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# Anti-Corrosion Coatings Based on $Nb_2O_5$ - a Comparison Between two Coatings Technology: Thermal Spray Coating and Epoxy Paint

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Niobium pentoxide ($Nb_2O_5$) has gained prominence as an anti-corrosive pigment. The performance of anti-corrosive coatings based on $Nb_2O_5$ was tested in an environment with an acid atmosphere and at high temperatures. For comparison, SAE 1020 carbon steel samples were coated with two anti-corrosive coatings based on $Nb_2O_5$: applied by thermal spray and epoxy paint. The samples were partially immersed in the laboratory for 720 h and 1440 h in a 40% (v/v) $H_2SO_4$ at 25°C, 60°C, and 80°C. An in-situ evaluation was carried out of chemical industry installations over 4383 h in microclimates with the presence of corrosive agents at temperatures up to 70°C. The results obtained showed that the $Nb_2O_5$ coatings applied by thermal spray offer better anti-corrosive performance under immersive conditions. In contrast, under conditions submitted to steam, both the $Nb_2O_5$ coatings applied by thermal spraying and epoxy-$Nb_2O_5$ paint show excellent anti-corrosive behavior.

**Keywords:** *Niobium pentoxide, thermal spray, epoxy paint, anti-corrosive coating, high temperatures, sulfuric acid.*

## 1. Introduction

Corrosive processes in industries that operate in aggressive environments cause wear and damage to structures and equipment, generating severe technical and economic consequences[1]. Several methodologies have been proposed to combat the problems caused by the corrosive process. Anti-corrosive coatings play an essential role in the protection methods due to their versatility and acceptable costs[2]. The coatings application protects against corrosion and is an economically viable alternative, ensuring a structure with good mechanical properties and adequate resistance to corrosion[3,4].

The technique of industrial painting is gaining prominence among the coating deposition technique for corrosion prevention and is one of the techniques most used nowadays. In the last few years, technological development in coatings has been intense, and the results obtained using industrial paints in the ambit of anti-corrosive protection are very representative. However, resin-based paint commonly available in the market does not show chemical resistance in highly aggressive environments or at temperatures above 100 °C[5-7]. Similarly to industrial painting, thermal spray technology is widely used in industrial applications, including aerospace, automotive, chemical, and petrochemical industries[7-10]. The thermal spray is a family of coating deposition techniques based on applying coating materials to a substrate to improve the properties of the surface on which it was applied[9,11-13]. Amongst the technologies available for the deposition of coatings by thermal spray flame spray is one of the most used for being a simple technique, cheaper, and capable of producing thicker coatings[14-16].

However, the protection effectiveness of coatings deposited by either painting or thermal spray can be compromised by the presence of defects on their surface, as well as an increase in porosity, interconnected cracks, and the formation of partially melted oxides[14]. Flaws such as cracks and porosity affect anti-corrosive performance and may act as preferred pathways to penetrate corrosive ions into the coating, reaching the metal substrate[12,17,18].

Due to the eventual presence of defects on the surface of the anti-corrosion coatings, increased research efforts have been dedicated to adding pigments that provide corrosion resistance in an aggressive environment. In this scenario, the niobium pentoxide stands out as an anti-corrosive pigment as well as a coating material due to its high resistance to corrosion in different media, its application at high temperatures, and its good mechanical properties[19-23]. $Nb_2O_5$ is an oxide coming from the niobium metal, which has as its characteristic the formation of a passive layer that can be made up of niobium pentoxide ($Nb_2O_5$), niobium dioxide ($NbO_2$), or the combination of niobium oxide (NbO) or these three oxides. The reactions from 1 to 3 describe the formation of these oxides[23,24].

$$Nb + H_2O \rightarrow NbO + 2H^+ + 2e^- \quad (1)$$

$$NbO + H_2O \rightarrow NbO_2 + 2H^+ + 2e^- \quad (2)$$

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$$2NbO_2 + H_2O \rightarrow Nb_2O_5 + 2H^+ + 2e^- \quad (3)$$

The excellent corrosion resistance of niobium is attributed to two main factors: the formation of a protective and adherent superficial film of stable oxide ($Nb_2O_5$), and the chemical inertia of niobium pentoxide, as demonstrated by Pourbaix diagram[24,25]. Thus, the steel structures covered with this oxide would be immune to corrosion[20,23,26]. Despite the resistance of the niobium in highly corrosive media having already been reported in the literature, few studies have tested $Nb_2O_5$-based coatings in environments with hydrofluoric acid (HF) or in acidic environments with high temperatures. The lack of results can be explained by the difficulty of working in the laboratory with HF, resulting in a gap in the behavior of the coatings. However, this combination of factors represents the reality of many environments and processes in the chemical industry, showing the importance of such study[26,27].

This study aimed to evaluate the anti-corrosive behavior of $Nb_2O_5$-based coatings in acidic environments. Therefore, a comparative study was carried out between the coating of $Nb_2O_5$ applied by thermal spray and an epoxy paint -$Nb_2O_5$ under test conditions close to those observed in chemical industries. Laboratory immersion tests, in-situ testing, characterization of these coatings, and mechanical tests were used to verify the influence of the temperature, and the exposure in an acid environment on the behavior of the coatings studied.

## 2. Experimental

### 2.1. Materials

The samples were made of SAE 1020 steel and coated with coatings based on niobium pentoxide ($Nb_2O_5$) using two techniques: applied by thermal spray and an epoxy paint-$Nb_2O_5$. The samples were manufactured in two dimensions: rectangular samples with 75 mm x 50 mm x 3 mm for laboratory testing and 120 mm x 75 mm x 3 mm for in-situ testing in the chemical industry. Table 1 shows the coatings studied in this work.

**Table 1.** Coating system applied to carbon steel.

| Coating | Paint system code | Thickness |
|---|---|---|
| $Nb_2O_5$ coating by thermal spray | TS | 250-300 µm |
| Epoxy paint-$Nb_2O_5$ | NP | 300 µm |

### 2.2. Application of coatings

Before applying the coatings, the carbon steel samples were cleaned and blasted to reach the Sa 2½ surface profile (near-white blast cleaning) as defined in ISO 8501[28].

Niobium pentoxide ($Nb_2O_5$ - 99.8% AMG Brazil purity) was applied through thermal spray by the Flame Spray process with the Terodyn 2000-FLA 002 equipment through the following steps:

I. Application of a 100 µm bond coat layer from the NiAl alloy.
II. $Nb_2O_5$ coating with thickness between 250-300 µm.
III. A layer of an epoxy resin-based sealant is cured with polyamine - to isolate the pores of the main coating.
IV. Application of epoxy-$Nb_2O_5$ paint at the ends of the samples.

Samples coated with epoxy paint-$Nb_2O_5$ (solid by mass: 96%, provided by EcoProtec©-Brazil) were painted and dried in the air at room temperature (23°C) and relative air humidity of 45%, with only one hand of the paint being applied to reach the desired thickness (300 µm). An extra layer of paint was applied to reinforce the coating at the edges of the samples. The samples were dried in the air for 7-days before being tested, according to the recommendation of the manufacturer.

