

25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019-0488

DEVELOPMENT AND USE OF COMPOSITE Nb₂O₅|Al AS COATING APPLIED BY THERMAL SPRAY ON 1020 AISI STEEL PROTECTION AGAINST CORROSION CAUSED BY SOIL IN BURIED STRUCTURES

Oscar Regis Junior

Sandra Mara Kaminski Tramontin

Luciano Augusto Lourenço

Department of Mechanics, Federal Technological University of Paraná, 84016-210, Ponta Grossa, PR, Brasil
regis@utfpr.edu.br, stramontin@utfpr.edu.br, lalouren@utfpr.edu.br

José Maurílio da Silva

Department of Research Civil Engineering, Institute of Technology for Development, CP19067, 81531-900, Curitiba, PR, Brazil

Ramon Sigifredo Cortes Paredes

Department of Mechanics, Federal University of Paraná, CP19011, 81531-9000, Curitiba, PR, Brazil

Abstract. *In this study the Nb₂O₅|Al corrosion resistance coating was developed and applied using a powder flame spray process on a AISI 1020 steel substrate. A galvanostatic electrochemical technique was employed with and without ohmic drop, in four different soils. These soils presented two different behaviors with respect to corrosiveness, two aggressive and two less aggressive. In order to compare the behavior of the coatings in different soils a cathodic hydrogen reduction reaction (equilibrium potential, overvoltage and exchange current density) was studied with emphasis on the effect of the ohmic drop.*

Keywords: *soil corrosion, surface coating, Nb₂O₅ coat.*

1. INTRODUCTION

Galvanizing buried structures normally confers reasonable protection against corrosion by the soil for several years but when they are in highly corrosive soils such protection becomes ineffective long before the end of their useful life.

Soil is a collection of natural bodies made up of three-dimensional and dynamic solids, liquids and gases, which are formed by mineral and organic materials that occupy most of the mantle surface of the continental extensions of the planet (EMBRAPA SOLOS, 1999). Their properties have a great influence on the electrochemical corrosion of buried metallic structures in light of the changes that can be observed in the anodic and cathodic processes. This influence can be caused by physical, chemical and biological, specific aggressiveness, properties as well as external factors, relative aggressiveness (Ferreira, C.A.M. et al., 2007).

Specific aggressiveness is closely linked to local properties such as resistivity, humidity, acidity or alkalinity, permeability and the presence of soluble salts and microorganisms. Relative aggressiveness is related to external factors such as current leakage and contact between different metals (Serra, E.T., 2006). These factors may act together and, for this reason, the corrosivity of soils is evaluated simultaneously for various physicochemical parameters, according to criteria in the literature (Silva, J.M and Brasil, S.L.D.C., 2009; Trabaneli, G. et al, 1972; Booth, G.H. et al 1967; Girard, R., 1970; Stratfull, R.F., 196; Department of Transportation, 1999).

Complementing the existing surface protection systems for buried structures, it was decided to evaluate the Nb₂O₅|Al composite as a surface coating applied by flame spray (FS), because of the versatility of this process.

The choice of the Nb₂O₅|Al composite was based on the characteristics of its constituent elements. The Nb₂O₅ is characterized by the formation of non-porous, stable, compact films with low dissolution and high resistance to corrosion in a wide variety of environments (Metals HandBook, 1987). In addition, the element aluminum (Al) it's resistance to corrosion is strictly related to the protective quality of the layer or film of aluminum oxide formed on its surface (passivation), (Rodríguez, R.M.H.P, 2003).

The FS process, which is used for the application of materials in powder form, has been well discussed in the literature (Habib, K.A. et al, 2006; Cano, C. et al, 2006; Uyulgan, B. et al, 2007; Cano, C. et al, 2008; Bandyopadhyay, P.P., 2008) and was used in this study to develop and validate a surface protection (based on Nb₂O₅|Al composite material) against the erosion processes on AISI 1020 steel, for its application in different types of soils.

The experimental evaluation was performed by comparing the results obtained from electrochemical techniques of uncoated AISI 1020 steel with AISI 1020 steel coated with Nb₂O₅|Al composite in four different soils. These were previously characterized according to criteria in the literature (Silva, J.M and Brasil, S.L.D.C., 2009; Trabaneli, G. et al, 1972; Booth, G.H. et al 1967; Girard, R., 1970; Stratfull, R.F., 196; Department of Transportation, 1999).

2. EXPERIMENTAL

The particle size of the Nb₂O₅|Al composite powder was established as being between 44µm and 63µm in diameter and its final composition was prepared using equal quantities of mass of the relevant powders (Regis Junior, O., 2010).

