International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Determining the Effect of the Main Alloying Elements on Localized Corrosion in Nickel Alloys using Artificial Neural Networks

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Abstract

Nickel base alloys are considered among candidate materials for engineered barriers of nuclear repositories. The localized corrosion resistance is a determining factor in materials selection for this application. This work compares the crevice corrosion resistance of several commercial nickel base alloys using artificial neural networks. The crevice corrosion repassivation potential of the tested alloys was determined by the potentiodynamic-galvanostatic-potentiodynamic (PD-GS-PD) method. The testing temperature was 60ªC and the chloride concentrations used were 0,1M, 1M and 10M.

The results indicate that the repassivation potential increases linearly with the PREN (Pitting Resistant Equivalent Number) at high chloride concentrations. We also found a linear relationship between the repassivation potential and the logarithm of the concentration of chloride.

Analysis from artificial neural networks presents distinctive patterns between the mayor alloying components and the chloride concentration and the repassivation potential. Predictions from artificial neural networks fit with successive tested commercial nickel alloys.

Keywords: Crevice corrosion; repassivation potential; chlorides; nickel alloys; artificial neural networks.

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1. Introduction

High-level nuclear waste contains radioactive isotopes with half-lives greater than 30 years. These residues are emitting radiation and heat and remain active for thousands of years. Therefore require a definitive management system that ensures isolation and confinement. The disposal is an important step in the management of radioactive waste and location of conditioned waste with no intentions of recovery, Carranza et al. (2009).

The deep geological disposals are the strongest alternative for the disposal of high level nuclear waste. Geological repositories are based on the multi-barrier principle, which is to bring a number of barriers, natural and engineered, between waste and the biosphere. Natural barriers must contribute to the isolation of the waste by minimizing the amount of water entering in the deposit and limits the transport of the waste through the natural system, for which the repository should be located above and below a very stable geological formation. The engineered barriers are designed specifically to prolong the isolation of the nuclear waste. The main barrier is the container, which must perform an excellent resistance to corrosion, good mechanical strength and considerable stability to heat and radiation.

Due to its high resistance to corrosion, both general and localized, and its mechanical properties, the alloys with a high Ni content such as C-22, 625 HYBRID-BC1 could form part of engineered barriers of these repositories. However, it is possible that these alloys may undergo crevice corrosion when in highly aggressive media, in particular media with high chloride concentration. The process of crevice corrosion can occur when the potential at which the alloy is subjected is equal to or greater than the potential of repassivation. This last parameter can be measured by the electrochemical technique PD-GS-PD (potentiodynamic - galvanostatic - potentiodynamic) Evans et al. (2007).

1.1. Nickel alloys

Nickel base alloys are widely used in the chemical industry because of its resistance to corrosion and also because stainless steels may suffer localized corrosion, leading to catastrophic failure in service. Most of the times, are the properties of resistance to localized corrosion the reason to choice such alloys: resistance to pitting, crevice corrosion and stress corrosion cracking.

However, nickel base alloys are not all equivalent, there are noticeable differences in behavior between the different families of alloys (Ni, Ni-Cu, Ni-Cr-Mo, Ni-Mo, Ni-Cr, etc..) And even within the same family. Only the selection based on a perfect knowledge of the environment and the characteristics of the alloys can avoid problems, Houlle (1994). Nickel alloys are reputed to be resistant to localized corrosion such as pitting corrosion, crevice corrosion and cracking. There have been very few reported failures in service due to localized corrosion in these alloys.

Nickel and its alloys have good resistance to atmospheric corrosion in natural fresh water and deaerated in non-oxidizing acids. They also have excellent resistance to corrosion caused by caustic alkali. Since nickel is ductile, with a hardenable matrix, is the basis of a variety of strong and corrosion resistant alloys, De Renzo (1985).

1.2. Resistance to pitting and crevice corrosion

The occurrence of localized corrosion (pitting and crevice) is the result of the combined effects of the metallurgical parameters and the medium. In acidic medium at elevated temperature, the foreknowledge of halogens and the formation of salt deposits lead to local depassivation pinholes or cracks. The electrochemical analysis of these phenomena reveals the existence of a critical potential. This potential is of great interest for industrial and nuclear applications, where the temperature and the potential occurrence of pitting or crevice corrosion are relevant parameters.

