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Fuzzy sets and Electrochemical Noise to Predict Corrosion Behavior of Ti Alloys

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Electrochemical noise (EN) and fuzzy sets were used to predict the corrosion behavior of titanium alloys. Ti-15Mo was analyzed to understand the trend of titanium alloyed with another material. This study employs an adaptive fuzzy set to approach and predict behavior of titanium alloys. A fuzzy set prediction model has been employed to establish the relationship between electrochemical noise signals and properties of Ti–15Mo alloy. The predicted results obtained with fuzzy sets showed a better agreement with the experimental results, having a less maximum relative error.

Keywords: Fuzzy sets, Electrochemical noise, Mechanical alloying, TEM, Corrosion.

1. INTRODUCTION

Titanium alloys are widely used in industry due to low density, high strength, toughness and good high-temperature properties. It is well known that the mechanical properties of titanium alloys depend directly on the chemical composition through the characteristics of the microstructure, but determination of the titanium alloys property is always very difficult and requires taking cautions and labor. Especially new types of titanium alloys are usually developed with the ‘‘trial-and-error’’ method, which wastes time and effort [1]. Fuzzy logic is used to solve various problems related to a wide range of applications, as providing flexible solutions. Designing a fuzzy system contains fuzzy sets which are defined by rule table and membership functions [2]; in this investigation a fuzzy system was designed. Also samples used in this research were made by powder metallurgy, because this is an important manufacturing method and developing models that can predict the characteristics of the products is remarkable for researchers. (PM) in many industries has not received the praise of which it is worthy, but for many years now, it has been an established process for the manufacture of precision quality engineering components. This method is sometimes the only manufacturing method which can be used for some parts manufacturing such as composite materials, porous materials, refractory metals and special high duty alloys [3]. (PM) is highly critical to be able to predict properties of products as variations of powder size, metal type, temperature, duration time, pressure, additive materials and other process parameters can affect the several characteristics of the product. Having a model permits describe the relationship between these parameters and the effect of input parameters variations on the output variables, helps to select the optimum input parameters and reach the optimum output. In this paper a (PM) method is widely used for production of Ti–15Mo alloys, after those samples were observed in TEM (Transmission Electron Microscopy) to understand the samples behavior with 8h of milling time. This milling time is very significant because in this analysis the most important changes were shown at these milling hours, under TEM analysis and electrochemical test.

Electrochemical Noise (EN) was used to know corrosion process; EN is a general term given to fluctuations in the potential and current generated spontaneously by corrosion processes. EN occurs naturally in the electrolyte/electrode interface due to the random ion movements and also originates from the occurrence of cooperative phenomena such as nucleation of pits [4].Electrochemical noise is associated with all degrees of freedom of the system. Likewise, it indicates a change in the thermodynamic and kinetic states of the interface and it is the only electrochemical technique that does not disturb the system [5].Electrochemical noises usually show complicated behaviors in time series data, to analyze nature, and to predict behavior; frequency analysis such as Fast Fourier Transform (FFT) has conventionally been used. However, frequency analysis is not always effective in estimating such complicated nonperiodic phenomena because frequency analysis is based on a linear predictive theory. Chaos analysis of the signal is carried out to determine the characteristics of corrosion phenomenon recently [6-7]. In some other investigations Fuzzy theory was used, this theory is a method that facilitates uncertainty analysis of systems where uncertainty arises due to vagueness or fuzziness rather than due to randomness alone [8]. This is based on superset of conventional (Boolean) logic that has been extended to handle the concept of partial truth–false values between completely true and completely false. It was introduced by Lotfi Zadeh in 1965 as a means to model the uncertainty of natural language. In classical set theory the membership of an element for a set is 0 or 1. It is impossible for membership functions to take any other value except 0 or 1. In this theory, the element may have a gradual degree of membership [9].

