

Article

Effect of Ti Content on Passive Film Formation and Growth Kinetics in $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ Metallic Glasses

A. G. Soriano Carranza ¹, L. A. Sánchez ², P. Roncagliolo ², A. Espinoza Vázquez ^{3,*}, C. Ramos ¹, G. A. Lara ¹, G. González ^{1,*}, F. J. Rodríguez Gómez ² and I. A. Figueroa ^{1,*}

¹ Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Cd. Universitaria, Ciudad de México 04510, Mexico; asoriano@pceim.unam.mx (A.G.S.C.); cramos@materiales.unam.mx (C.R.); laragab@unam.mx (G.A.L.)

² Departamento de Ingeniería Metalúrgica, Facultad de Química, Universidad Nacional Autónoma de México, Ciudad de México 04510, Mexico; luissanchezmartinez20@gmail.com (L.A.S.); proncagliolo@quimica.unam.mx (P.R.); fxavier@unam.mx (F.J.R.G.)

³ Unidad Anticorrosión, Instituto de Ingeniería, Universidad Veracruzana, Veracruz 94292, Mexico

* Correspondence: araespinoza@uv.mx (A.E.V.); josegr@unam.mx (G.G.); iafigueroa@unam.mx (I.A.F.)

Abstract

In this study, the effect of Ti content on the electrochemical behavior and passive film growth mechanism of $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ ($x = 10, 15$, and 20 at.%) metallic glasses produced via melt spinning was investigated. Structural characterization via X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed the fully glassy nature and chemical homogeneity of all alloys. Electrochemical performance was evaluated in a 3.5 wt.% NaCl solution using potentiodynamic and potentiostatic polarization, as well as electrochemical impedance spectroscopy (EIS). The results showed that increasing Ti content improves corrosion resistance by reducing corrosion and passive current densities and increasing charge-transfer resistance. The $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy exhibited the best electrochemical performance, associated with the formation of a more stable and protective passive film. The passive film growth mechanism was analyzed using the High-Field Model (HFM). A linear relationship between inverse capacitance and anodic potential confirmed that ionic transport through the oxide layer governs passive film growth. The calculated electric field strength decreased systematically with increasing Ti content, suggesting the formation of passive films with lower defect density and enhanced barrier properties. These results demonstrate that adding Ti significantly enhances the passivation behavior of Ni-Nb metallic glasses and promotes the formation of stable oxide films with improved corrosion resistance in chloride-containing environments.

Keywords: metallic glasses; Ni-Nb-Ti alloys; passivation; electrochemical impedance spectroscopy; high-field model; corrosion; passive film



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1. Introduction

Titanium and its alloys are among the most widely used metallic biomaterials for orthopedic and dental implants owing to their excellent corrosion resistance, high specific strength, favorable biocompatibility, and long-term chemical stability in physiological environments. Their outstanding corrosion performance is primarily attributed to the spontaneous formation of a thin, compact, and highly adherent passive oxide film, predominantly composed of TiO_2 , which effectively limits metal dissolution and ion release under physiological conditions [1–3], including in chloride-containing electrolytes such as

3.5 wt.% NaCl, commercially pure titanium (CP-Ti) and Ti-6Al-4V, which typically exhibit corrosion current densities in the range of $0.02\text{--}0.10\ \mu\text{A cm}^{-2}$ and corrosion potentials between -350 and -200 mV vs. SCE, reflecting the high stability of their native passive films. Likewise, advanced β -type biomedical alloys, including Ti-29Nb-13Ta-4.6Zr and Ti-Nb-Zr systems, generally present even lower corrosion current densities ($0.01\text{--}0.05\ \mu\text{A cm}^{-2}$) together with more noble corrosion potentials (approximately -250 to -100 mV vs. SCE), owing to the formation of compact $\text{TiO}_2/\text{Nb}_2\text{O}_5$ mixed passive layers with enhanced resistance to chloride attack [1,4,5]. Despite these advantages, conventional titanium alloys, particularly Ti-6Al-4V, still present important limitations for long-term implant applications. One of the major drawbacks is the considerable mismatch between the elastic modulus of the alloy (approximately 110 GPa) and that of cortical bone (10–30 GPa), which promotes stress shielding, bone resorption, and eventual implant loosening [6,7]. In addition, concerns regarding the potential release of cytotoxic alloying elements such as Al and V have stimulated the development of next-generation Ti-based biomaterials containing non-toxic β -stabilizing elements, including Nb, Ta, Zr, and Mo, which offer improved mechanical compatibility and corrosion resistance [8–10].

Among alternative metallic biomaterials currently under investigation, metallic glasses have attracted considerable attention for their unique combination of high strength, high elastic limit, excellent corrosion resistance, and structural homogeneity. Unlike conventional crystalline alloys, metallic glasses are free of grain boundaries, precipitates, and crystallographic defects that frequently act as preferential sites for localized corrosion [11,12]. Their chemically homogeneous, amorphous structure promotes the formation of compact, compositionally uniform passive films, thereby enhancing corrosion resistance in aggressive environments. In particular, Ni-Nb-based metallic glasses exhibit excellent glass-forming ability and remarkable chemical stability. At the same time, the incorporation of Ti has been reported to further enhance passivation by forming thermodynamically stable Ti-rich oxide species that reinforce the protective passive layer [13,14].

Previous investigations have demonstrated the promising corrosion performance of Ti-containing metallic glasses in chloride-containing and physiological environments. Pang et al. reported that Ni(Co)-Nb-Ti-Zr bulk metallic glasses exhibited extremely low corrosion rates in NaCl solution due to the formation of Nb- and Ti-rich passive films. Likewise, Jiang et al. showed that increasing the Ti content in Ni-Nb-Ti metallic glasses significantly enhanced pitting resistance and reduced passive current densities in acidic media. More recently, studies on Ti-based metallic glasses have confirmed that the addition of Ti promotes the development of TiO_2 -rich passive layers with high chemical stability. At the same time, Nb contributes to the formation of highly protective Nb_2O_5 species, resulting in passive films with improved resistance to chloride-induced degradation [15–18]. These findings demonstrate the beneficial role of Ti in passive film stabilization. However, the mechanistic influence of Ti concentration on passive film growth and electrochemical stability in Ni-Nb-Ti metallic glasses has not yet been fully established.

The corrosion resistance of passive alloys is governed not only by the chemical composition of the oxide film but also by its growth kinetics, defect structure, and transport properties. Several theoretical models have been proposed to describe passive film formation, among which high-field ionic conduction models have proven particularly successful for metals and alloys. According to these models, the growth of the passive film is controlled by the migration of ionic defects under the influence of the intense electric field established across the oxide layer [19,20]. The High-Field Model (HFM) predicts that ionic transport through the passive film follows an electric-field-assisted mechanism, establishing a linear relationship between the inverse capacitance of the oxide film and the applied formation potential. This approach has been successfully employed to investigate passive film growth

on titanium and Ti-based alloys, providing valuable information regarding electric field strength, film thickness evolution, and the mechanisms governing passivation [19,21].

Although the electrochemical behavior of conventional titanium alloys has been extensively investigated, considerably less attention has been paid to understanding the kinetics of passive film growth in Ni-Nb-Ti metallic glasses. In particular, the influence of Ti concentration on the electrochemical characteristics, defect chemistry, and growth mechanism of passive films has not been addressed in depth. Furthermore, no systematic study has combined electrochemical characterization, surface chemical analysis, and High-Field Model calculations to elucidate how Ti modifies the formation, stability, and protective properties of passive films in Ni-Nb-Ti metallic glasses. Addressing these issues is essential for establishing the relationships between alloy composition, passive film characteristics, and corrosion resistance, thereby providing fundamental knowledge for the design of advanced corrosion-resistant metallic glasses with potential biomedical applications.

