Corrosion behavior of AISI 316 L borided and non-borided steels immersed in a simulated body fluid solution

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ABSTRACT

The corrosion resistance of AISI 316 L borided and non-borided steels was evaluated during 10 days of immersion in a simulated body fluid (Hanks' solution). The FeB/Fe$_2$B layer was developed using the powder-pack boriding process at 1223 K and 6 h of exposure. First, the electrochemical behavior on the surface of borided and non-borided steels was assessed using Electrochemical Impedance Spectroscopy, EIS. After the corrosion tests, the surface of both types of samples were analyzed by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectrometry (EDS) and X-Ray Photoelectron Spectroscopy (XPS), to establish the corrosion mechanisms, the composition and the electrochemical species developed over the surface, after 10 days in the simulated body fluid solution (SBFS), respectively. According to the electrochemical study, the AISI 316 L borided steel provided a reasonable corrosion resistance notwithstanding, the non-borided steel exhibited higher resistance values. Finally, it was concluded that the decrease of corrosion resistance of AISI 316 L borided steel was caused by a rather complex combination of chemical interactions amongst boron-bearing species, sulfates and phosphates taking place initially over the borided surface and subsequently through pits and cracks after 10 days of immersion in Hanks' solution.

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1. Introduction

AISI 316 L stainless steel has been successfully applied in medicine due to its biocompatibility and relatively low cost [1]. Different surface engineering techniques can be performed to increase the corrosion resistance of the base metal, in particular when exposed to electrolytes simulating a body fluid [1–8], which lead to diverse applications as biomaterial.

The powder-pack boriding is a surface thermochemical treatment, which improves the hardness, wear and corrosion resistance of diverse metallic materials. Further, because of its low cost and ease of processing, compared with other thermochemical treatments [9–17], boriding has been successfully applied to a wider sort of steels.

Boriding can enhance the corrosion resistance of ferrous materials if it leads to the formation of boride coatings on the surface component. Boride coatings passivate in non-oxidizing dilute acids and alkaline media [15–16]. For industrial applications, it is important to consider that the corrosion resistance of boride-coated steel components greatly depends on the amount of microcracking in the coating and the specific coating-solution conditions [18–21].

Likewise, boride coatings corrode by either direct chemical or physical mechanisms. In the case of chemical attack of boride coatings, the composition of the environment may cause the coating to either become soluble or to be changed into soluble corrosion (chemical species) products. Thus, the importance to understand and to know the chemical species formed on the surface of boride coatings is related to the direct information of the oxidation/reduction behavior, and therefore, the corrosion and/or metal release mechanisms.

Particularly, a study of the corrosion resistance on AISI 316 L borided steel exposed to a simulated body fluid solution (SBFS) during 1 and 168 h was developed by Kayali et al. [2], using the potentiodynamic polarization technique. For AISI 316 L steel, the corrosion resistance was higher compared to the borided steel. This effect was attributed to the porosity of borided coatings and to the development of soluble complex salts over the surface of borided steel. Nevertheless, in the study of Kayali et al. [2], the chemical species formed during the corrosion tests on the material were not reported.

Moreover, during the work proposed in [2], the wear resistance of AISI 316 L borided and non-borided steels were estimated using the ball-on-disk system in dry and wet (SBFS) mediums. A decrease in the

wear rates both in dry and wet mediums was observed in AISI 316 L borided steel when increasing boriding temperature. In the dry medium, the wear rates of borided steels were 30 times lower than that of AISI 316 L steel, while in the SBFS medium were 3 times lower.

In comparison with the work proposed in [2], in this study, the corrosion resistance of AISI 316 L borided and non-borided was estimated during 10 days of immersion in the Hanks' solution using the Electrochemical Impedance Spectroscopy (EIS) technique. The days of immersion in the Hanks' solution were selected to verify the behavior of the corrosion resistance of both non-borided and borided steels, the evolution and type of the chemical species developed on the surface, and corrosion mechanisms formed by the electrolyte-surface system by the aid of SEM, EDS and XPS techniques. In this case, similar days of immersion in a SBFS were proposed by different authors [2–8] to estimate the corrosion resistance of coatings formed on the surface of AISI 316 L steel. The corrosion results were analyzed by means of Nyquist and Bode plots in order to fit a suitable electrical equivalent circuit to estimate the electrochemical parameters for both, borided and non-borided samples immersed in the SBFS medium. Finally, from all the experimental evidence, electrochemical reactions are proposed to explain the behavior of corrosion resistance of the borided steel after 10 days in the Hanks' solution.

2. Experimental procedure

2.1. The powder-pack boriding process

Commercial samples of medical grade AISI 316 L steel, with 25.4 mm OD and 6.35 mm long were used in this study. The chemical composition of the steel is given in Table 1.

Prior to boriding, the specimens were ground sequentially using 100–2000 grit SiC papers then ultrasonically cleaned in isopropyl alcohol. The samples were packed in a stainless steel container (AISI 304) in contact with commercial Ekabor 2 powder mixture. During the boriding process, the container was transferred to a resistance furnace at 1223 K and was kept for 6 h. At the end of the process, samples were kept within the container and cooled down to room temperature.