2. MATERIALS AND METHODS

2.1 Materials and experimental procedure

Pure materials (Alfa Aesar): Titanium (99.5% purity), Molybdenum (99.5% purity) powders. The first step was the preparation by milling with the corresponding quantity of metal powder in a high energy SPEX 8000M connected to a hardened steel container with 13 mm(Ø) balls as milling media and an inert Ar atmosphere. Pressed samples were mounted, polished and etched using standard metallographic techniques in order to carry out the microstructural observations by using a scanning electron microscope (SEM) JEOL-5800-LV, without sintering process. The structural changes of powders during the milling process were determined by X-ray diffraction (XRD). A Panalytical X'Pert PRO diffractometer (40 kV, 35mA) with Cu Kα radiation (λ= 0.15406 nm) was used for the measurements.

2.2 Preparation of the simulated biofluids

Consolidated bulk products were in the form of bottom of 5g of powder, with composition of Ti 85, Mo 15 in balance. The electrolyte used for simulating human body fluid condition was Ringer's solution, prepared using laboratory grade chemicals and distilled water. The composition of Ringer's solution was (in g/l) 9NaCl, 0.24 CaCl2, 0.43 KCl and 0.2 NaHCO3. This electrolyte was used because the corrosion resistance in physiological solutions which model the human body fluid is one of the basic criteria to choose the material as implant, in this case titanium. The corrosion behavior of titanium alloys was investigated in simulated physiological solutions elsewhere [10-11]. It is known that the integrity of passive oxide layer is influenced by the wear, observing that wearing accelerate corrosion behavior of Ti alloys in the physiological environments, even becoming more severe than for corrosion only [12].

2.3. Eletrochemical Test.

The tests were made in a potentiostat/galvanostat/ZRA Solartron 1287. The electrode of Ti-15Mo was coated with epoxy resin and then was rinsed in Ringer's solution. Samples were immersed in Ringer's solution for half an hour for stabilization and the open circuit potential was measured during this period with a multimeter; the OCP samples were -350 and -160 mV vs SCE. All tests were performed at ± 37 ºC; this temperature was used to simulate human body temperature. Analysis was done according to ASTM G199. The statistical analysis was achieved in time intervals of 2048 seconds. The time intervals were selected from the last section from the records, where stabilization was reached.

2.4 Fuzzy model

Modeling of systems by fuzzy logic can be employed in a number of ways. There are rule-based fuzzy models, fuzzy linear regression models, or fuzzy models using cell structure [13]. This research focuses only on rule-based fuzzy models, where the relations between variables are represented. In 1986, FRVs (Fuzzy Random Variables) were introduced by Puri and Ralescu as a valuable and well-formulized model to deal with probabilistic and statistical problems involving fuzzy data. Formally, FRVs have been presented as an extension of random sets and variables, but in practice they correspond to an intermediate level of precision between either real or random variables [14-15].The differences between classical set and fuzzy logic theory can be explained in mathematical language as

$$\mu(x) = \begin{cases} 1, & \text{if } x \in a \\ 0, & \text{if } x \notin a \end{cases} \qquad (1)$$

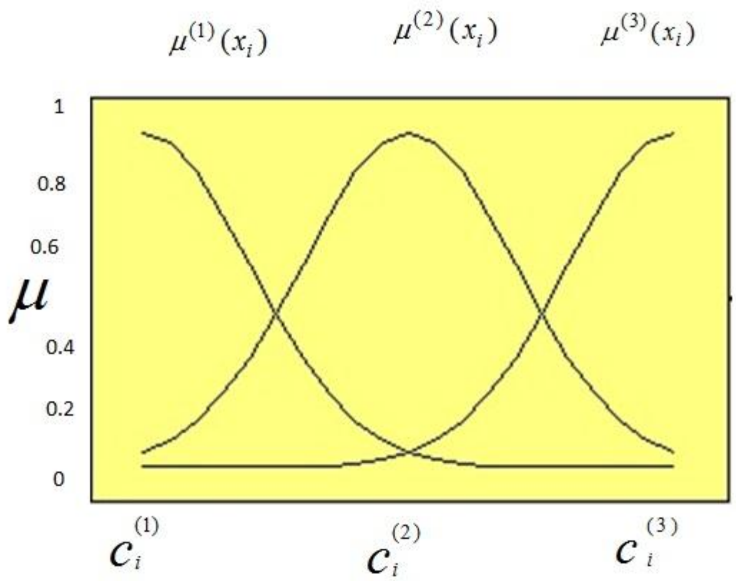

Figure 1. Membership functions of fuzzy model.

