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Analysis of Corrosion Degradation of TiCrN Coatings Subjected to High Temperatures

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In order to provide a procedure for corrosive problems in industrial devices, Thin films of titanium chromium nitride were deposits onto 316LVM steel substrates using a multi target magnetron sputtering system with radio frequency, sources from Titanium and Chromium sputtering targets of high purity (99.99%). The corrosion analysis was performed by electrochemical impedance spectroscopy and Tafel polarization curves, where it is determined that the coatings are adhered to the substrate and evaluated in a solid solution at different temperatures ranging from 600°C to 700°C, The substrate and coatings morphology were performed by scanning electron microscopy (SEM) being a different topography for each one of the evaluated temperatures, this due to the corrosive effect and the high temperatures that generated processes of obtaining oxides as also of carbides due to the corrosive phenomenon of the coatings, the effect of the corrosive phenomenon was also determined by the change in the crystal structure as the temperature increases, XRD analysis were done on thin films samples, the change of microstructure changes due to defects such as porosities and cracks generates easy access connections for solid solution ions, which facilitates the entry into the coating-like material in contact with the corrosive salts.

Keywords: Coatings, corrosion, high temperatures, corrosive salts, magnetron sputtering.

1. INTRODUCTION

The binary materials TiN and CrN in previous studies showed an increase in the life time and in the speed of work, in relation to materials that were not coated. From these hard coatings, TiN and CrN, several techniques or methods have been developed to obtain coatings with better properties [1-2]. Accordingly, in the selection of a coating for a given application the following aspects must be taken into account: "Meet the properties of the material to be used as substrate; recognize the environment and working conditions to which the coating will be exposed, select the material for the coating taking into account its chemical stability, adhesion to the substrate, hardness, coefficient of friction and costs, among others [3]. Select the best deposition technique that provides the desired characteristics. For this application an indicator in this case is required its resistance to the wear reason why the hardness must be superior to the 30GPa, additionally, their high oxidation-corrosion resistance is required [4]. The great interest in producing multilayers is then to achieve hard coatings having high hardness, low brittleness, to improve the adhesion between the substrate coating, besides low chemical reactivity and low coefficient of friction between many more advantages like: Increased compatibility between substrate film, ability to overcome the lack of toughness in a coating and thermal barriers [5].

Thin film coatings of titanium nitride type chromium, have played a significant role in the industrial sector where resistance to high temperature and aggressive environments is required in union with abrasive wear [6]. These coatings must work as thermal barriers, since they are multilayer systems formed by a ceramic coating that acts like thermal insulation; thin titanium nitride layer is then deposited on the sacrificial layer [7]. Which improves the adhesion and corrosion resistance of the metal substrate in most cases are 316L steel. Coatings ceramic types must have a high coefficient of thermal expansion which is one of the parameters of design that must be taken into account, the most commonly used method for obtaining these thin-film coatings is physical vapor deposition (PVD), through which coatings are obtained in this case multilayers based on transition metals such as titanium and chromium, which allow to improve the surface properties of the material used as substrate. One of the main advantages of multilayer coatings is that each of the layers fulfills a specific function on the surface of the material, either by improving its hardness, adhesion, resistance to corrosion and wear properties of the titanium are melting point 1668°C and expansion coefficient $8.35*10^{-6}$/K, and the melting point 1857°C and expansion coefficient $6.66* 10^{-6}$/K. Additionally when combined with non-metal, in this case Nitrogen, it is possible to find an oxidation resistant system at high temperatures, so they provide protection against temperature, corrosion, or wear [9]. Another of the materials used to mitigate surface damages is chromium nitride, CrN, due to its excellent mechanical and tribological properties (coefficient of friction comparable to TiN when in contact with steel) [10]. High chemical and thermal stability with an oxidation temperature around 700 ° C, which make this coating useful in a wide variety of industrial applications [11]. The purpose of this work is to study the performance of multilayer coatings such as Titanium Chromium Nitride (TiCrN), Subjected to different temperatures from 600 ° C to 700 ° C to evaluate the potential for corrosion resistance as a protective barrier at high temperatures In function of the multilayer structures.

