

Electrochemical Behavior Of Nb In Aqueous Solutions Of Different pH

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Abstract

The electrochemical behavior of niobium in aqueous solutions of pH covering the range 2-12 in naturally aerated solutions was investigated. The general behavior of the niobium electrode is the passivation in all aqueous solution leading to the low corrosion rate. The equilibrium electrode potential is a linear function of the solution pH. The slope of the linear relation nearly -0.04 V/pH. EIS investigations have shown that the metal undergoes active dissolution in alkaline aqueous solutions since the equilibrium between film formation and film dissolution shifted towards the film dissolution as the pH of the solution shifted towards the alkali media. The corrosion behavior of niobium can be simulated to a Randle equivalent circuit model. The oxide film formed on the Nb electrode is more stable in the acidic media more than that in the neutral and basic media. The interaction of this film with the H^+ and OH^- in solutions with different pH was discussed.

Keywords: niobium, passivation behavior, metal dissolution, corrosion, effect of pH.

1. Introduction

Refractory elements, in particular Nb and Ta, are important alloying additions in nickel-base and iron-nickel-base super-alloys. They are responsible for much of the strength associated with these heat resistant alloys. [1] Many investigations have been directed towards the production of corrosion-resistant materials to be used as efficient anodes in the manufacture of chlorine and caustic soda [2, 3]. Valve metals in general are known to form stable oxide films in aqueous media [4]. Niobium is one of these metals [5] and has been subjected to extensive studies, most of which were concerned with the kinetics of the oxide film on its surface [6-15]. Few studies have been directed towards the stability of these oxide films in aggressive media [16,17]. Randall *et al.* [18] investigated the structure of the

anodic oxide film formed on niobium using radioactive isotope techniques. The structure changes in the oxide film during the anodization of the metal were studied by Lakhiani and Shreir [19]. Stfitzle and Heusler [20] investigated the semiconducting properties of the anodic oxide film formed on niobium; they reported that the oxide film behaves as a weakly dissociated extrinsic semiconductor. The present study was performed to obtain additional information on the corrosion behavior of niobium. The impedance and polarization measurements were employed to study the electrochemical behavior controlling the corrosion rate of the anodized niobium electrode in aqueous solutions of different pH's. The corrosion rates were measured by means of the polarization measurements. Measurements were conducted under optimized conditions.

2. Materials and Methods

The working electrode were prepared from Spectroscopically pure niobium rods (Aldrich-Chemie), mounted in glass tubes of appropriate internal diameter by an epoxy resin leaving a front surface area of 0.20 cm² to contact the electrolyte. The electrochemical cell was an all glass three electrode electrolytic cell with a large area Pt counter- and saturated calomel, SCE, reference electrodes. Before each experiment the working electrode was abraded using successive grades emery papers down to 2000 grit then washed with triple distilled water and transferred quickly to the electrolytic cell. The electrochemical measurements were carried out in aqueous solutions, where analytical grade reagents and triply distilled water were always used. The test electrolytes were freshly prepared aqueous solutions of different pH's (buffer solutions). The buffer solutions were prepared according to the following compositions :

pH	Composition
2	44.2 mL 0.1 M COOKC ₆ H ₄ COOH + 54.3 mL 0.1 M HCl.
5	102 mL 0.1 M COOKC ₆ H ₄ COOH+ 48.1 mL 0.1 M NaOH.
7	113.6 mL 0.1 M KH ₂ PO ₄ + 56.8 mL 0.1 M NaOH.
9	100 mL 0.2 M KH ₂ PO ₄ + 103.5 mL 0.2 M NaOH.
12	100 mL 0.2 M KH ₂ PO ₄ + 163.7 mL 0.2 M NaOH.

The polarization experiments and electrochemical impedance spectroscopic investigations, EIS, were performed using a Voltalab PGZ 100 “All in one” potentiostat/ Galvanostat system. The potentials were measured against and referred to the saturated calomel reference, SCE, (0.245 V vs. the standard hydrogen electrode, SHE). All potentiodynamic polarization experiments were carried out using a scan rate of 10 mV/ s to achieve quasi-stationary conditions. The impedance, Z, and phase shift, Θ , were recorded in the frequency domain 0.1-10⁵ Hz. The superimposed ac-signal was 10mV peak to peak. To achieve reproducibility, each experiment was carried out at least twice. Details of experimental procedures are as described elsewhere [21-22].

