Research Article

EIS Evaluation of Fe, Cr, and Ni in NaVO_3 at 700°C

**O. Sotelo-Mazón,¹ J. Porcayo-Calderon,^{1,2} C. Cuevas-Arteaga,¹ J. J. Ramos-Hernandez,³
J. A. Ascencio-Gutierrez,² and L. Martinez-Gomez^{2,4}**

¹ Universidad Autonoma del Estado de Morelos, CIICAp, Avenida Universidad 1001, 62209 Cuernavaca, MOR, Mexico

² Instituto de Ciencias Fisicas, Universidad Nacional Autonoma de Mexico, Avenida Universidad s/n, 62210 Cuernavaca, MOR, Mexico

³ Facultad de Química, Universidad Nacional Autónoma de México, 04510 México, DF, Mexico

⁴ Corrosion y Proteccion, Buffon 46, 11590 Mexico, DF, Mexico

Correspondence should be addressed to J. Porcayo-Calderon; jporcayoc@gmail.com

Received 27 May 2014; Accepted 14 October 2014; Published 10 November 2014

Academic Editor: Damien Boyer

Copyright © 2014 O. Sotelo-Mazón et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Due to the depletion of high-grade fuels and for economic reasons, use of residual fuel oil in energy generation systems is a common practice. Residual fuel oil contains sodium, vanadium, and sulphur as impurities, as well as NaCl contamination. Metallic dissolution caused by molten vanadates has been classically considered the main corrosion process involved in the degradation of alloys exposed to the combustion products of heavy fuel oils. Iron and nickel base alloys are the commercial alloys commonly used for the high temperature applications, for example, manufacture of components used in aggressive environments of gas turbines, steam boilers, and so forth. Therefore, because the main constituents of these materials are Fe, Cr, and Ni, where Cr is the element responsible for providing the corrosion resistance, in this study the electrochemical performance of Fe, Cr, and Ni in NaVO_3 at 700°C in static air for 100 hours was evaluated.

1. Introduction

Corrosion is the deterioration of a material by its reaction with the environment. This negatively affects the properties that must be preserved [1]. High temperature corrosion was recognized as a serious problem in 1940 due to the degradation of water-wall tubes in boilers of steam generating plants operating at high temperatures ($600\text{--}1100^\circ\text{C}$). Since then, the problem has been observed in boilers, internal combustion engines, gas turbines, fluidized bed combustion, and waste incinerators. Degradation suffered by metallic components of boilers, gas turbines, and furnaces is caused mainly by molten salts as thin salt films. Molten salts are formed by combustion of residual fuel oils, and they are deposited on metal surfaces of boiler equipment such as superheater and reheater, which can be at temperatures above 600°C . These temperatures correspond to the liquids of many combustion products from residual fuel oils, which include compounds of vanadium, sulfur, and oxygen, such as sodium sulfate-vanadium pentoxide ($\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$) mixture solution [2–8].

This accelerated attack results from condensation of films containing molten salts such as sulfates, chlorides, vanadates, and carbonates. Particularly, vanadium (V), sodium (Na), and sulfur (S) are the common impurities of low grade petroleum fuel used in oil-fired power stations. During combustion, vanadium is oxidized to form different oxides, among which vanadium pentoxide (V_2O_5) is the most common and forms several compounds of low melting temperature while sulfur is involved with sodium and make sodium sulfates [9]. Efficiency and availability of power plants depend upon the behavior of the materials they use. All materials in contact with water or steam must have physical and chemical properties to resist both high pressure and temperature and the effect of the ashes, which are a product of the oil burning. The latter leads to the failure of the materials in contact with them [4, 6, 7].

The corrosion performance of an alloy depends greatly upon its chemical composition. Generally speaking, for conditions involving high temperatures, the required materials can develop protective oxides such as chromium oxide

(Cr₂O₃), aluminum oxide (Al₂O₃), and silicon oxide (SiO₂). These oxides must have good adherence, low gas permeability and high thermodynamical stability to offer good corrosion resistance [10, 11], and low diffusion coefficients [12]. In addition to this, protective oxides must have a low solubility in the melted ashes. It has been suggested [13] that Cr, Al, and Si greatly reduce corrosion rates due to a slow dissolution of their oxides in liquid ashes.