2. EXPERIMENTAL DETAILS

The TiCrN thin films were made using the Magnetron Sputtering Reactive D.C technique on an international AJA equipment, the equipment consists of two circular flat magnetrons 2 "in diameter, with a DC power supply, with two targets: Ti and Cr targets with 99.9% purity were used. For the pumping system of the fume hood turbomolecular pump has been used, assisted by a rotary pump. The base pressure was on the order of 10^{-9} mbar. Before the coating is obtained a pre-sputteting process is performed of each target by the bombardment of air ions for the cleaning of the target of possible superficial oxides. The pressure of Ar during the deposit was constant, for Ti it was 5.4 * 10^{-3} mbar and for Cr of 1.19 * 10^{-3} mbar. The power applied to the magnetron was 50 W. The substrates used were 316LVM stainless steel. Each substrate prior to deposition has degassed at 390 K for 90 minutes to eliminate possible air pollution and cooled to room temperature.

The electrochemical tests of the coatings were performed using Tafel curves techniques and EIS Electrochemical Impedance spectroscopy, the Tafel test is based on the application of an overvoltage around the equilibrium potential which was measured during a 5 hour potential stabilization time, the measurement of the current, subsequent to the measurement of stabilization potential readings were made by electrochemical impedance spectroscopy EIS, by means of an alternating signal of 10 mV between the working electrodes and the reference electrode, immersed in an electrolyte, measuring the phase difference between the stimulus (voltage) and the response (current) varying the frequencies from 0.001Hz to 300 MHz, for the Tafel polarization curves tests, potential variations in the 250mV range were made in the anodic and cathodic region with respect to the corrosion potential value at Scan rate of 0.5 mV s^{-1}.

The treatments were carried out at temperatures between 500 and 700 ºC, in an oven that has adapted the corrosion cell, with the purpose of evaluating the deterioration determined as corrosive wear that is accelerated when the system components reach the melting temperature of the salt deposit, which exerts a fluxing action on the protective oxide, deteriorating it by dissolution and favoring the transport of oxidant species towards the metal and metal ions towards the salt, unleashing the stage of propagation or accelerated attack. *The corrosive surface attack was observed via scanning electron microscopy (SEM) with a JSM 6490LV JEOL equipped with an optic light with a magnification range of 400X–100000X and a high sensibility detector (multi-mode) for scattering electrons.*

To evaluate microstructural changes and coatings when treated at high temperatures, it has been carried out using the X-ray diffraction technique, using a diffractometer. The position and intensity of the diffraction lines characteristic of each phase, are tabulated in a data bank. This equipment is coupled with a computer equipped with a Data collection software for XRD that incorporates the system of control of the apparatus and the handling and processing of data. X-ray diffractograms were made with a wavelength of 1.54059 Ǻ ($K\alpha_1$ (100) Cu radiation with Nickel filter) and a detector collimator of 0.05 mm. The recording conditions used for all analyzes were: voltage of 40 kV, intensity of 25 mA.

All the diffractograms were recorded for values of 2θ between 30° - 70°, in the continuous recording mode. *Generally, a step interval of 0.03 ° has been used every 10.2 seconds. The configuration used was Bragg-Brentano (θ/2θ) in beam mode, Cu Kα radiation (λ = 1.5405 Å), acceleration voltage of 40 kV and a current of 50 mA.* The diffractometer has a secondary monochromator to eliminate the K rad radiation and the background fluorescence, at room temperature. The indexing and position of the peaks was performed with the help of the database JCPDF 87-0633 and JCPDF 77-0047, taken from the ICDD charts for TiN and CrN.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Investigation