3. Results and Discussion

3.1. Open Circuit measurements:

The open-circuit potential (OCP) of Nb electrode was recorded over a period of 180 min in stagnant naturally aerated aqueous solutions of different pH covering the pH 2,5,7,9 and 12. The results of these experiments are presented in **Figs.1** and the recorded values of the steady state potential, E_{ss}, in the different solutions are summarized in **Table 1**. In these solutions the electrode potential gets more positive (more noble) with time indicating the tendency of the metal for passivation and the formation of a passive layer at the electrode/ electrolyte interfaces. In all cases the steady state is reached in about more than 60 min from the electrode immersion, where a large increase at the moment of electrode immersion was recorded, then a gradual increase with time until a steady state is reached were recorded. The steady potential shifts in the negative direction by increasing the pH of the solution, this indicates that the passivation process depend on the pH of the solution.

To compare between the open circuit potential behavior of Nb electrode in the three

different zones, the recorded data of pH =2,7 and 12 are presented in **Fig. 2**. The figure reflect clearly the corrosion and passivation behavior of Nb electrode in acidic, neutral and basic solution as was mentioned, in acidic solution of pH= 2, the electrode potential get more positive with time more than in pH =7 and pH=12 this indicates that a passive film developed on the metal surface.

The steady state potential, E_{ss}, measured after 180 min of the electrode immersion in different aqueous solutions covering the pH 2,5,7,9 and 12 was plotted against the pH of the solution and presented in **Fig. 3**. The results reveal that E_{ss} is pH dependent over the pH range from pH=2 to the pH=12. The linear relation of this figure can be formulated as:

$$E_{ss} = \alpha - \beta \text{ pH} \quad (1)$$

Where α is a pH independent value of E_{ss} obtained by the extrapolation of the linear relation at pH=0. The value of α was found to be +64 mV. The slope β of the linear relation presented in **Fig. 3** is 0.04 V/pH which was calculated from the familiar Nernst equation for pH indicator electrodes which is given by:

$$E = E^0 - 0.059/n \text{ pH} \quad (2)$$

where E⁰ is the pH-independent (or the standard) electrode potential and n is the number of electrons involved in the steady electrode process. which means that the Nb electrode can be used as pH indicator and the extrapolated value of 64 for the constant α , is an indication that the metal surface is covered by a barrier film which consists most probably of a mixed oxide .[23]

3.2. Potentiodynamic measurements:

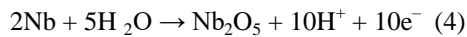
The electrochemical behavior of Niobium was investigated under polarization conditions, the linear polarization and Tafel extrapolation techniques were used. Unless otherwise stated, the polarization experiments were carried out at a scan rate of 10 mV/s. **Fig. 4** presents the potentiodynamic polarization curves of the Nb electrode after holding the metal at the open circuit potential in naturally aerated solutions of pH = 2, 5, 7, 9 and 12. The values of the corrosion parameters, corrosion potential, E_{corr}, corrosion current density, i_{corr}, Tafel slopes, β_a & β_c and corrosion rate were calculated and presented in **Table 2**. The calculated anodic Tafel slopes are in all cases (acidic, neutral and basic solutions); in the range \approx 60-240 mV/decade which indicate that the corrosion process is under activation control [24].

It is clear that the corrosion potential is shifted to more negative values as the pH increases . It is

noticed that the Nb surface subjected to anodic passivation by increasing pH and a very low corrosion rate that presented in **Table 2**. The corrosion current density, i_{corr} , increases with increasing the pH of solution which indicates metal dissolution at high pH values metal dissolution occurs via the reaction:



while in the passive region the film thickness grows according to the reaction:

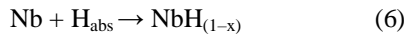


The progress of each reaction depends on the concentration of the alkali and surface pretreatment and initial electrochemical conditions.

