Vol. **132** (2017) *ACTA PHYSICA POLONICA A* No. 3

Special issue of the 3rd International Conference on Computational and Experimental Science and Engineering (ICCESEN 2016)

Effect of Boronizing on the Oxidation Resistance of 316L Stainless Steel

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The effect of boronizing treatment on oxidation at high temperature on 316L stainless steel was studied at 850, 900, 950, and 1000 °C in air, for holding times between 0.25 and 24 h. The oxidation resistance of unboronized and boronized specimens was studied isothermally by thermogravimetric analyzer. The oxidation rate constant represented as a parabolic rate constant K_p was evaluated. Optical microscopy, X-ray diffraction, and the scanning electron microscopy were used for surface characterizations. The experimental results show that boronized coating increases the resistance of stainless steel 316l about twice and prevents oxygen from penetrating into the stainless steel substrate at the temperatures between 850 and 1000 °C.

DOI: 10.12693/APhysPolA.132.518

PACS/topics: 316L stainless steel, boronizing, high temperature oxidation, oxidation kinetics, rate constant

1. Introduction

Austenitic stainless steels are widely used in industry when it is necessary to corrosion resistance at elevated temperatures. The corrosion resistance of these steels is achieved through their chemical compositions which contain significant quantities of chromium and nickel. In some cases thermochemical surface treatments or other diffusion treatments including boronizing are applied to stainless steel to increase their resistance properties to corrosion and high-temperature oxidation. The inserted boron reacting with the base material to form borides plays a prominent role in the field of corrosion and tribology and they can be made by the parts involved through various means and techniques [1, 2]. Research work [3–9] found that the boronizing became a conventional surface treatment such as nitriding and carburizing and it is currently applied in many branches of industry and shows advantageous properties such as high resistance to adhesive and abrasive, and provides good resistance to most acids. Although many researchers have investigated boron including properties and performance of boron coating at room temperature, the influence of a boron on high temperature oxidation resistance of a metal and alloy substrate in terms of kinetics mechanisms is still limited [10, 11].

This article will provide a better understanding of the high-temperature oxidation process in relation to boron coating by focusing on the oxidation reaction rates as basis for the explanation on reaction mechanisms. In this article the surface diffusion with boron on low carbon stainless steel 316L was studied. The oxidation kinetics on unboronized and boronized stainless steel 316L specimens at 850, 900, 950, and 1000 °C were studied by thermogravimetry.

2. Experimental procedures

In this work, low carbon austenitic stainless steel (SS) 316L was used as substrate material for boronizing treatment. The chemical composition 316L stainless steel is 0.024% C, 1.15% Mn, 0.38% Si, 0.033% P, 0.028% S, 17.2% Cr, 2.79% Mo, and 12.35% Ni by weight. The stainless steel coupon was cut into small pieces, we chose cylindrical specimens with a diameter of 19.80 mm and thicknesses between 3 and 5 mm. After coating, the samples are then abraded on a series of silicon carbide abrasive paper with particle size from 90 to 1000, and then polished on felt fabrics with a diamond paste. The surface prepared specimens were divided into two groups: unboronized and boronized for the boronizing process. The boriding treatment of 316L stainless steel was carried out in a powder consisting of 90% SiC, 5% B_4C, and 5% $NaBF_4$. Processing conditions ($T = 950$ °C during 4 h) allow, according to previous work, to obtain an average borided layer thick enough (> 90 μm). The unboronized and boronized specimens were oxidized at temperatures between 850 °C and 1000 °C in air, for holding periods of 0.25 to 24 h. After the oxidation tests, the quantification of the effect of temperature and holding time on these specimens was done by metallographic observations and gravimetric analysis. The measure of mass change during oxidation tests allow to extract the parabolic oxidation rate constant (K_p) which allows efficient comparison of oxidized specimens (unboronized and boronized specimens).

3. Results and discussions

3.1. Boronizing treatment

It should be noted that the morphology of borided layer formed on 316L SS has not the shape of the needle-like oriented perpendicular to the surface that always encountered during the boriding carbon steels. This is justified, according to some authors [12–17] by the presence of a significant amount of alloying elements (Cr, Ni, Mo, etc.) in 316L SS, which delays the diffusion of

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boron atoms in their favorite directions (002) and leads to the formation of a front (layer/substrate interface) more or less regular between the formed layer and the rest of material [15, 16]. The various means used for characterization of the borided layer formed on the surface of 316L SS show that the layer formed on the surface is composed of a complex layer (many phases) as shown in Fig. 1. The average thickness of borided layer formed on the surface of 316L SS is about 60 μm, which corresponds to 0.32 mg/cm^2. The X-ray diffraction (XRD) and the scanning electron microscopy (SEM) observation showed that the borided layer formed on the surface of 316L SS contains significant amounts of chromium and nickel. The presence of chromium and nickel in the borided layer leads to the formation of a complex layer of borides. Thus, there was the presence of FeB, Fe_2B, CrB, Ni_2B_3, $(Fe, M)_2B$ where M may be Cr or Ni. Palombarini and Carbucicchio [12] and Goeuriot et al. [15] showed that the presence of substantial proportions of chromium and nickel in borided steels leads to the formation of borides of chromium and nickel. When the chromium content in the steel exceeds 13% (by mass), the FeB phases and Fe_2B dissolve considerable amounts of chromium. The distribution of different phases in borided layers becomes rather irregular, probably due to non-equilibrium conditions related to the formation of the layer when the average chrome content is 8% in the layer of (Fe, Cr)B and 9% (by mass) in the layer of $(Fe, Cr)_2B$ [17].