In figure 1, the results of the tests are observed by evaluating the behavior of the coatings that are used to reduce heat transfer, using the Nyquist diagrams, a system response is obtained as the response to an alternating current signal varying over a wide range of frequencies, the impedance in materials especially in those that are not good conductors of electricity, in this case when treating a ceramic type coating due to the combination of the two metals Titanium and Chromium and nonmetal Nitrogen [12], this response is related to the variation of the frequency according to the characteristics of the material and the chemical nature of the joints, because of this the variation of the reactance of the system can be related to the development of the layer of nitrides, The reduction of the anchor layers and ceramic coating, cracking and oxide formation at grain boundaries, which is obtained due to the temperature of the test [13]. To determine their best behavior and for the purpose of controlling cracking of the coatings it was adequate to perform coefficient of thermal expansion measurements which was determined using a high temperature dilatometer, To 600 ° C was obtained $3.21*10^{-6}$/K, 650 ° C with a value of $3.57*10^{-6}$/K and for 700 ° C was generated $3.64*10^{-6}$/K [14].

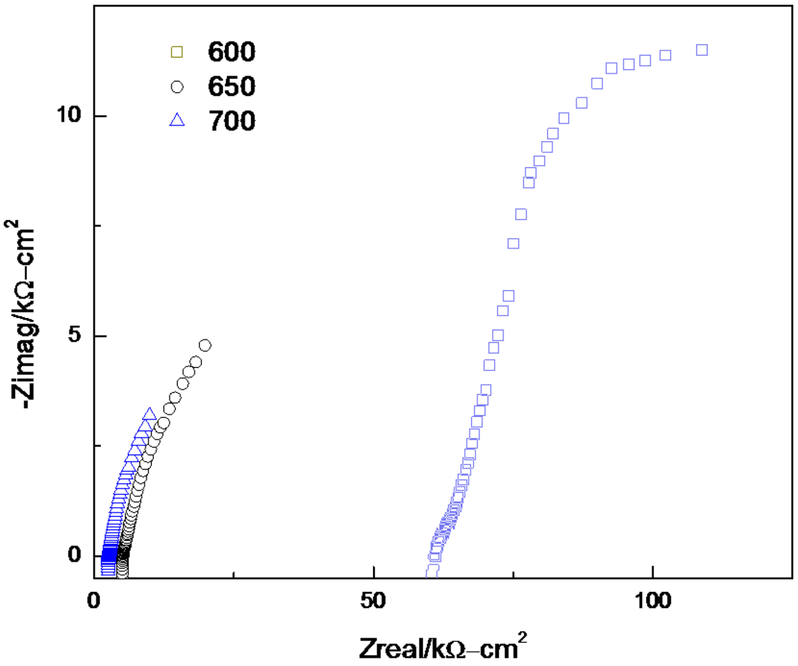

Figure 1. Impedance diagram corresponding to *TiCrN coatings*, evaluated at three different temperatures in the range of 600 ° C to 700 ° C.

With these results, it is evidenced the use as a thermal barrier, with the electrochemical impedance spectroscopy technique it can be identified that the coatings evaluated at 3 temperatures, have a double layer, when observing the thin film evaluated at 600 ° C an adequate value of total impedance is observed, due to the two constant phase elements present in the evaluation performed, the coatings evaluated at 650 ° C and 700 ° C have a similar behavior and is due to the magnitude of impedances decreases by 1 order of magnitude in the oxidation behavior of the coating, this process of decreasing its electrochemical response is associated with the change of coefficient of expansion, due to stabilizing the impedance value between 650 ° C and 700 ° C [15-16], this due to the oxidation process since the salts melt at those temperatures and generate an accelerated process of atomic diffusion, the effect of the roughness of the coated surface generates a dispersion of the frequency generating a non-uniform distribution in the current density, this is due to the fact that pore size and surface roughness have a nanometer scale so a dispersion can be generated in the system frequency [17].

In figure 2, polarization curves for hard coatings in the form of coatings in thin layers are observed which were deposited on 316LVM steel substrates, for the purpose of achieving the desired surface properties such as high hardness and corrosion resistance, this type of coating is of ceramic characteristic with a strong ionic character [18]. Corrosion kinetics were determined by the Tafel polarization curves. The basic factors which involve the prediction of oxidation, both at room temperature and at high temperatures are thermodynamic and kinetic [19]. Thermodynamics allows to predict corrosion phenomena that compounds can be formed under equilibrium conditions, while kinetics allows the determination of the rate of growth of the different layers on the surface of the coating. Oxidation processes at high temperatures are very complex given the great variety of physical and chemical phenomena which occur in such processes, therefore, it is very difficult to follow a general kinetic model which allows to describe completely the phenomena of oxidation and corrosion that occur at high temperatures [20].