### 2.3. Immersion test

To understand and compare the behavior of the coatings under different conditions, the samples were submitted to immersion tests at different temperatures, 25°C, 60°C, and 80°C. Half of the samples were partially immersed for 720 h and 1440 h in an acid solution of 40% (v/v) $H_2SO_4$. The conditions were chosen based on the corrosive medium found in the chemical industry: a highly acidic medium with $H_2SO_4$ and $HF^-$. However, only $H_2SO_4$ was used to perform the test due to the $HF^-$ toxicity and high corrosivity, making it challenging to handle in the laboratory. The tests were conducted to evaluate the behavior of the coatings in the liquid phase, steam, and in the liquid/steam interface, according to norm ASTM G31[29]. Conditions are outlined in Table 2.

During the immersion test, defects such as color change and the formation of small bubbles were not considered as parameters for discontinuation of the test. The test was interrupted when the coatings were peeled and cracked.

**Table 2.** Immersion test conditions.

| Conditions | Test solution | Temperature (°C) | Immersion time (hours) |
|---|---|---|---|
| C1 | 40% $H_2SO_4$ | 25 | 720 |
| C2 | | 25 | 1440 |
| C3 | | 60 | 720 |
| C4 | | 60 | 1440 |
| C5 | | 80 | 720 |
| C6 | | 80 | 1440 |

### 2.4. In-situ testing

As described in Table 3, the in-situ tests were carried out at the industrial installations of a chemical industry that

**Table 3.** In situ test condition.

| Conditions | Test solution | Temperature (°C) | Immersion time (hours) |
|---|---|---|---|
| C7 | $F^-$ | 70 | 4373 |
| C8 | CaO | 25 | 4373 |
| C9 | Organic solvent | 25 | 4373 |
| C10 | Boric acid and $F^-$ | 25 | 4373 |
| C11 | $NH_3$ | 70-80 | 4373 |

produces niobium and tantalum oxides. The samples were then allocated to micro-environments that are part of the production of these oxides as described in the following topics:

- Condition C7: The microclimate described by the C7 condition consists of the digestion stage. In this step, there is a process of acid lixiviation of the raw material, using a 70% solution (v/v) HF and a working temperature of approximately 70°C. Because of the chemical products used in this process, the environment shows a high fluoride ion ($F^-$) concentration in the air.
- Condition C8: The C8 microclimate corresponds to the effluent treatment station. The waste treatment process corresponds to the last stage in the production process of the oxides. It consists of neutralizing the acid effluents with calcium oxide (CaO), precipitation of the contaminants, and decantation. Due to the presence of calcium oxide, the atmosphere of this microclimate is classified as basic.
- Condition C9: The C9 microclimate consists of the extraction process. The liquor resulting from the digestion process is forwarded to the liquid-liquid extraction stage through a selective organic solvent.
- Condition C10: This microclimate corresponds to the stage of the precipitation of the niobium (Nb) in the form of hydroxides, followed by the drying and calcination for obtaining the oxides. The solution originating from the extraction stage is precipitated in an acidic aqueous environment at room temperature. The primary acids found in this environment are boric acid and fluoride acid (HF).
- Condition C11: The microclimate corresponds to the precipitation stage of the tantalum (Ta) in the form of hydroxides. The precipitation of the tantalum occurs in a basic environment and with temperatures that vary between 70° C and 80° C, the main contaminant being ammonia hydroxide ($NH_3$).

### 2.5. Coating degradation/failure assessment

Coatings were visually analyzed after the immersion and in-situ tests according to ISO 4628[30], where the main defects of the coatings were assessed as polishing, cracking, peeling, and spoiling of the coating. The standard classifies defects according to type, quantity, and dimension and can vary from 0 to 5, with 5 being the largest. Besides, the samples were analyzed using a scanning electron microscope (SEM) using HITACHI TM 3000 equipment to assess the degradation of the coatings and possible alterations after the tests. To verify the integrity of the film after the tests, the samples were cut cross-sectional in the region of the sample in the immersion region. Samples of each tested coating were selected as a reference condition for comparative purposes.

### 2.6. Mechanical tests

The tensile strength of the coatings was determined using the Positest AT-A Pull-Off Defelsko model, according to ISO 4624[31]. The measures were performed in triplicate to ensure repeatability.

## 3. Results

Below are the results obtained from the experiments performed in this study. Firstly, the results obtained after the immersion test in the laboratory will be exposed, followed by the results of the in-situ test and by the mechanical characterization of the coatings based on $Nb_2O_5$ applied by thermal spray (TS) and by the epoxy paint $Nb_2O_5$ (NP).

### 3.1. Coatings degradation analysis after immersion test

Figure 1 presents the TS coatings samples after the immersion test as outlined in Table 2.

The TS REF sample represents the reference sample of the $Nb_2O_5$ coating applied by thermal spray, and this sample was not tested. Based on a comparison with the reference sample, it was possible to note that the samples coated with $Nb_2O_5$ by thermal spray (TS) did not form blisters, peeling, or cracks. Changes in the tonality of the immersion region were observed in the conditions tested at temperatures of 25°C and 60°C (C1 to C4).

The samples submitted to the 80°C (TS C5 and TS C6) test showed a marked color change in the immersion region, the formation of blisters, corrosion points on the surface of the coating, cracks, and delamination at the edges of the sample. These observed defects did not propagate to a region exposed to steam, as highlighted by the arrows in Figure 1.

Figure 2 presents a set of cross-section images of TS samples after exposure under the conditions studied.

The formation and nucleation of cracks and blisters in the transversal cut of the samples tested at 25°C (TS C1 and TS C2) were not verified. The samples exposed to the immersion test at 60°C (TS C4) showed delamination after transversal cutting, as shown in Figure 2. The increase in temperature in the immersion tests led to a reduction in the coating thickness, as can be observed more clearly in the C6 (80°C) condition in Figure 2.

Figure 3 presents the samples of the NP coatings after the immersion test as set out in Table 2.

The NP REF sample represents the reference sample of the epoxy coating-$Nb_2O_5$. This sample was not submitted