To ensure proper adhesion of the coatings to the substrate the surface was prepared so that when the particles were projected, at the moment of impact they would totally adhere and they would be entirely free from residual impurities (Kanouff, M.P. et al, 1998).

A METCO 6P-II pistol was used in the spray process under the conditions specified in Table 1. It was attempted to achieve an average thickness of 250-450 µm per deposited layer.

Table 1. Parameters used in the FS process for the application of the Nb₂O₅|Al composite on AISI 1020 steel (Regis Junior, O., 2010).

Variables	Pre-heating	Distance of projection	Flow O ₂	Flow C ₂ H ₂	Flow N ₂	Feed rate	Air pressure
Values	120 °C	150 mm	55[*1]	45[*2]	15[*3]	30 g/min	60 psi

[*1] 55 = 106.82 feet³/h # [*2] 45 = 87.41 feet³/h # [*3] 15 = 29.14 feet³/h

Four soil types were studied, and for their ratings and their aggressiveness (aggressive or less aggressive) there was the need for experimental determination of the parameters recommended in the literature (Habib, K.A. et al, 2006; Cano, C. et al, 2006; Uyulgan, B. et al, 2007; Cano, C. et al, 2008; Bandyopadhyay, P.P., 2008).

In terms of physical and chemical parameters, the following were studied: soil resistivity as a function of the amount of added water; conductivity; the pH and surge of hydrogen in conditions of minimal resistivity (evaluated as total acidity); the concentration of sulphate and chloride. For electrochemical parameters, the rest potential (E_{Rep}) of the steel in the medium; cathodic potentiodynamic curves and the current density (i_p) required for protection of the specimen, respectively.

The effectiveness of the sprayed material was analysed by electrochemical techniques to obtain the polarisation curves of carbon steel, with and without coating and immersed in four different soil types, using the electrochemical parameters of reduction of hydrogen, experimentally obtained and complemented through the literature (Panossian, Z., 2008; Silva J.M., 1994).

The measurements of E_{Reps} with time were obtained by immersion of the reference electrode (copper/saturated copper sulphate) and the working electrode (AISI 1020 carbon steel with and without the coating of the Nb₂O₅|Al composite) in the four studied soils, each within an electrochemical cell at ambient temperature. With the aid of a multimeter, data were collected of these potentials relative to the reference electrode and as a function of time. The results were presented in a graphical form and analyzed.

For the construction of the electrochemical curves, using galvanostatic techniques with and without ohmic fall, an increase of current injected by galvanostat/potentiostat, model EG&G PARC 175 and an EG&G PARC 175 universal programmer, was performed to obtain the potentials in closed circuit conditions (E_{on}) for each increment

After E_{on} stabilization, it was necessary to obtain the potentials in E_{off} open circuit conditions for each current increment. Therefore, the interruption of injected current was performed by galvanostat (Glass, G.K, 1999). With this interruption, the E_{on} dropped sharply to a certain value, passing to a slight stabilization over time. The E_{off} value reading was considered to be the first resultant potential immediately after turning off the galvanostat key. For each increment in current, the E_{off} potential was measured. Having obtained the E_{off} values, the graphical part of the potentiodynamic polarization was carried out under conditions of closed and open circuit (potentials due to the increased current density).

Based on the physicochemical parameters of the soils and the criteria in the literature, they were classified into aggressive (A and B), and less aggressive (C and D).

The Nb₂O₅|Al coating provided better protection for the AISI 1020 steel, resulting in an increased ohmic drop and overvoltage of hydrogen values that were more positive in all soils, except soil "A" (-68mV).

The value of the density of the protection current afforded by the coating was less than that of the uncoated steel for all soils, possibly due to the dissolution of aluminum in the studied soils.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of soils

After completion of the laboratory tests, it was possible to analyze the aggressiveness of the soils based on existing criteria in the literature (Silva, J.M and Brasil, S. L. D.C., 2009; Trabaneli, G. et al, 1972; Booth, G.H. et al 1967; Girard, R., 1970; Stratfull, R.F., 196; Department of Transportation, 1999). The summary of the values obtained are shown in Table 2 for soils A, B, C and D. From these values, the soils were classified as: **aggressive**: “A” due to high acidity; and “B” due to the resistivity value obtained in saturated conditions and, **slightly aggressive**, “C” and “D”.