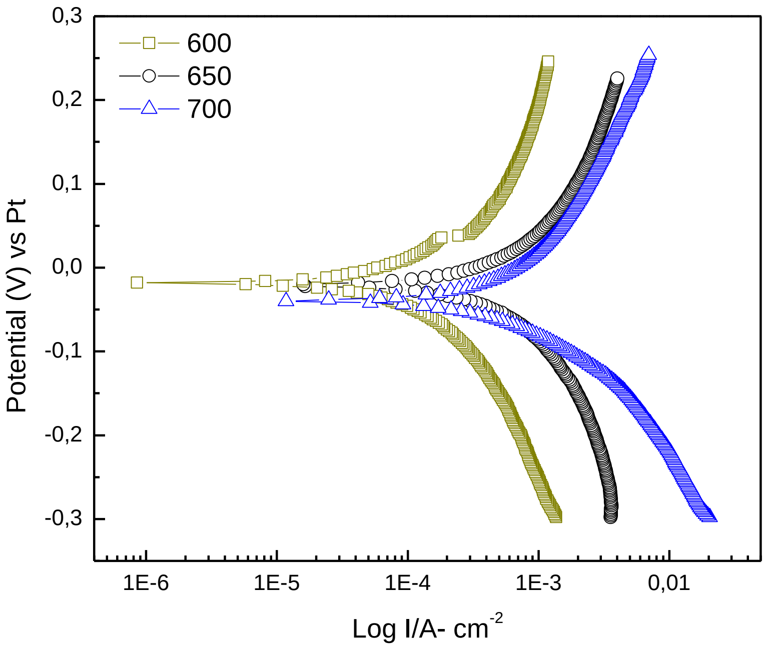

Figure 2. Potentiodynamic curves corresponding to steel coated with titanium nitride chromium after evaluating them at three different temperatures, the decrease of the corrosion potential towards active zones is observed as the temperature increases.

Table 1. Corrosion parameters obtained from the Tafel curves corresponding to the coatings exposed to temperatures from 700 to 600°C

	B_A mV	B_C mV	Icorr µA/cm^2	Vcorr µmy
600°C	42.04	-37.43	0.980	170.73
650°C	180.09	-102.18	0.0380	388.02
700°C	110.84	-87.49	0.0702	956.66

The rate of corrosion is directly related to the attack speed which increases substantially with temperature because the electrochemical parameters observed in the potentiodynamic curves indicate greater dissolution as the temperature increases, this is because the surface film increases as a result of the oxide-metal reaction due to the transport of anions through the oxide which behaves as a solid electrolyte [21]. The resistance of the TiCrN coating to a specific environment is determined by factors such as thermodynamic stability, the ionic defects of the structure are related to the porosity caused by increasing or decreasing the temperature during the test [22].

The good protective characteristics of the coating are due to high thermodynamic stability due to the nanostructure achieved by the bonds formed between titanium, chromium and nitrogen, achieving a system that neither evaporates nor dissolves within the evaluated atmosphere additionally an adequate coefficient of thermal expansion is had which contributes to a low diffusion coefficient of the reactant species so that the coating has a slow corrosion rate [23]. It is observed that by increasing the melting temperatures adequate adhesion to the base metal is obtained which can be considered as a sufficient plasticity at high temperature to resist fracture with the differential thermal expansion stresses [24]. In this work it was possible to establish that the effects of increasing the speed of degradation are due to the oxides as well as the carbides and the mixtures of these species. For the formation of a controlled corrosion layer by the diffusion process the rate of degradation of the oxide can be altered by the modification of the concentration of defects involved.