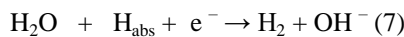
The cathodic branch of the potentiodynamic curve represents the evolution of hydrogen gas, Under cathodic polarization, a part of hydrogen, which is generated on the Nb electrode, is absorbed on the electrode surface and when its amount becomes large, a niobium hydride will be formed. This process may be expressed by the equation:



A part of the absorbed hydrogen penetrates into the surface forming niobium hydride:



The other part of absorbed hydrogen is liberated by electrochemical desorption:



Therefore, the oxide films existing on the Nb electrode affect its behavior during cathodic polarization.[25] while the anodic branch corresponding to niobium passivation and formation of a stable oxide film. It is clear from, The value of corrosion rate measurements that the corrosion of Nb is generally small .these value are in acidic solutions ≈ 0.28 mm/Y , in neutral solutions ≈ 0.49 mm/Y and in basic solutions ≈ 2.9 mm/Y, Which means that by increasing the PH the equilibrium between the film formation (passivation) and film dissolution is shifted towards the dissolution process.

3.3. Electrochemical impedance measurements:

Steady-state EIS can be used to confirm the results of corrosion rate measurements performed by conventional polarization techniques. Both Bode and Nyquist diagrams can be used to display and analyses the EIS data. All impedance data in the whole frequency domain are explicitly represented in the standard Bode plots. Nyquist plots illustrate the difference between the R_p values of the investigated alloys in various solutions [26-29]. The experimental impedance results obtained with the Nb electrode

after 180 min of the electrode immersion in different aqueous solutions of pH 2,7 and 12 are presented **Fig.5 a, b** The Bode plot shows one phase maximum at intermediate frequencies with a single time constant. The intermediate time constant is attributed to the presence of a protective surface film. The broadness of these phase maxima decrease by increasing the pH of solution, which means that the passive film formation process is shifted towards the dissolution process as we approach the alkali media. The same result is also presented as Nyquist plots where the diameter of the semi- circle decreases with increasing the pH of the solution (**cf.Fig.5, b**). These results are in good agreement with the results of the open circuit potential and polarization measurements.

The impedance data were analyzed using software provided with the impedance system for the simple equivalent circuit model, presented in **Fig.6**. The calculated equivalent circuit parameters are presented in **Table. 3**. The deviation of the value of α from unity is very small which means that we are dealing with a homogeneous surface. It is noticed that C_{dl} increases as the solution pH increases.

The impedance data in **Table. 3** show a decrease in R_{ct} as the pH increases which indicate an increase in the corrosion of the electrode in basic media. This behavior can be explained on the basis that the main constituent of the passive film is Nb_2O_5 , the dissolution of this passive film is dependent on the potential and the pH of the solution.

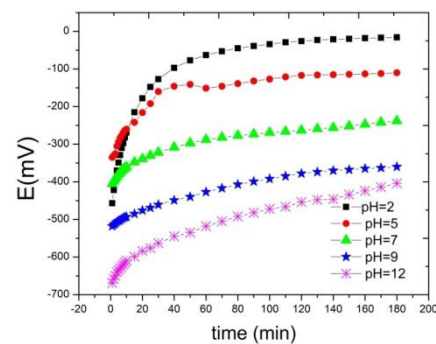


Fig. 1: Variation of the open-circuit potential for Nb electrode with time in solutions different pH at 25^o C.

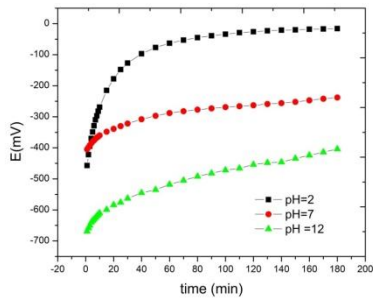


Fig. 2 : Variation of the open-circuit potential for Nb electrode with time in solutions of pH=2,7 and 12 at 25⁰ C.

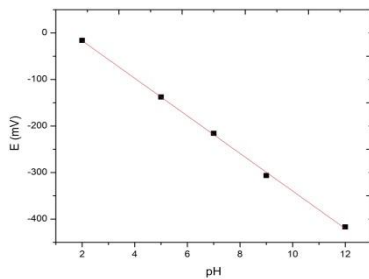


Fig.3: Variation of the steady state potential for Nb electrode with solutions of different pH at 25⁰ C.