Therefore, the present work investigates the effect of Ti content on the passivation behavior and passive film growth kinetics of $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ ($x = 10, 15, \text{ and } 20 \text{ at.}\%$) metallic glasses produced via melt spinning. Electrochemical techniques, including potentiodynamic polarization, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy (XPS), were employed to characterize the passive films formed under anodic polarization. In addition, the High-Field Model was applied to analyze the passive film growth mechanism and to determine the influence of Ti concentration on the electric field strength, growth kinetics, and protective properties of the passive oxide layer.

2. Materials and Methods

2.1. Alloy Preparation

Master alloys with nominal compositions $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ ($x = 10, 15, \text{ and } 20 \text{ at.}\%$) were prepared from high-purity metals ($\geq 99.9 \text{ wt.}\%$) by arc melting under a high-purity argon atmosphere. To ensure chemical homogeneity, each ingot was remelted at least five times. Then, metallic glass ribbons were produced by melt spinning onto a copper wheel at a tangential wheel velocity of 25 m s^{-1} . The obtained ribbons have thicknesses in the range of 25–30 μm .

2.2. Structural Characterization

The structural characterization of the melt-spun metallic glasses was performed via X-ray diffraction (XRD) in a Siemens D5000 diffractometer (Siemens, Karlsruhe, Germany), using $\text{Cu-K}\alpha$ radiation in a 2θ range from 20° to 80° at a scanning rate of $1.2^\circ \text{ min}^{-1}$.

Transmission electron microscopy (TEM) analyses were conducted using a JEOL ARM-200F microscope (JEOL Ltd., Tokyo, Japan) operated in high-resolution mode (HRTEM). Selected area electron diffraction (SAED) patterns were acquired to further confirm the glassy nature of the alloys. Thin foils for TEM observation were prepared via focused ion beam (FIB) milling. In addition, energy-dispersive X-ray spectroscopy (EDS) was employed to evaluate the chemical homogeneity of the ribbons.

The SEM observations were performed using a JEOL JSM-7600F field-emission scanning electron microscope (JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 10 kV in secondary electron (SE) imaging mode.

2.3. Electrochemical Characterization

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell using a Biologic SP300 potentiostat/galvanostat (Bio-Logic Science Instrument, Seyssinet-Pariset, France). The metallic glass ribbons were used as the working electrode, a platinum mesh as the counter electrode, and a saturated calomel electrode

(SCE) as the reference electrode. All experiments were performed in naturally aerated 3.5 wt.% NaCl solution at room temperature.

Before each electrochemical test, the working electrode surface was cathodically reduced at -1.0 V vs. SCE for 120 s to remove the naturally formed oxide film. Subsequently, the samples were stabilized at open-circuit potential (OCP) for 1 h before testing. Potentiodynamic polarization tests were performed from -0.4 V below vs. OCP up to 1.5 V vs. SCE at a scan rate of 0.333 mV s $^{-1}$. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values were determined via Tafel extrapolation. Potentiostatic tests were conducted at constant potentials of 0.6 V and 0.9 V vs. SCE for 3600 s to evaluate the kinetics of passive film growth and steady-state current behavior.

Electrochemical impedance spectroscopy (EIS) measurements were performed at OCP and under anodic polarization conditions over a frequency range from 10^5 to 10^{-2} Hz using a sinusoidal perturbation amplitude of 10 mV. The impedance spectra were fitted using equivalent electrical circuit models in order to determine the electrochemical parameters associated with passive film formation. Each electrochemical experiment was performed at least three times to ensure reproducibility, and the reported values correspond to the mean $\pm$ standard deviation.

2.4. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5000 VersaProbe II system (Physical Electronics, Chigasaki Kanagawa, Japan) equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). The X-ray beam was operated at 25 W and 15 kV, with a beam diameter of 100 μm . The spectrometer was calibrated using the Au 4f $_{7/2}$ (84.0 eV), Ag 3d $_{5/2}$ (368.2 eV), and Cu 2p $_{3/2}$ (932.6 eV) photoelectron peaks with a full width at half maximum (FWHM) of 0.56 eV for the Ag 3d $_{5/2}$ peak. The base pressure in the analysis chamber during measurements was maintained below 1×10^{-9} Torr.

2.5. Passive Film Analysis by the High-Field Model

The passive film growth mechanism was analyzed using the High-Field Model (HFM), which assumes that ionic transport through the oxide layer controls film growth under anodic polarization conditions. The effective capacitance (C_{eff}) values were calculated from the constant phase element (CPE) parameters using the modified Brug relationship:

$$C_{\text{eff}} = [Q (1/R_s + 1/R_{\text{ct}})^{n-1}]^{1/n} \quad (1)$$

where C_{eff} is the effective film capacitance, Q and n are the CPE parameters, R_s is the solution resistance, and R_{ct} is the charge transfer resistance. This approach corrects for non-ideal capacitive behavior arising from surface heterogeneity and frequency dispersion effects [22,23].

The passive film thickness (d) was estimated assuming a parallel-plate capacitor model:

$$d = (\epsilon_0 \epsilon_r A) / C_{\text{eff}} \quad (2)$$

where ϵ_0 is the vacuum permittivity (8.85×10^{-14} F cm $^{-1}$), ϵ_r is the relative dielectric constant of the oxide layer, and A is the geometric surface area (1 cm 2). A dielectric constant of $\epsilon_r = 41$ was adopted for the passive films, based on the following considerations: (i) the XPS analysis confirms that the passive films are predominantly composed of TiO $_2$ -rich mixed oxides; (ii) amorphous TiO $_2$ films typically exhibit dielectric constants in the range of 40–85 [24,25]; (iii) mixed Ti-Nb oxides have reported dielectric constants of 30–50 depending on composition [26,27]; and (iv) Nb $_2$ O $_5$ exhibits dielectric constants of $\sim$ 40–50

for amorphous films [28]. The selected value of 41 lies within this range and is consistent with the TiO₂-rich nature of the passive films.

According to the HFM, the inverse capacitance is proportional to the passive film thickness and should be linearly related to the applied formation potential [21]. The E_0 is the electric field strength across the passive film (V cm^{−1}), which was estimated from the slope of the C^{-1} versus potential relationship:

$$d(C^{-1})/dU = (\epsilon_0 \epsilon_r E_0)^{-1} \quad (3)$$

The validity of the HFM approach was confirmed by the linearity of the C^{-1} vs. U plots. The calculated electric field values were within the range typically reported for passive oxide films under high-field conditions (10⁶–10⁷ V cm^{−1}) [29,30].

3. Results

3.1. Structural Characterization

3.1.1. X-Ray Diffraction Analysis

The vitrification of the alloys was evaluated with X-ray diffraction. Figure 1 shows the diffraction patterns obtained for the three studied compositions. In all cases, the diffractograms exhibit broad diffuse halos without sharp Bragg reflections, confirming the absence of long-range atomic order and demonstrating the successful formation of a vitreous structure.