The oxidation of TiCrN coatings demonstrate thermal stability since the rate of reaction kinetics with which chemical reactions occur is low in the range of 600 ° C to 700 ° C, the values of deterioration; Indicate that the coating has not been consumed, this is because nitrides combined with Cr and Ti have excellent corrosion resistance, in this case oxidation resistance [25].

3.2 Scanning Electron Microscopy Characterization (SEM)

In figure 3 the growth of multilayer nano-structured TiCrN coatings is observed indicating that the step controlling the growth of the layer is the reaction-deposition process where the metals are mixed with the nitride, this is a physical process which allows the growth of a layer of a solid compound at the interface formed between the substrate and the layer [26]. Therefore, ternary compounds that may form on the surface of the steel substrates generate a surface with a very low porosity. The movement of atoms in the PVD deposition process allows a higher mass transfer rate to be achieved compared to other techniques used in nitride blends. Thus, the influence of the diffusion in physical form on the rate of deposition is lower and the stage which limits the rate of deposition is the solid state diffusion [27]. Therefore, if there is a balance between the surface layer and the decrease in porosity. The growth of the layers was perfectly described by a multilayer model.

Figure 3. Micrograph corresponding to multilayer TiCrN coatings where the homogeneity of the surface is observed due to the low porosity value.

In Figure 4, 5 and 6, the analyzes are observed by scanning electron microscopy of the test specimens after the three tests indicating the formation of a layer associated with the oxides and carbides which are in conditions of operation of the thermal barriers, which generally work at temperatures between 600 and 700 ° C. In figure 4 it is observed that the particles adhered to the surface are minimal, this is due to the suitable stability that is obtained at 600 ° C, and from the coating to the outer layer due to this effect a kinetic low of the corrosion is obtained [28]. In the micrographic analysis of the images 4, the formation of a compact oxide layer was observed composed mainly of the molten salts. It was determined that high diffusion was present from the interior of the substrate to the outer layer of oxide, although they are present in very low amounts in the metal matrix [28]. The effect of titanium and chromium together with the nitrogen atoms is that they are the major responsible for maintaining stability and influence the kinetics of growth of the oxide layer which has been generated at 600 ° C and the exposure time [29].

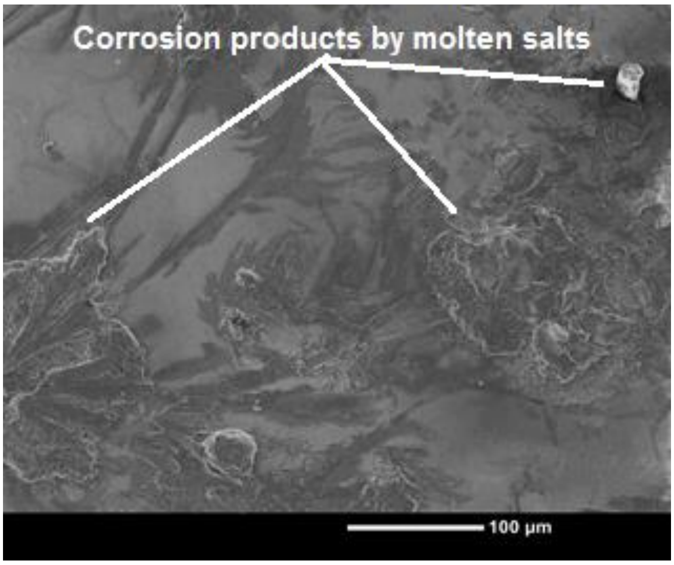

Figure 4. Micrograph of the TiCrN coating wherein the deposition of the salts on the coated material is observed in the zones analyzed no superficial damage is observed.

In Figure 5, oxidation-carburization is observed the chromium titanium nitride creates a decrease in the level of adhesion of the corrosive salts which comes in this highly fuel environment. In Figure 5, on the right side a highly compact oxide layer is observed in the central part of the micrograph the oxide layer at the interface with the gaseous environment begins to fracture and to decompose and observe the detachment of the protective film although it does not reach the point of detachment from the metal, and at the interface with the matrix of the substrate still remains compact. This is because low carbon and oxygen diffusion occurs through microstructural defects which occur on the surface of the oxide layer as discontinuities on its outer part and also the oxidation level tends to increase with the exposure time, which is considered responsible for this type of behavior [29].