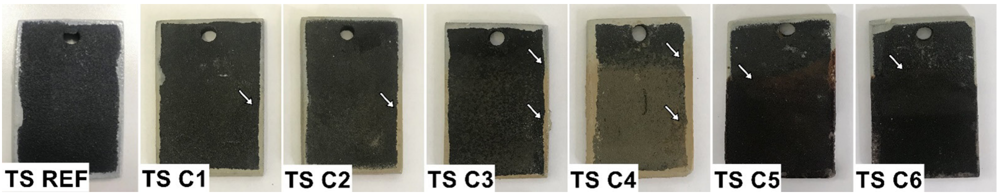


**Figure 1.** Specimens of $Nb_2O_5$ coating by thermal spray (TS) after immersion test.

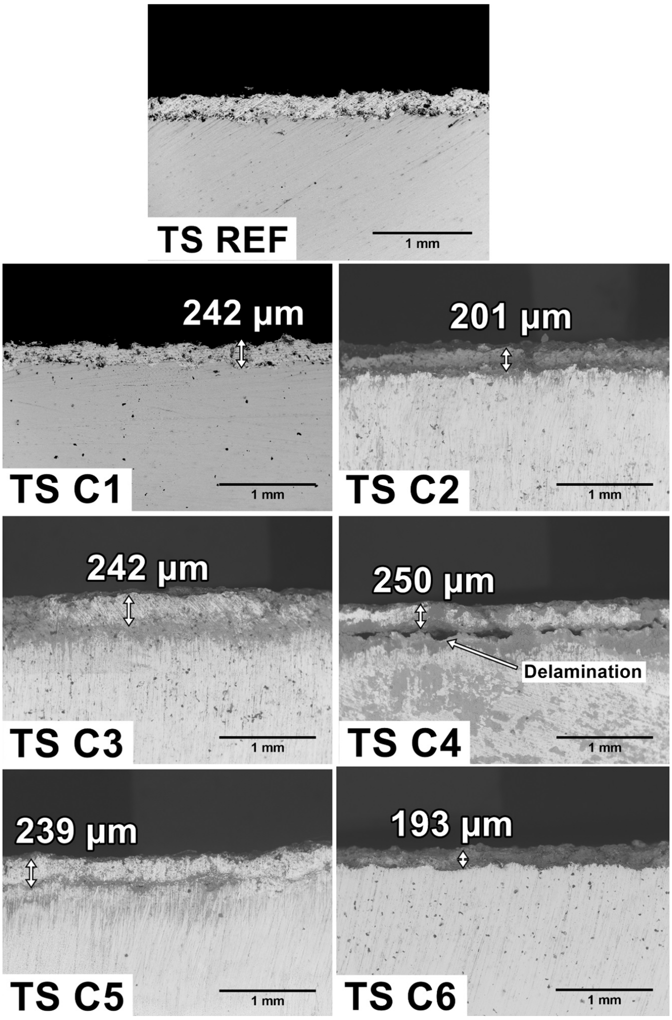


**Figure 2.** SEM images of $Nb_2O_5$ coating by thermal spray (TS) samples exposed to immersion test.

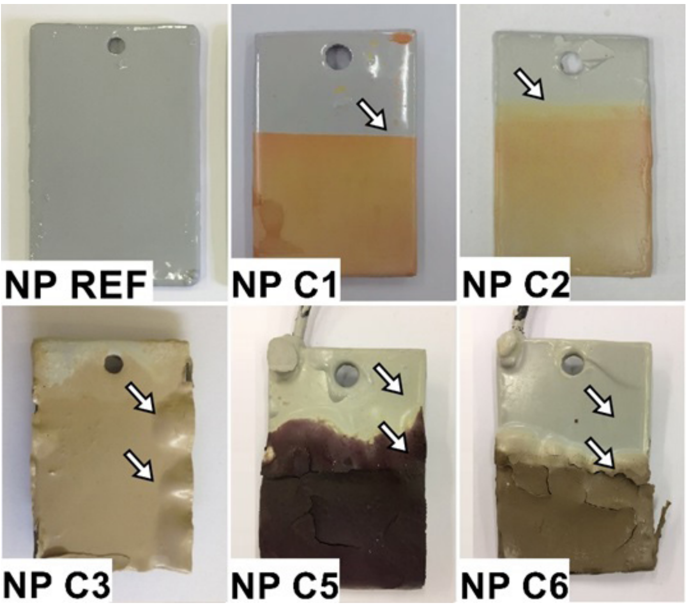


**Figure 3.** Epoxy-$Nb_2O_5$ paint (NP) test specimens after immersion test.

to the immersion test. The samples coated with epoxy paint -$Nb_2O_5$ (NP) showed slight tonality changes in the immersion region, as can be seen in the highlights of conditions C1 (25°C, 720 h) and C2 (25°C, 1440 h).

The increase in the immersion time (1440 h) led to the formation of fissures on the side of the sample. These fissures did not propagate through the sample surface, as indicated by the arrows in the NP C2 sample. The change in tonality after exposure in an acid environment has already been reported in the literature[26].

The increase in the temperature caused more significant degradation of the samples coated with epoxy paint -$Nb_2O_5$ (NP) compared to the samples tested at 25°C. Based on ISO 4628[30] standard, the incidence of low-density blisters was observed at the edges of the sample after 720 h of testing (NP C3) and cracks and displacements in these regions, as indicated in Figure 3. Accelerated formation of corrosion products was observed after 1440 h of immersion (NP C4), making it impossible to analyze the specimens under these conditions.

The samples submitted to the immersion test in an acid solution at 80°C suffered a more accelerated degradation process, with a remarkable change in the color and cracks at the edges of the samples, as highlighted in Figure 3. Due to these defects, the test was interrupted before the set time, samples NB C5 and NB C6 remaining 624 h and 720 h in immersion, respectively.

The results obtained showed that the increase in temperature accelerates the degradation process of the epoxy-$Nb_2O_5$ (NP) paint, in most cases in the immersion region. There was a process of coating degradation in these areas, with an incidence of blisters, and cracks, especially at the edges of the sample. However, these defects did not propagate to the steam region, thus indicating the resistance of the NP coating applied to structures and equipment exposed to acid environments in the steam phase at temperatures up to 80°C.

As there was a failure incidence in the immersion region, the samples were cut down transversal in the steam region and analyzed via SEM. Figure 4 presents a set of cross-section images of the NP samples after exposure under the conditions studied.

After the immersion test, no morphological changes, such as blisters or crack development, were found in the epoxy-$Nb_2O_5$ (NP) paint under any tested condition. However, it was possible to verify the occurrence of the delamination of the samples after the cut for analysis. As the corrosive process on the metal substrate was not observed, the delamination process probably occurred due to the shear force when preparing the samples for the analysis.

The immersion tests showed that the $Nb_2O_5$ coating applied by thermal spray (TS) presented resistance to superior corrosion in the sample immersion region compared to the epoxy-$Nb_2O_5$ (NP) paint. In the steam region, however, both the coatings showed good anti-corrosive performance, with no defects observed, as shown in Figure 1 and Figure 3.

Although both coatings have niobium pentoxide as an anti-corrosive pigment, the coating applied by thermal spray (TS) is composed only of $Nb_2O_5$, while in the samples NP, the niobium pentoxide acts only as an anti-corrosive pigment in an epoxy resin matrix. One of the

