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Susceptibility of M5™ (ZrNbO) alloy to pitting corrosion at different temperatures

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Abstract

Corrosion of fuel cladding is a major concern in the nuclear industry. Zirconium alloys are the standard materials for nuclear fuel tubing due to its notable low neutron absorption cross-section. The M5™ alloy is currently employed for the production of nuclear fuel cladding in Brazil. Pitting corrosion has been associated with the intergranular stress corrosion cracking of these materials. In this regard, the study of pitting corrosion behavior of M5™ alloy is of great technological interest in order to allow the development of safer nuclear fuel claddings. The aim of this work was to evaluate the pitting corrosion behavior of M5™ alloy at different temperatures. Electrochemical measurements comprised potentiodynamic polarization and electrochemical impedance spectroscopy analyses. The tests were conducted in 5.0 wt.% NaCl solution at room temperature, 40 °C and 60 °C. The corrosion resistance was shown to be dependent on the testing temperature. The M5™ alloy showed good corrosion resistance with only a slight decay as the temperature increased.

Keywords: M5™ zirconium alloy, pitting corrosion, temperature

Introduction

Zircaloy-4 is traditionally used as fuel-cladding material for pressurized water reactors (PWR) worldwide due its low neutron absorption cross-section (1,2). It is considered as one of the most critical components of the reactor's core (3). This material oxidizes during irradiation in a PWR due to contact with the primary water, forming a zirconia layer which can reach a thickness of up to 100 μm (4). In spite of the relative stability of the passive film formed on zirconium alloys (5), some authors reported that foreign ions can be incorporated into this film (6). The stability of the oxide film formed on zirconium alloys was found to be relatively low in aqueous electrolytes containing chlorides (7), giving rise to stress corrosion cracking and intergranular stress corrosion cracking phenomena (8,9). In this context, corrosion is a major concern regarding the safe use of fuel-cladding materials. Several authors have investigated the dependence of pitting corrosion on the applied potential, scanning rate and concentration of aggressive ions. Shibata et al. (10) observed that the pitting potential of Zircaloy-4 increases with the scanning rate in 5 wt.% NaCl solution. They have also observed

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that the incorporation of chlorides into the passive film is favored with increased anodic polarization. Satpati et al. (11) mention that the pitting potential of Zircaloy-2 varies with temperature.

The M5™ alloy was developed in the 1980's. The absence of tin in its chemical composition and the controlled contents of iron, oxygen and sulfur lend it a low corrosion rate in high burn-up and high duty irradiation conditions (12). If, in on hand, there are several reports about the corrosion behavior of zircaloy type alloys, on the other hand, there is an absence of literature reports regarding the influence of temperature on the pitting corrosion resistance of the M5™ alloy.

The present work aims at fulfilling this gap by investigating the effect of temperature on the susceptibility of the M5™ alloy to pitting corrosion in NaCl solution. The electrochemical behavior of the samples was assessed by electrochemical impedance spectroscopy and potentiodynamic polarization curves.

Methodology

The material used in this work was a tube cladding made of M5™ zirconium alloy, kindly provided by INB (Indústria Nucleares do Brasil). The nominal chemical composition of the alloy is shown in Table 1.

Table 1 – Chemical composition of the M5™ alloy used in this work.

Element	Mass (%)
Nb	0.80 – 1.20
O	0.11 – 0.17
S	0.01 – 0.035
Zr	Bal.

The working electrodes for the electrochemical tests were prepared by encapsulating the specimens into cold curing epoxy resin. The specimens were prepared by mechanical grinding with progressively finer SiC paper up to 1000 grit size. All the electrochemical measurements were performed with an Autolab PGSTAT 100 potentiostat/galvanostat. The electrolyte was a NaCl 5 wt.% solution. The tests were conducted under three different temperatures: room temperature, 40 °C and 60 °C. A conventional three-electrode cell was used for measurements with a platinum wire as the counter-electrode, a standard calomel electrode (SCE) as the reference and M5™ alloy as the working electrode. All the potentials mentioned in this work are referred to the SCE.

First, the open circuit potential was monitored for 1 h to ensure a stable electrochemical condition. EIS measurements were performed over the frequency range of 100 kHz to 10 mHz, with an acquisition of 10 points per decade of frequency, at the open circuit potential (OCP), and an amplitude of the perturbation signal of 10 mV (rms). Next, potentiodynamic polarization curves were obtained at a scanning rate of 1 mV s⁻¹. The potential range was from -0.25 versus the open circuit potential up to +1.0 V. The curves were obtained right after the EIS measurements. A set of three different specimens was polarized at each testing

temperature. The results presented here are representative of the mean electrochemical behavior observed for each period. The corrosion morphology after the potentiodynamic polarization tests was observed by optical microscopy.