Table 2. Physicochemical results used for soil classification (Regis Junior, O., 2010)

PARAMETERS	Soil			
	A	B	C	D
Minimum resistivity ($\Omega.m$)	14	40	110	350
Chloride (mg/Kg)	40	3	60	10
Sulphate (mg/Kg)	15	5	< 1	10
pH	4.18	5.73	5.87	5.85
Water content (%)	44	30	24	31
Saturation humidity (%)	38	44	39	28
Total acidity (meq/l)	1.84	0.08	0.08	0.08

3.2 Electrochemical characterization of the Nb₂O₅/Al composite

3.2.1 E_{rep} vs Cu/saturated Cu(II) reference electrode

The Figure 1 shows the profile of the behavior of the E_{rep} variation of coated and uncoated AISI 1020 carbon steel (Nb₂O₅/Al) placed in soils saturated with H₂O and dependent on insertion time. Note that the AISI 1020 steel showed a E_{rep} variation in the most cathodic sense in relation to its initial potentials after immersion in each soil. A similar phenomenon can be observed in the AISI 1020 steel coated with the composite Nb₂O₅/Al subjected to "A" and "B" soils (aggressive).

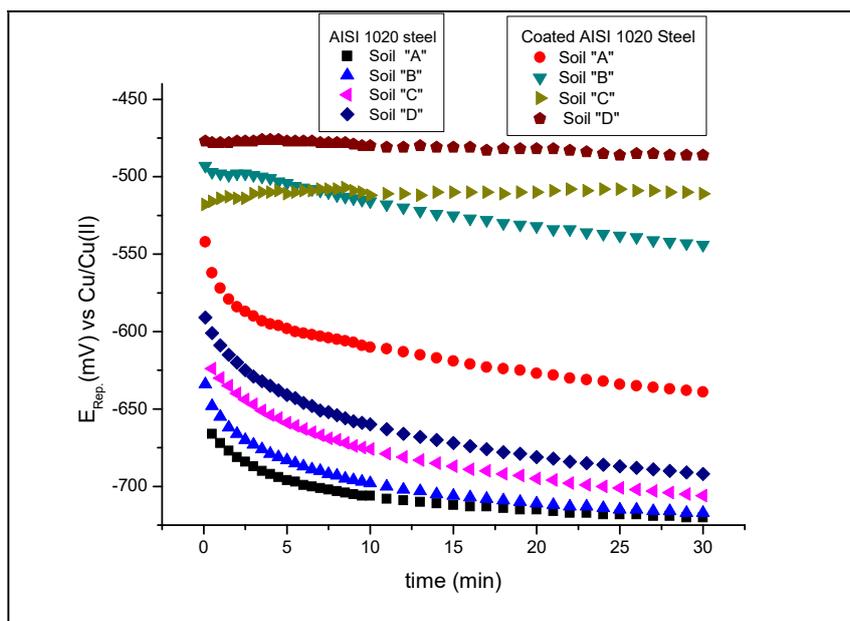


Figure 1. Rest potentials (E_{rep}) of coated and uncoated AISI 1020 carbon steel (Nb₂O₅/Al) for the soils saturated with H₂O E_{rep} vs Cu/Cu(II) (Regis Junior, O., 2010).

When analyzing the AISI 1020 steel in soils, it was observed that the initial potential and the E_{rep} after 30 minutes were related to the pH and resistivity of the soil. The greater the amount of soil resistivity, the less negative was the value of the initial potential. For the more resistive soils, it was found that there was a greater variation in the cathodic sense of the potential of the steel.

The soil "D" showed the highest minimum resistivity, 350 Ω .m. This explains the greater variation in the evolution of the potentials of the steel in this soil.

The E_{rep} of the AISI 1020 steel coated with the Nb₂O₅/Al composite showed a slight trend to more positive values in the soil "C", which seems to be an indication that the aluminum was oxidizing, forming a passive film on the surface and modifying to its exposed area with the passage of time. In the soil "D", the E_{rep} of coated AISI 1020 steel hardly evolved.

When analyzing the coated steel in the soils, it was observed that the initial potentials and E_{Rep} (after 30 min) showed less negative values than the initial potentials and rest values of the uncoated AISI 1020 steel. This indicates that the coating provided protection to the substrate against corrosion by the soil.

3.2 Electrochemical characterization of the cathodic reaction of hydrogen reduction

3.2.1 Overvoltage of hydrogen (η_{H_2})

The table 3 presents the values of the hydrogen overvoltage of AISI 1020 and the coating in the studied soils. These values were obtained by the electrochemical parameters of the cathodic reaction of hydrogen reduction for a E_{Rep} of 30 minutes exposure.

