

Corrosion Resistance of Mo₃Si with Niobium Additions in Hydrochloric Acid

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Abstract

In the present work, the electrochemical behavior of molybdenum-silica-niobium alloy produced by arc cast technique is presented, keeping silica constant (at 24 wt %), using different niobium concentrations (5, 10, 15 & 20 wt %) as alloying elements. These samples were immersed in an electrochemical solution of 10 % by volume hydrochloric acid. The corrosion behavior was obtained using electrochemical techniques, namely: open circuit potential, polarization curves and electrochemical current noise. The potential behaviour as a function of time allows to determine the activity of the alloy as a function of its content, the polarization technique was used to obtain characteristic electrochemical parameters and the electrochemical current noise the type of attack while comparing them with the corrosion surface morphological features. Surface images showed different corrosion morphologies, being the most attacked the sample without niobium additions. It was found that niobium additions result in a better corrosion resistance when its concentration is increased in the alloy.

Keywords: polarization curves, electrochemical noise, hydrochloric acid, molybdenum, silica, niobium.

Introduction

Materials under highly corrosive environments such as oxidizing electrolytic media, high temperatures and structural stresses are being damaged under these extreme conditions, producing a high cost of investment. The constant demand for new materials to support several service conditions is increasing in a fast way. In the search of resistant materials, recently a new kind of alloys are being developed which provide good physical and mechanical properties, able to be used in hard technological processes, extending the service life and usefulness of them [1, 2]. Among these needed materials are the intermetallic compounds

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based on the Mo-Si system which are interesting materials to operate as structural ones under aggressive aqueous corrosion such as acid conditions in the chemical industry, and under high temperature as resistant heating elements and oxidation-resistant surface materials, specially MoSi₂. The molybdenum silicide alloys provide such good properties for these harsh conditions.

Molybdenum silicides have been studied with ternary alloy additions [3-7] obtaining an improvement in their resistance to different corrosive electrolytes and oxidation atmospheres. The main problem among many intermetallic compounds is their poor ductility and resistance at room temperature which produce a considerable limitation in structural applications specifically for Mo₃Si. Having alloys with good properties that can help to improve their performance under these requirements, will give a guideline into the use of them with different additions of a third alloying element, that will provide an improvement in the physical and mechanical properties of the alloy and also good corrosion resistance, for better service under extreme conditions.

Until now, these specific molybdenum silicides, i.e. Mo₃SiNb_x, have not been explored in relation to their corrosion resistance. For this reason, the purpose of the present work is to report the response of the molybdenum silicide alloys (Mo₃Si) with niobium additions under aggressive corrosion conditions.

Experimental procedure

The detailed alloy manufacturing was described elsewhere [1,2]. In order to perform the experimental work, each alloy sample with 5, 10, 15 and 20 % (atomic wt %) niobium additions, was cut using a diamond-disc cutter. As a control sample, an alloy without niobium addition was also prepared. Table 1 presents the alloys composition and the approximate area exposed was 1 cm² for each alloy.

Table 1. Mo-Si-Nb alloys composition (wt. %).

Alloy	Si	Nb	Mo
1	24	0	76
2	24	5	71
3	24	10	66
4	24	15	61
5	24	20	56

For the experiments (see Fig. 1), two 'identical' working electrodes, a saturated calomel reference and auxiliary graphite electrodes were set up and used simultaneously. The working electrodes were coupled to a conductive wire, and then inserted within a glass tube of 12 cm in length, to isolate the wires of the electric union from the electrolyte. The glass tubes were fixed with epoxy resin employed to encapsulate the metal samples. The exposed surface were grinded up to 600 emery paper and polished with alumina powder (0.5µm) to obtain a mirror like smooth surface. In this work, the electrodes were immersed into an

electrochemical cell containing a 10 % hydrochloric acid electrolyte, at room temperature. The samples were evaluated using open circuit potential measurements as a function of time, electrochemical current noise and polarization curve techniques. Duplicate experimental measurements were performed and the average values were obtained and presented.