Results and discussion

EIS data of the M5™ zirconium alloy in NaCl 5 wt.% solution at different temperatures are shown in Figure 1. The data are represented as Nyquist plots. The inset in Figure 1 shows the same data with expanded scales to more clearly resolve the plot referred to the solution temperature of 60 °C.

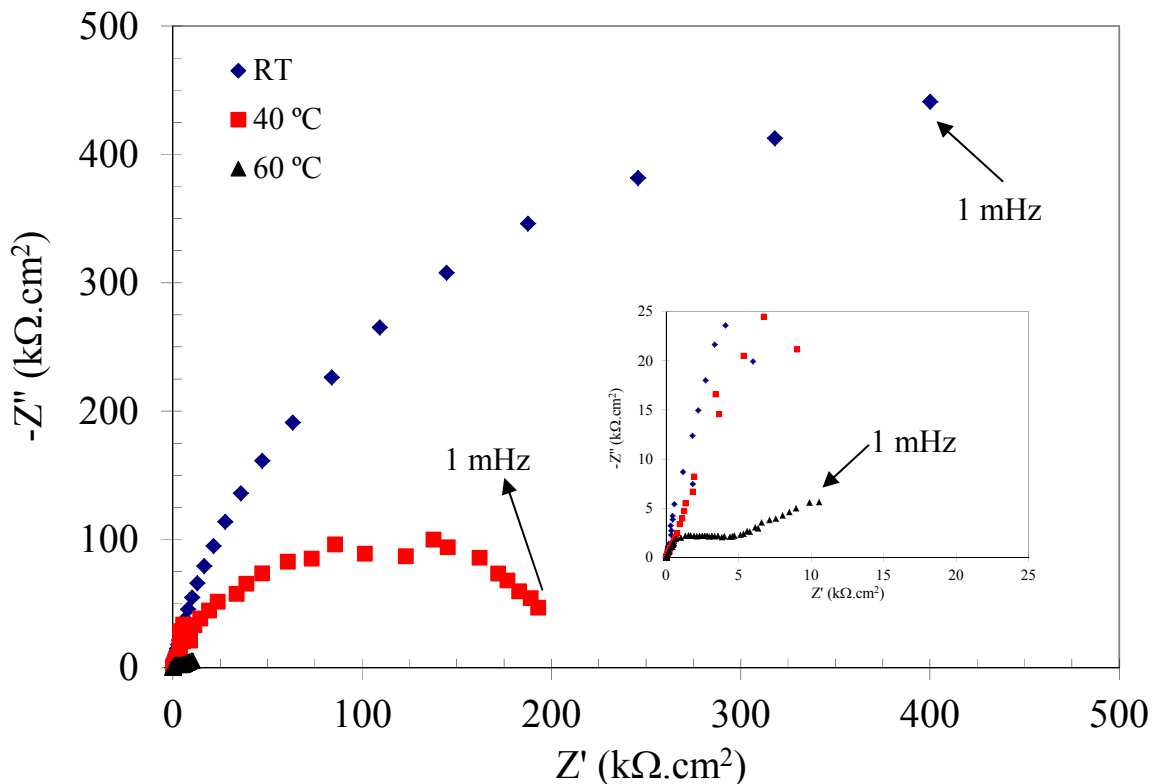


Figure 1. Nyquist plots of the M5™ zirconium alloy in NaCl 5 wt.% solution at different temperatures.

The Nyquist plot obtained at room temperature shows the presence of one single capacitive loop characterized by high impedance which is typical of electrodes with high corrosion resistance (13). In the case of zirconium alloys the high corrosion resistance is associated with the presence of a passive oxide layer in aqueous electrolytes. By increasing the solution temperature to 40 °C there was a decrease of the impedance values. The EIS data are still characterized by one single capacitive loop. However, this loop is more flattened than that obtained at room temperature, presenting a smaller radius which is associated with a decreased corrosion resistance (14). By further increasing the solution temperature to 60 °C the corrosion mechanism seems to change in comparison with lower temperatures. There was a steep decrease of the impedance values. The presence of a diffusion tail can be observed at the lowest frequencies as can be promptly seen in the inset of Fig. 1. Thus, it is suggested that

the more elevated temperature is likely to facilitate the onset of corrosion processes, promoting the penetration of aggressive species from the electrolyte through the passive film on the surface of the electrode. In fact, Sumathi et al. (15) have shown that the corrosion rate of zircaloy-2 increased with temperature in HMnO_4 and H_2SO_4 solutions as well as the polarization resistance determined from EIS measurements.