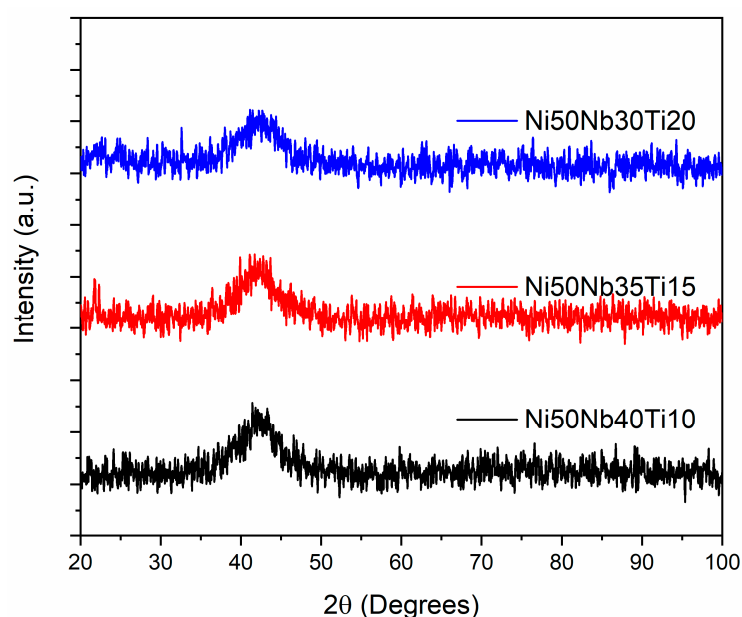


Figure 1. XRD patterns for Ni₅₀Nb_{50−x}Ti_x metallic glasses.

The fully glassy nature of the ribbons indicates that the cooling rate achieved during melt spinning was sufficiently high to suppress crystallization during solidification. Similar diffraction behavior has been reported for Nb-containing metallic glasses, where the combination of multicomponent alloying and rapid solidification promotes glass formation by hindering atomic diffusion and crystalline nucleation [14,16,31]. No significant differences in the vitreous structure were observed as a function of Ti content, suggesting that Ti addition within the studied compositional range does not affect the glass-forming ability of the Ni-Nb system.

3.1.2. Transmission Electron Microscopy

The vitreous structure of the alloys was further confirmed via transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Representative TEM micrographs and EDS analyses are presented in Figure 2. The TEM images revealed a homogeneous contrast, with no evidence of crystalline precipitates or nanocrystalline regions. In agreement with the XRD results, the corresponding SAED patterns exhibited a diffuse halo ring characteristic of amorphous materials.

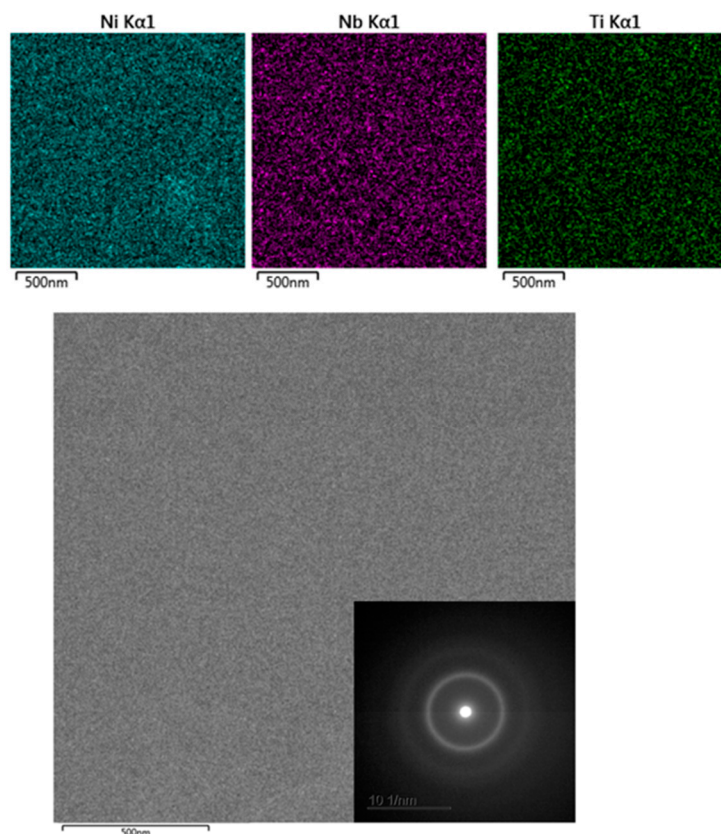


Figure 2. EDS mapping and TEM image (bright field and SAED) for $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses.

EDS analysis confirmed the chemical homogeneity of the metallic glass ribbons at the nanoscale, indicating that the alloying elements were uniformly distributed throughout the vitreous matrix. The at.% for each alloy is reported in Table 1. The absence of detectable compositional segregation or nanocrystallization is particularly important for corrosion resistance, as structural heterogeneities often serve as preferential sites for localized electrochemical attack.

Table 1. Atomic percent composition obtained via EDS.

Alloy	Element	At. %
$\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$	Ti	10.12 ± 0.03
	Ni	49.68 ± 0.08
	Nb	40.20 ± 0.03
$\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$	Ti	15.05 ± 0.01
	Ni	50.02 ± 0.04
	Nb	34.93 ± 0.05
$\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$	Ti	20.01 ± 0.03
	Ni	50.19 ± 0.07
	Nb	29.80 ± 0.04

The homogeneous amorphous structure obtained in this work provides an appropriate model system for evaluating the intrinsic effect of alloy composition on passive film formation and electrochemical behavior, minimizing the influence of microstructural defects such as grain boundaries or secondary phases.

3.2. Potentiodynamic Polarization Behavior

The corrosion behavior of the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses was evaluated by potentiodynamic polarization in 3.5 wt.% NaCl solution. The polarization curves are shown in Figure 3, and electrochemical parameters obtained via Tafel extrapolation are summarized in Table 2.

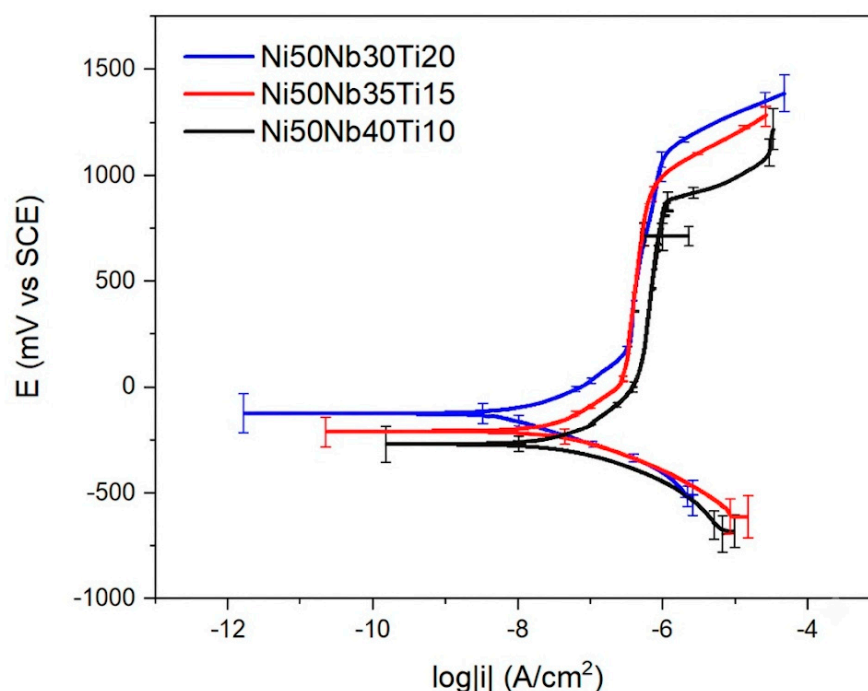


Figure 3. Potentiodynamic polarization curves for $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses evaluated in 3.5 wt.% NaCl.

Table 2. Electrochemical parameters obtained via Tafel extrapolation.