Iron base alloys and nickel-based superalloys are commonly used for high temperature applications, for example, the manufacture of components used in aggressive environments of gas turbines, steam generators, and so forth. The excellent mechanical performance and good corrosion resistance of superalloys, especially nickel-based superalloys, make them useful for components exposed to aggressive environments at high temperature in industrial gas turbines and other energy conversion systems [3, 14]. A significant number of nickel-base alloys have been developed to meet the many demands and applications involving high temperature corrosive environments. By adding adequate amounts of chromium (Cr), aluminum (Al), or silicon (Ni) to form a protective scale of chromia (Cr₂O₃), alumina (Al₂O₃), or silica (SiO₂), these alloys can be highly resistant to vanadium (V), sulfur (S), and oxygen (O) attack at elevated temperatures. On the other hand, Fe-Cr-Ni alloys also meet these requirements and some of them are exposed to multioxidant species containing appreciable partial pressure of sulfur and low partial pressure of oxygen, or environments where sulfur- or vanadium-containing molten salts are present [6].

Therefore, in order to understand the corrosion performance of an alloy, it is important to study the behavior of its pure elements (Fe, Cr, and Ni) that are part of it. This is because these elements are the main components of both austenitic stainless steels as the Ni-based superalloys. On the other hand, chromium is the main alloying element to ensure the corrosion resistance of these materials [15].

2. Experimental Procedure

Pure Fe, Cr, and Ni, 99.99%, were used for this research. Rectangular parallelepiped specimens of 10 mm × 5 mm × 5 mm were cut down using a diamond tipped blade. Sample surfaces were grounded using silicon carbide sandpaper. Grinding process began with 120-grit sandpaper until all major scratches and burs were removed. The process was continued with 220-, 400-, and 600-grit sandpaper until all surfaces were uniform. Once the grinding was complete, samples were washed with distilled water then by ethanol in an ultrasonic bath for 10 minutes before the tests.

Impedance measurements were carried out using an ACM Instruments zero-resistance ammeter (ZRA) coupled to a personal computer. The amplitude of input sine-wave was ±10 mV and frequencies ranged from 10,000 Hz to 0.01 Hz. A typical three-electrode arrangement was used with two platinum wires as reference electrode and counter electrode. For electrical connection of the working electrode a Ni20Cr wire was spot welded. Ceramic tubes were used for isolating the electrical wire from the molten salt; the gap between

the ceramic tube and electrical connection wire was filled with refractory cement. Size, preparation of specimens, and corrosive mixtures were the same for electrochemical tests. A 30 mL alumina crucible was used for containing the corrosive salt and placed inside an electrical furnace. When the test temperature was stabilized, the three electrochemical cell electrodes were introduced inside the molten salt. For the corrosion tests sodium metavanadate was used, NaVO₃. The corrosion test was carried out for 100 hours at 700°C, and the atmosphere above the melt was static air.

After testing, corroded specimens were mounted in thermosetting resin, metallographically polished, and then cross section analyzed by scanning electron microscopy to investigate the morphology and distribution of reaction products. X-ray mapping and microprobe analysis were carried out using an X-ray energy dispersive (EDX) analyzer connected to a Zeiss DSM960 scanning electron microscope.