The corrosion behavior of the M5TM alloy was further characterized by potentiodynamic polarization. Potentiodynamic polarization curves of the M5TM alloy in NaCl 5 wt.% solution at different temperatures are shown in Figure 2. The electrochemical parameters determined from these curves are presented in Table 2.

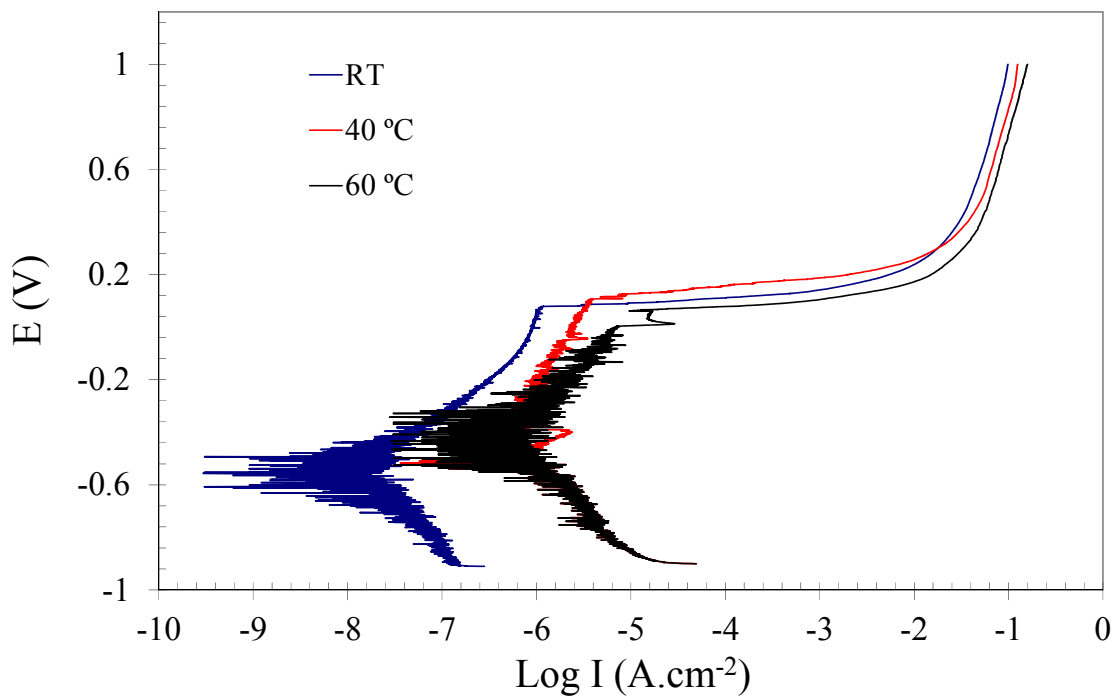


Figure 2. Potentiodynamic polarization curves of the M5TM zirconium alloy in NaCl 5 wt.% solution at different temperatures.

Table 2 – Electrochemical parameters determined from the potentiodynamic polarization curves shown in Figure 2.

Temperature	E_{corr} (mV)	I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)	E_b (mV)	Passive range (mV)
RT	-546	$6,23\cdot 10^{-9}$	79	625
40 °C	-520	$5,01\cdot 10^{-7}$	111	501
60 °C	-445	$7,58\cdot 10^{-7}$	12	457

The corrosion current densities (I_{corr}) are progressively increasing with the solution temperature. The polarization curves are characterized by a passive range which became shorter as the solution temperature increased. This indicates that the susceptibility to pitting corrosion is influenced by the temperature of the electrolyte. In the same way, the corrosion rate, associated with the values of I_{corr} , is also increased with temperature. It is noteworthy

that the corrosion resistance at room temperature is very high, denoted by the low magnitude of I_{corr} (in the range of nanoampères). Even at higher temperatures, the magnitude of I_{corr} is very low, revealing the high corrosion resistance of the M5™ alloy in the testing conditions. The corrosion morphology of the M5™ alloy after the potentiodynamic polarization tests is shown in Fig. 3. Representative images of the samples polarized at room temperature and 60 °C are presented.