Fig. 1 shows a schematic diagram of structure of the fuzzy logic system used in this research. The first step of fuzzy logic system is to employ the inputs or some inputs into a fuzzification process.

The fuzzification comprises the process of transforming crisp values into grades of membership for linguistic terms of fuzzy sets; the input data (digital, precise/imprecise) will undergo some translation into linguistic quantity such as, very low, low, medium, high, and very high. In fuzzy logics parameters are not completely true or completely false. The parameters can be defined with the ‘‘degree of truth”. In Fig 1, rule aims in:

$$If\ \ x_1 \text{ is } \quad \text{and } x_2\ C_i^{(1)} \quad \text{and} \ldots C_i^{(2)} \ldots x_n \text{ is } \quad \text{then } y\ C_n^{(j)} \qquad (2)$$

Where: j is the number of rule, $x1$, $x2$, . . ., x_n are the input variables and y is the output variable.

The output is a fuzzy degree of membership in the qualifying linguistic set, always the interval between 0 and 1[16]. In fuzzy logic, membership function is allowed to have a value between 0 and 1, as shown in Fig. 1. This number can change continuously in the range of (0 1). In some projects, researchers have presented nero-fuzzy models by combining both fuzzy parameters and neural network models [17]. In rule-based fuzzy model, the number of input sets is equal to the input variants. For this system the electrolyte type and duration of the milling time process are the input variations. So two input sets are selected. The model has only one output variable respected to the predicted value (Localization Index-IL), this value explain the type of corrosion (located, mixed, generalized). The schematic representation of the designed model is shown in Fig. 2 where input variables, Mamdani algorithm and output variable is represented.

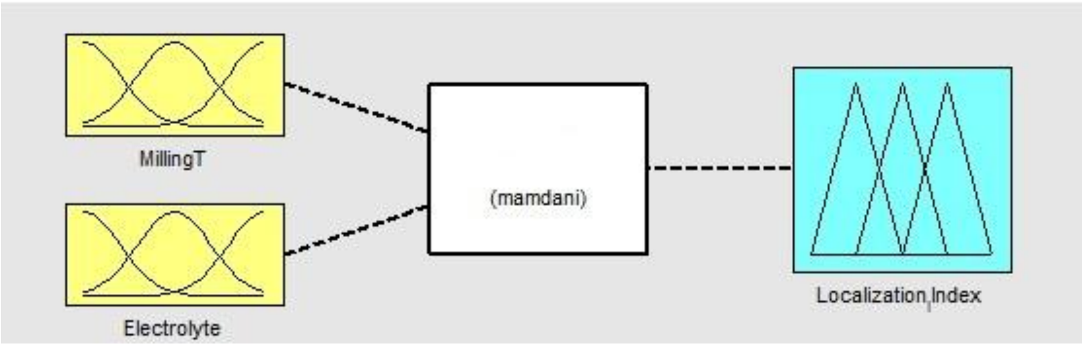

Figure 2. Schematic presentation of designed rule-based fuzzy system.

3. RESULTS AND DISCUSSION

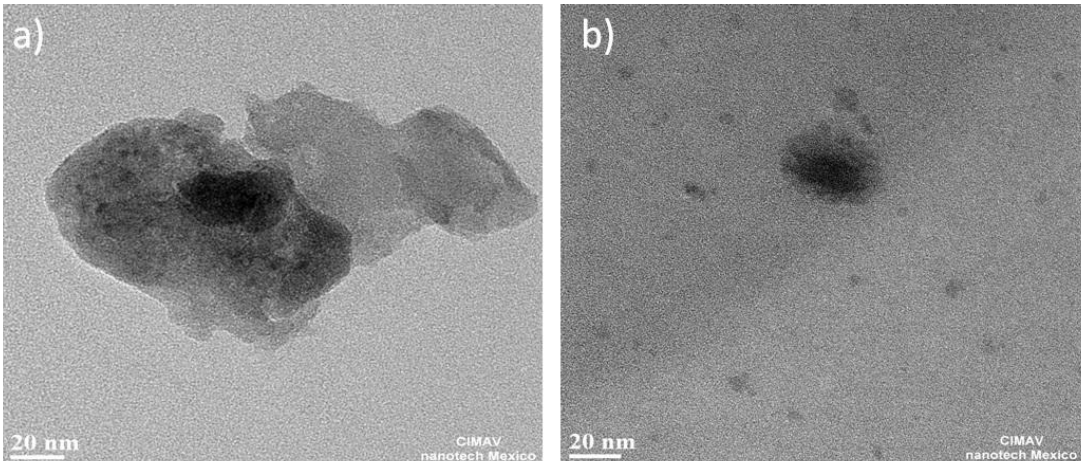

Figure 3. Representative view TEM image of a nanoparticle at a) 3h and b) 5h.