2. Experimental procedure

2.1. Commercial nickel alloys used

Assays were performed in order to test crevice corrosion susceptibility by using the PD-GS-PD method on alloy C-22, C-22HS, HYBRID-BC1, 625, G35, G30 and 718. The chemical composition of these alloys can be seen in Table 1

Table 1: Chemical composition of nickel-based alloys used

Alloy	Ni	Cr	Mo	W	Fe	Co	Si	Mn	C	V	Al	B	Cb+Ta	PREN
625	62	21	9	0	5	1	0,5	0,5	0,1	0	0,4	0	3,7	50,7
G-30	43	29,8	5	2,7	15	5	0,8	1,5	0,03	0	0	0	0,9	50,8
G-35	55	33	8	0	2	0	0,6	0,5	0,05	0	0,4	0	0	59,4
C-22	56	22	13	3	3	2,5	0,08	0,5	0,01	0,35	0	0	0	69,85
C-22 HS	61	21	17	1	2	1	0,08	0,8	0,01	0	0,5	0,006	0	78,75
718	52	18	3	0	19	1	0,35	0,35	0,05	0	0,5	0,009	5	27,9
HYBRID-BC1	62	15	22	0	2	0	0,08	0,25	0,01	0	0,5	0	0	87,6

2.2. Determination of repassivation potential crevice corrosion

Using the PD-GS-PD method was determined crevice corrosion susceptibility of the alloys HYBRID-BC1, C-22HS, C-22, 625, G-35 and 718 in solutions of NaCl 1 mol/L and 0.1 mol/L and in $CaCl_2$ 5 mol/L, at a temperature of 60°C. Assays were performed in triplicate. Photographs were taken of the test specimens, and observed under the optical microscope.

The results obtained were analysed, yielding the quantitative relationships between the repassivation potential and chloride concentration for each alloy. Moreover, a quantitative relationship was established between the repassivation potential and PRE (Pitting Resistance Equivalent). The PRE is a function of the contents of Cr, Mo and W of the alloy, defined as PRE =% Cr + 3,3 (% Mo + 0.5% W) Kehler and Scully (1995).

PD-GS-PD assays consists of three consecutive steps: (1) a potentiodynamic polarization (to 0.167 mV/s) in the anodic direction to achieve an anodic current of 30 uA ($2\mu A/cm^2$ approx.), (2) the application of a constant anodic current of 30 uA for 2 hours and (3) a potentiodynamic polarization (to 0.167 mV/s) in the cathodic direction to intersect the curve of the alloy passivity. The repassivation potential crevice corrosion for this technique is a potential defined by the intersection of the two sweeps, the stage 1 and 3

The specimens used were PCA (Prism Crevice Assemblies) or holed plates with cracks forming ceramic coated with a film of polytetrafluoroethylene (PTFE), specially designed for the study of crevice corrosion. The exposed area was approximately 14 cm2. The samples were polished with abrasive paper 600, one hour before each experiment. They were cleaned with alcohol. We applied a torque of 5 Nm to cracks forming. All electrochemical experiments were carried out in an electrochemical cell of 500 mL with three electrodes (ASTM G 5). The experiments were performed in $CaCl_2$ 5mol/L solution and NaCl 1 mol/L and 0.1M mol/L at 60°C. The solutions were deaerated by bubbling nitrogen for one hour before the experiment and all through the assay. A saturated calomel electrode (SCE) was used as the reference electrode and as counter electrode was used a platinum foil welded to a wire of platinum or a graphite electrode. The samples were examined with an optical microscope after completion of the tests and some of them were observed in the scanning electron microscope (SEM). The assembly of PD-GS-PD assay is shown in Fig. 1a and 1b
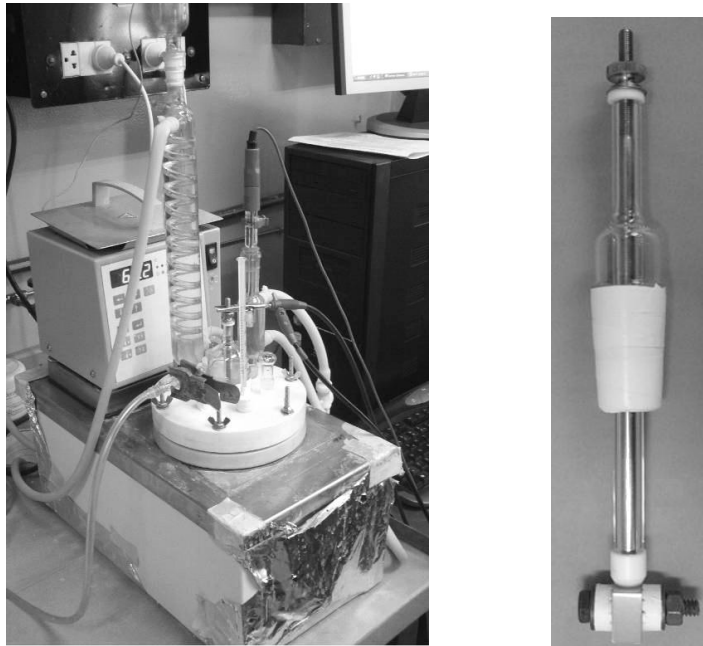
Fig. 1. (a) Essay PD-GS-PD for specimens PCA type of nickel base alloys; (b) PCA type specimen mounted for testing PD-GS-PD