Table 3. Values of the hydrogen overvoltage obtained by electrochemical parameters of cathodic reaction of hydrogen reduction of the coatings and of the AISI 1020 steel for E_{rep} in a time of 30 min. exposure in the respective studied soils (Regis Junior, O., 2010)

		Soils			
		Agressive		Less aggressive	
		A	B	C	D
AISI1020 steel	$E_{rep,t=30}^{steel}$ (mV)	-722	-717	-706	-692
	$\eta_{H_2, E_{Re p, t=30}}^{steel}$ (mV)	-151	-53	-34	-21
Composite	$E_{rep,t=30}^{Nb_2O_5/Al}$ (mV)	-639	-544	-511	-486
	$\eta_{H_2, E_{Re p, t=30}}^{Nb_2O_5/Al}$ (mV)	-68	120	161	185

Using the E_{rep} of AISI 1020 ($E_{rep,t=30}^{A_{Co}}$) in a 30 minute, time period to obtain the hydrogen overvoltage ($\eta_{H_2, E_{Re p, t=30}}^{A_{Co}}$), it was observed that the results showed that this presented a negative overvoltage for all soils. Analyzing these values starting from the E_{rep} of the steel coated with the Nb₂O₅/Al ($E_{rep,t=30}^{Nb_2O_5/Al}$) composite, it was observed that the overvoltage ($\eta_{H_2, E_{Re p, t=30}}^{Nb_2O_5/Al}$) became positive for all the coatings in all soils, except soil "A" (-68mV). The positive and less negative values of the hydrogen overvoltage obtained for the coated steel, which is the parameter related to the reduction of hydrogen ions existing in soil moisture, showed that the coatings provided better protection against corrosion for the steel in the soil.

3.2.2 Exchange current density of hydrogen (i_{H_2/H^+}^0)

The value (i_{H_2/H^+}^0) of steel exposed to sea water is 0.1 μ A/cm² and in drinking water it is 1 μ A/cm² (Panossian, Z., 2008; White, R.E. et al, 1983). This proves that in the most aggressive medium, with the exception of soil "B", the exchange current density was lower. This fact was verified with the steel and the coating when exposed to the soils listed in Table 4. The value of (i_{H_2/H^+}^0) for the steel coated with the composite was obtained in a manner similar to that

conventionally adopted for steel without coating. Although the reaction zone is not the same, the values obtained showed a high similarity.

Table 4. Summary of the values of exchange current density of hydrogen obtained by electrochemical parameters of the cathodic reaction of hydrogen reduction of and uncoated steel and coating with Nb₂O₅|Al (Regis Junior, O., 2010)

	Soils			
	Aggressive		Less aggressive	
	A	B	C	D
	i_{H_2/H^+}^0 ($\mu A/cm^2$)			
AISI 1020 steel	5.4	28.2	19.5	12.6
Nb ₂ O ₅ Al	5.4	28.1	17.4	10.5

3.3 Corrosion potential (E_{corr})

The table 5 shows the E_{corr} values for the AISI 1020 steel and the steel coated with the Nb₂O₅|Al composite in the different studied soils. This table also presents the ohmic drop verified in the systems. The difference between the E_{Rep} and the E_{corr} provided the value of the ohmic drop (IR) in the system.

Table 5. Values of corrosion potentials (E_{corr}) and the ohmic drop (IR) of uncoated AISI 1020 steel and AISI 1020 steel coated with Nb₂O₅|Al composite in soils (Regis Junior, O., 2010)

	Soils			
	Aggressive		Less aggressive	
	(A)	(B)	(C)	(D)
	E_{corr} (mV)	E_{corr} (mV)	E_{corr} (mV)	E_{corr} (mV)
AISI 1020 steel	-797	-755	-768	-780
Nb ₂ O ₅ Al	-828	-757	-773	-772
	IR (mV)	IR (mV)	IR (mV)	IR (mV)
AISI 1020 steel	75	38	62	88
Nb ₂ O ₅ Al	189	213	262	286

Also shows that the E_{corr} of the steels coated with the Nb₂O₅|A composite in the studied soils was more cathodic than that of the uncoated steel, with the exception of soil "D". For this examination, it was observed that there was a variation of the ohmic drop for the uncoated steel and the steel coated with Nb₂O₅|Al buried in the four soils. This ohmic drop was directly related to the resistivity of the soils.

For soil "D" ($\rho_{min} = 350 \Omega.m$) the largest ohmic drop was observed in both the uncoated steel (88 mV) and the steel coated with composite (286 mV).

Thus, it follows that the Nb₂O₅|Al coating on the steel buried in the four soils presented an increase in ohmic drop, confirming the efficiency of the coating.

3.4 Current density for the protection of steel and coatings in the soil (i_p^{IR}) with the interference of the ohmic drop in the reduction processes

The Table 6 shows a summary of the (i_p^{IR}) values of the steel with and without coating in the studied soils.

