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Technical Report

Electrochemical Noise Study of Ni-Mo Alloys Fabricated by Mechanical Alloying and Densified by Spark Plasma Sintering

F. Almeraya-Calderon[1,2]*, R.G. Bautista-Margulis*[3]*. C.G. Nava-Dino*[4]*. G. López-Ocaña*[3]*, C. Gaona-Tiburcio*[2]*, S.D. De la Torre*[5]*, J. Castañeda-Avila*[4] *and A. Martínez-Villafañe*[1,*]

[1] Departamento de Integridad y Diseño de Materiales Compuestos. Centro de Investigación en Materiales Avanzados. S.C. CIMAV. Miguel de Cervantes No. 120, Complejo Industrial Chihuahua, C.P 31109, Chihuahua, Chihuahua, México.
[2] Universidad Autónoma de Nuevo León. FIME - Centro de Innovación e Investigación en Ingeniería Aeronáutica. Av. Universidad s/n. Ciudad Universitaria. San Nicolás de los Garza, Nuevo León, México.
[3] Universidad Juárez Autónoma de Tabasco, División Académica de Ciencias Biológicas, C.P. 86040, Villahermosa, Tabasco, México.
[4] Universidad Autónoma de Chihuahua, Facultad de Ingeniería. Chihuahua, Circuito No 1., Campus Universitario 2 Chihuahua, Chih.
[5] Centro de Investigación e Innovación Tecnológica (CIITEC)-IPN, D.F. México, Cerrada de Cecati S/N, Col. Santa Catarina Azcapotzalco, CP 02250, México D.F.

[*]E-mail: martinez.villafane@cimav.edu.mx

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The mechanical alloying (MA) method by the low energy ball milling process has been used to fabricate Ni-Mo based electro-active powder. Nanometric-sized Mo particles have been embedded into agglomerated amorphous matrix. The spark plasma sintering (SPS) process has been used to densify the powder in < 6 min at heating rates of about 250°C min^{-1} from 400 to 1300°C, applying loads of 120 MPa. High performance porous nickel electrodes having new phases with a particle size range between 1.0 and 8.7 μm have been obtained after rapid SPS operations. The electrochemical noise (EN) technique has been used to study the behavior of Ni-Mo alloy in KOH 30% solution at 70°C. In this study, the preliminary electrochemical analysis of the porous nickel electrodes was reported.

Keywords: Electrochemical Noise, Ni-Mo, Mechanical Alloying, Spark Plasma Sintering (SPS)

1. INTRODUCTION

The mechanical alloying (MA) has shown to be an effective process, that offers the possibility directly of obtaining novel structures from the milling [1-3]. The main advantages of the SPS process over traditional sintering techniques are the super fast heating and cooling rates that it can develop and the relatively high pressure applied on the samples. Depending on the electrical properties (nature) of the material being treated it is possible to reach full density and control its porosity while retaining its metastable character and the small crystal size of precursor powder (reduced grain growth). Therefore, it is possible to keep the high activity and performance of the material [4,5].

It has been reported that nickel-based alloys, when suitably prepared, are useful catalysts (electrodes) for the hydrocarbon conversion and the improvement of the alcohol, just to mention some examples. The relative inefficiency of the electrodes is one of the most outstanding factor of energy dissipation and high cost of the electrolytic hydrogen production. For that reason, in many cases the investigation has been focused to the control and understanding of the hydrogenation/dehydrogenation phenomena, which depends widely on the type of electrochemical reactions that happen in the interface electrode/electrolyte. Concerted efforts have been conducted to the development of electrocatalytic materials that are active, efficient and stable. Evidently, these characteristics are function of their composition and preparation method. For example, the Ni-Mo alloys widely have been studied in the alkaline media due to its demonstrated catalytic response [8-13]. It is worth noting that the hydrogen evolution reaction (HER) process occurring at the electrode/electrolyte interface reveals the electrocatalyst performance. On searching for active systems the smaller the hydrogen overpotential, the better is the electrocatalyst. The overpotential, i.e. the voltage shift (polarization) caused through an electrochemical cell by the passage of current, can properly be estimated using electrochemical techniques like linear sweep voltammetry (LSV), Tafel and resistance polarization (Rp). In this research work, a preliminary study of electrochemical noise measurements behavior of Ni-Mo alloys obtained by mechanical alloying and densified by spark plasma sintering has been carried out.