3. Results and discussion

The results obtained in the essays of susceptibility to crevice corrosion by the PD-GS-PD method for alloys C-22, HYBRID-BC1, C-22HS, 625, G35 and G30 are shown in Figure 2

Figure 2a shows the curve obtained in the PD-GS-PD test for G30 alloy in NaCl 1mol/L solution at 60°C. In the figure can differentiate the 3 stages of the assay.

Figure 2b shows repassivation potentials (E_{CO}) versus the concentration of chlorides in the solution. The E_{CO} decreased with increasing chloride concentration. The relationship between E_{CO}, the chemical composition of the alloys and the chloride concentration of the solution are of great importance. E_{CO} also increased with the PRE (Pitting Resistance Equivalent) of the alloys. However G35 and G30 alloy presented a higher resistance to low concentrations of chlorides than other alloys with higher PRE.
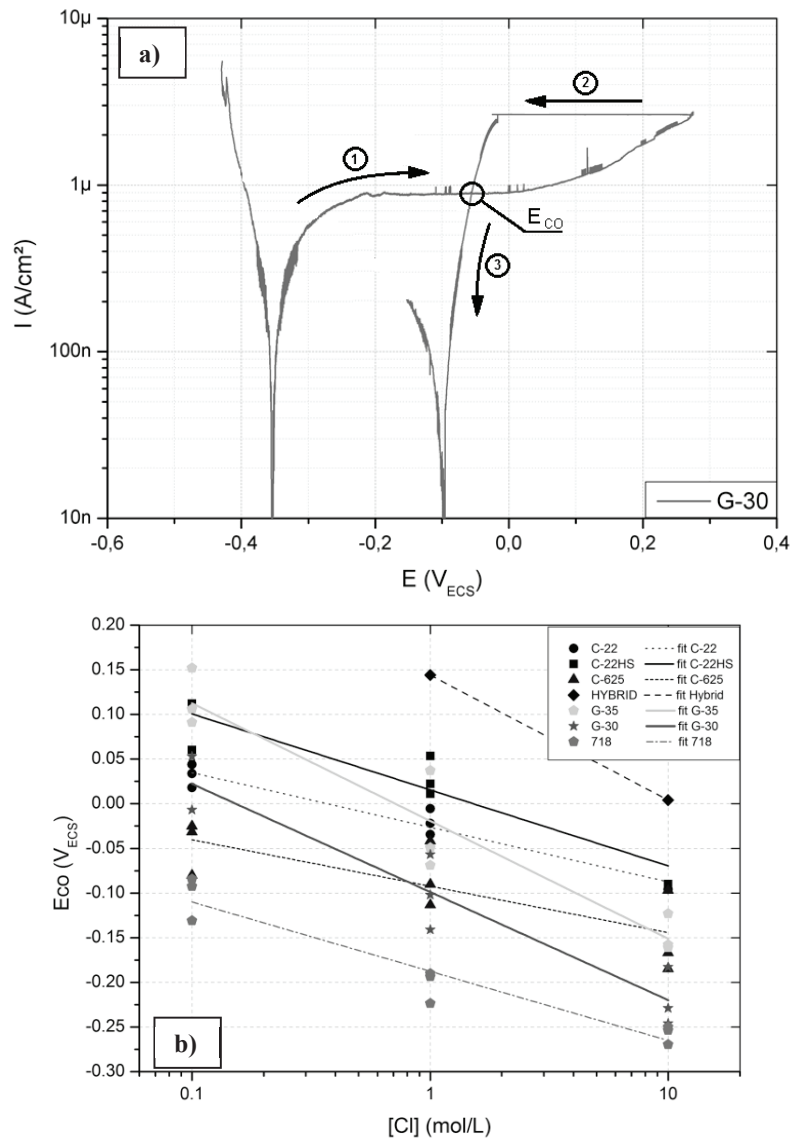
Fig. 2. (a) Current versus potential in PD-GS-PD essay; (b) Repassivation potentials versus the concentration of chlorides