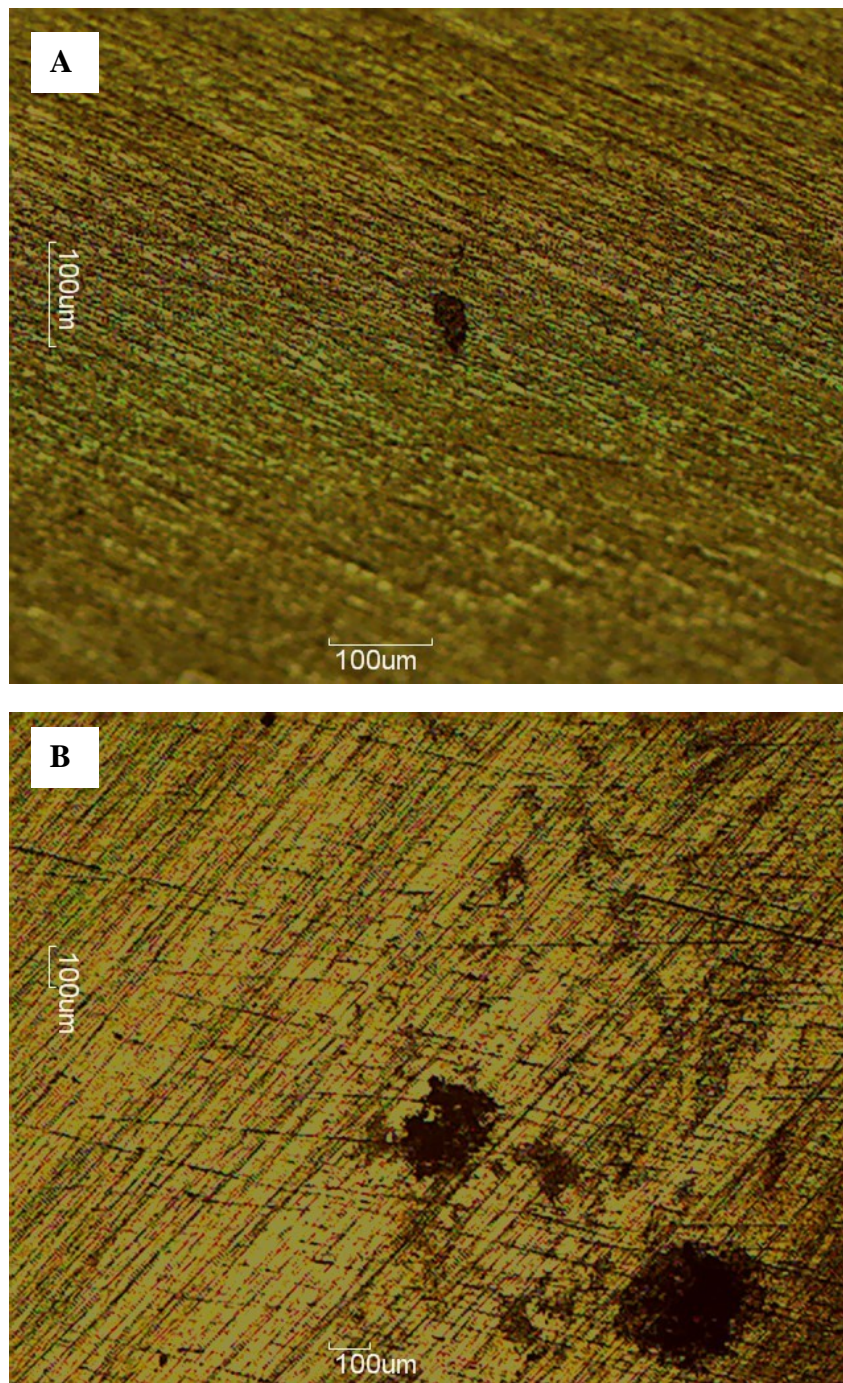


Figure 3. Corrosion morphology of the M5™ alloy zirconium alloy after the potentiodynamic polarization tests: a) room temperature; b) 60 °C.

The images reveal that the corrosion was more intense for the sample polarized at 60 °C as inferred from the more intense localized attack in the bottom right part of Fig. 3b. This result corroborates those obtained from the electrochemical tests.

Conclusions

The pitting corrosion susceptibility of the M5™ zirconium alloy has been evaluated. The influence of the solution temperature on the corrosion properties was assessed. It was observed that corrosion current density increased whereas the passive range decreased with temperature. EIS results pointed to a sharp decrease of the impedance as the solution temperature increased. The results suggest that the passive film of the M5™ alloy becomes less stable as the temperature increases. If, in one hand, this can be a concern for nuclear applications, on the other hand, the results indicated that the corrosion current densities are low, even at 60 °C.

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