3. Results and Discussion

3.1. Electrochemical Impedance Spectroscopy. During immersion in the NaVO₃ molten salt the impedance measurements were performed. Figures 1 to 3 show results, in both Nyquist and Bode format. Impedance spectrum is related to the transient behavior of a specific electrochemical interface, and it reflects dialectic behavior, oxidation-reduction reactions and mass migration across the electrochemical interface, which is determined by the electrical and chemical properties of the corrosive medium, and the electrode materials [16]. It is said that analysis of the Bode diagram is simpler than the Nyquist diagrams. Bode format minimizes the dispersion of the experimental data and shows a clearer description of the frequency-dependent behavior of the electrochemical system, which only is implicit in the Nyquist diagrams. In addition, Bode diagrams are most appropriate for analysis and extrapolation of the experimental data at low frequencies. From the Bode diagram can also be identified the following basic elements in order to establish the configuration of the equivalent circuits describing the electrochemical system [17]: resistors (*R*) that appear as plateaus, and in this case $|Z| = R$ and $\phi \rightarrow 0^\circ$, capacitors (*C*), where $|Z|$ is a straight line with a -1 slope and $\phi \rightarrow 90^\circ$, and elements associated with diffusion, where $|Z|$ has a -0.5 slope and $\phi = 45^\circ$. In general, three frequency regions referring to the high, intermediate, and low frequency values are obtained from Bode diagrams [18, 19]. In the higher frequency region ($f > 1000$ Hz), the Bode plot exhibits a plateau (horizontal line) of the $|Z|$ values with the phase angle approaching 0° . This is the response of the electrode ohmic or solution resistance, R_s , which includes the electrolyte resistance, cell geometry, impedance of the conductors, and the reference electrode. In the middle frequency region (1000 to 10 Hz), the spectrum displays the maximum phase angle approaching -90° and a linear slope of about -1 in $\log |Z|$ as $\log(f)$ decreases. This is the characteristic response of capacitive behavior of the electrode and describes the dielectric properties of the electronically conducting surface film. In the lower frequency region ($f < 10$ Hz) are detected the electron charge transfer process,

FIGURE 1: Evolution of the Nyquist and Bode plots of the EIS response of the Fe in NaVO₃ at 700°C.

the mass transfer processes, or other relaxation processes taking place at the film-electrolyte interface or within the pores of the surface film.

Concerning to Fe, from Nyquist plot one relaxation at beginning of the corrosion process (0 hours) was observed. However after that, an additional relaxation was observed in the rest of corrosion test. Diameter of both capacitive semicircles increases as time elapses. Increasing of these capacitive loops denotes both an increase in the corrosion resistance and formation of a protective layer on the alloy surface. This behavior indicates that the corrosion process was under charge transfer from the metal to the electrolyte through the double electrochemical layer. This is most evident from the Bode plot, where one of them is observed in the middle frequency region and the other one in the low frequency region. The relaxation observed in the middle frequency region (10–1000 Hz) has a low impedance and capacitance. This may be related to the growth of a corrosion product layer. In the low frequency region an increase in the impedance module is observed. In addition, this is associated with an increase of the maximum phase angle. It is known that the

magnitude of the maximum phase angle is associated with a more capacitive response of the protective oxide. Then, this behavior can be associated with the growth of a protective oxide or by the accumulation of a corrosion products layer which limited the penetration of the corrosive agent. On the other hand, apparently an additional relaxation can be observed at frequencies higher than 1000 Hertz, as confirmed by Nyquist plots. An incomplete semicircle in Nyquist plots, corresponding to a capacitive behavior, was exhibited in this frequency region. It has been argued that the incomplete capacitive semicircle at high frequency region was associated with the TEL (thin electrolyte layer) thickness [20, 21]. However, in this case it is considered that the emergence of the incomplete semicircle is associated both with the location of the working electrode with respect to the bottom of the alumina crucible, or due to the partial evaporation of the molten salts. In both cases, the result is the formation of an apparent TEL on the working electrode surface, which would justify the emergence of this semicircle. In all cases, the plateau zone at the low frequency region was not defined.

FIGURE 2: Evolution of the Nyquist and Bode plots of the EIS response of the Cr in NaVO₃ at 700°C.