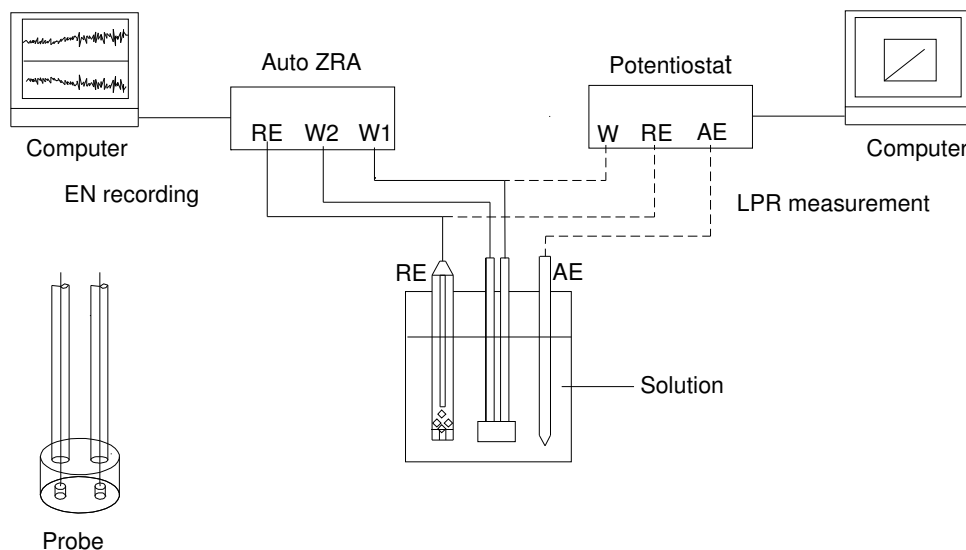


Figure 1. Experimental setup.

The electrochemical noise and polarization curve measurements were made using an electrochemical AC Gill ACM Instruments equipment. For polarization curves a saturated calomel reference electrode (SCE) and a graphite auxiliary electrode were used in a typical electrochemical cell arrangement. All potentials are referred to the standard calomel reference electrode. The polarization curves were obtained polarizing 500 mV above and below with respect to the free corrosion potential (E_{corr}) at a sweeping rate of 100 mV/min. To corroborate the reproducibility of the data collected through the electrochemical measurements, tests were repeated but with a slower sweeping rate of 6 mV/min, giving similar results.

Electrochemical noise measurements (ENM) were obtained using a three 'identical' electrodes set-up. Electrochemical noise data were recorded at 0.5 reading/second to produce current-time records of 1024 data points. Data processing includes trend removal of the signal by minimum square linear fitting and Hanning windowing, prior to obtain the current noise spectra using the Fast Fourier transformer (FFT) [8].

Results and discussion

The free corrosion potential behaviour as a function of time for the different alloys is presented in Fig. 2. The noblest potential obtained corresponds to the sample composition without Nb at around 40 mV SCE, remaining so till the end of the test. Less noble but very stable values correspond to the 20 % Nb alloy

composition, followed by the the 10 % and 15 % in the range between 0 and – 50 mV SCE respectively. All of these samples present steady state behaviour all along. The 5 % Nb sample showed the most negative or active potential, starting at around -110 mV SCE becoming slightly more negative after 300 minutes of immersion, reaching near -250 mV SCE remaining so till the end of the experiment.