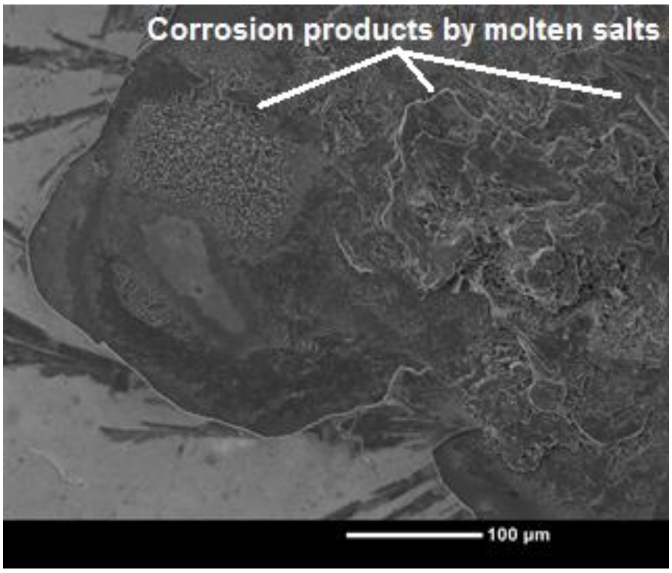

Figure 5. Micrograph corresponding to the chromium titanium nitride coating evaluated at 650 ° C, where the effect of the dissolution of the corrosive salts is observed.

In figure 6 a higher loss of corrosion resistance as a function of temperature is observed this is because the salts melt at this temperature value and generate greater degradation of the coating, generating porosity on the coating, and achieving the detachment of the upper part of the multilayers, but nevertheless the adhesion with the substrate is conserved which generates a protection which functions as a thermal barrier. Therefore, this type of multilayer coating is very useful because it increases temperature input to the matrix and consequently substrate efficiency depending on the time when the combustion temperatures are close to 700 ° C, the surface observation of Figure 6 indicates that there is a wear by hot corrosion. In this dissolution mechanism there is detachment of metal-oxide interface forming detachment of the material [30]. This makes the oxide-salt interface the peeling and dissolution of the protective layer are accelerated whereby part of the coating layers can be detached. Therefore it was observe severe corrosion products by molten salts when the corrosive temperature was increased to 700 °C.

Figure 6. Micrograph of the coating worn by the effect of the corrosive salts after prolonged exposure and at a temperature of 700 ° C.

3.3 Crystallography Characterization by XRD

In figure 7, the X-ray diffraction spectrum is observed corresponding to 316LVM steel used as substrate it is observed that the structure of the material is cubic structure centered in the faces (FCC), indicating a material with some structural defects but which has important mechanical properties such as hardness and ductility as well as contraction or thermal expansion, for this type of properties have been used for applications where high temperature changes are required. In figure 7, a typical spectrum of austenitic steels is observed widely used in the metalworking industry due to its properties as the excellent resistance to corrosion, high hardening for cold work and good formability [31]. Applications in boilers involves taking into account phenomena of modification and degradation occurring on the surface, as a consequence of a mechanical action (wear) Chemical or Electrochemical (corrosion) and thermal, so a change in the surface is required.