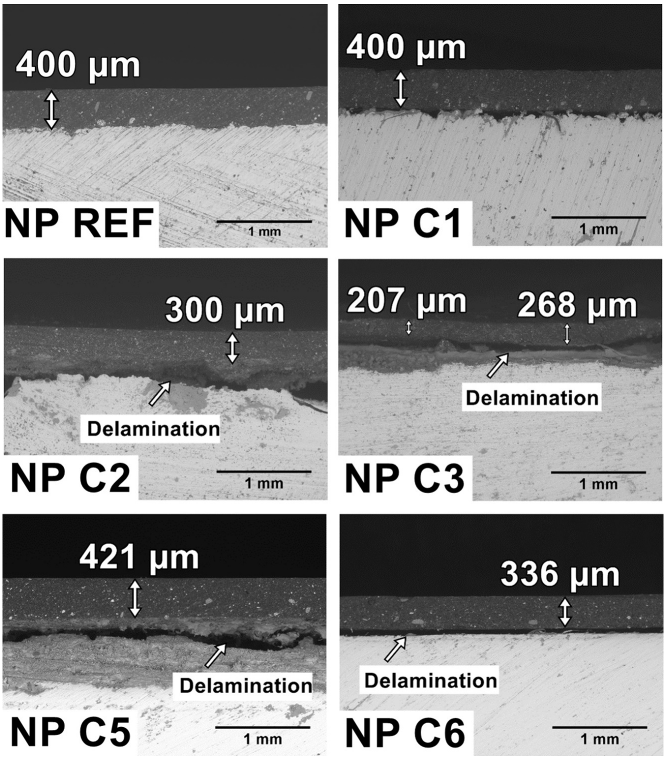


**Figure 4.** SEM images of epoxy-$Nb_2O_5$ paint (NP) samples exposed to immersion test.

major inconveniences of the coating applied by thermal spraying by the Flame Spray technique is the probable porosity formation due to the process. The PETROBRAS N-2568 standard[32] determines the application of an epoxy varnish sealant for applications at a temperature of up to 120°C to minimize the porosity of the coatings applied by thermal spraying. The application of this epoxy sealant in the $Nb_2O_5$ coating applied by the Thermal Spray process probably acted as a barrier, reducing the porosity of the coating and promoting the excellent performance of the TS samples in the immersion and steam region.

## 3.2. Coatings degradation analysis after the in-situ test

In-situ testing is beneficial in evaluating the resistance to corrosion of coatings in industrial environments, providing good results in the medium and long term. In-situ tests make it possible to verify the behavior of coatings under real conditions of application. The chemical industry micro-climates where the samples coated with $Nb_2O_5$ were installed are described in Table 3. The samples remained in these microclimates for 4383 hours. After this period, the samples were removed, cleaned with Clark's solution, and visually assessed.

Figure 5 presents the TS coatings samples after the in-situ tests, as outlined in Table 3.

The TS REF sample represents the reference sample of the $Nb_2O_5$ coating applied by thermal spraying, i.e., this sample was not submitted to the test and served as a visual comparison for the samples tested. The samples coated with $Nb_2O_5$ by thermal spray (TS) submitted to the microclimate C7 (Figure 5) were removed after 168 hours of exposure due to accelerated degradation observed during the test. Defects at the edges of the samples, peeling, and the delamination of the coating left the metal substrate exposed, speeding up the corrosive process.

When exposed to the microclimates exposed to the ambient temperature C8, C9, and C10 (Figure 5), the TS samples showed excellent anti-corrosive behavior, showing only eventual changes in tonality after 4383 h. Niobium pentoxide ($Nb_2O_5$) showed excellent anti-corrosive behavior in the thermal spray (TS) samples in environments with the presence of contaminants such as CaO, organic solvent, $NH_3$, and boric acid (TS C11), with no changes in tonality, even at high temperatures.

Figure 6 presents a set of cross-section images of TS samples after exposure under the conditions studied. It was impossible to carry out the microscopic analysis of the TS sample submitted to the C7 microclimate due to the high degradation rate of these samples.

No microscopic or morphological changes were identified in the coating after the in-situ test in the micro-climates tested (from C8 to C11).

Figure 7 presents the samples of the NP coatings after the in-situ test as set out in Table 3.

Likewise verified for the samples coated with niobium pentoxide applied by thermal spray (TS), when submitted to the C7 micro-climate, the epoxy-$Nb_2O_5$ (NP) paint samples showed accelerated degradation, so the test was interrupted after 168 h of exposure. The presence of hydrofluoric acid in the gaseous phase at a high concentration and temperature of 70 °C were determinant factors for the acceleration of the corrosive process.

The samples exposed to the micro-climates at the ambient temperature C8, C9, and C10 showed excellent anti-corrosive behavior after 4383 h. Niobium pentoxide ($Nb_2O_5$) proved to be a tremendous anti-corrosive pigment for paint in environments with contaminants such as CaO, organic solvent, and boric acid (NP C11), not showing any failures or changes in the tonality of the coating.

