the service demand in temperatures that do not cause grain growth depends on the efficiency of the boron diffusion, which is the reason for further investigating the process. Among the possibilities, it can be cited the use of electric currents in boronizing salt baths, the use of superplastic deformation, and the addition of rare earth (RE) elements [7].

The use of RE elements finds references in several articles and publications since the 1980s, notably for the thermochemical treatments of carburizing and nitriding [8 – 19]. In the gas carburizing process, for example, the addition of cerium chloride to the process reagents increased the concentration and depth of carbon penetration compared to the conventional process [16]. In the salt bath nitriding process it is to be found the addition of RE elements in the form of cerium or lanthanum chlorides, resulting in improved hardness and layer thickness [18]. Similar results have also been reported for plasma nitriding [19].

The boronizing process with RE additions finds references for the use of cerium, lanthanum and neodymium [20 – 22], however with mixed results. The addition of neodymium, for example, revealed an increase in the thickness of the layers only at process temperatures above 1133 K [22].

The effect of RE elements on the boride layers formed varies with the RE element itself and the compound used [23]. Thus, this work aimed to compare the layers thickness and the hardness resulted from RE oxides and nitrates added to the boronizing process.

2. EXPERIMENTAL PROCEDURE

The specimens were prepared from an AISI 1045 steel bar supplied in the standardized state, with a diameter of 50 mm, which was turned to a diameter of 15mm and face-faced in discs on the lathe for a height of 6 mm. These discs were then ground on their flat faces in 220, 400, and 600 mesh grade sandpaper and a 1200 mesh SiC paper. The boron donor medium used was a mixture (in wt.%) of 5% B₄C, 5% KBF₄ and 2,5% RE, formulated as RE-oxides of La₂O₃, Nd₂O₃ and RE-nitrates of Nd(NO₃)₃, Sm(NO₃)₃ or Gd(NO₃)₃, all diluted with SiC [23].

The specimens were boronized in a tubular electrical furnace under argon flux at 1173 K for 4 h and slowly cooled inside the furnace. The surface layers were characterized by optical microscopy (Olympus model BX51M) and by X-ray diffraction (XRD) with Cu-K α radiation of 1.54060 Å and 0.02° interval step mode using a Rigaku model Multiflex diffractometer.

The thickness of the boride layers measured on the cross-section of the specimens was determined through the average of randomly selected peaks in different regions and the microhardness values of the layers were determined by the mean of ten indentations, located at the same depth below the surface, using a microhardness tester with Vickers penetrator (Fischerscope model HM2000) with an indentation load of 30 g applied for 20 s [23].

3. RESULTS AND DISCUSSION

The layers formed after boronizing with RE-oxides at 1173 K for 4h, investigated by optical microscopy at the cross-section of the specimen are shown in Fig.1. It can be seen the presence of two different regions near the surface, a saw-toothed boride layer and below it, a pearlitic-rich diffusion zone. At the immediate interface between the boride layer and the diffusion zone, it can also be seen some ferrite-induced phases, which are typically formed after the silicon present on the AISI 1045 steel is expelled by the formation of the iron boride layer. Similarly, the increased participation of the pearlitic phase below this iron boride layer is related to the migration of carbon atoms towards the core, migration induced by the formation on the surface of the iron boride phases [24].

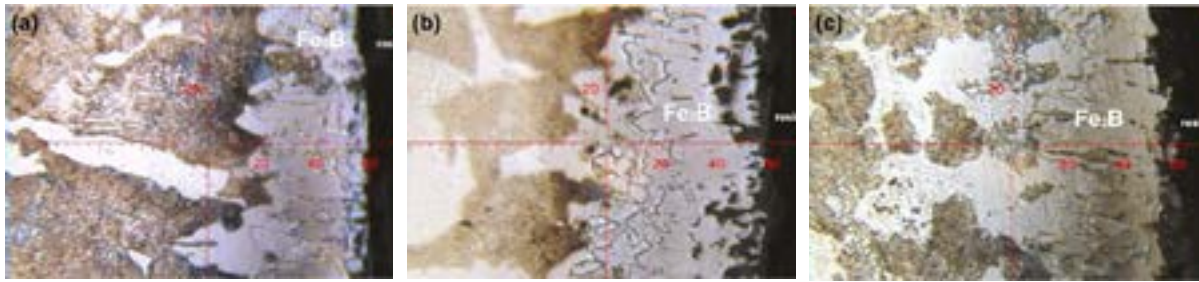


Fig.1. Micrographs of the boride layer of the AISI 1045 specimens treated at 1173 K for 4 h, (a) boronized, (b) La-boronized and (c) Nd-boronized.

The thickness of these boride layers, measured by optical microscopy at the cross-section of the specimens is presented in Table 1 [23].

Table 1 – Boride layer hardness and layer depth for boronizing process with and without RE-oxide additions

Process	RE Ionic Radius (Å)	Vickers Hardness (kg/mm ²)	Depth (µm)
B	-	1802.6 ± 52.9	36.5 ± 2.3
B + La	1.160	1711.5 ± 27.7	50.2 ± 4.4
B + Nd	1.109	1730.9 ± 40.8	47.6 ± 4.1

The results show that the use of lanthanum and neodymium oxides in the boronizing process at 1173 K leads to the formation of thicker boride layers, in agreement with other publications of boronizing with the additions of lanthanum [21] and neodymium [22]. The microhardness values measured are similar to those found in the literature for the iron borides [7].