Regarding Cr, from Nyquist plot two capacitive-like semicircles were observed: one of them in the middle frequency region and the other one in the low frequency region. Diameter of the capacitive semicircles increases up to 25 hours and then they decrease as time elapses. This behavior shows that initially there was an increase in corrosion resistance due to the growth of a protective oxide, and subsequently the aggressiveness of the salt decreased its protective capacity. This is consistent with the Bode plot, in the low frequency region there is an initial increase and then a decrease in both impedance module and maximum phase angle. This behavior was caused by the aggressiveness of the molten salt, which favored the protective oxide dissolution and reducing its protective capacity. This behavior indicates that the corrosion process was under charge transfer from the metal to the electrolyte through the double electrochemical layer. Again, additional relaxation was observed at high frequency region, and the plateau zone at the low frequencies region was not defined.

Nyquist plot for Ni shows one capacitive-like semicircle at beginning of the corrosion process (0 hours), and after

that two capacitive-like semicircles are observed. In this case, the diameter of both capacitive semicircles increases as time elapses. Increasing of these capacitive loops denotes both an increase in the corrosion resistance and formation of a protective layer on the alloy surface. This behavior indicates that the corrosion process was under charge transfer from the metal to the electrolyte through the double electrochemical layer. From the Bode plot, one relaxation is observed in the middle frequency region and the other one in the low frequency region. Impedance and capacitance of the relaxation observed in the middle frequency region (10–1000 Hz) increase as time elapses. This may be due to the growth as thickening of a corrosion product layer. In the low frequency region an increase in the impedance module is observed. In addition, this is associated with an increase of the maximum phase angle, which shows a more capacitive response of the protective oxide. This behavior is associated with the growth of a protective oxide on the material surface. In this case also at high frequency region an additional relaxation was observed, and the plateau zone at the low frequency region was not defined.

FIGURE 3: Evolution of the Nyquist and Bode plots of the EIS response of the Ni in NaVO_3 at 700°C .

3.2. SEM Analysis. Although the electrochemical methods are extremely useful in studying corrosion processes, they alone do not provide enough information to elucidate the mechanism of the system under study. Therefore the use of complementary techniques has been suggested, that is, scanning electron microscopy (SEM), auger electron spectroscopy (AES), among others, in order to clarify both the morphology of the attack and the chemical composition and distribution about the elements present. Combination of these methods provides the information to understand the reactions occurring on the surface [22]. Therefore in this study the cross section of the working electrodes was studied using scanning electron microscopy (SEM) to clarify both the morphology and the elements distribution.

Figure 4 shows the cross-sectional aspect of Fe and mapping elements for Fe, V, and O, after the corrosion test. Fe was not able to develop a stable protective layer. The presence of a thick layer of corrosion products is noted (greater than 200 microns). Vanadium salts penetrated the corrosion products layer and continuously reacted with both Fe and

iron oxides. On the corrosion products surface the presence of crystals associated with V and Fe is observed; these are possibly iron metavanadate. The aspect observed justified the continuous increase in impedance module shown in Figure 1. The increase observed in the charge transfer resistance was not due to the formation of a passive layer on its surface, but rather it was due to the accumulation of a thick layer of corrosion products which limited the access of the molten salt.

Figure 5 shows the cross-sectional aspect of Cr and mapping elements for Cr, V, and O, after the corrosion test. It is observed that chromium was not able to develop a stable passive layer on its surface. This was because the chromium oxide was continuously dissolved by the molten salt. Cr mapping shows the presence of this element through the whole layer of corrosion products. That agrees with EIS measurements (Figure 2), where initially there was an increase in the charge transfer resistance and then a steady decline.

Figure 6 shows the cross-sectional aspect of Ni and mapping elements for Ni, V, and O, after the corrosion test.

FIGURE 4: Cross-sectional aspect of Fe and elements distribution after corrosion test.

Presence of a passive layer of NiO is observed onto the nickel surface. It is possible that its growth rate was greater than its dilution rate in the molten salts. According to the elements mapping onto passive layer there are a large amount of corrosion products, possibly nickel metavanadate, and in the outer zone the presence of a thick layer of the corrosive salt is observed. The capacitive-like semicircles observed in the EIS measurements (Figure 3) correspond to the presence of the protective oxide layer and corrosion products. The increase in its diameters is the result of the thickening of both layers.