Alloy	E_{corr} (mV vs. SCE)	i_{corr} ($\mu\text{A cm}^{-2}$)	Ba (mV dec^{-1})	Bc (mV dec^{-1})	E_{pass} (mV vs. SCE)	E_{pit} (mV vs. SCE)
$\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$	-257 ± 23	0.048 ± 0.004	260 ± 23	142 ± 13	25.95 ± 0.67	813.75 ± 0.97
$\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$	-191 ± 13	0.034 ± 0.002	220 ± 15	137 ± 10	63.32 ± 0.38	871.98 ± 0.92
$\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$	-152 ± 8	0.014 ± 0.001	227 ± 12	143 ± 8	100 ± 0.25	872.10 ± 0.94

All metallic glasses exhibited typical passive behavior, characterized by a low passive current density over a wide anodic potential range, indicating the formation of protective oxide films on the alloy surfaces. The cathodic branches of the polarization curves exhibited similar behavior across all compositions, suggesting that the addition of Ti does not significantly alter the cathodic reaction kinetics under the conditions evaluated.

A clear compositional dependence was observed in the anodic response as the Ti content increased from 10 to 20 at.%, the corrosion potential shifted toward more noble values, while the corrosion current density systematically decreased. The $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy shows the highest corrosion resistance, with the lowest i_{corr} and passive current density values.

The passivation potential (E_{pass}) also varied with alloy composition, indicating differences in the kinetics of passive film stability. The $\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$ alloy exhibited the lowest E_{pass} value (25 mV vs. SCE), suggesting that passivation was initiated at relatively low anodic overpotentials. In contrast, the $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy required a higher potential to achieve complete passivation (210 mV vs. SCE). Although a higher E_{pass} may indicate a delayed transition into the passive state, once passivation was established, this alloy exhibited the lowest passive current density and the greatest passive stability, indicating that the resulting oxide film was considerably more protective. This behavior suggests that the early stages of oxidation involve the formation of a thicker or more chemically stable mixed oxide layer before reaching steady-state passivation.

The pitting potential (E_{pit}) provides additional evidence of the beneficial effect of Ti on localized corrosion resistance. Increasing the Ti content shifted E_{pit} from approximately 814 mV vs. SCE for $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$ to about 872 mV vs. SCE for both Ti-containing alloys with 15 and 20 at.% Ti. This increase of nearly 60 mV indicates that higher anodic polarization is required to initiate chloride-induced passive film breakdown, reflecting enhanced resistance to pitting corrosion. The absence of a significant increase in E_{pit} between 15 and 20 at.% Ti suggests that the beneficial effect reaches a plateau once sufficient Ti is incorporated into the passive film. At the same time, further improvements are mainly reflected in lower passive current densities rather than in additional increases in the breakdown potential.

The reduction in passive current density (i_{pass}) as Ti content increases indicates the formation of a more protective passive film with lower ionic transport through the oxide layer. Ti is well known for promoting the formation of highly stable TiO_2 -rich passive films with excellent resistance to chloride-containing media [13,19,20,31]. In addition, previous studies have demonstrated that incorporating Nb into Ti-based systems stabilizes mixed Ti-Nb oxides, thereby improving both film compactness and corrosion resistance [21–33].

The passive current densities (i_{pass}) obtained were on the order of $10^{-7} \text{ A cm}^{-2}$, which is consistent with highly passive metallic systems evaluated in chloride-containing media [4,10,33]. These low current densities indicate limited anodic dissolution and confirm the excellent passivation ability of the studied metallic glasses.

Overall, the polarization results demonstrate that the addition of Ti has a beneficial effect on the passivation behavior of Ni-Nb metallic glasses, promoting the formation of more stable passive films with enhanced resistance against chloride-induced localized corrosion.

3.3. Potentiostatic Analysis of Passive Film Growth

The growth kinetics of the passive films formed on the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses were investigated by potentiostatic polarization at 0.6 and 0.9 V vs. SCE. Representative current-time transients are presented in Figure 4, and the corresponding electrochemical parameters are summarized in Table 3.

For all studied metallic glass alloys, the potentiostatic transients exhibited an initial rapid decrease in current density followed by a gradual stabilization toward steady-state conditions. This behavior is characteristic of passive film formation processes in which the anodic current progressively decreases as the oxide layer thickens, thereby limiting ionic transport across the metal/electrolyte interface.

At 0.6 V vs. SCE, the $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy exhibited the lowest steady-state current and charge densities, indicating the formation of a more protective passive film that requires lower ionic transport during growth. In contrast, the Nb-rich alloy presented higher steady-state currents, suggesting a less compact passive layer.

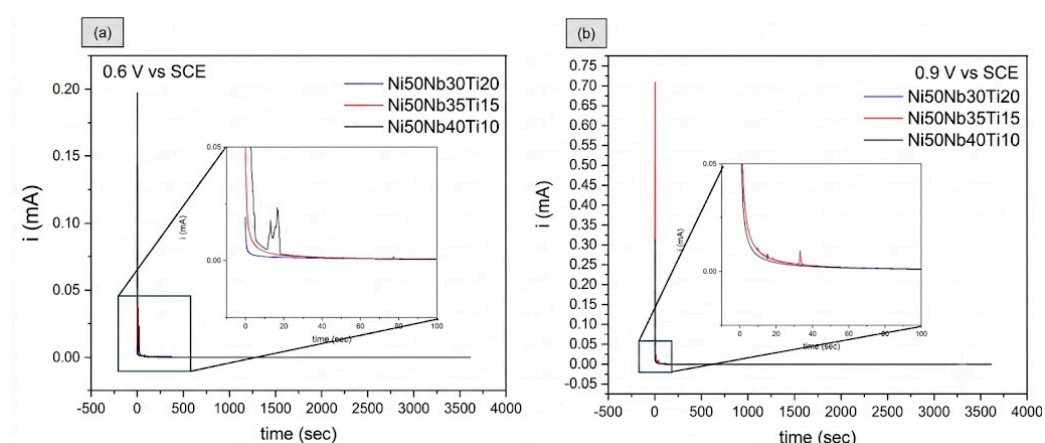


Figure 4. Potentiostatic curves at (a) 0.6 V and (b) 0.9 V vs. SCE for the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses.

Table 3. Electrochemical parameters of $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ glassy alloys in 3.5 wt.% NaCl after 3600 s at different applied potentials.

Alloy	Potential (V vs. SCE)	Initial Current Density (A cm^{-2}) $\times 10^{-4}$	i_{ss} (A cm^{-2}) $\times 10^{-6}$	Charge Density (mC cm^{-2})	Passive Film Thickness (nm)	Electric Field Strength (V cm^{-1}) $\times 10^6$
$\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$	0.6	2.00 ± 0.18	2.50 ± 0.22	5.0 ± 0.4	2.00 ± 0.4	3.00 ± 0.4
$\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$	0.6	1.60 ± 0.11	1.10 ± 0.08	3.2 ± 0.2	2.04 ± 0.2	2.94 ± 0.2
$\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$	0.6	1.10 ± 0.06	0.40 ± 0.02	2.1 ± 0.1	2.07 ± 0.3	2.90 ± 0.3
$\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$	0.9	12.0 ± 1.1	7.00 ± 0.62	12.8 ± 1.1	1.88 ± 0.1	4.79 ± 0.1
$\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$	0.9	8.00 ± 5.6	4.00 ± 0.28	9.5 ± 0.7	2.29 ± 0.4	3.93 ± 0.4
$\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$	0.9	5.00 ± 0.27	2.00 ± 0.11	6.7 ± 0.4	2.44 ± 0.2	3.70 ± 0.2

Increasing the applied potential to 0.9 V resulted in higher current densities and larger accumulated charge values for all tested compositions. This behavior is consistent with high-field ionic conduction models, in which the electric field across the passive film enhances defect migration and promotes oxide growth under anodic conditions [34,35].