The microstructure of a Ti-15Mo alloy depends strongly on mechanical milling process and their corrosion resistance as a result of the electrochemical fluctuations thrown by EN test which can lead to significant variability (uncertainty) in values of the material parameters. This grade of uncertainty can be solved by fuzzy set system. EN knew as spontaneous fluctuations of the electrical quantities [17].

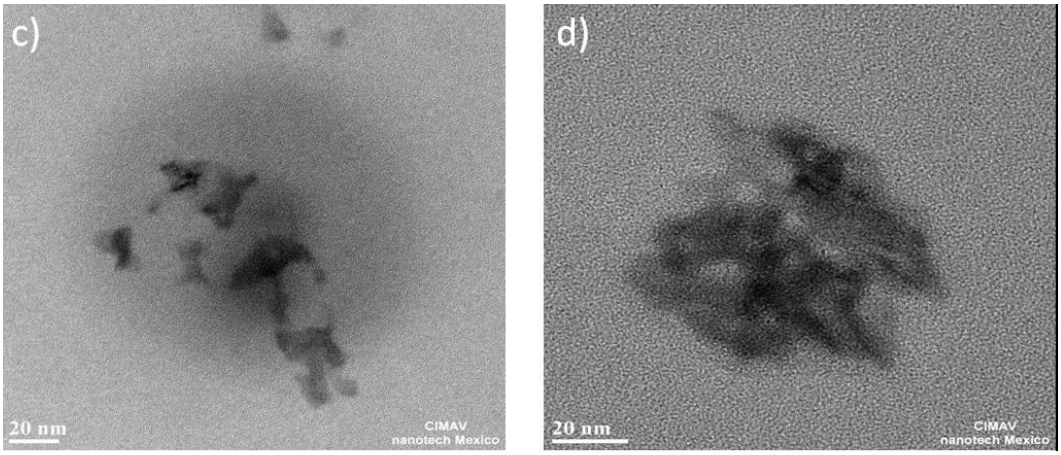

Figure 4. TEM image of Ti-15Mo at 8h milling c) y d).

In Figs. 3 and 4, it is possible to observe differences inTi-15Mo samples, increasing milling time particles start to reduce its size and change its shape; this factor it is important because shape and porosity could be a factor to reduce or increase corrosion resistance of samples. Fig. 3 shows Ti-15Mo alloy with 3h and 5h of milling time; while in Fig. 4, Ti-15Mo different samples of 8h milling time are shown. This demonstrates that similar milling time can change the particle size and some possibilities of corrosion response. Fig. 5 shows an energy dispersive spectrometer studies (EDS) of 8 milling time samples.

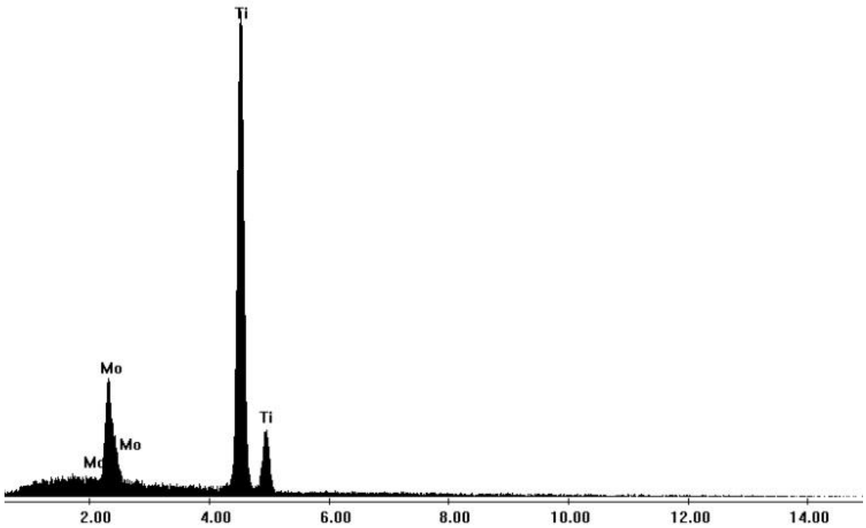

Figure 5. EDS studies of Ti-15Mo at 8h milling.