It is important to point out that the electrochemical results and the SEM analysis complement each other to elucidate a corrosion mechanism, which leads to a better understanding of the performance of these pure metals in NaVO₃ molten salt. Therefore, and considering the natural trend of chromium, nickel, and iron to develop a protective oxide on their metallic surfaces, it is possible to establish that the degradation of Cr, Ni, and Fe was throughout the following reactions:

Through these reactions the metallic oxides were dissolved. The melting points of the metallic vanadates formed are 760°C, 810°C, and 1220°C, respectively. Therefore, the excellent performance of Ni is because to the formation of Ni₃V₂O₈, which is considered a refractory compound with a high melting point, and therefore it decreases the corrosiveness of the NaVO₃ [23]. The corrosive aggressiveness of NaVO₃ is due to its low melting point (650°C), and its fluidity produces that the different species have major interaction between them, and therefore the electrochemical reactions are carried out more quickly. Nevertheless, the presence of Ni₃V₂O₈ reduces the fluidity of the NaVO₃. Whereas the melting points of FeVO₄ and CrVO₄ are smaller, then it is expected that the corrosion rate of Fe and Cr is bigger than that of Ni.

The corrosion results described above imply clearly that Ni is very effective in improving the corrosion resistance in NaVO₃. It is well known that the corrosion protection of any material performing in molten salts depends on the chemical stability of both the metallic elements and their compounds such as oxides and vanadates. This is explained because the breakdown of the protective oxide can occur by dissolution into the molten salts and the degradation rate can be fast if the oxide has a high solubility. Considering that V and O₂ are the main species of the NaVO₃-O₂ system that contribute to the degradation of materials, the construction of phase

FIGURE 5: Cross-sectional aspect of Cr and elements distribution after corrosion test.

TABLE 1: Chemical reactions and equilibrium constants for the Fe-Na-V-O system at 700°C.

Number	Reaction	log 10 K
1	$4 \text{Fe}_3\text{O}_{4(s)} + \text{O}_2 = 6 \text{Fe}_2\text{O}_{3(s)}$	10.9158
2	$4 \text{NaVO}_{3(s)} = 2 \text{V}_2\text{O}_{4(s)} + 2 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-39.7131
3	$\text{Na}_3\text{VO}_{4(s)} = \text{NaVO}_{3(s)} + \text{Na}_2\text{O}_{(s)}$	-10.1885
4	$2 \text{Na}_3\text{VO}_{4(s)} = \text{V}_2\text{O}_{3(s)} + 3 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-47.6241
5	$2 \text{NaVO}_{3(s)} = \text{V}_2\text{O}_{3(s)} + \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-27.2471
6	$2 \text{V}_2\text{O}_{3(s)} + \text{O}_2 = 2 \text{V}_2\text{O}_{4(s)}$	14.7810
7	$2 \text{FeVO}_{4(s)} + \text{Na}_2\text{O}_{(s)} = \text{Fe}_2\text{O}_{3(s)} + 2 \text{NaVO}_{3(s)}$	15.5865
8	$2 \text{Fe}_2\text{O}_{3(s)} + 2 \text{V}_2\text{O}_{4(s)} + \text{O}_2 = 4 \text{FeVO}_{4(s)}$	8.5400

stability diagrams of these species with the elements (Fe, Cr, and Ni) is a useful tool for understanding the corrosion behavior at high temperature. Figures 7, 8, and 9 show the phase stability diagrams for the M-Na-V-O (M = Fe, Cr, Ni) system at 700°C. The procedure to generate the diagrams is described elsewhere [24]. Tables 1, 2, and 3 show the set of chemical reactions used for their calculation.