Although thicker films were formed at higher potentials, film thickness alone does not necessarily guarantee improved corrosion resistance. The protective properties of passive films are influenced by structural characteristics such as defect concentration, compactness, and chemical composition. In this case, the Ti-rich alloy maintained the lowest steady-state current density even at 0.9 V, indicating better barrier properties compared with the Nb-rich compositions.

The improved passivation behavior associated with higher Ti content is consistent with the high thermodynamic stability of TiO_2 , which exhibits low ionic conductivity and excellent resistance to chloride attack [31,33]. The synergistic interaction between Ti and Nb oxides may contribute to the stabilization of the passive layer by reducing defect density and enhancing film compactness.

3.4. Electrochemical Impedance Spectroscopy

The electrochemical response of the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses was investigated via electrochemical impedance spectroscopy (EIS) at different anodic potentials. The Nyquist diagrams presented in Figure 5 exhibit the typical response of highly passive systems, characterized by capacitive semicircles associated with the passive oxide layer formed on the alloy surface.

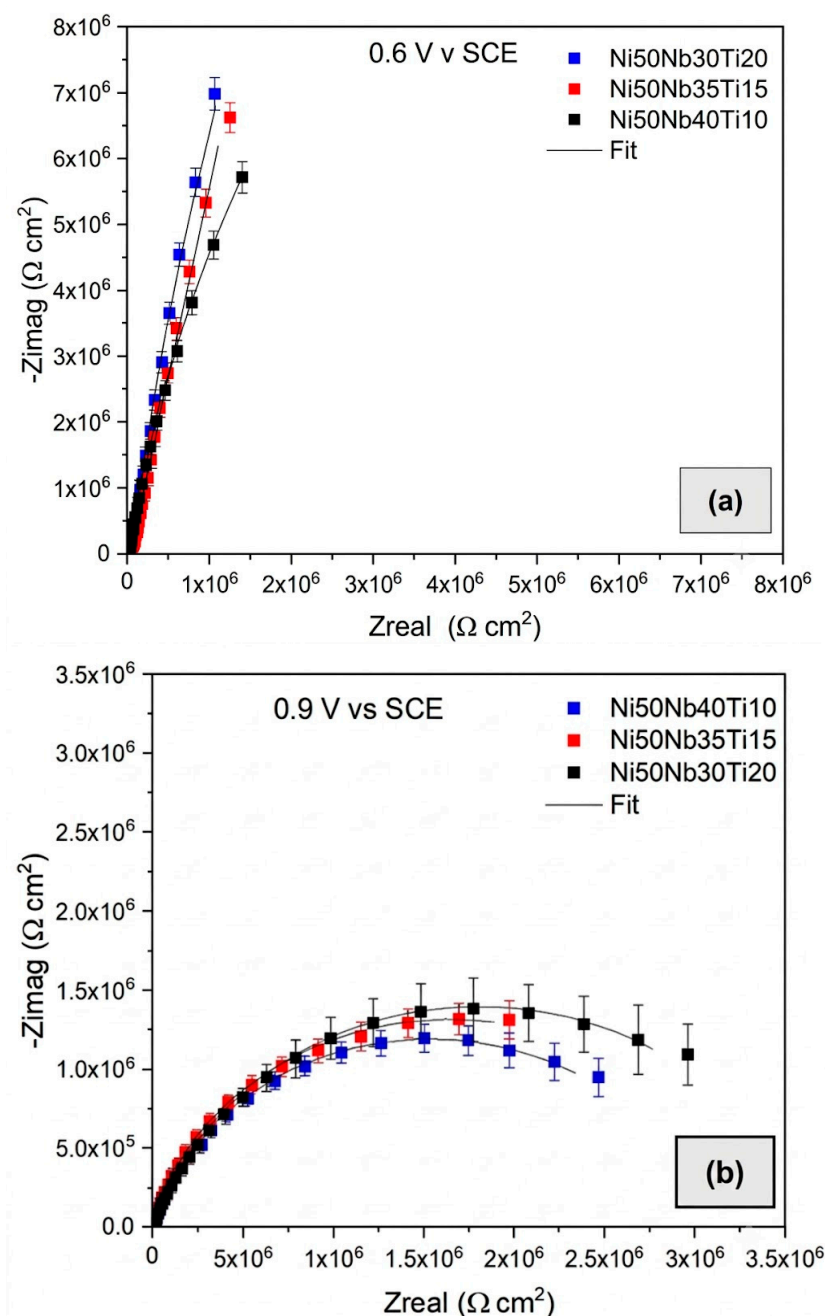


Figure 5. Nyquist diagrams for $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses immersed in 3.5 wt.% NaCl at (a) 0.6 V and (b) 0.9 V vs. SCE.

The impedance spectra were fitted using the equivalent electrical circuit shown in Figure 6, consisting of the solution resistance (R_s) connected in series with a parallel combination of charge transfer resistance (R_{ct}) and a constant phase element (CPE). The fitted electrochemical parameters are summarized in Table 4.

The depressed capacitive semicircles observed in the Nyquist plots indicate non-ideal capacitive behavior associated with surface heterogeneities and frequency dispersion. The CPE exponent values ($n = 0.98\text{--}0.99$) confirm that the passive films do not behave as ideal capacitors, which is common for electrochemical oxide layers formed on metallic materials.

At 0.6 V vs. SCE, the charge-transfer resistance values were on the order of $10^8 \Omega \text{ cm}^2$, indicating highly stable passive films with excellent corrosion resistance. Increasing the applied potential to 0.9 V produced a significant decrease in R_{ct} , suggesting enhanced ionic transport and increased anodic dissolution kinetics under stronger anodic polarization.

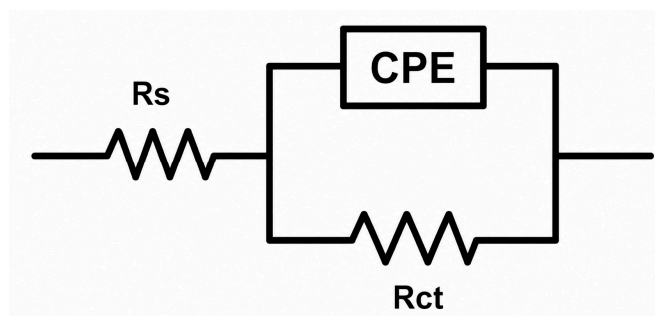


Figure 6. Equivalent electrical circuit used for fitting.

Table 4. Electrochemical parameters obtained via EIS.

Alloy	Potential (V vs. SCE)	R_{ct} ($\Omega \text{ cm}^2$) $\times 10^6$	C_{dl} ($\mu\text{F cm}^{-2}$)	n	χ^2
Ni ₅₀ Nb ₄₀ Ti ₁₀	0.6	180 $\pm$ 0.12	19.37 $\pm$ 0.060	0.988 $\pm$ 0.072	0.00054
Ni ₅₀ Nb ₃₅ Ti ₁₅	0.6	219 $\pm$ 0.21	17.92 $\pm$ 0.028	0.989 $\pm$ 0.061	0.00024
Ni ₅₀ Nb ₃₀ Ti ₂₀	0.6	306 $\pm$ 0.19	17.64 $\pm$ 0.018	0.989 $\pm$ 0.045	0.00015
Ni ₅₀ Nb ₄₀ Ti ₁₀	0.9	2.97 $\pm$ 0.26	18.85 $\pm$ 0.034	0.989 $\pm$ 0.080	0.00062
Ni ₅₀ Nb ₃₅ Ti ₁₅	0.9	3.05 $\pm$ 0.21	17.27 $\pm$ 0.038	0.997 $\pm$ 0.062	0.00015
Ni ₅₀ Nb ₃₀ Ti ₂₀	0.9	3.14 $\pm$ 0.17	16.37 $\pm$ 0.015	0.998 $\pm$ 0.048	0.00032

Among the studied alloys, the Ni₅₀Nb₃₀Ti₂₀ composition consistently exhibited the highest R_{ct} values and the lowest effective capacitance, indicating the formation of thicker, more protective passive films. Lower capacitance values are generally associated with increased oxide thickness and reduced dielectric response of the passive layer.