EN measurement has been shown to be uniquely capable of monitoring rapidly changing electrochemical processes and has emerged as a promising technology in the recent years; it is also a powerful technique to obtain more information about the coating formation mechanism (TiO_2) but, some factors as instability of the test electrode during the measurement period is a problem that can affect many electrochemical techniques, in this case mechanical milling process could produce relevant changes in the result to understand the corrosion resistance of the samples.

Electrochemical noise measurements (ENM) can also be used for the determination of the corrosion resistance, because this technique takes advantage of naturally occurring fluctuations of current and electrode potential in an electrochemical cell. No external perturbation is applied to the system, and the experimental set-up can be easily designed to carry out continuous, automated measurements. Several parameters, such as noise current, noise potential and noise resistance, obtained by ENM can be related to the protective performance of the coating[18]. The proposed system utilizes two fuzzy interfaces to quantify the exposure condition, IL and corrosion type.

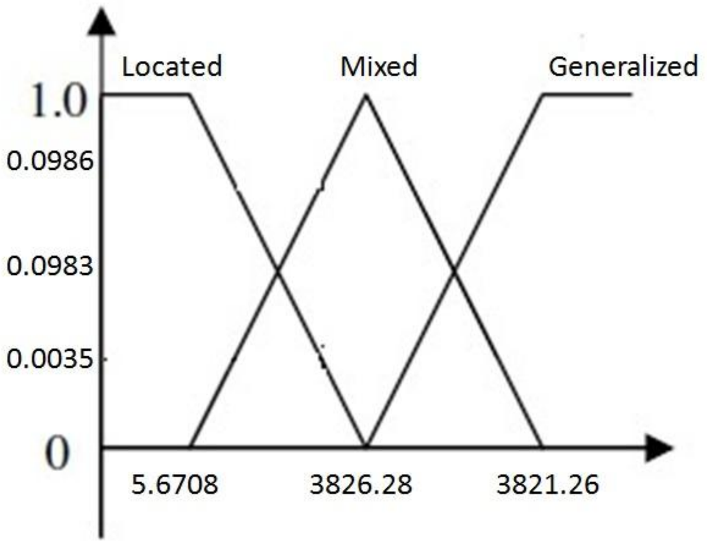

Figure 6. Membership function.

Matlab software was used to construct the fuzzy system. Electrochemical fluctuations occur spontaneously in current and potential measurements, and contain information on the corrosion mechanism. This information may be understood by the fuzzy system which permits analyze the corrosion process and changes into the microstructure of the samples. In the present study it is assumed that the membership functions of the fuzzy material parameters are triangular as shown schematically in Fig. 6, and EN signals of 3 different and significant samples of Ti-15Mo at 8h milling are observed in Fig. 7 with red, blue and black color. The results revealed that corrosion could be mixed and generalized. The value of fuzzy system is initially set at 1, so each domain therefore begins with three regions: located, mixed, and generalized. The values of IL are shown in Fig. 6. The solid lines delineate the fuzzy regions within this fuzzy domain.

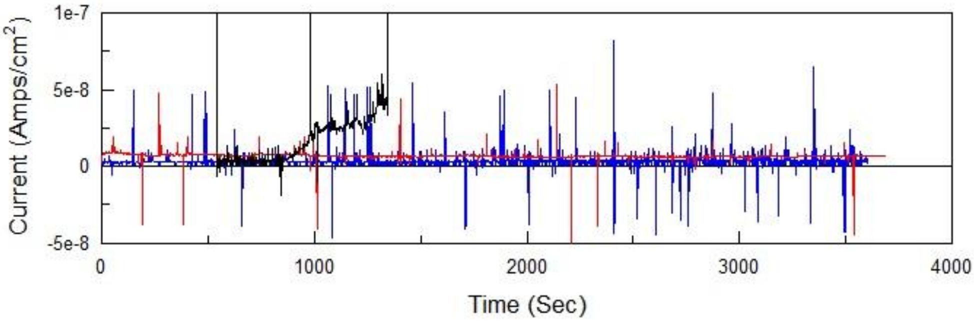

Figure 7. Electrochemical noise of Ti-15Mo 8h in Ringer's solution.