From the figures it is observed that from the thermodynamic viewpoint Fe shows the higher affinity to oxygen and vanadium. In any condition of partial pressure of oxygen and sodium oxide activity (basicity), it will form nonprotective corrosion products of iron oxides or iron vanadates. Furthermore, in normal operation conditions of oil-fired power

stations, Cr always form chromium vanadates nonprotective, and only in conditions of low partial pressure of oxygen and low basicity, the chromium oxide will be stable. On the other hand, notwithstanding that Ni forms nickel vanadates in a wider range of conditions of partial pressure of oxygen and basicity, than those of the Cr, the formation of this compound increases its corrosion resistance due its melting point as it has been discussed. Therefore, the corrosion resistance of Ni is greater in $\text{NaVO}_3\text{-O}_2$ environments where the Fe and Cr would be corroding continuously. Therefore, in conditions of environments of oil-fired power stations at 700°C temperatures where NaVO_3 is the predominant species, the Ni-rich alloys will show better performance

FIGURE 6: Cross-sectional aspect of Ni and elements distribution after corrosion test.

TABLE 2: Chemical reactions and equilibrium constants for the Cr-Na-V-O system at 700°C.

Number	Reaction	log 10 K
1	$4 \text{NaVO}_{3(s)} = 2 \text{V}_2\text{O}_{4(s)} + 2 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-39.7131
2	$\text{Na}_3\text{VO}_{4(s)} = \text{NaVO}_{3(s)} + \text{Na}_2\text{O}_{(s)}$	-10.1885
3	$2 \text{Na}_3\text{VO}_{4(s)} = \text{V}_2\text{O}_{3(s)} + 3 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-47.6241
4	$2 \text{NaVO}_{3(s)} = \text{V}_2\text{O}_{3(s)} + \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-27.2471
5	$2 \text{V}_2\text{O}_{3(s)} + \text{O}_2 = 2 \text{V}_2\text{O}_{4(s)}$	14.7810
6	$2 \text{CrVO}_{4(s)} + \text{Na}_2\text{O}_{(s)} = \text{Cr}_2\text{O}_{3(s)} + 2 \text{NaVO}_{3(s)}$	16.7790
7	$2 \text{Cr}_2\text{O}_{3(s)} + 2 \text{V}_2\text{O}_{4(s)} + \text{O}_2 = 4 \text{CrVO}_{4(s)}$	6.15498

TABLE 3: Chemical reactions and equilibrium constants for the Ni-Na-V-O system at 700°C.

Number	Reaction	log 10 K
1	$2 \text{Ni}_{(s)} + \text{O}_2 = 2 \text{NiO}_{(s)}$	16.3501
2	$4 \text{NaVO}_{3(s)} = 2 \text{V}_2\text{O}_{4(s)} + 2 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-39.7131
3	$\text{Na}_3\text{VO}_{4(s)} = \text{NaVO}_{3(s)} + \text{Na}_2\text{O}_{(s)}$	-10.1885
4	$2 \text{Na}_3\text{VO}_{4(s)} = \text{V}_2\text{O}_{3(s)} + 3 \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-47.6241
5	$2 \text{NaVO}_{3(s)} = \text{V}_2\text{O}_{3(s)} + \text{Na}_2\text{O}_{(s)} + \text{O}_2$	-27.2471
6	$2 \text{V}_2\text{O}_{3(s)} + \text{O}_2 = 2 \text{V}_2\text{O}_{4(s)}$	14.7811
7	$3 \text{NiO}_{(s)} + 2 \text{NaVO}_{3(s)} = \text{Ni}_3\text{V}_2\text{O}_{8(s)} + \text{Na}_2\text{O}_{(s)}$	-15.3293
8	$6 \text{NiO}_{(s)} + 2 \text{V}_2\text{O}_{4(s)} + \text{O}_2 = 2 \text{Ni}_3\text{V}_2\text{O}_{8(s)}$	9.0546

FIGURE 7: Thermodynamic stability diagrams for Fe-Na-V-O at 700°C.

FIGURE 9: Thermodynamic stability diagrams for Ni-Na-V-O at 700°C.

FIGURE 8: Thermodynamic stability diagrams for Cr-Na-V-O at 700°C.

compared with those richer in Fe or Cr. This kind of analysis is very important in order to determine the different corrosion processes that materials and alloys may experience; however, taking into account the microenvironment created under the molten salts it can modify the actual corrosion reaction pathways.