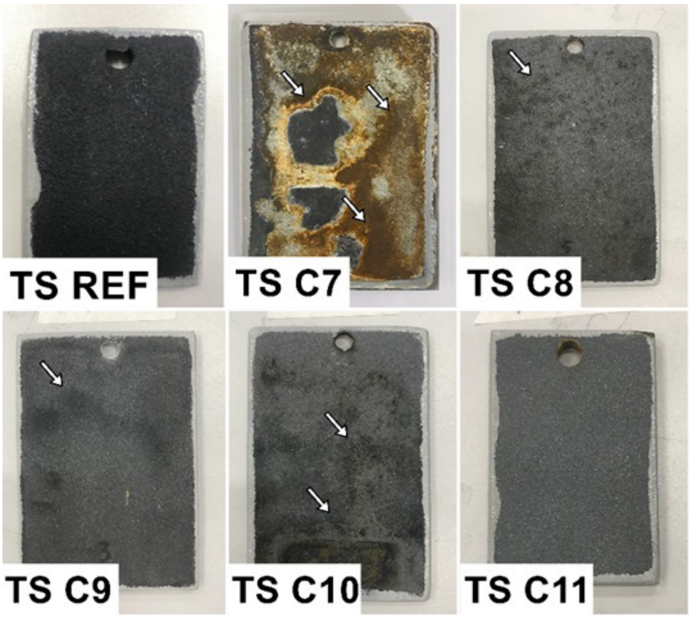


**Figure 5.** Specimens of $Nb_2O_5$ coating by thermal spray (TS) after in-situ test.

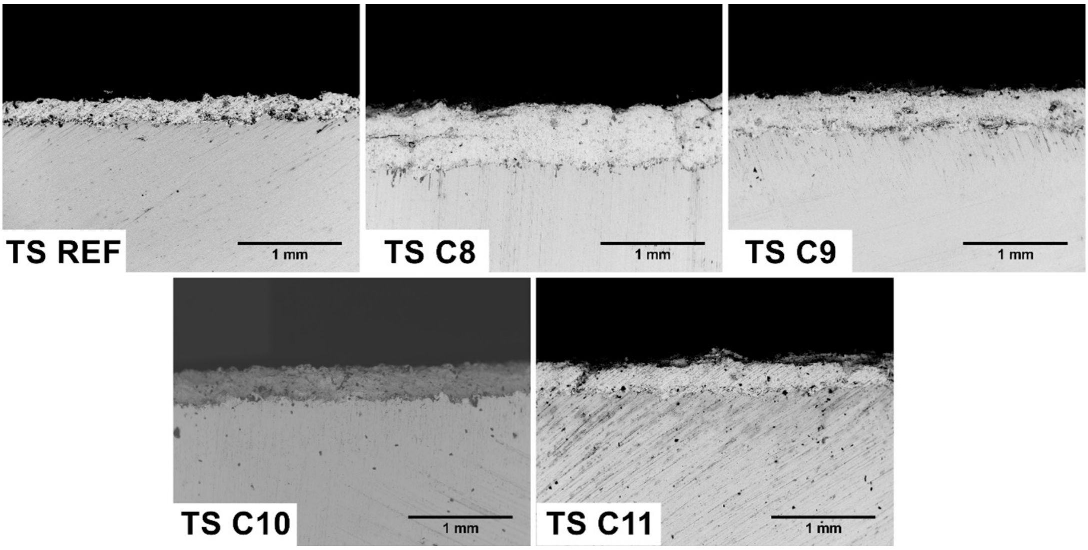


**Figure 6.** SEM images of $Nb_2O_5$ coating by thermal spray (TS) samples exposed to in-situ test.

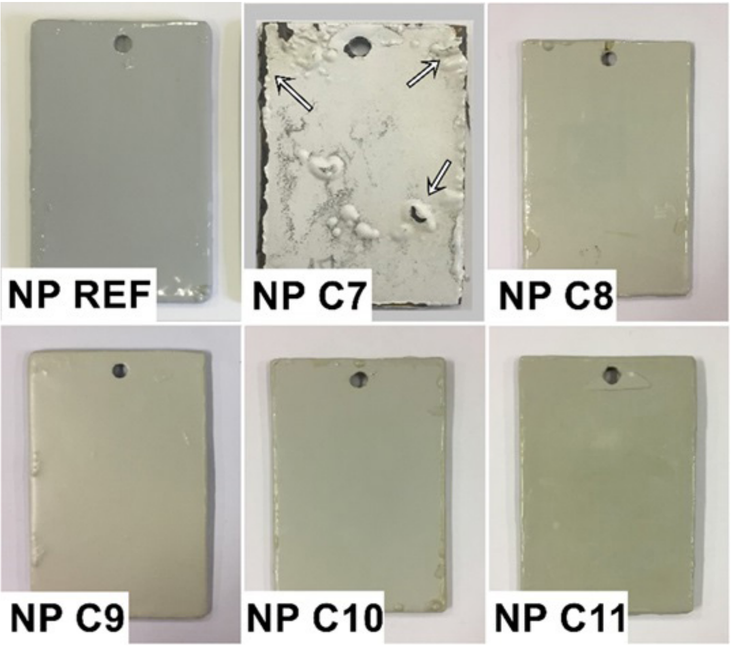


**Figure 7.** Epoxy-$Nb_2O_5$ paint (NP) test specimens after in-situ test.

Images of the NP samples were carried out after exposure in the micro-climates studied (Figure 8) to verify the morphological changes of the film after the in-situ tests.

After the in-situ tests in the micro-climates studied, no microscopic or morphological changes were identified in the paint. No formation of blisters, cracks, or detachment of the coating can be observed in Figure 8.

It was possible to observe that the samples coated with epoxy paint-$Nb_2O_5$ had a lower incidence of defects than the samples coated with $Nb_2O_5$ applied by thermal spraying, as seen when comparing Figure 5 and Figure 7. The samples in-situ tests were exposed to the steam phase, and the results obtained were in line with those observed in the steam region of the immersion tests (Figure 1 and Figure 3).

### *3.3. Mechanical properties of coatings*

The adhesion of the coatings was assessed through the test of resistance to pull-off tensile strength. The method is based on applying a tensile force in a direction perpendicular to the plane of the coated substrate until a failure occurs due to rupture of the coating or its interface with the substrate. An adhesive is used between the coating and the dolly on the extraction equipment. The metallic substrate is considered layer A, the coating as layer B, the adhesive as layer Y, and

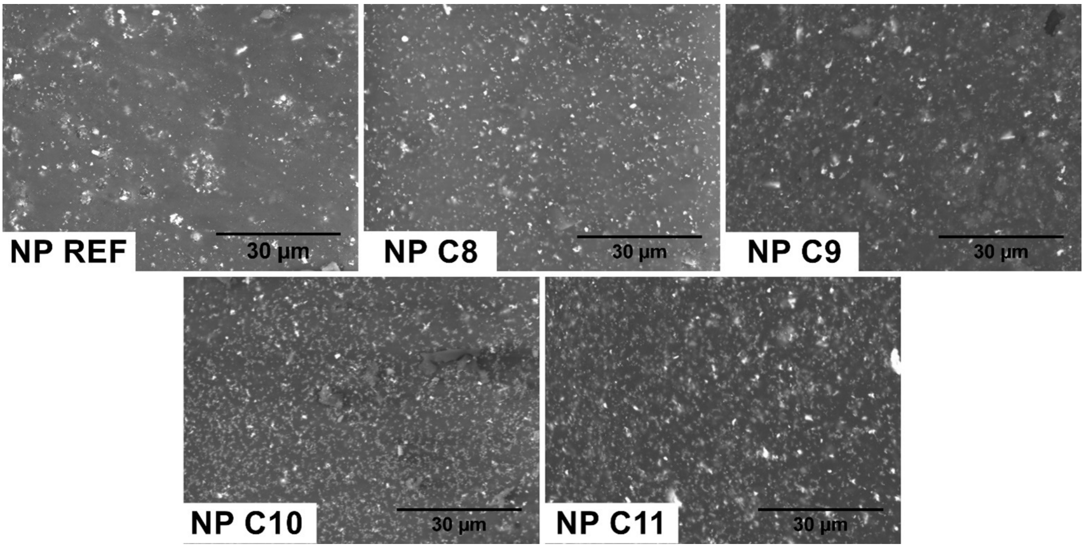


**Figure 8.** SEM images of epoxy-$Nb_2O_5$ paint (NP) samples exposed to in-situ test.

the dolly surface as layer Z. In a single-layer coating, when there is a failure in the interface between the substrate and the coating, this failure is called A/B. Type B/Y defects occur between the coating and the adhesive, and the Y/Z type defects, which occur between the adhesive and the dolly, are common. Different types of defects can occur in the same extraction area. The tensile strength then characterizes adhesion to the coating at the moment of rupture and by visual inspection of the type of failure that occurs during the test execution. According to ISO 4624[31], defects can be cohesive between coating layers or stickers on interfaces.

Table 4 shows the average Pull-Off tensile strength values of the TS and NP samples after the immersion tests.

The samples coated with $Nb_2O_5$ applied by thermal spray (TS) presented a significant variation in the results of Pull-Off tensile strength after the immersion tests, with values lower than observed in the literature for $Nb_2O_5$ coatings applied by the Flame Spray method[33,34].

The samples submitted to the most aggressive immersion condition, C6 (80° C, 1440 h), showed the least resistance to Pull-Off tensile strength between the samples coated with $Nb_2O_5$ applied by thermal spray (TS). This reduction in resistance may result from the formation of blisters and nucleation corrosion after carrying out the immersion test. Although the Pull-Off tensile strength values were lower than in the literature, the TS samples presented an average Pull-Off traction resistance value higher than the samples coated with epoxy-$Nb_2O_5$ (NP) paint, as described in Table 4. The NP samples showed relaxation in the immersion region, making it impossible to test the resistance to pull-off traction in this area. The test was carried out in the region exposed to the steam phase. Despite showing less resistance to traction, the NP samples showed, in their majority, adhesive defects of type B/Y, this sort of failure indicates that the paint remained in the metallic substrate.

The Pull-Off traction resistance test was also performed on the TS and NP samples after the in-situ test under the conditions set out in Table 3. The average values are shown in Table 5.

The TS samples tested in-situ showed, in their majority, cohesive defects in the coating, in which a failure inside the coating was observed after the tensile test. The Pull-Off traction resistance values of the TS samples after the in-situ test (Table 5) were much higher than those observed after the immersion test. The mechanical resistance on the samples submitted to the C7 condition was not analyzed because these samples showed accelerated degradation of the coatings (TS and NP). It was possible to verify a variation in the Pull-Off tensile strength resistance values under the conditions tested in-situ and the reference condition (Table 5). According to the literature[31,34,35], the variation in the resistance values to pull-off traction may result from different factors such as the heterogeneity of the coatings, the preparation of the metallic substrate, the application of the coating, or the degradation of the unfused surface layer of $Nb_2O_5$.