The random fluctuations of the potential or the current of a material subject to corrosion, can be evaluated by means of the technique of electrochemical noise. With this technique the state of the system in study is not altered, since any external disturbance is not applied to make the measurements. Also, electrochemical noise is an inversely proportional behavior at the frequency interval, to smaller frequency greater amplitude [14].

The electrochemical noise seems to reflect the individual sum of the random events, and the average square value (quadratic root r.m.s.) of the amplitude of these events, or standard deviation. In addition it has been seen that it provides the digital track with the amount of dissolved metal, depending on the combination atmosphere [15]. The electrocatalyst-metaestable alloy structure and properties, generally are studied by the reaction of hydrogen evolution in alkaline solutions [16], it is therefore that the objective of the present work is to obtain the corrosion behavior of the Ni-Mo alloy obtained by alloyed mechanic, and to evaluate them by means of the electrochemical noise technique, in the presence of KOH to 30 % and at 70 °C.

2. EXPERIMENTAL PROCEDURE

2.1. Powder Synthesis and Sintering.

Detailed explanation of the experimental sequence for powder synthesis and its SPS-treatment has been reported elsewhere [17-18]. Elemental Ni and Mo powders 99.99% pure of < 100μm in size were ball milled in a horizontal low-energy mill, set up at 120 rev.min^{-1} with stainless steel balls of 9 mm ϕ. A concentration of Ni-43at%Mo was selected for this study. Milling was performed for 800h under Ar atmosphere and the ball-to-powder weight ratio was set up 50:1. A commercial Dr. Sinter equipment (1020-Sumitomo Mining-Japan) was used at vacuum conditions while On/Off pulsed current cycles at 12/2 for the compacting runs. A cylindrical graphite die set of 8mm ϕ was used so that a maximum axial pressure of 120 MPa could be applied during the run. Before each SPS run, specimens were cold pre-compressed at 15 MPa.

2.2. Electrochemical Test.

A commercial potentiostat/galvanostat/ZRA operated by a personal computer was used to conduct electrochemical noise measurements. The working electrode (W) of the electrochemical cell is SPS-treated Ni-Mo specimen, which was coupled to a Cu wire. Specimens of various densities and open porosity were mounted in epoxy resins as to expose a face of 8 mm ϕ directly to KOH 30% high grade solution, which was kept stirred at 70°C during all the electrochemical noise analysis. The testing solution was nitrogen-bubbled at least 1h before and during the measurements. The counter electrode (CE) is a pure Pt wire and the reference electrode is a saturated calomel electrode (SCE, $Hg/Hg_2Cl_2/KCl$ sat). Electrochemical potential and current noise measurements (EPNM and ECNM respectively) were obtained at a sample rate of 0.5 reading/s to produce records of 1024 points. Fast Fourier Transform (FFT) analysis was applied to the experimental time series using a digital algorithm.

Table 1. Some features of mechanically alloyed Ni-43at% Mo powder densified by SPS.