The higher electrochemical performance of the Ti-rich alloy is consistent with the polarization and potentiostatic results, confirming that Ti promotes the formation of passive films with improved barrier properties and enhanced resistance against chloride-induced corrosion.

3.5. XPS Characterization of the Passive Film

The analysis of survey spectra (Figure 7) and high-resolution XPS data reveals significant changes in the surface chemical composition of the Ni₅₀Nb₃₀Ti₂₀ metallic glass following anodic polarization under passive conditions (0.6 V and 0.9 V vs. SCE), as compared to the open-circuit potential (OCP) state. The survey spectrum in Figure 7 confirms the presence of the constituent matrix elements (Ni, Nb, Ti) alongside a prominent “O 1s” signal. The increase in oxygen content observed under polarized conditions evidences the growth of a protective oxide layer that effectively mitigates anodic dissolution processes [36–38].

At the open-circuit potential (OCP), the high-resolution Ni 2p_{3/2} spectrum (Figure 8a) exhibits a predominant, narrow peak centered at approximately 852.6 eV, characteristic of nickel in its metallic state (Ni⁰) [39]. Upon the application of anodic potentials of 0.6 V and 0.9 V vs. SCE, a drastic decrease in the intensity of this metallic peak is observed (Figure 8a). This marked attenuation, coupled with the absence of significant peaks corresponding to nickel oxide (NiO) or nickel hydroxide (Ni(OH)₂) in the ~854–856 eV region, demonstrates that nickel undergoes preferential dissolution into the electrolyte, thereby enabling the selective enrichment of passive-film-forming elements (Nb and Ti) at the metallic glass surface [38].

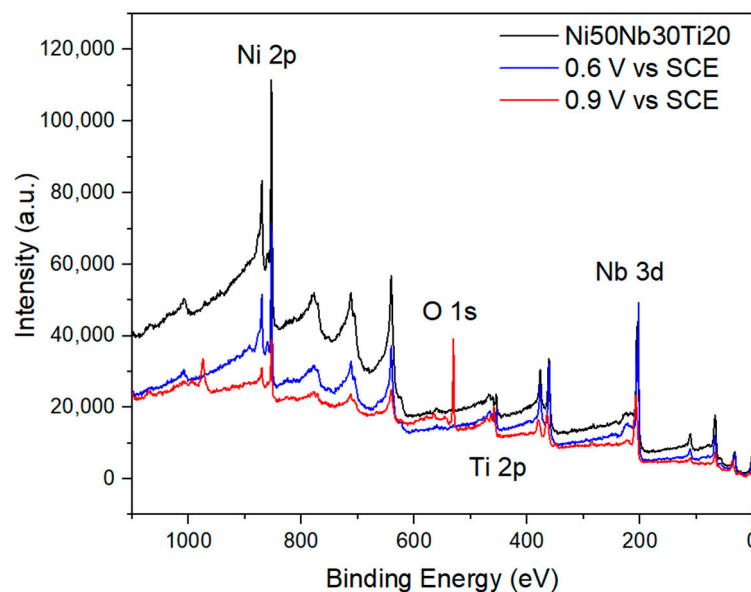


Figure 7. Survey XPS spectra for the $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ metallic glass at different polarization potentials.

XPS analysis of Nb-Ti-Ni alloy surfaces

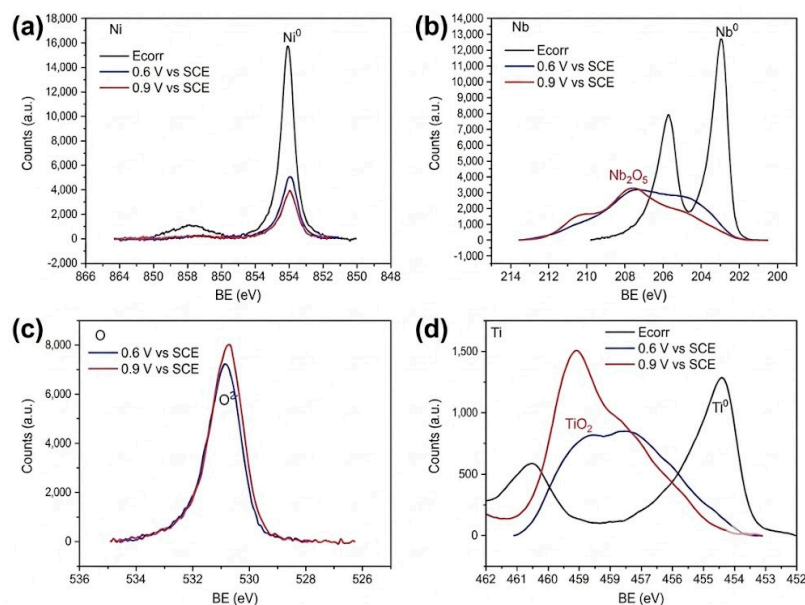


Figure 8. High-resolution XPS spectra for (a) $\text{Ni } 2p_{3/2}$, (b) $\text{Nb } 3d$, (c) $\text{O } 1s$, and (d) $\text{Ti } 2p$ for the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses at different polarization potentials.

The Nb 3d spectrum at OCP (Figure 8b) exhibits a well-defined doublet with the Nb $3d_{5/2}$ peak positioned at 202.2 eV, which corresponds directly to metallic niobium (Nb^0) within the glassy matrix. However, under anodic polarization conditions at 0.6 V and 0.9 V (Figure 8b), the metallic doublet completely disappears and is replaced by a broad signal shifted toward higher binding energies, with the Nb $3d_{5/2}$ peak centered at ~207.4 eV. This transformation confirms the complete surface oxidation of niobium to form niobium pentoxide (Nb_2O_5 , Nb^{5+} state) [40], which constitutes the thermodynamic backbone of stability and provides robust protection against localized corrosion in aggressive media [41,42].

The high-resolution Ti 2p spectrum at OCP (Figure 8d) reveals the metallic state (Ti^0) at approximately 454.3 eV. Following polarization at 0.6 V and 0.9 V vs. SCE, the elemental state is suppressed and a dominant doublet emerges, with the Ti $2p_{3/2}$ component positioned at 458.9 eV (Figure 8d), a value indicative of the formation of titanium dioxide

(TiO₂, Ti⁴⁺ state) [43]. This observation correlates directly with the high-resolution O 1s spectrum (Figure 8c), which exhibits a symmetric and intense peak at 530.5 eV, associated with lattice oxygen in metal oxides (O^{2−}). Collectively, these findings support a synergistic passivation model mediated by a compact mixed-oxide film [37].

The spectroscopic results demonstrate that a selective passivation mechanism governs the excellent corrosion resistance of the Ni₅₀Nb₃₀Ti₂₀ alloy at high anodic potentials. While Ni actively dissolves at the metal/electrolyte interface, Nb and Ti undergo instantaneous preferential oxidation due to their high thermodynamic affinity for oxygen [38,44]. The segregation and growth of this amorphous Nb₂O₅-TiO₂ bimetallic film—which remains free of crystalline phases or grain boundary defects owing to the disordered nature of the glassy substrate—acts as a highly effective barrier against ionic diffusion and pitting attack [37].