When submitted to high-temperature microclimate (C11), both the coatings (TS and NP) showed adhesive defects with coating removal. These failures indicate a reduction in coating adhesion, which can damage the coatings. After the test, however, no corrosion was detected in the metal substrate. This result corroborates with a visual and microscopic evaluation that the niobium coating in an environment without fluoride acid was not affected by corrosion during the period tested, even when exposed to high temperatures.

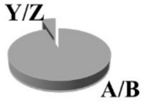
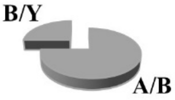
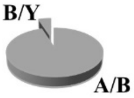
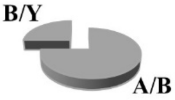
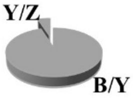
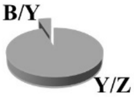
## 4. Discussions

### *4.1. Analysis of the degradation of coatings after immersion test*

Resistance to corrosion of anti-corrosion coatings depends on several factors, including the preparation of the metal substrate, the type and application of the coating, and the exposure conditions such as temperature and presence of chemical agents.

After the acid immersion test with the niobium pentoxide-based coatings, the results showed that both $Nb_2O_5$ applied by

**Table 4.** Adhesion resistance of $Nb_2O_5$ based coatings applied by thermal spray (TS) and epoxy-$Nb_2O_5$ paint (NP) after the immersion test.

| Conditions | Pull-Off | | Conditions | Pull-Off | |
|---|---|---|---|---|---|
| | Tensile Strenght (MPa) | Failure nature | | Tensile Strenght (MPa) | Failure nature |
| TS REF | 12.57 ± 1.880 |  | **NP REF** | 6.8 ± 1.980 |  |
| TS C1 | 10.62 ± 1.250 |  | **NP C1** | 7.1 ± 1.558 |  |
| TS C2 | 9.12 ± 0.450 |  | **NP C2** | 5.3 ± 0.570 |  |
| TS C3 | 9.06 ± 0.980 |  | **NP C3** | 7.0 ± 0.754 |  |
| TS C4 | 9.13 ± 1.790 |  | **NP C4** | - | - |
| TS C5 | 9.82 ± 1.460 |  | **NP C5** | 7.9 ± 1.970 |  |
| TS C6 | 7.39 ± 1.770 |  | **NP C6** | 6.0 ± 0.123 |  |

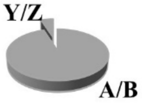
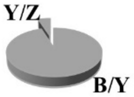
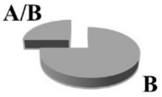
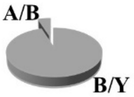
thermal spray (TS) and epoxy-$Nb_2O_5$ (NP) showed defects in the immersion region after the test, even at room temperature.

Both coatings showed a change in tonality in the region immersed in the acid solution after the test was performed. This behavior was more evident in the tests carried out at high temperatures. This change, already reported in the literature[26,36,37], can be associated with changes in the surface morphology caused by chemical agents, such as sulfuric acid and/or physical agents, such as temperature. The epoxy resin present in the coatings plays different roles. While in the NP samples, the epoxy resin is the vehicle of the paint responsible for checking the barrier property, in the TS samples, this resin was applied to reduce the porosity of the coating produced by the thermal spray process.

Besides the thermal degradation of the epoxy resin, contact with humidity and temperature increases the free volume of the polymer chains of the epoxy resin, facilitating penetration of water and consequently reducing the barrier property. This behavior occurs because standard resins do not show sufficient resistance when used in environments with high humidity and temperature[37-40].

Under these conditions, the paints can show pores and channels that act as an open path for the electrolyte to reach the substrate[40]. This model describes the degradation process of coatings involving the spontaneous formation of conduction paths through the coating by hydrolysis reactions, followed by the start of corrosion. According to Morsch et al.[40], the coatings can contain intrinsic "hydrophilic" regions or

**Table 5.** Adhesion resistance of $Nb_2O_5$ based coatings applied by thermal spray (TS) and as epoxy-$Nb_2O_5$ paint (NP) after the in-situ test.

| Conditions | Pull-Off | | Conditions | Pull-Off | |
|---|---|---|---|---|---|
| | Tensile Strenght (MPa) | Failure nature | | Tensile Strenght (MPa) | Failure nature |
| TS REF | 12.57 ± 1.880 |  | **NP REF** | 6.8 ± 1.980 |  |
| TS C8 | 23.10 ± 3.040 |  | **NP C8** | 8.720 ± 1.890 |  |
| TS C9 | 19.65 ± 2.190 |  | **NP C9** | 8.480 ± 0.147 |  |
| TS C10 | 20.08 ± 2.000 |  | **NP C10** | 8.497 ± 0.580 |  |
| TS C11 | 14.70 ± 4.620 |  | **NP C11** | 9.750 ± 1.547 |  |

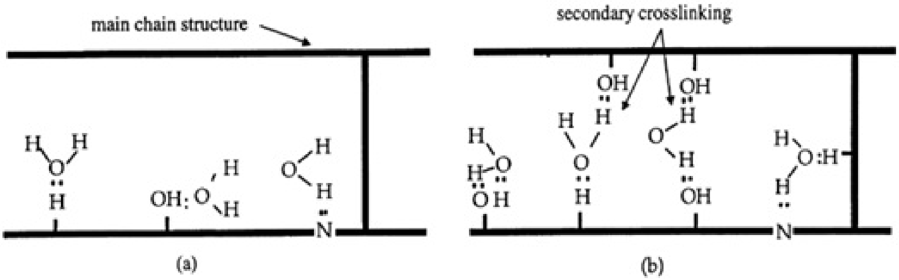


**Figure 9.** Illustrative scheme of possible water bonds with the epoxy resin polymer chains as proposed by Zhou and Lucas[37].

regions with a low density of reticulation within the polymer network, where the transport of water and ions occurs freely. Thus, it is believed that corrosion starts when the polymer tension relaxation joins up with these hydrophilic regions to create a sticking path through the coating.

Zhou and Lucas[37] explain the degradation of the epoxy resin by forming two types of hydrogen bonds by the water absorbed when subjected to high humidity and temperature environments. Figure 9a shows a unique hydrogen bond between the water network and the epoxy, corresponding to Type I water. Type I water diffuses into the polymer chains of the epoxy resin and disturbs the forces of van der Waals, resulting in greater mobility and swelling of the chain following. In this case, the water acts as a plasticizer. Figure 9b shows the model when the water molecules form multiple hydrogen bonds with resin polymer chains. In this case, Type II connected water formation has higher activation energy and is more difficult to remove by desorption. The authors state that the increase in temperature results in an increase in the free volume of the coatings, facilitating the entry of water into the material. The ingress of water promotes the plasticizing of the material by breaking van der Waals bonds. Still, it can also form multiple hydrogen bonds with the polymer chains, making the material hardened.