Table 1. Electrochemical noise (EN) of Ti-15Mo.

Specimen Ti-15Mo	R_n (ohm.cm^2)	Localization Index IL	Corrosion Type	Fuzzy System
8h A	3821.26	0.0983	Mixed	8h-9 elements in electrolyte (Located)
8h B	3826.28	0.0986	Mixed	3h-9 elements in electrolyte (Mixed)
8h C	5.67089E-05	0.0035	Generalized	5h millig-6 elements in electrolyte (Generalized)

The main properties of EN have been usually described by statistical parameters (noise resistance), as well as by parameters obtained from spectral analysis (noise impedance), and the theory of chaos (the correlation dimension and the largest Lyapunov exponent). All these parameters are, however, calculated by means of mathematical techniques that are based on the assumption of the stationary of signals, so that the reliability of estimated parameters could be questionable in specific cases[19]; these questionable parameters as the milling time was one of the variables that in this research were studied by fuzzy system. EN measurements do not need any externally imposed perturbation to the electrochemical system that could change its specific properties [20-21]. Some mechanisms relates to impact and velocity of ball milling by making flakes in the surface of samples viewed by SEM [22]. In this research this flakes are shown in different ways decreasing o increasing milling time (Fig. 3 and Fig. 4). The analysis of the records (current and / or potential) obtained by this technique is essential to getinformation about the studied system [23-24]. There is not a unique way of doing this analysis, but it depends on the expected form of corrosion and on the experimental setup. Sometimes it is necessary to perform various types of data analysis to evaluate which parameters are useful to a particular case (Cottis and Turgoose, 1999). Electrochemical noise records may be contaminated with unwanted noise sources, like power line noise, reference electrode noise, voltage spikes. Using a fuzzy system is possible to predict part of the random behavior of the alloy [25-26], as shown in table 1, where the results of IL, corrosion type and fuzzy system are observed.