3.6. Morphological Characterization by SEM

After the electrochemical tests, the corroded surfaces of the metallic glass ribbons were examined via scanning electron microscopy (SEM) to evaluate the surface morphology and identify corrosion features associated with passive film formation and localized attack. Scanning electron microscopy (SEM) analysis of the Ni₅₀Nb_{50−x}Ti_x metallic glass after potentiostatic polarization at 0.6 V (Figure 9) vs. SCE revealed a surface that, despite exhibiting a fine texture at 500×, remained essentially free of localized corrosion attack, maintaining its overall integrity and homogeneous appearance. This observation is consistent with the formation of a stable, compact passive film, which is a hallmark of the corrosion resistance of Ni–Nb–Ti-based bulk metallic glasses (BMGs) in the passive regime [45]. The absence of pitting or deep crevices at this potential strongly suggests that 0.6 V lies well below the pitting potential (E_{pit}) for this alloy, allowing for effective passivation driven by the enrichment of Ti and Nb oxides (TiO₂ and Nb₂O₅) within the passive layer, which are known to provide superior barrier properties even in chloride-containing media [46].

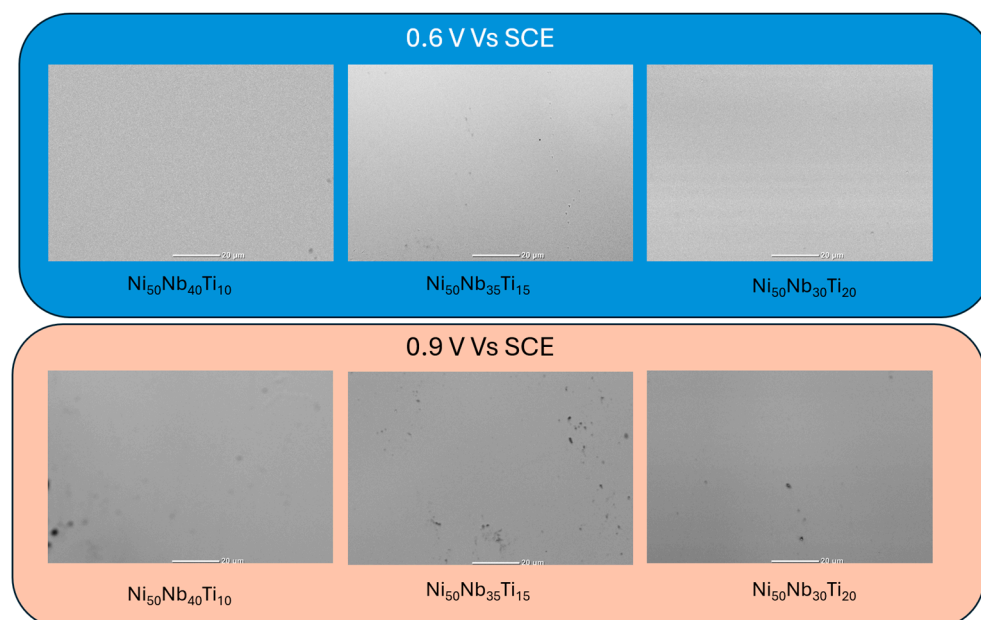


Figure 9. SEM images for polarized Ni₅₀Nb_{50−x}Ti_x at different potentials.

In contrast, the samples polarized at 0.9 V vs. SCE (Figure 9) exhibited a markedly different, severely degraded morphology, characterized by a rough, eroded surface topology. This transition from a pristine to a heavily attacked surface is a clear indication that the

applied potential of 0.9 V exceeds the E_{pit} for the $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$ glass, leading to the localized breakdown of the passive film [47].

The initiation of these pits is likely associated with nanoscale heterogeneities or local compositional fluctuations inherent to the amorphous structure, which can act as preferential sites for chloride ion adsorption and subsequent film rupture; once initiated, the autocatalytic mechanism of pit growth, driven by localized acidification and chloride enrichment, proceeds rapidly, leaving behind the characteristic porous morphology observed [48].

The comparative morphological analysis unequivocally demonstrates that the passive film stability of the $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$ metallic glass is critically potential-dependent. While the alloy shows excellent resistance to uniform corrosion at 0.6 V due to a highly protective oxide layer, anodic polarization to 0.9 V triggers a catastrophic transition to localized corrosion. This behavior is consistent with the defect-generation model for passive films, in which an increase in anodic potential increases the concentration of cation vacancies within the oxide, facilitating the ingress of aggressive Cl^- ions and leading to the eventual rupture of the barrier layer and the onset of severe pitting corrosion [17]. Therefore, the SEM results not only confirm the broad passivation window of the $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$ alloy at moderate anodic potentials but also highlight its pronounced sensitivity to overpotentials, providing crucial morphological evidence for predicting its long-term durability in aggressive electrochemical environments.

3.7. Passive Film Growth Mechanism

3.7.1. Effective Capacitance and Passive Film Thickness

Because the impedance response of the passive films exhibited non-ideal capacitive behavior, the effective capacitance (C_{eff}) was calculated from EIS fitting of the constant phase element parameters using the modified Brug relationship (Equation (1)). This approach allows a more accurate estimation of the real electrochemical capacitance in systems presenting frequency dispersion effects [30,31].

The passive film thickness was estimated assuming a parallel-plate capacitor model (Equation (2)) with a dielectric constant of $\epsilon_r = 41$, a value commonly employed for amorphous TiO_2 passive layers and lying within the range reported experimentally for passive titanium oxides (40–85). For mixed Ti-Nb oxides, values between 30 and 50 have been reported depending on the relative oxide fractions [26,27]. The dielectric constant of Nb_2O_5 is typically ~40–50 for amorphous films (Cavigliasso et al., 1998) [28], while TiO_2 exhibits values of 40–86 depending on structure and deposition conditions [15,25]. Since the passive films formed on the Ni-Nb-Ti alloys are expected to be amorphous mixed oxides with Ti as the predominant cation (as confirmed via XPS), a value of 41 was selected. This value is consistent with the dielectric behavior of amorphous TiO_2 -rich passive films reported in the literature.

The calculated capacitance (Table 3) values showed a clear dependence on both alloy composition and applied potential. In general, increasing the Ti content resulted in lower effective capacitance values, whereas increasing the anodic potential produced a further decrease in capacitance. Since capacitance is inversely proportional to oxide thickness in the parallel-plate capacitor model, these results indicate the formation of thicker passive films in the Ti-rich alloys and under higher anodic polarization.

The $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy exhibited the lowest capacitance among the compositions studied, suggesting the formation of a thicker, more compact passive layer. This behavior is consistent with the potentiostatic and EIS results, which showed lower passive current densities and higher charge-transfer resistance values for this alloy.

The improved protective behavior associated with Ti enrichment can be attributed to the formation of Ti-rich oxide layers with reduced ionic conductivity and lower defect concentration. TiO_2 is known to possess excellent dielectric and barrier properties, which help limit ionic transport through the passive film [15,22].

3.7.2. Validation of the High-Field Model

The passive film growth mechanism was analyzed using the High-Field Model (HFM), which assumes that ionic migration through the oxide layer is controlled by the electric field established across the passive film [49].

According to the HFM, the inverse capacitance is proportional to passive film thickness and should exhibit a linear relationship with the applied formation potential. Figure 10 presents the relationship between C^{-1} and the applied potential for the studied alloys. In all cases, a nearly linear dependence was observed, supporting the applicability of the High-Field Model to describe passive film growth in Ni-Nb-Ti metallic glasses.