4. Conclusions

EIS measurements, as well as SEM analysis and thermochemical analysis, show that Ni present the best performance in NaVO_3 at 700°C. Nickel is the only material able to develop a stable passive layer and its corrosion products have a high melting point. $\text{Ni}_3\text{V}_2\text{O}_8$ is an effective barrier for the penetration of corrosive salts and it also decreases the corrosivity of the NaVO_3 . Both chromium and iron are not able to form a stable passive layer, and this favored its continuous degradation. From EIS measurements, an incomplete capacitive semicircle in Nyquist plots was exhibited at high frequency region. It was argued that the emergence of this incomplete semicircle is associated with the formation of an apparent TEL on the working electrode surface.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

Financial support from Consejo Nacional de Ciencia y Tecnología (CONACYT, México) (Project 299143, and Ph.D. scholarship to O. Sotelo-Mazon, registration no. 227517) is gratefully acknowledged.

References

- [1] T. S. Sidhu, S. Prakash, and R. D. Agrawal, "Hot corrosion and performance of nickel-based coatings," *Current Science*, vol. 90, no. 1, pp. 41–47, 2006.
- [2] J. G. González-Rodríguez, M. Salazar, J. Porcayo-Calderon, G. Rosas, and A. M. Villfane, "Effect of Li, Ce and Ni on the corrosion resistance of Fe₃Al in molten Na₂SO₄ and NaVO₃," *High Temperature Materials and Processes*, vol. 23, no. 3, pp. 177–183, 2004.
- [3] C. Cuevas-Arteaga, J. Uruchurtu-Chavarín, J. González, G. Izquierdo-Montalvo, J. Porcayo-Calderón, and U. Cano-Castillo, "Corrosion evaluation of Alloy 800 in sulfate/vanadate molten salts," *Corrosion*, vol. 60, no. 6, pp. 548–560, 2004.
- [4] V. M. Salinas-Bravo, J. Porcayo-Calderón, T. Romero-Castañón, G. Domínguez-Patino, and J. G. Gonzalez-Rodriguez, "Corrosion behavior of Fe-Si metallic coatings added with NiCrAlY in an environment of fuel oil ashes at 700 °C," *Materials and Corrosion*, vol. 56, no. 7, pp. 481–484, 2005.
- [5] O. L. Arenas, J. Porcayo-Calderon, V. M. Salinas-Bravo, A. Martinez-Villafañe, and J. G. Gonzalez-Rodriguez, "Effect of boron on the hot corrosion resistance of sprayed Fe40Al intermetallics," *High Temperature Materials and Processes*, vol. 24, no. 2, pp. 93–100, 2005.
- [6] J. G. Gonzalez-Rodriguez, S. Haro, A. Martinez-Villafañe, V. M. Salinas-Bravo, and J. Porcayo-Calderon, "Corrosion performance of heat resistant alloys in Na₂SO₄-V₂O₅ molten salts," *Materials Science and Engineering A*, vol. 435–436, pp. 258–265, 2006.
- [7] V. M. Salinas-Bravo, J. Porcayo-Calderon, and J. G. Gonzalez-Rodriguez, "Corrosion monitoring using electrochemical noise and linear polarization resistance in fuel oil combustion gas environment," *Russian Journal of Electrochemistry*, vol. 42, no. 5, pp. 560–565, 2006.
- [8] A. Luna-Ramirez, J. Porcayo-Calderon, G. Salinas-Solano, C. D. Arrieta-Gonzalez, V. M. Salinas-Bravo, and L. Martinez, "Electrochemical performance of Fe-Al intermetallic alloys with addition of Li, Ni and Ce in NaVO₃ at 700°C," *International Journal of Electrochemical Science*, vol. 8, no. 4, pp. 4641–4653, 2013.
- [9] G. Sorrel and W. B. Hoyt NACE Publication, 1956.