Table 6. Summary of the values of the current density required for protection of steel and coatings in soils (Regis Junior, O., 2010)

	Soils			
	Aggressive		Less aggressive	
	A	B	C	D
	$i_p^{IR} (\mu A/cm^2)$	$i_p^{IR} (\mu A/cm^2)$	$i_p^{IR} (\mu A/cm^2)$	$i_p^{IR} (\mu A/cm^2)$
AISI 1020 steel	16.7	128.0	43.0	25.9
Nb ₂ O ₅ Al	9.9	61.6	39.9	21.4

When comparing the Nb₂O₅|Al coatings with uncoated steel in the soils it was observed that there was no improvement in relation to the uncoated steel, when assessed by this parameter, because it gave a lower current density required for protection. One of the likely factors for this decrease in i_p^{IR} values in the coated steels is the possible dissolution of aluminum in the studied soils.

4. CONCLUSION

Based on the physicochemical parameters of the soils and the criteria in the literature, they were classified into aggressive (A and B), and less aggressive (C and D).

The Nb₂O₅|Al coating provided better protection for the AISI 1020 steel, resulting in an increased ohmic drop and overvoltage of hydrogen values that were more positive in all soils, except soil "A" (-68mV).

The value of the density of the protection current afforded by the coating was less than that of the uncoated steel for all soils, possibly due to the dissolution of aluminum in the studied soils.

5. ACKNOWLEDGMENTS

The technical team would like to thank the UTFPR/PG, UFPR, Fundação Araucária, CNPq and the , Institute of Technology for Development - LACTEC.

6. REFERENCES

- Bandyopadhyay, P.P.; Hadad, M.; Jaeggi, C.; Siegmann, St.; *SCTEEJ SM*. 2008, 203, 35.
- Booth, G.H.; Cooper, A.W.; Cooper, P.M.; Wakerley, D.S.; *British Corrosion Journal* 2. 1967, 104,7.
- Cano, C.; Garcia, E.; Fernandes, A.L.; Osendi, M.I.; Miranzo, P.; *Journal of the European Ceramic Society*. 2008, 28, 2191.
- Cano, C.; Osendi, M.I.; Belmonte, M.; Miranzo, P.; *SCTEEJ SM*. 2006, 201, 307.
- Department of Transportation; "Method for Estimating the Service Life of Steel Culverts – Test 643", 1999, California, US.
- EMBRAPA SOLOS; "Sistema Brasileiro de Classificação de Solos", Rio de Janeiro, Brasil, 1999.
- Ferreira, C. A.M.; Ponciano, J.A.C.; Vaitsman, D.S.; Pérez, D.V.; *STENDL 24/YR*. 2007, 308, 250.
- Girard, R., *Corrosion Trait. Protec. Fin.*, 1970, 18, 75.8.
- Glass, G. K.; *Corrosion* 55 (1999), doi:10.5006/1.3283989.
- Habib, K.A.; Saura, J.J.; Ferrer, C.; Damra, M.S.; Giménez, E.; Cabedo, L.; *SCTEEJSM*. 2006, 201, 1436.
- Kanouff, M. P.; NEISER Jr., R. A.; ROEMER, T. J.; *Journal of Thermal Spray Technology*. 1998, 2, 219.
- Metals HandBook – ASM; Vol.6, *Welding and Brazing and Soldering*, 8th ed., 1987.
- Panossian, Z.; *INTERCORR*, Recife, Brasil, 2008.

Regis Junior, O.; *Tese de Doutorado*, Universidade Federal do Paraná, Brasil, 2010.

Rodriguez, R.M.H.P; *Tese de Doutorado*, Universidade Federal do Paraná, Brasil, 2003.

Trabanelli, G., Zucchi, F., Arpaia, M., *PACHAS M*, 1972, 3, 43.

Serra, E. T.; *Corrosão e proteção anticorrosiva dos metais no solo*, CEPTEL, Rio de Janeiro, 2006.

Silva J. M.; *Tese de Doutorado*, Universidade Federal de São Carlos, Brasil, 1994.

Silva, J. M; Brasil, S. L. D. C.; *Corr. Prot. Mater.* 2009, 29, 1.

Stratfull, R. F., *CORRAK*, 1961, 17, 10.

Uyulgan, B.; Dokumaci, E.; Celik, E.; Kayatekin, I.; Ak Azem, N.F.; Ozdemir, I.; Toparli, M.; *Journal of Materials Processing Technology*. 2007, 190, 204.

White, R.E.; Bockris, J.O'M.; Conway, B.E.; *Modern Aspects of Electrochemistry*, 15th ed., Plenum Press: New York, 1983.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.