The results of the lab immersion test showed that the $Nb_2O_5$ coating applied by thermal spray (TS) had a lower incidence of defects compared to the samples of the epoxy-$Nb_2O_5$ (NP) paint, as shown in Figure 1 and Figure 3. It was possible to note a pattern in the formation and propagation of defects in both coatings: the beginning of the formation of the defects occurred at the edges of the samples, the defects concentrated in the immersion region of the samples without propagation of the defects for the region exposed to the steam phase.

The incidence of defects in the extremities of the samples reflects the difficulty of access for the proper preparation of the surface and an inefficient coating layer application. Thus, when analyzing these regions in laboratory tests, care must be taken as these defects make it difficult to perform and correctly interpret the results.

A thickness reduction of the samples coated with $Nb_2O_5$ by thermal spray (TS) after the immersion test in the laboratory was observed, as shown in Figure 2. The process of applying the thermal spray coating using the Flame Spray method is characterized by factors such as low acceleration of the particle, a lower deposition temperature, and inadequate control of the surrounding atmosphere. These factors may lead to a more significant formation of porosity, interlacing cracks, the formation of oxide, low cohesion between the spills, and lower adherence to the metallic substrate[8,14,41-43]. Thermal treatments are generally employed to improve the properties of the coatings produced by thermal spray. In this work, an attempt was made to minimize the adverse effects of the porosity of the coating based on $Nb_2O_5$ by applying a layer of epoxy resin sealant. However, as already discussed, this layer could not confer the coating the appropriate barrier property when immersed in acid solution. Exposure of the coating over time in an acid solution with temperature also reduced the Pull-Off traction resistance of the TS samples, as shown in Table 4. Studies reported that the change and adjustment of the parameters for applying the coating by thermal spray could reduce the porosity and increase the adhesion force of the coating to the metallic substrate[30,36,37].

The failures observed in the epoxy-$Nb_2O_5$ (NP) paint samples after the laboratory immersion test started and spread due to the inefficient layer on the edges of samples. These unprotected regions allowed the solution to penetrate the coating, leading to the formation of blisters and the removal of the paint. Through Figure 3 analysis, it is possible to infer that NP samples anti-corrosive behavior were affected by the increase in temperature, with a higher incidence of blisters, and a marked change in the tonality of the paint. At room temperature, however, the NP samples show no defects. Serenario et al.[26] carried out immersion tests in the laboratory with acid and saline solutions for 3000 hours at room temperature and did not verify failures in the epoxy paint - $Nb_2O_5$. The epoxy paint - $Nb_2O_5$ also showed no defects after 3500 hours of testing in chambers with 100% moisture and salt spray.

Although both tested coatings showed defects after the test in the immersion region, these defects did not propagate to the region exposed to the steam phase. These results may indicate that the $Nb_2O_5$-based coatings show good anti-corrosive behavior when exposed to environments exposed to the corrosive atmosphere in a vapor phase. However, this coating should be reconsidered for immersion application, and attention should be given to good surface preparation and optimizing the application of the coatings to obtain satisfactory results.

## *4.2. Analysis of the degradation of coatings after in-situ testing*

Testing coatings under actual operating conditions is essential and provides practical results in the medium and long term. The niobium-based coatings showed excellent results after the tests were carried out on almost all the selected microclimates of the chemical industry. The samples submitted to the C7 microclimate (Figure 5 and Figure 7) were removed after 168 hours of exposure. Both the $Nb_2O_5$ coating applied by thermal spray (TS) and the epoxy-$Nb_2O_5$ (NP) paint showed high degradation leading to the interrupting of the test. This degradation can be attributed to the characteristics of the microclimate: the presence of hydrofluoric acid in the gas phase closed environment and a temperature of 70 °C.

Niobium pentoxide ($Nb_2O_5$) is widely used due to its unique chemical and physical characteristics, such as high chemical stability, high resistance to corrosion in acidic and alkaline media, and good optical and electrical characteristics[22,33,44,45]. However, niobium and tantalum pentoxide reacts with hydrofluoric acid forming the soluble fluorides $H_2NbF_7$ and $H_2TaF_7$, respectively, as shown in the following reactions[27].

$$Ta_2O_5 + 14HF \rightarrow 2H_2TaF_7 + 5H_2O \tag{4}$$

$$Nb_2O_5 + 14HF \rightarrow 2H_2NbF_7 + 5H_2O \tag{5}$$

The presence of hydrofluoric acid triggers the lixiviation of the niobium pentoxide, leading to its degradation 26 as observed in the TS samples (Figure 5). However, the NP samples did not show corrosive errors due to the lixiviation process. According to Serenario et al.[26], the resistance of the paint to this process may be due to the formulation of the paint, which, in addition to the niobium pentoxide pigment, responsible for chemical stability, has the addition of the epoxy resin, which gives the property of the paint barrier. In the case of the epoxy paint-$Nb_2O_5$ (NP), film degradations occurred due to the adhesion and application defects at the edges, resulting in paint peeling and consequent degradation of the metallic substrate.

The two coatings based on $Nb_2O_5$ (TS and NP) showed excellent anti-corrosive behavior when exposed to the C8 and C9 microclimates, with the presence of CaO and organic solvent, respectively. The presence of some marks and changes in tonality was observed but without defects such as blisters and flaking. The TS sample showed a more accentuated color change when submitted to the C10 microclimate, where HF- is present. However, the concentration of hydrofluoric acid in this environment is residual and has not caused the lixiviation process of the niobium pentoxide. When submitted to the microclimate with a high temperature of C11, both coatings (TS and NP) showed good mechanical behavior, with the occurrence of defects not observed after the exposure period.

The occurrence of adhesive defects in the Pull-Off tensile strength test in the TS and NP coatings indicates that there has been a reduction in the adherence of the coating. Adherence failure was not desirable in an anti-corrosive coating. Even in the samples where adhesive defects on the coating were observed, corrosion points in the metallic substrate were not verified at any of the tested coatings.

The results obtained in the in-situ test showed that both niobium-based coatings showed an excellent anti-corrosive performance when submitted to conditions in-situ, and have shown promising results even when submitted to higher temperatures. This response of the niobium-based coatings to the aggressive environments of the chemical industry is very significant. It represents a possible reduction in the cost of applying and maintaining the coating. In the chemistry industry, where coatings were tested, commercial paint is used to cover most structures and equipment. However, every six months, it is necessary for the painting to be redone. The results obtained in this study show the anti-corrosive efficiency of TS coating and NP paint in environments with acid and basic contaminants.

### 4.3. Niobium pentoxide as an anticorrosive pigment

The excellent resistance to the corrosion of the metallic niobium in different media is attributed by literature to the presence of a film with a stable oxide surface, protector, and strongly adherent ($Nb_2O_5$) that is instantly formed in the air[23,25]. According to the Eh-pH diagram proposed by Pourbaix (Figure 10a), the chemical inertia of the niobium and its oxides is one of the primary points that make it a pigment highly efficient to support various aggressive media at room temperature[20,23,46]. However, the niobium Pourbaix diagram covers a limited pH range in water and room temperature. These conditions cannot be taken as a reference for analyzing oxide formation in acidic or temperature media.