- [10] W. J. Quadackers and M. J. Bennet, "Oxidation induced lifetime limits of thin walled, iron based, alumina forming, oxide dispersion strengthened alloy components," *Materials Science and Technology*, vol. 10, no. 2, pp. 126–131, 1994.
- [11] I. Wolf, H. J. Grabke, and P. Schmidt, "Carbon transport through oxide scales on Fe-Cr alloys," *Oxidation of Metals*, vol. 29, no. 3–4, pp. 289–306, 1988.
- [12] H. W. Grünling and R. Bauer, "The role of silicon in corrosion-resistant high temperature coatings," *Thin Solids Films*, vol. 95, no. 1, pp. 3–20, 1982.
- [13] J. R. Wilson, "CORROSION 76," Paper 12, NACE International, Houston, Tex, USA, 1976.
- [14] H. Singh, D. Puri, and S. Prakash, "An overview of Na₂SO₄ and/or V₂O₅ induced hot corrosion of Fe- and Ni-based superalloys," *Reviews on Advanced Materials Science*, vol. 16, no. 1–2, pp. 27–50, 2007.
- [15] T. Tzvetkoff and P. Gencheva, "Mechanism of formation of corrosion layers on nickel and nickel-based alloys in melts containing oxyanions—a review," *Materials Chemistry and Physics*, vol. 82, no. 3, pp. 897–904, 2003.
- [16] C. Liu, Q. Bi, A. Leyland, and A. Matthews, "An electrochemical impedance spectroscopy study of the corrosion behaviour of PVD coated steels in 0.5 N NaCl aqueous solution: part I. Establishment of equivalent circuits for EIS data modelling," *Corrosion Science*, vol. 45, no. 6, pp. 1243–1256, 2003.
- [17] V. Freger and S. Bason, "Characterization of ion transport in thin films using electrochemical impedance spectroscopy: I. Principles and theory," *Journal of Membrane Science*, vol. 302, no. 1–2, pp. 1–9, 2007.
- [18] J. E. G. Gonzalez and J. C. Mirza-Rosca, "Study of the corrosion behavior of titanium and some of its alloys for biomedical and dental implant applications," *Journal of Electroanalytical Chemistry*, vol. 471, no. 2, pp. 109–115, 1999.
- [19] S. Tamilselvi, V. Raman, and N. Rajendran, "Corrosion behaviour of Ti-6Al-7Nb and Ti-6Al-4V ELI alloys in the simulated body fluid solution by electrochemical impedance spectroscopy," *Electrochimica Acta*, vol. 52, no. 3, pp. 839–846, 2006.
- [20] Q. Cheng and Z. Chen, "The cause analysis of the incomplete semi-circle observed in high frequency region of EIS obtained from TEL-covered pure copper," *International Journal of Electrochemical Science*, vol. 8, no. 6, pp. 8282–8290, 2013.
- [21] A. Nishikata, Y. Ichihara, and T. Tsuru, "An application of electrochemical impedance spectroscopy to atmospheric corrosion study," *Corrosion Science*, vol. 37, no. 6, pp. 897–911, 1995.
- [22] Y. van Ingelgem, A. Hubin, and J. Vereecken, "Investigation of the first stages of the localized corrosion of pure copper combining EIS, FE-SEM and FE-AES," *Electrochimica Acta*, vol. 52, no. 27, pp. 7642–7650, 2007.
- [23] E. Rocca, L. Aranda, M. Moliere, and P. Steinmetz, "Nickel oxide as a new inhibitor of vanadium-induced hot corrosion of superalloys—comparison to MgO-based inhibitor," *Journal of Materials Chemistry*, vol. 12, no. 12, pp. 3766–3772, 2002.
- [24] J. J. Ramos-Hernandez, J. Porcayo-Calderon, V. M. Salinas-Bravo, C. D. Arrieta-Gonzalez, J. G. Gonzalez-Rodriguez, and L. Martinez-Gomez, "Phase stability diagrams for high temperature corrosion processes," *Mathematical Problems in Engineering*, vol. 2013, Article ID 542061, 7 pages, 2013.