In Figures 3a, 3b and 3c are shown the specimens of C-22, C-22HS and 625 after testing. It can be observed marks from the occluded areas attacked by the crevice corrosion on the specimen.
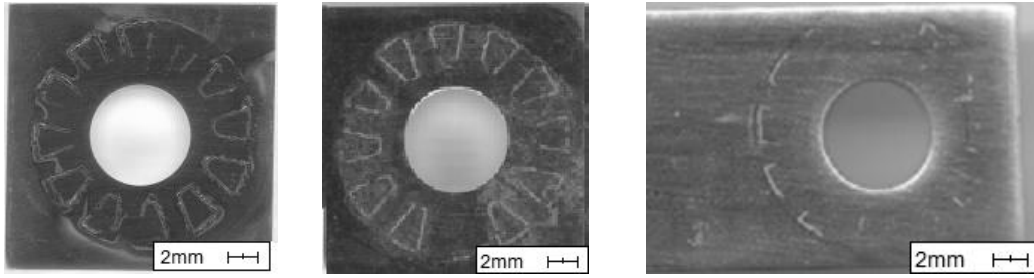
Fig. 3. (a) Specimen of C-22 after the test; (b) Specimen of C-22 HS after the test; (c) Specimen of 625 after the test

To analyze the results was implemented a method of adjustment by artificial neural network using Back Propagation method. The network consisted of 7 entries defined as the percentage of Ni, Cr, Mo, W, Fe, Co of alloys used and the chloride concentration of solution in the different assays, two inner layers of neurons 5 and 2 outputs denoted as the E_{CO} and the PRE.

We performed a training step with 37 essays of 5 different composition alloys (C-22, C-22HS, G35, G30 and 625) and adjusted performing 1 million iterations. Figure 4 shows a basic diagram of a neural network for adjusting a parameter.
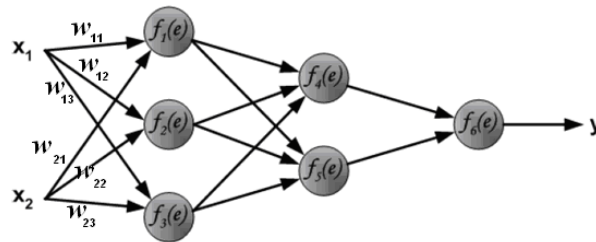

Fig. 4. A basic scheme of an artificial neural network

The neural network adjusts the weights (w_{11}, w_{12}, etc ...) of the input variables (X_1, X_2, etc ...), then performs a summation (equation 1) of the weights multiplied by the input variables and then evaluates this sum through the bipolar sigmoid activation function (equation 2) and so on with the other layers