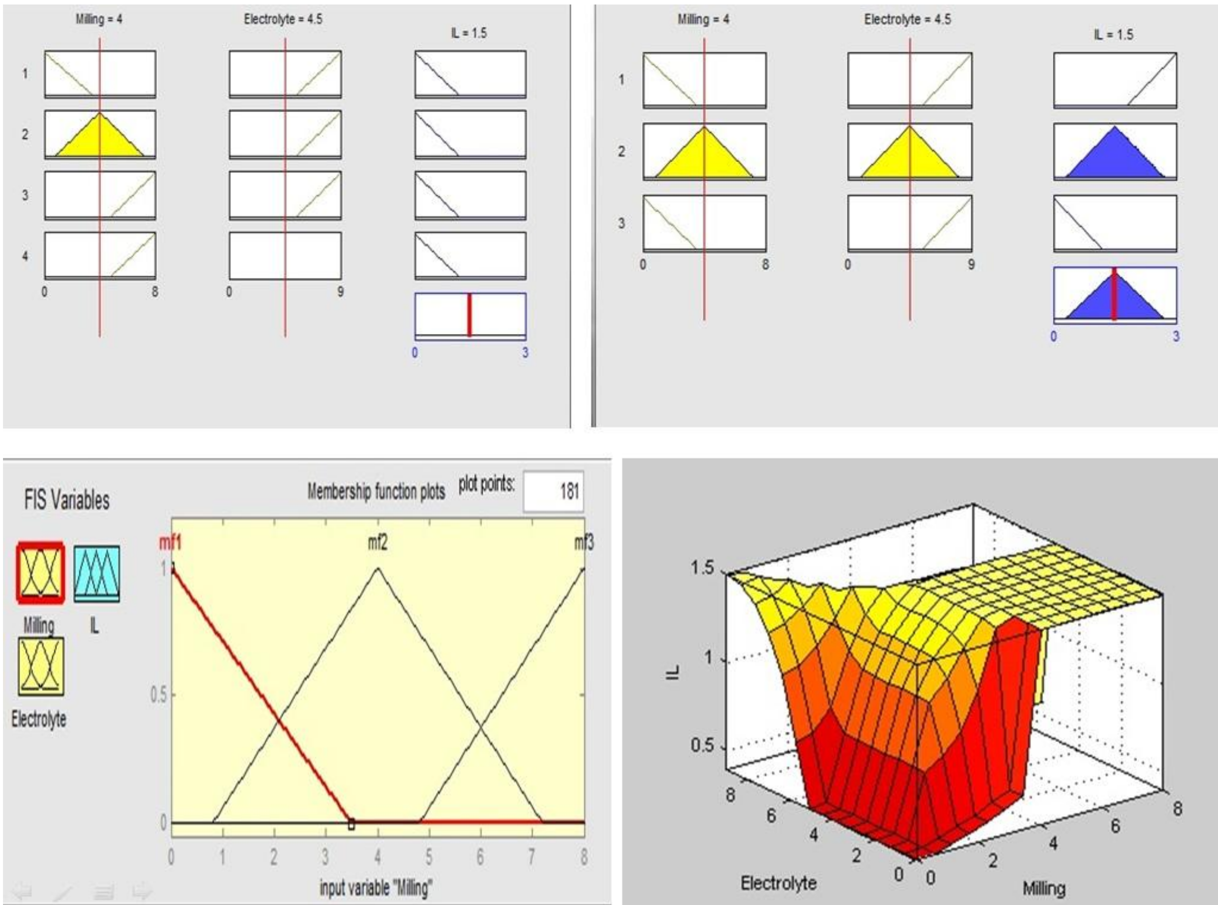

Figure 8. Membership function, variables and graph of fuzzy system.

The mechanical properties of materials such as molybdenum prealloys are a complex function of chemical composition and fabrication techniques. Many probers have reported the feasibility of soft computing techniques to deal with such a complexity. Among the soft computing different methods, artificial neural network and fuzzy logic have proven fitness for high accuracy prediction of mechanical properties of complex systems [27].The performance of fuzzy inference system can be highly influenced by the type and shape of membership function [28]. In some studies the crystallization behavior occurred after the sintering process [29], but these studies were performed on green samples only. In Fig. 8, construction of fuzzy system is observed with 8 possible variables in electrolyte type (consider a variable as a number of components of electrolyte), milling variable consider 8 possible situations (number of hours), IL values in graph (0.001-0.01/ 0.001-0.1/ 0.1-1.0) is observed as a (0.5-1-1.5 values). This numbers are considered to get close to the real values obtained in lab test. Finally, graph surface in colors red, orange and yellow present the possibilities of corrosion type may occur (as explained in table 1).

4. CONCLUSIONS

Based on the current experiments and fuzzy system design, the following conclusions have been made:

- Analysis of the signals obtained by EN and the cathodic process could affect the corrosion mechanism and the corresponding EN signals.
- Electrochemical Noise (EN) technique was employed to study the passivation of Ti-15Mo green samples alloy, finding good resistance corrosion.
- There are several electrochemical methods to evaluate the corrosion protection performance of alloys, such as EIS (electrochemical impedance spectroscopy), LP (linear polarization) and EN (electrochemical noise) according to other studies made with Ti-15Mo. Hence mechanical milling hours is important to determine the kind of corrosion type. Other investigations related to mechanic milling explain significant changes for milling time variations [30].
- Results obtained by analysis of noise data and fuzzy system in time and frequency domains were satisfactory. Also, these values observed in IL ranges are feasible to study by the fuzzy logic rules.
- The average of shape particles and corrosion type correspond to the impacts of balls during mechanical milling process.
- The significant milling time and microstructural changes during fabrication can be utilized to explain the EN results of Ti-15Mo green samples. The compaction pressure influence of the green samples can lead to fuzzy systems without sintering samples, but it can change by the sintering technique. At this point, other investigations related to mechanical milling coincide that the morphology and size of the powders particles depend strongly on milling time [31].

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