To verify the behavior of the metallic niobium when submitted to environments with temperature, Asselin et al.[47] developed an Eh-pH diagram for the metallic niobium in mediums at 25° C, 75° C and 95° C. The diagram proposed (Figure 10b) includes stability regions for $NbO_3^-$ (methanobate) and $Nb(OH)_4^+$ (anthhydroxide). According to the authors, although the metallic niobium forms a passive film at temperatures below 95°C when exposed to concentrated solutions of HCl and $H_2SO_4$, it undergoes the corrosion process generated by the competition involving Nb oxidation in $Nb_2O_5$ and the chemical dissolving of $Nb_2O_5$ in $Nb(OH))_4^+$.

Also, according to Asselin et al.[47], as the temperature increases, the methaniobate stability region ($NbO_3^-$) increases, and the chemical balance between $Nb_2O_5$ and $NbO_3$- increases to more acidic values. The dissolution of $Nb_2O_5$ in strongly acidic solutions may be the reason for the formation of niobium tetrahydroxide ($Nb(OH)_4^+$). The dissolving reaction in acid solutions (at pH below 0.5 to 25°C) could then proceed as a chemical dissolution of metastable niobic pentoxide (Equation 1) or an electrochemical dissolution of niobic dioxide (Equation 2).

$$Nb_2O_5 + 3H_2O + 2H^+ = 2Nb\left(OH\right)_{4^+} \quad \text{(Eq.1)}$$

$$NbO_2 + 2H_2O = 2Nb\left(OH\right)_{4^+} + e^- \quad \text{(Eq.2)}$$

Santandrea et al.[48] developed a study through computer simulation of Eh-pH diagrams for the niobium in different media, with the addition of sulfur (S), sodium chloride (NaCl), and variation of the temperature. The simulations generated by his work evidenced the appearance of stable chemical species such as the NbS, $NbS_2$, and $NbO_2Cl$ (Figure 11). The authors pointed out that it is necessary to study the kinetics for their formation or see if these species are formed under simulated conditions.

Although different Eh-pH diagrams for niobium have been proposed over the years, in practice, most of the situations found in the field are very likely to fit in the classical Pourbaix diagram[23] with the Nb, NbO, $NbO_2$, and $Nb_2O_5$ species, i.e., with a wide range of stable and passive $Nb_2O_5$ film formation.

The defects observed in the TS and NP samples can be associated with other factors such as the preparation of the samples that can cause the coatings to detach, the defects of the resin used as a sealant in the TS samples, and as a

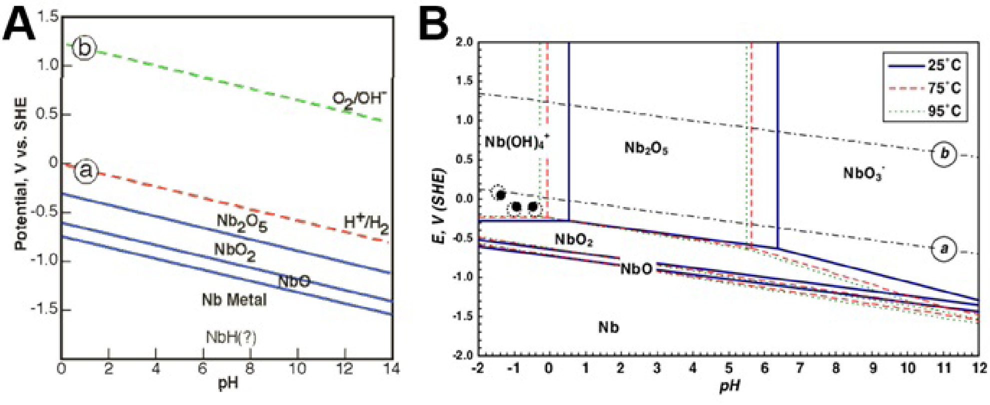


**Figure 10.** A) Eh-pH diagram of the Nb-$H_2O$ system at 25 ° C and 1 atm pressure according to Pourbaix (RICKER, 2009); B) Eh-pH diagram for the Nb-$H_2O$ system at 25, 75 and 95 ° C. (•) represents the corrosion potential at 75 ° C and (○) represents the potential at 95 ° C, according to Asselin et al.[47]

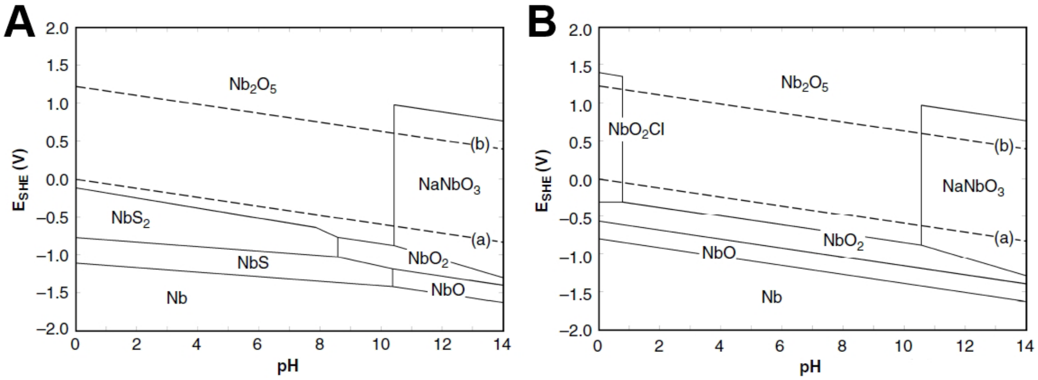


**Figure 11.** E-pH diagrams for Nb species in the A) Nb-Na-S-H2O system at 25°C, concentrations: niobium 10-6 mol/L, sodium 0.22 mol/L, and sulfur 0.20 mol/L; B) Nb-Na-Cl-H2O system at 25°C, concentrations: niobium 10-6 mol/L, sodium 0.16 mol/L, and chlorine 0.17 mol/L (Santandrea et al.[48]).

matrix in the NP samples, as well as being associated with defects in the application of the coatings.

## 5. Conclusions

The objective of this research was to conduct a comparative analysis of the performance of different $Nb_2O_5$-based coatings. Lab and in-situ tests were conducted. As a result, the following conclusions were drawn:

- The defects originated at the edges of the specimen, and the application of an inefficient layer of the coatings in this region may be responsible for the defects.
- The increase in the temperature during the laboratory immersion test brought about more significant degradation in both coatings, resulting in the formation of blisters, cracks, and a reduction in Pull-Off tensile strength.
- There is no evidence of the propagation of the defects from the immersion region to the vapor region.
- The combination of humidity and temperature can cause a degradation of the epoxy resin, thus reducing the barrier property of the coating.
- The $Nb_2O_5$ coating applied by thermal spray (TS) showed more excellent resistance to corrosion in a medium with humidity and temperature. Still, it is necessary to optimize the application parameters and select a sealant compatible with the application to reduce the porosity of this coating.
- In environments with fluoride acid (HF), niobium pentoxide undergoes the lixiviation process. In these environments, the epoxy-$Nb_2O_5$ paint showed greater resistance to corrosion than the coating applied by thermal spray. The outstanding behavior is because niobium pentoxide acts on an epoxy resin matrix in the case of paint.
- Factors such as the preparation of the metal substrate and the coating application are essential to ensure good anti-corrosive performance.

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