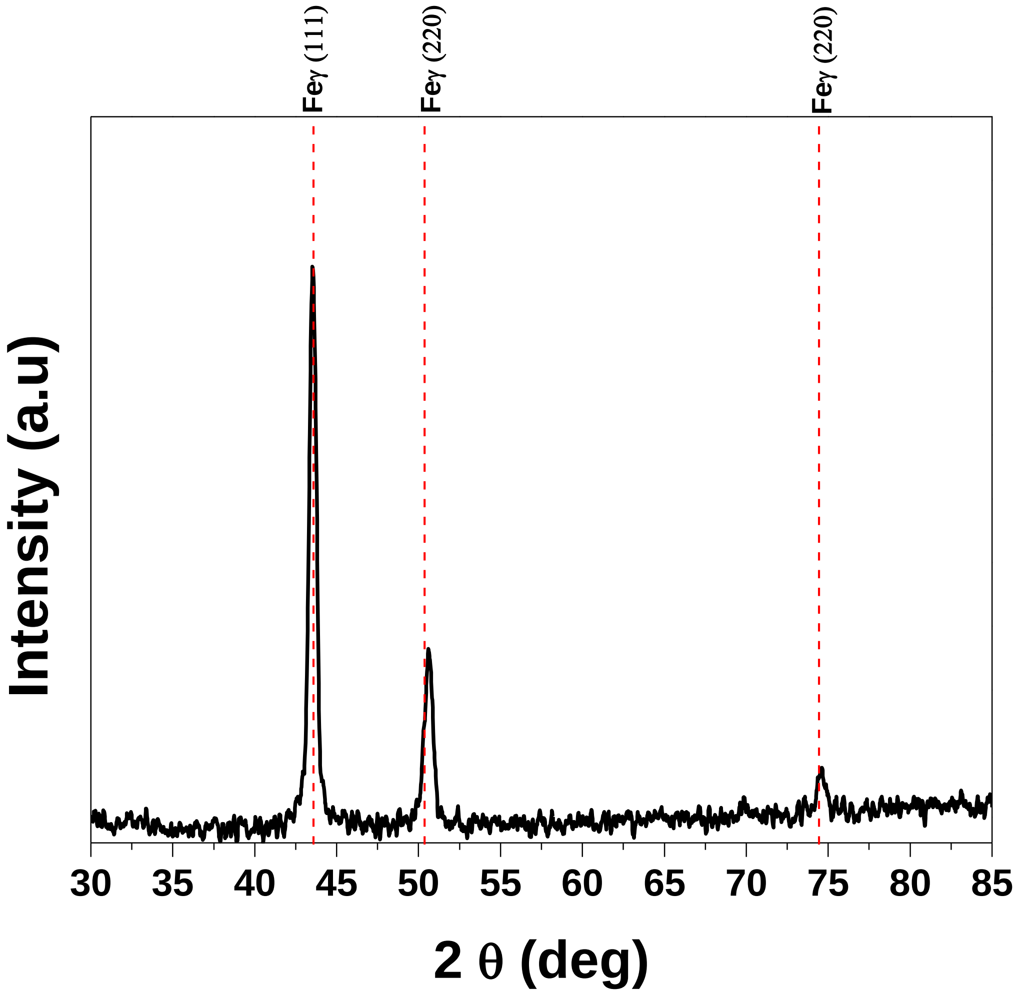

Figure 7. X-ray diffraction spectrum corresponding to 316LVM steel without subjecting it to corrosion tests at high temperatures.

The spectra shown on the surface of the coatings in Fig. 8, for TiCrN respectively showed the presence of elements such as Ti, Cr, N and O. The areas of the peaks were used in order to calculate the composition of the coatings. The values obtained indicate that the coatings were sub-stoichiometric close to the stoichiometric range. The presence of oxygen in these materials is frequently encountered during the process of high temperature and oxygenation. Figure 8 shows a spectrum at the top where the defined peaks of NCr and NTi are obtained after the respective corrosion tests at 600 ° C, Observing the structure of TiCrN in cubic phase shows first to be very stable in the same figure 8, the spectrum corresponding to the coating subjected to 650 ° C is observed, a different structure is observed due to the formation of predominant Cr_2O_3 and CrO_2 Chromium oxide, these oxides generate a protection and is due to the large amount of charge accumulated in the nitrogen atoms, no link creation or destruction is observed for this reason must present a strong bond between the chromium, oxygen and nitrogen, at the bottom is the spectrum corresponding to the coating evaluated at 700 ° C, where it is observed that most peaks do not have the same intensity and is due to the effect of the reaction of the corrosive salts on the surface, where they have been deposited on the coated material [32].