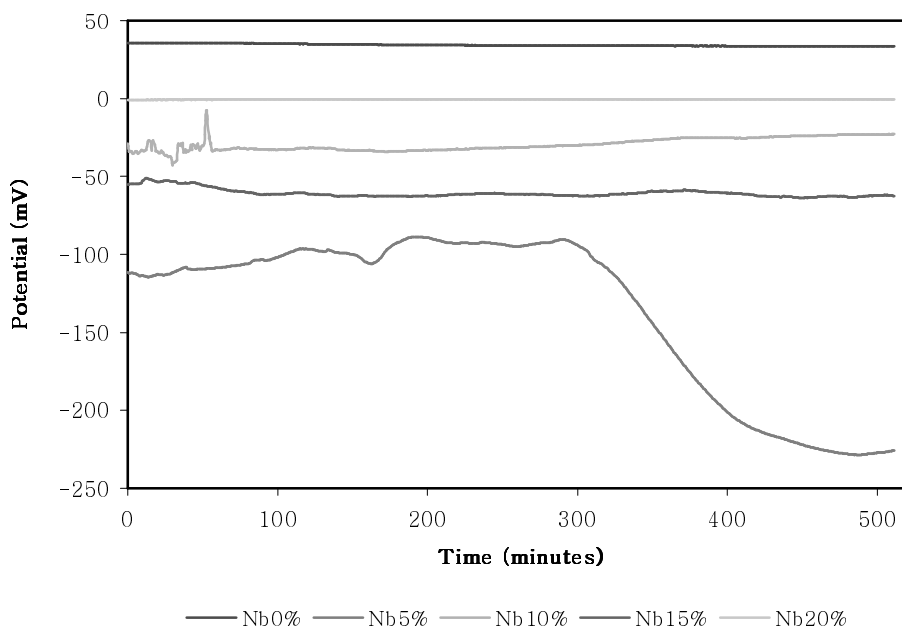


Figure 2. Corrosion potential as a function of time for different alloys.

Fig. 3 presents the potentiodynamic polarization curves obtained with a potential range between -500 to +500 mV around the corrosion potential. The corrosion potential becomes more positive as the niobium content is increased up to 20 %. The most positive corrosion potentials were obtained for the sample with 20 % niobium, being as noble or positive as the one observed for the sample without niobium (around 0 mV SCE). For the 5 % sample is -270 mV, for the 10 % niobium sample is -50 mV, while for the 15 % sample it is -150 mV; very similar with what was found with the open circuit potentials as a function of time. The cathodic branch for all the samples presents a Tafel and a concentration polarization region, with two slopes, changing at much more negative potentials. These are probably associated to mixed control, charge transfer and hydrogen evolution process.

In the anodic branch a non Tafel low polarization high current density increase can be seen for all the samples with different niobium concentrations. Two peaks are present very near the corrosion potential, possibly associated to oxidation and reduction of alloy compounds. At more positive potentials, a decrease in current density was observed, associated to the formation of a second passivation region. The anodic branch presents a passivation region of about 200 mV in the sample without niobium addition, initiating in 180 mV up to 380 mV. For the 5 % niobium sample this passivation potential diminishes to a value near to 0 mV,

whereas for those samples with 10% and 15% niobium concentration the potential rose up to 100 mV and for the 20 % sample the passivation potential increased to values close to 200 mV.

On the other hand, the passive current density is lower for the concentration of 20 % niobium with a value of 10^{-4} mA/cm², whereas for the 15 % Niobium concentration the passive current density increases three orders of magnitude up to 10^{-1} mA/cm². Finally, for concentrations of 5 % and 10 % Niobium and without it, the passive current density is in the order of 10^{-1} mA/cm². The passivation region for all the alloys shows a slight increase in the passive current density towards more positive potentials. This indicates that the corrosion products responsible for the passivation are not completely stable.

The pitting potentials for the samples tested, are the noblest at 300 mV for the sample without niobium, and for the samples with niobium additions the pitting potential increases as a function of concentration from 100, 175 to 250 mV respectively, reaching the transpassive region. The 20 % Niobium concentration sample did not show a pitting potential and transpassive region in the potential sweep range considered. This result indicates the beneficial effect of niobium additions, at least up to 20% wt.