Sample code	Powder Treatment (SPS)	Bulk Density g/cm^3	Open Porosity %
A	400 °C/3 min	5.77	30.0
B	650°C/4 min	6.32	24.14
C	650°C/4 min + PLS (5°C(min) 1000°C/30 min	6.44	6.730
D	800 °C/5 min	6.96	10.44
E	850 °C/3.5 min	7.90	6.50
F	1000 °C/4 min	8.60	0.040
G	1300 °C/5 min	7.27	10.52

3. RESULTS AND DISCUSSION

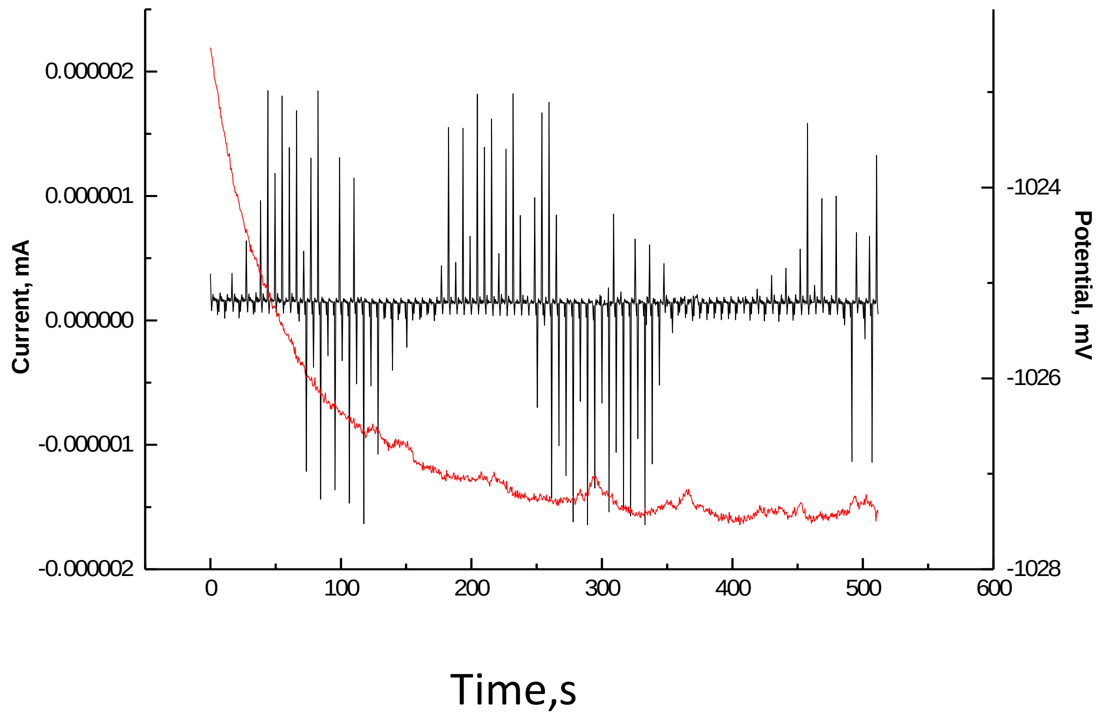
The results of the chemical composition of the alloy appear in table 2, which were analyzed by X ray Fluorescence.

Table 2. Chemical analysis of Ni-Mo powders, milled for 800 hours (weight %).

Ni	Mo	Si	Fe	Al	Cr
62.41206	36.52835	0.42877	0.35766	0.22903	0.04410

The generated electrochemical results revealed that the electrochemical behavior of the material was being submissive to the action of KOH at 30% and 70°C. Next the series of time of noise in current and potential for each one of the samples evaluated and sinterized under different conditions of temperature appeared.