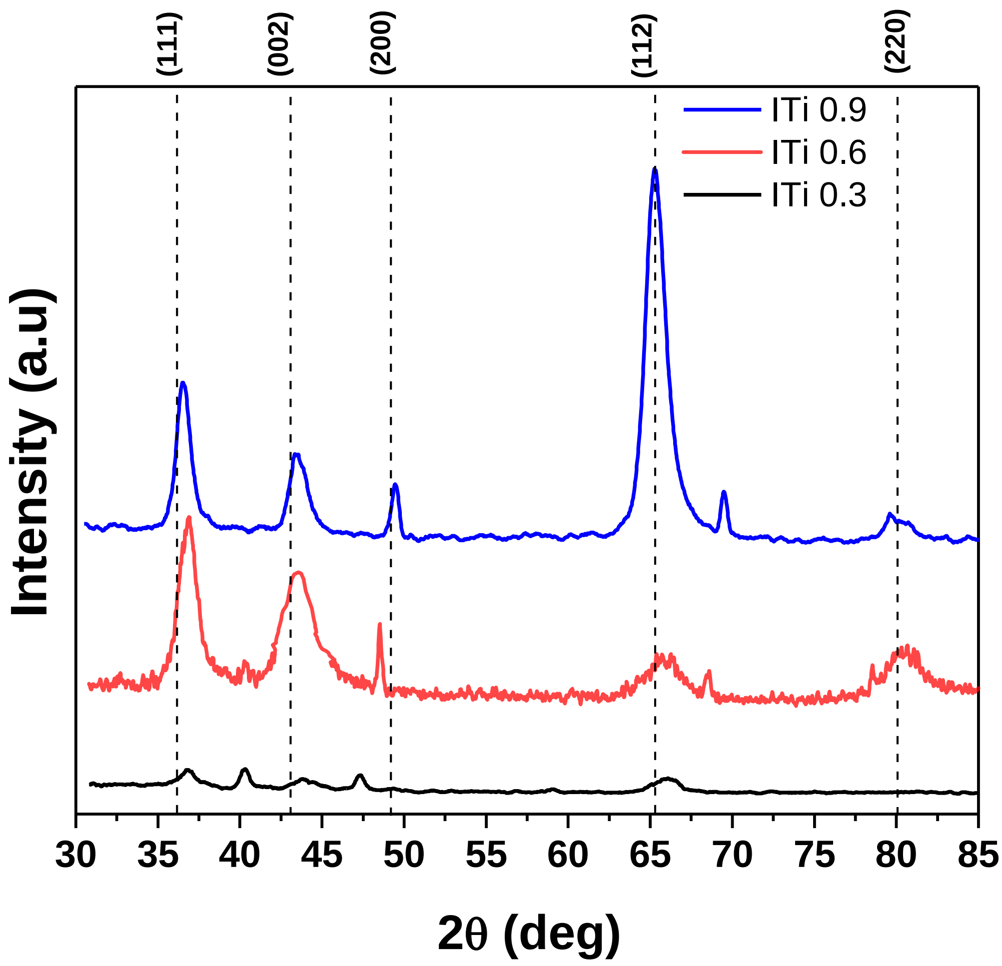

Figure 8. Spectra corresponding to the coatings after the corrosion test at high temperatures evaluated between the ranges of 600 ° C to 700 ° C.

4. CONCLUSIONS

By means of electrochemical impedance spectroscopy it was possible to evaluate the degradation effect of the coatings of titanium nitride chromium, determining the effective thermal barrier result because in the temperature range evaluated, a minimum variation of the coefficient of thermal expansion was achieved.

The polarization curves allowed to determine the values of corrosion rate, in each of the systems evaluated in contact with the corrosive salts, there is a direct relationship that relates the temperature to the rate of corrosion, Indicating the increase directly, the lower corrosion rate has a uniformity in the generated oxide layer, which is interpreted as adequate adhesion of the coating to the substrate, the intermediate corrosion rate exhibits a hot corrosion wear due to peeling of the metal -

oxide interface. Finally, the sample with the highest corrosion rate presents porosity in the coating which contributes to be considered unfavorable properties.

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