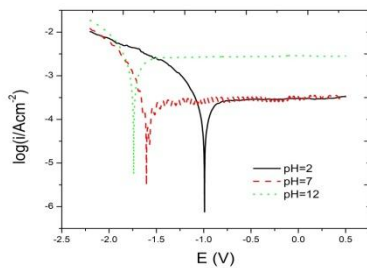


Fig.4: potentiodynamic polarization curves of Nb electrode after electrode immersion in solutions of pH=2,7and 12 and scan rate 10 mV/sec at 25°C.

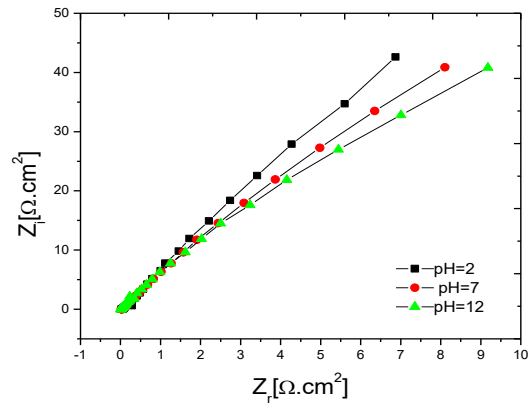
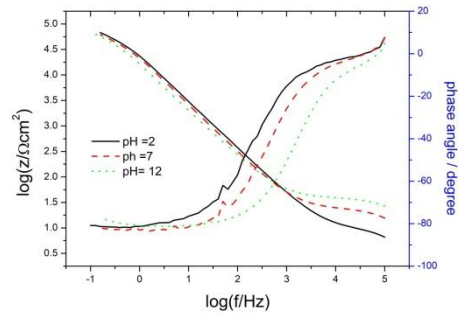


Fig. 5: Impedance plots of Nb electrode after 180 min electrode immersion in solutions of pH=2,7 and 12 at 25°C.

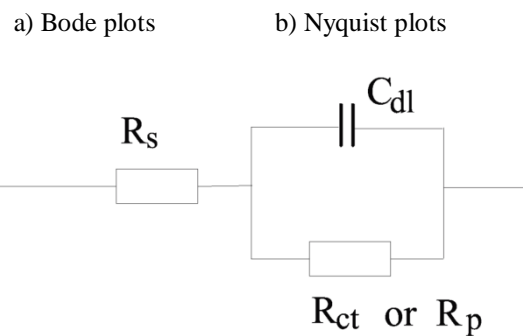


Fig. 6: Equivalent circuit model for a simple electrochemical cell (Randles Model).

Table 1: The stead state potential, E_{ss} for Nb electrode as a function of solution pH at 25°C.

pH	E _{ss} (mV)
2	-16

5	-110
7	-238
9	-360
12	-404

Table 2 : corrosion parameters of Nb electrode in solution of pH =2,7 and 12 at 25°C.

pH	E_{corr} (mV)	i_{corr} (mA/cm ²)	R_p (ohm.cm ²)	β_a (mV/dec)	β_c (mV/dec)	Corrosion rate (mm/Y)
2	-1098.8	0.039	1030	47.4	-151.4	0.288
7	-1604.0	0.067	147.13	54.0	-84.6	0.49
12	-1739.4	0.40	46.32	127.9	-107.7	2.9

Table 3 : Equivalent circuit parameters of Nb electrode in aqueous solutions of pH=2,7 and 12 at 25°C.

pH	R_s (Ω . cm ²)	R_{ct} (Ω . cm ²)	C_{dl} (μ F/ cm ²)	α
2	57.26	1369	1.162	0.999
7	38.43	820.1	1.226	0.999
12	9.008	543.9	1.84	1

5. Conclusions

- 1-The Nb electrode generally show passivation process in all aqueous solution that's leads to the low corrosion rate.
- 2-The electrode form a passive layer which is more stable in acidic media than that formed in neutral and basic media.
- 2-The value of the corrosion current density increases by increasing the pH of the solution hence the corrosion rate is very small in acidic media than that in neutral and basic media.
- 3- The Nb electrode can be used as pH indicator.
- 4- The electrode surface is covered by a barrier film which consists most probably of a mixed oxide.
- 5- The EIS Electrochemical impedance spectroscopy measurements in a good agreement with the results

obtained from potentiodynamic and open circuit potential measurements.

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