$$e_j = \sum_{i=1}^{n} x_i w_{ji} \tag{1}$$

$$f(e_j) = \frac{2}{1 + \exp(-e_j)} - 1 \tag{2}$$

In Figures 5. 6 and 7 show a mapping in composition of Cr Mo from two settings of the neural network and compared with the actual values of E_{CO}
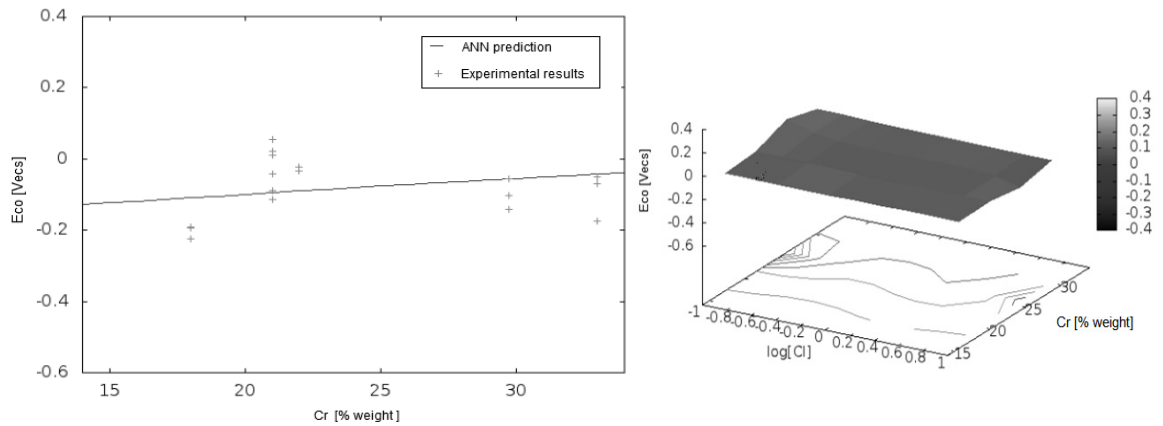
Fig. 5. (a) Repassivation potential Vs Cr content in a 1mol/L NaCl solution; (b) Mapping in composition of Cr content and chloride concentration from artificial neural network prediction.
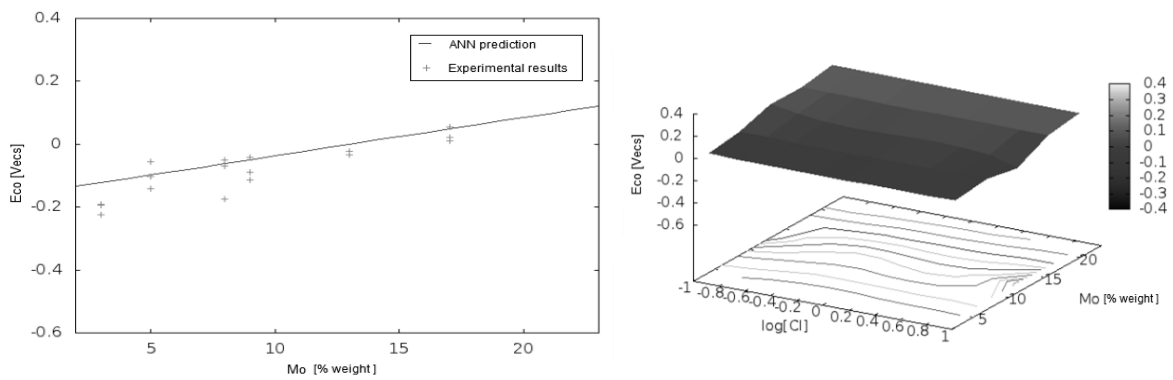

Fig. 6. (a) Repassivation potential Vs Mo content in a 1mol/L NaCl solution; (b) Mapping in composition of Mo content and chloride concentration from artificial neural network prediction.
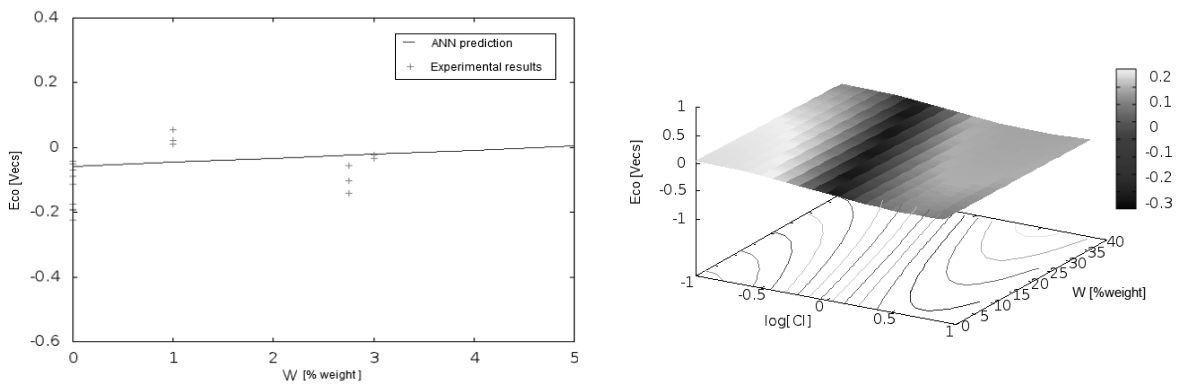

Fig. 7. (a) Repassivation potential Vs W content in a 1mol/L NaCl solution; (b) Mapping in composition of W content and chloride concentration from artificial neural network prediction.

4. Conclusions

Values of E_{CO} were obtained for different nickel-base alloys using the PD-GS-PD method and a linear behavior was observed between the susceptibility to crevice corrosion and the logarithm of the concentration of chlorides in the solution.

It was observed that PRE can be associated as a parameter relating to the crevice corrosion resistance at high concentrations of chlorides in the nickel base alloys studied.

Adjustments of data through the neural network results in maps of composition and susceptibility to crevice corrosion. However with a greater amount of data we may obtain a final adjustment on the surfaces of the superalloy composition versus the repassivation potential.

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