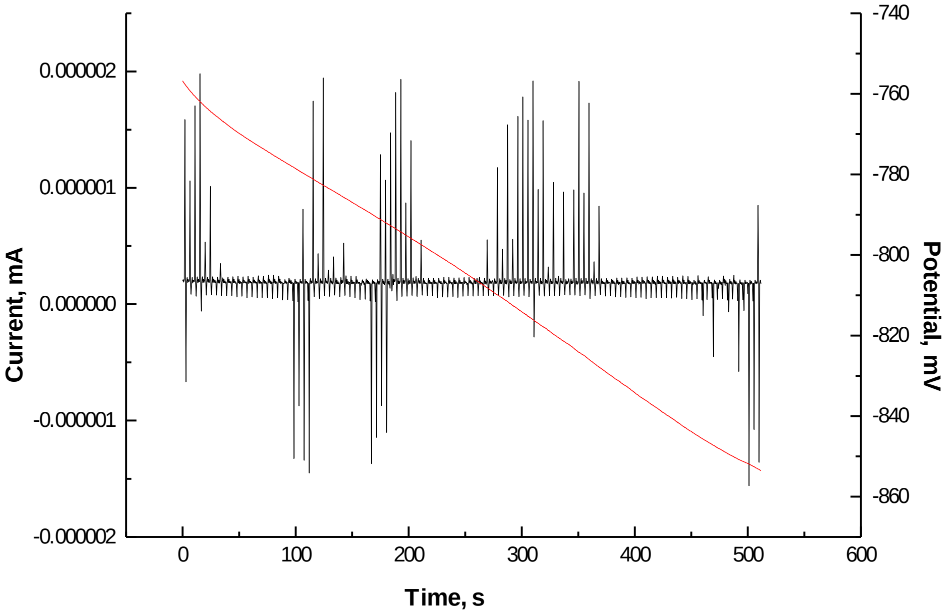
As illustrated in graph 1, the potential showed a tendency to diminish from the -1022 mV, but it went away returning constant near 1027 mV. Also, are possible to be appreciated transitory of high frequency and low amplitude.



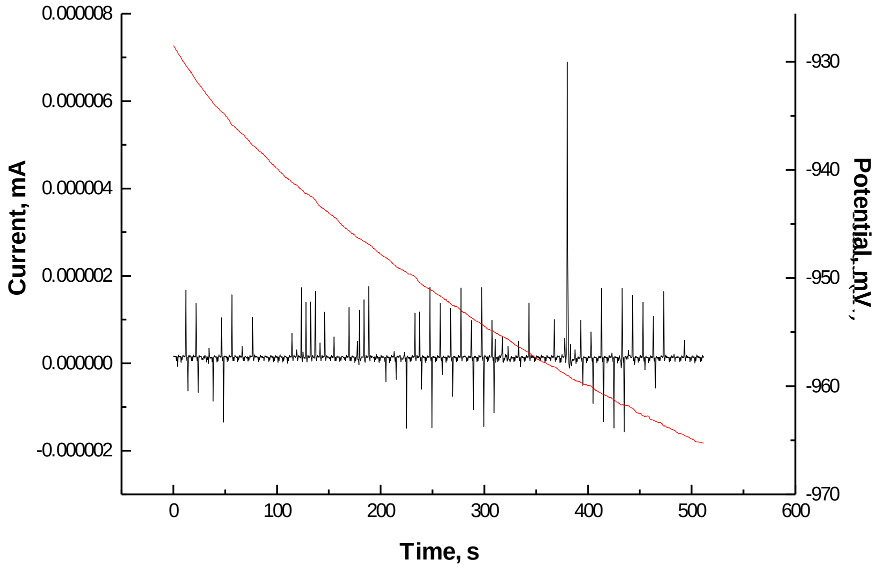
Graph 1. Time series of electrochemical noise in current and potential for sample A.

With respect to sample B, sinterized at 650°C, a slight decrease in the values of potential is appraised, fluctuating between 986 and 992 mV, also tending to diminish with time without reaching stability some of them. The transitory ones also were of high frequency and low amplitude.

When the alloy was at 650°C during 4 minutes and 1000°C by in form half an hour combined, by a side diminished the potential of corrosion to 760 mV, in addition which throughout the test maintained a tendency towards more negative values, reaching 860 mV. With respect to the transitory ones that can be appreciated, these are of VLF and amplitude, representing a straight line, as shown in graph 2.