The phases present in the boronized layers were investigated through X-ray diffraction analysis and the results found are shown in the Fig.2.

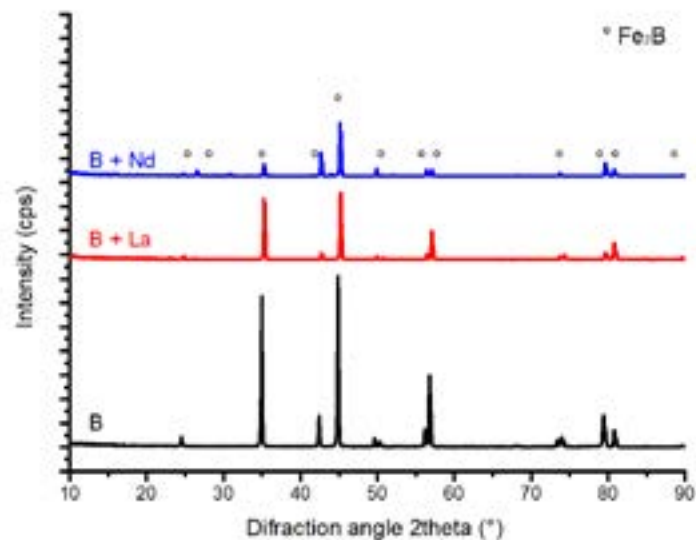


Fig.2. XRD patterns of the boronized specimens with additions of La₂O₃ and Nd₂O₃

The diffractograms of the boronized, La-boronized, and Nd-boronized samples showed the presence of the iron boride phase Fe₂B. The presence of RE elements phases in the diffractograms is not observed, a result that is consistent with other publications, that reported the use of EDS [22], XPS [23], and Auger analysis [25] on the surface of the boronized samples to detect RE elements on the layers. This finding can be explained by the very small amount of RE phases close to the surface, being their presence in higher amounts reported at about 30 μm below the surface, which is beyond the X-ray penetration depth [22].

The addition of RE oxides to the boronizing process at 1173 K resulted in an increase in the boride layer thickness formed. The morphological analysis of these layers revealed an increase in the porous zone near the surface of the samples boronized with RE oxides, an outcome that could be associated with the diffusion of oxygen into the lattice of the boride phases formed. The reduction of the porosity was accomplished through the use of RE nitrates, as it can be seen in Fig.3, that show the micrographs of the layers formed on the samples boronized at 1173 K with additions of neodymium, samarium and gadolinium nitrates, respectively.



Fig.3. Micrographs of the boride layer of the AISI 1045 specimens treated at 1173 K for 4 h, (a) Nd-boronized, (b) Sm-boronized and (c) Gd-boronized.

The thickness of these boride layers, measured by optical microscopy at the cross-section of the specimens is presented in Table 2.

Table 2 – Boride layer hardness and layer depth for boronizing process with RE-nitrate additions

Process	RE Ionic Radius (Å)	Vickers Hardness (kg/mm ²)	Depth (μm)
B	-	1802.6 ± 52.9	36.5 ± 2.3
B + Nd	1.109	1821.7 ± 27.1	54.1 ± 4.1
B + Sm	1.079	1847.1 ± 33.6	56.3 ± 4.4
B + Gd	1.053	1848.2 ± 31.2	64.2 ± 4.3

The comparison of layer depths of the Nd-boronizing process, carried out at 1173 K by 4 h, as to be seen in Fig.1 and Fig.3 showed that the addition in the form of nitrates results in the formation of thicker layers (54.1 μm) when compared to that obtained with the addition of neodymium in the form of oxides (47.6 μm). Furthermore, the micrographs presented in Fig.3 revealed, as well, that the addition of samarium and gadolinium nitrates resulted in increasingly thicker boride layers. The electronic configuration of the RE elements, with its outermost 6s² sublevel, always filled, results in an “outward appearance” identical among them, resulting in similar chemical properties of the elements in the lanthanide series. Thus, the variation of boron diffusion observed as a formation of thicker layers with the addition of RE elements with smaller ionic radius, as the data gathered in Table 1 and 2 show, allows to correlate the boron diffusion ratio as being proportionally inverse to the ionic radius of the RE element added. This correlation and the mechanism of influence of RE elements in the boronizing process is further investigated in other publications and is reported to be related to the formation of

distinct RE-borides in the layer [23].

4. CONCLUSIONS

In this work, RE-boronizing of the carbon steel AISI 1045 at 1173 K for 4 h was investigated through the use of various RE elements, added to the reagents of the powder-pack boronizing process in the form of RE-oxides or RE-nitrates. The results obtained at the samples led to the following conclusions:

- The addition of RE elements to the boronizing process in the formulation of oxides increased the thickness of the boride layers by 38% for La_2O_3 and 30% for Nd_2O_3 ;
- RE nitrates are more effective in the increase of the boride layer thickness, 38% for $\text{Nd}(\text{NO}_3)_3$ in comparison with 30% for Nd_2O_3 samples;
- The additions of RE nitrates to the boronizing process increased the thickness of the boronized layers formed by 54% ($\text{Sm}(\text{NO}_3)_3$) and 76% ($\text{Gd}(\text{NO}_3)_3$)

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