The sample was subjected to metallographic characterization in order to reveal the microstructure of the boride coating. Firstly, the remaining boron powder mixture was manually and ultrasonically removed from the steel sample. Then, the sample was cut transversely with a precision diamond cutter machine (LECO VC50) and mounted in bakelite. The mounted sample was ground with SiC abrasive waterproof sandpapers starting from the rougher sandpaper R80 to R2000. Afterward, a manual polishing machine was used (Extec, LABPOLDU8) with alumina powder of 0.3–0.05 μm to polish the surface until a mirror finishing was achieved. Finally, the polished sample was etched with Villela's reagent during 1 min to reveal the microstructure of the boride coating.

The boride coating was observed by scanning electron microscopy (SEM) using a JEOL JAX-8200 instrument: the coating thickness measurements were collected from a fixed reference on the surface of AISI 316 L borided steel with the aid of Image-Pro PLUS V6.0 software. The total (FeB + Fe$_2$B) coating thickness ranged 27 ± 1 μm approximately, for the particular boriding conditions as given in Fig. 1.

In addition, the AISI 316 L borided steel before immersion in the SBFS was characterized through X-Ray diffraction (XRD) using an X'PERT PRO PANanalytical instrument. A standard scan procedure (CuKα radiation at λ = 0.154 nm) was applied over the surface. The collected data were analyzed with the aid of X'Pert HighScore V. 2.2d software according to the JCPDS (Joint Committee of Powder Diffraction Standards) database
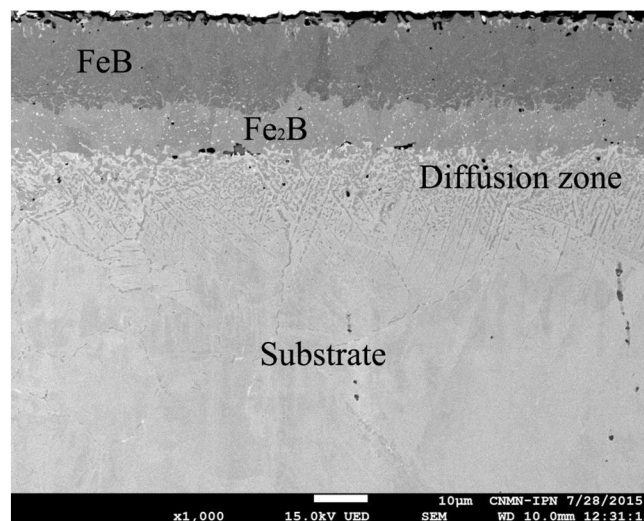

Fig. 1. SEM cross-sectional view of AISI 316 L borided steel.

to identify the compounds developed on the surface of AISI 316 L borided steel.

2.2. Corrosion tests

The electrochemical impedance spectroscopy tests were conducted on borided and non-borided steels using a SBFS (the composition of Hanks' solution is given in Table 2). A commercial workstation (Zahner Zennium instrument) with Thales software running on a PC was used to collect the electrochemical data during 10 days of immersion at room temperature. The standard cell used for the EIS tests comprised: the reference electrode (Ag/AgCl), an AISI 316 L steel cylindrical rod as counter electrode, and the samples as working electrodes, as shown in [17]. The surface area of borided and non-borided steels exposed to the electrolyte was 1 cm^2. The frequency range was established from 8 MHz to 2 mHz using a sinusoidal input of ± 10 mV. Electrochemical parameters were calculated for both borided and non-borided steels by fitting the appropriate equivalent electrical circuit to the experimental data using Zsim software.

2.3. Characterization of borided and non-borided surfaces by SEM and XPS techniques

The surface and cross-section of samples (borided and non-borided) immersed in the SBFS after 10 days of exposure were analyzed using a JEOL JAX-8200 Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) to identify features of the corrosion mechanisms and the presence of chemical elements. Acquisition of EDS data was done at an accelerating voltage of 15 kV at different working distances. Furthermore, the evolution of the corrosion damage on the surface and cross-section of borided and non-borided steels exposed to

Table 1
Chemical composition of AISI 316 L steel.

Element	C	Mn	Si	P	S	Cr	Ni	Mo
(wt%)	0.03	2.0	1.0	0.045	0.03	16.0–18.0	10.0–14.0	2.0–3.0

Table 2
Chemical composition of the Hanks' solution.

Compound	Nomenclature	Composition (g L^{-1})
Sodium bicarbonate	NaHCO$_3$	0.35
Magnesium sulfate	MgSO$_4$.7H$_2$O	0.2
Calcium chloride	CaCl$_2$.2H$_2$O	0.14
Potassium dihydrogen phosphate	KH$_2$PO$_4$.3H$_2$O	0.06
Sodium hydrogen phosphate	Na$_2$HPO$_4$.2H$_2$O	0.06
Sodium chloride	NaCl	8
Potassium chloride	KCl	0.4
Glucose	C$_6$H$_{12}$O$_6$.H$_2$O	2