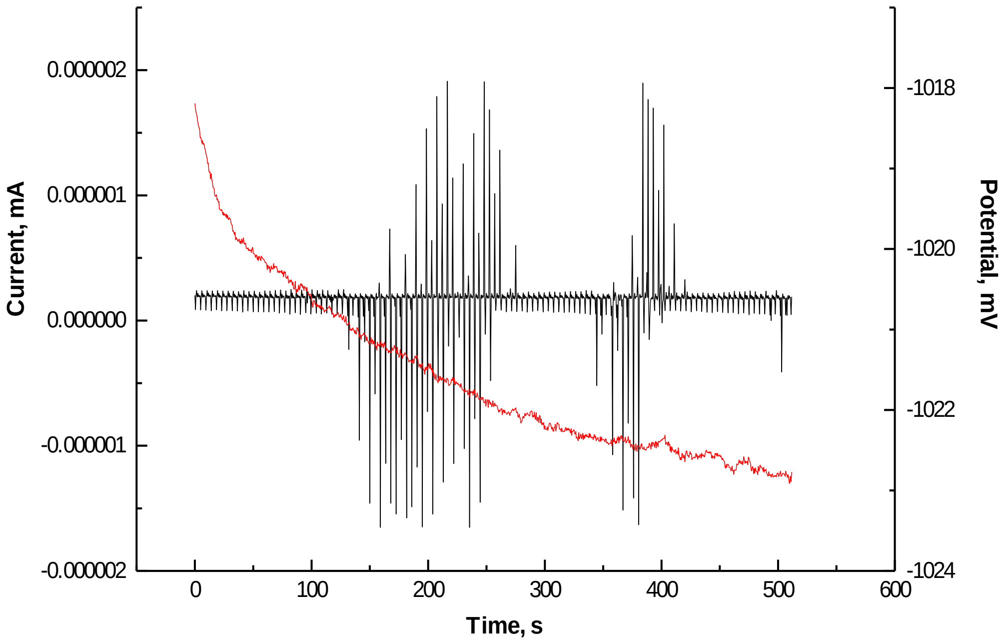
Graph 2. Time series of electrochemical noise in current and potential for sample C.



Graph 3. Time series of electrochemical noise in current and potential for sample D.

In graph 3 the obtained series of time for sample D, sinterized at 800°C by 5 minutes appear. The potential ones again reaches the values between 930 and 970 mV. Similar to the case of sample C, also this series of time is practically a straight line without transitory, because these are of very low frecuency and amplitude.

It becomes evident that the signal obtained when evaluating sample G, treated at 1300°C, appeared transitory of high frequency and low amplitude again, similar to the case of the sample A. To the potential of corrosion in this case practically stayed between -1018 and -1023 constant mV, always with tendency to diminish in the time.



Graph 4. Time series of electrochemical noise in current and potential for sample G.

From these results, it was found that the Rp of noise is higher for the samples with smaller percentage of porosity (C and D), meaning that the speed of corrosion is smaller as a result of less existing anodic sites. This leads, in turn, to a smaller degradation due to the smaller porosity of the material, that is, a smaller superficial area to be in contact with.