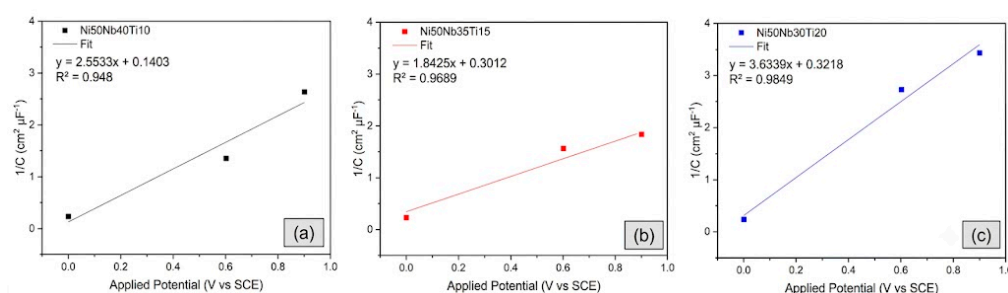


Figure 10. C^{-1} vs. U plot for the $\text{Ni}_{50}\text{Nb}_{50-x}\text{Ti}_x$ metallic glasses (a) $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$, (b) $\text{Ni}_{50}\text{Nb}_{35}\text{Ti}_{15}$ and (c) $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$.

The observed linearity indicates that ionic transport through the passive layer constitutes the rate-controlling step during anodic oxidation. Similar behavior has been reported previously for Ti and Ti-based alloys, in which oxygen-vacancy migration through the oxide film governs the kinetics of passive-layer growth under anodic polarization conditions [28,32–34].

The absence of significant deviations from linearity suggests that the passive films formed on the studied alloys behave as compact barrier-type oxides rather than porous or dissolution-dominated films within the evaluated potential range.

3.7.3. Electric Field Strength and Influence of Ti Content

The electric field strength across the passive film E_0 was estimated from the slope of the C^{-1} versus potential relationship using Equation (3), and the results are reported in Table 3. The obtained values were within the range typically reported for passive oxide films formed under high-field conditions, confirming the validity of the HFM approach.

A decrease in E_0 was observed as Ti content increased. The Ti-rich alloy exhibited the lowest electric field values, suggesting modifications in the dielectric properties and defect structure of the passive film. Lower electric field values imply that passive film growth can proceed at lower driving forces for ionic migration, which is generally associated with more stable and less defective oxide layers.

This behavior may be related to the formation of mixed Ti-Nb oxides with improved structural compactness and lower oxygen-vacancy concentrations. Previous studies have shown that Ti additions can reduce ionic defect mobility within passive films, thereby decreasing steady-state current density and improving corrosion resistance [22,33].

In addition, the passive film thickness increased with applied potential for all studied alloys, reaching the highest values for the $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ composition. The formation of

thicker passive films with enhanced protective properties further supports the beneficial role of Ti in stabilizing the oxide layer.

The relationship between electric field strength and defect density in passive films is grounded in the Point Defect Model (PDM) [19]. According to this model, the electric field across the passive film is the driving force for ionic transport, particularly for the migration of oxygen vacancies and metal interstitials. The high-field conduction law relates the ionic current density to the electric field exponentially (Equation (4)):

$$i = A \exp(BE) \quad (4)$$

where E is the electric field strength, and A and B are constants related to the activation energy for defect migration and the charge of the migrating species [19]. Under steady-state conditions, the concentration of point defects (particularly oxygen vacancies) is determined by the balance between generation at the metal/film interface and consumption at the film/electrolyte interface. A higher electric field accelerates defect migration, which, if generation exceeds consumption, leads to defect accumulation and increased defect density [19].

The electric field strength is also inversely related to film thickness for a given applied potential ($E = \Delta U/d$). Thus, a lower electric field, as observed for the Ti-rich alloy ($2.90 \times 10^6 \text{ V cm}^{-1}$ for $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ at 0.6 V versus $3.0 \times 10^6 \text{ V cm}^{-1}$ for $\text{Ni}_{50}\text{Nb}_{40}\text{Ti}_{10}$), implies either a thicker film or a lower potential gradient across the film. Thicker films with lower defect densities are characteristic of more stable, compact oxide layers. The addition of Ti promotes the formation of TiO_2 , which has a lower ionic conductivity and higher thermodynamic stability compared to Nb_2O_5 , resulting in reduced defect generation and lower steady-state defect concentrations [5,33]. Consequently, the lower electric field values observed for Ti-rich alloys are consistent with the formation of passive films with reduced oxygen vacancy concentrations and improved barrier properties.

4. Discussion

The results obtained in this study demonstrate that the addition of Ti significantly improves the passivation behavior and corrosion resistance of Ni-Nb metallic glasses in chloride-containing solutions. Structural characterization confirmed that all studied alloys retained a fully vitreous structure after melt spinning, eliminating microstructural heterogeneities commonly associated with localized corrosion in crystalline alloys.

The electrochemical results consistently showed that increasing Ti content promotes the formation of more stable passive films. The shift of the corrosion potential toward more noble values, together with decreases in the corrosion and passive current densities, indicates a progressive improvement in the protective character of the oxide layer as the Ti concentration increases.

The potentiostatic and impedance analyses revealed that the Ti-rich alloy forms passive films with lower ionic conductivity, higher charge-transfer resistance, and greater thickness. These characteristics are indicative of compact barrier-type oxide layers with enhanced resistance to chloride penetration and reduced defect density.

A major finding of this work is the experimental validation of the High-Field Model for passive film growth in Ni-Nb-Ti metallic glasses. The linear relationship observed between inverse capacitance and formation potential confirms that ionic transport through the passive film controls the kinetics of oxide growth under anodic polarization conditions.

The electric field values obtained in this work are comparable to those previously reported for passive Ti-based systems [30], indicating that similar high-field ionic migration processes govern the passivation mechanism of the studied metallic glasses. The decrease in electric field strength with increasing Ti content suggests that Ti modifies the dielectric

properties and defect structure of the passive layer, thereby facilitating the formation of thicker, more stable oxide films.

The improved electrochemical performance of the Ti-rich alloy is likely attributable to a synergistic effect between TiO_2 and Nb_2O_5 species within the passive film. TiO_2 provides excellent barrier properties and chemical stability, while Nb-containing oxides may contribute to film stabilization and enhanced corrosion resistance [20–22].

From a biomaterials perspective, the obtained results indicate that Ni-Nb-Ti metallic glasses exhibit promising corrosion resistance for potential biomedical applications. However, additional studies involving direct surface chemical characterization, ion release measurements, and biological evaluation are necessary before considering any medical application.

5. Conclusions

X-ray diffraction and transmission electron microscopy confirmed the vitreous nature of all studied alloys, demonstrating that the melt-spinning process successfully suppressed crystallization and produced chemically homogeneous metallic glass ribbons.

Potentiodynamic polarization results showed that increasing Ti content improves corrosion resistance in 3.5 wt.% NaCl solution. The $\text{Ni}_{50}\text{Nb}_{30}\text{Ti}_{20}$ alloy exhibited the most noble corrosion potential together with the lowest corrosion and passive current densities, indicating the formation of a more protective passive film.

Potentiostatic polarization and electrochemical impedance spectroscopy corroborated that Ti-rich alloys develop passive layers with higher charge-transfer resistance and lower effective capacitance, consistent with the formation of thicker and more compact oxide films with enhanced barrier properties.

The passive film growth mechanism was successfully described using the High-Field Model (HFM). The linear relationship between inverse capacitance and applied potential confirmed that ionic transport through the oxide layer controls passive film growth under anodic polarization conditions. The calculated electric field strength values were within the range reported for passive Ti-based systems under high-field conditions. Increasing Ti content resulted in lower electric field values, suggesting a reduction in defect density and improved stability of the passive layer.

The excellent electrochemical behavior observed for the Ti-enriched alloys is attributed to the formation of stable mixed Ti-Nb oxide films with reduced ionic conductivity and enhanced resistance against chloride-induced degradation.

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