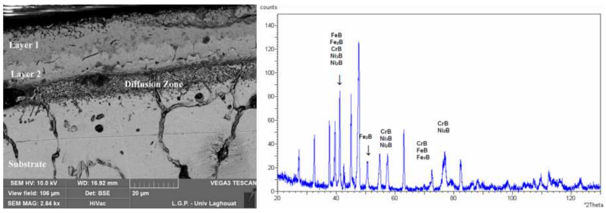

Fig. 1. SEM microstructure of borided layer after boriding treatment at 950 °C for 4 h (a), and X-ray diffraction diagram of borided layers formed on 316L SS (b).

The various means used to characterize borided layer on the surface of 316L SS show that the formed layer consists in a complex layer of several phases. The complexity borides formed on the treated surface may be of great benefit for hot oxidation. Generally, coatings used as thermal barrier are several successive layers deposited on each other.

3.2. Oxidation tests

The optical microscopy observations of samples exposed to hot oxidation allowed us to make the following observations:

- For untreated samples, there is absence of compact oxide layer (Fig. 2a).
- For the borided samples, we observed the presence of a layer on the surface even after 24 h of oxidation at 1000 °C (Fig. 2b).

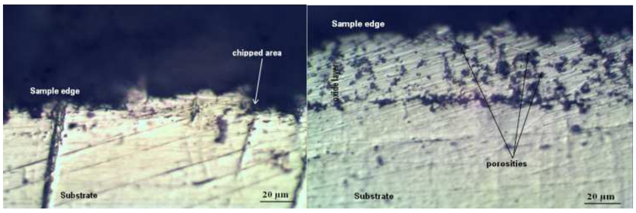

Fig. 2. Optical micrograph of untreated surface of 316L SS(a), and borided layers formed on 316L SS (b) after hot oxidation tests.

The layer formed on the surface of the borided samples can be responsible for the good behavior of the latter during the hot oxidation tests.

3.3. Study of the oxidation kinetics

Changes in mass gain per unit area as a function of time and temperature of hot oxidation tests on borided and untreated samples of 316L SS are given in Fig. 3.

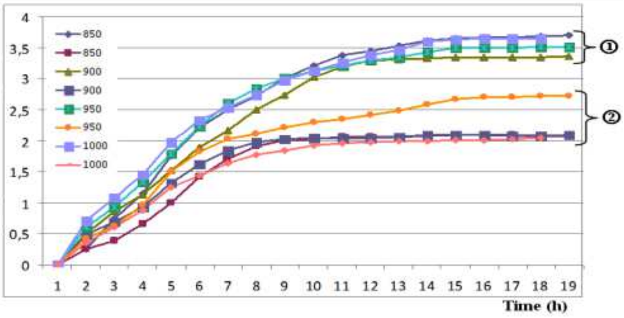

Fig. 3. Change in mass gain per unit area as a function of time and temperature after hot oxidation tests. 1 — untreated samples, 2 — borided samples.

According to the literature [18, 20], the parabolic shape is typical oxidation phenomenon controlled by oxygen diffusion through an oxide layer. Analysis of obtained results from curves, allows us to say that the gain of mass on borided samples are far lower than those on untreated samples, although they have the same parabolic shape. We can see that the stabilization of mass gains curves of borided samples starts after 8 h oxidation, while for untreated samples this stabilization begins for periods which exceed 15 h. A quantification of the effect of boronizing on oxidation resistance of 316L SS, considering the mass gain per unit area as a criterion, allowed us to say that the mass gain recorded on borided samples is almost half of that recorded on untreated samples.

The growth kinetics controlled by the diffusion regime is described by the parabolic law

$$\Delta m^2 = K_p t$$

where Δm is the mass of the oxidized sample taken per unit area, K_p is called parabolic oxidation constant practically.

Values of oxidation constant (K_p) as a function of temperature for untreated and borided specimens are given in Table I.

TABLE I

Values of oxidation constant K_p [$\times 10^{-10}$ g^2 cm^{-4} s^{-1}] as a function of temperature for untreated and borided specimens.

Temperature [°C]	850	900	950	1000
untreated specimens	2.41	2.45	1.32	1.96
borided specimens	12.2	11.3	8.7	10.3

The obtained results using comparison of K_p confirm the obtained results in the first comparison. To get an idea about the chemical composition of oxide layers formed, we have followed a method proposed by several researchers [20–23] and that takes into account the constant parabolic oxidation K_p and the chemical composition of the material (especially its chromium content). The formed oxides are: magnetite (Fe_3O_4), hematite (Fe_2O_3), chromia (Cr_2O_3) and spinels $Fe_{2-x}Cr_xO_4$. The presence of magnetite in the oxide layer slightly alters its resistance to hot oxidation because of the weak compactness of the magnetite and the presence of porosity in the product. The presence of boron atoms in large quantities in the surface layer leads to the formation of oxides containing boron, which explains the improved to hot oxidation resistance of borided samples.

4. Conclusions

The boronizing treatment of 316L SS, the characterization of formed layers on the surface and hot oxidation testing performed on borided and untreated samples allowed us to advance the following conclusions:

1. The oxidation kinetics of borided and untreated 316L SS at high temperature (850–1000 °C) obeys a parabolic function in both cases.
2. Thermogravimetry results revealed that boronizing treatment increases oxidation resistance of 316L SS of about twice.
3. The kinetics rate constant of boronized layers on 316L SS show that the boronizing treatment is effective in slowing oxygen diffusion, thus giving lower reaction rate of boronized samples compared to untreated ones.
4. The improvement of hot oxidation resistance is obtained by forming a layer of oxides and more compact (less porous) products on boronized surface.

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