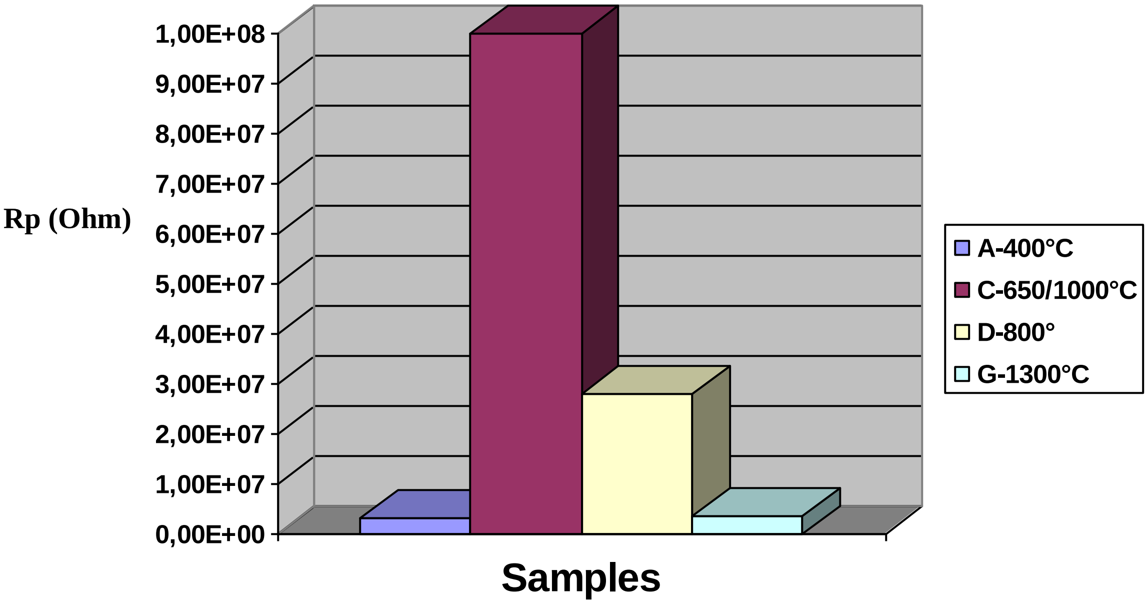
Regarding the temperature of the samples, the materials presented a transitory LF and low amplitude (as seen in samples C and D) as increasing the temperature. At 1300°C (as shown in sample G), a high amplitude and transitory LF was found, behaving very similarly to that encountered at 400°C.

Based on the porosity of the samples and the applied temperature sintering, the results obtained for the calculation of the Rp of electrochemical noise can be seen in graph 5.

$$Rp = \sigma E / \sigma I$$

Where: σE = standard deviation of noise in potential

σI = standard deviation of noise in current



Graph 5. Results obtained for the Rp of electrochemical noise.

The smaller value of Rp was obtained in the sample with greater porosity (To, 30%), whereas the greatest value was found in sample C, treated in combined form at 650 and 1000°C, and whose porosity was 6.7%. In the range of 800 and 1000°C, the sinterized pieces were developed very close to the Rp values (2.1é7 and 3.7e7 ohms).

The processing of powder through the MA technique usually ends up with a material highly mechanically-energised [1-5]. Unless effective annealing is carried out in the so refined powder product its microstructure will be inevitably unstable and thus reactive. In this work, it was attempted to prepare non-eroding Ni_Mo electrodes while retaining such *metastability* via rapid SPS densification operations [5,15,16]. Thereby not only the atoms in the bulk but also those placed at the surface of the resultant Ni_Mo electrodes are under tension or strain due to alteration of their lattice structure and interatomic forces of attraction. The electrochemical analysis of these electrodes revealed that the equilibrium potential *E*o of the set electrochemical cell adopted a value in the negative scale in the aqueous KOH solution. This suggests that the W-electrodes became negatively charged because a positive charged metal ion passed into solution. In such a case the system might be locally depolarised at the electrode-electrolyte interface with the cathodic reaction becoming energetically more favourable as long as the negative potential predominates.

The fact that E_{final} resulted more negative reveals thermodynamic irreversibility in the system. That is, supplying current into the surface of the negatively charged Ni_Mo electrodes makes that the potential difference, naturally created across the Helmholtz double layer to increase. Consequently the field strength existing at the electrode-electrolyte interface increases and Ni ions are pulled out of the solution across the double layer in an attempt to cancel out the superimposed overpotential[16-18].

4. CONCLUSIONS

The technique of alloyed mechanic metaestables Ni-Mo alloys with different densities and reactivity were prepared and applied. After employing the electrochemical noise technique, it was concluded that greater superficial areas, therefore greater porosities, the reaction of hydrogen evolution favored these materials in the presence of KOH at 70°C. The series of time of electrochemical noise are a useful tool in the evaluation and performance of these materials, improving their effectiveness as catalysts.

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