Potential (mV)

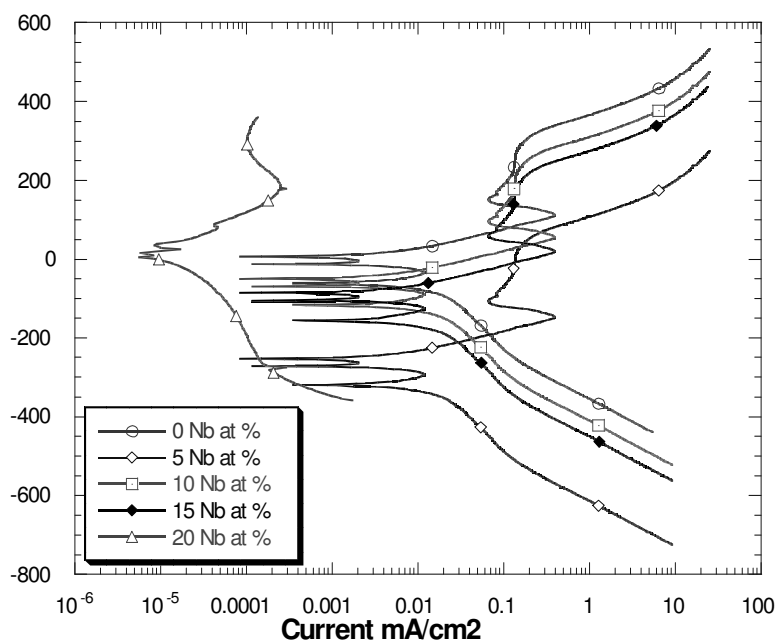


Figure 3. Potentiodynamic polarization curves for the alloys.

The electrochemical current noise as a function of time series and corresponding spectra obtained after trend removal is similar for all the samples, and an example is presented in Fig. 4. It is clearly observed at free corrosion conditions high amplitude, high frequency transient peaks of very short duration, which indicates that samples are more susceptible to film breakdown repassivating

events and to localized corrosion attack. This is consistent with the polarization curves where two peaks are present near the corrosion potential, this being associated to film formation for all the samples tested. For comparison, Fig. 4 presents the current noise and FFT spectrum for samples with and without 20 % niobium addition, in which a higher noise level could be observed for the former sample. When niobium is added to the alloys, the transitory peaks diminish gradually in amplitude and frequency as a function of niobium concentration, which suggests that niobium confers higher corrosion resistance to these alloys with such additions [1, 9].

Table 2 presents the electrochemical parameters for all the samples tested showing the corrosion potential, current density, pitting potential and the noise current standard deviation for the different niobium atomic percentages present in the alloy. It is possible to observe clearly the relation between the electrochemical parameters and the niobium concentration in the alloy.

Table 2. Electrochemical corrosion parameters.

Parameters	0%Nb	5%Nb	10%Nb	15%Nb	20%Nb
E_{corr} (mV)	0	-200	-150	-50	10
I_{corr} (mA/cm ²)	1.58E-01	6.32E-02	4.75E-02	6.30E-03	2.38E-03
I_{passive} (mA/cm ²)	0.1	0.09	0.09	0.08	0.0003
Pitting potential (mV)	300	100	175	250	-
σ_{ECN} (mA/cm ²)	9.2 E-5	5.1 E-5	6.0 E-5	3.1 E-5	1.5 E-5

From Tafel extrapolation, the values of the corrosion current density (I_{corr}) obtained from the polarization curves as a function of niobium concentration were plotted and presented in Fig. 5. It can be observed that the I_{corr} diminishes when the niobium concentration is increased in an exponential way. This corrosion current density based on the niobium concentration percentage can be expressed in the following form:

$$I_{\text{corr}} = 0.1827e^{-0.2244 (\% \text{ Nb})}$$

Fig. 5 shows the corrosion current density diminishing when the niobium concentration is increased, i.e., the corrosion rate is inversely proportional to the Niobium concentration.

Image analysis

Analysis by optical microscopy indicates surface and grain boundary corrosion attack for the specimen without Nb addition, as seen in Fig. 6. This figure shows the corrosion products due to the electrochemical attack in the corrosive environment of hydrochloric acid.

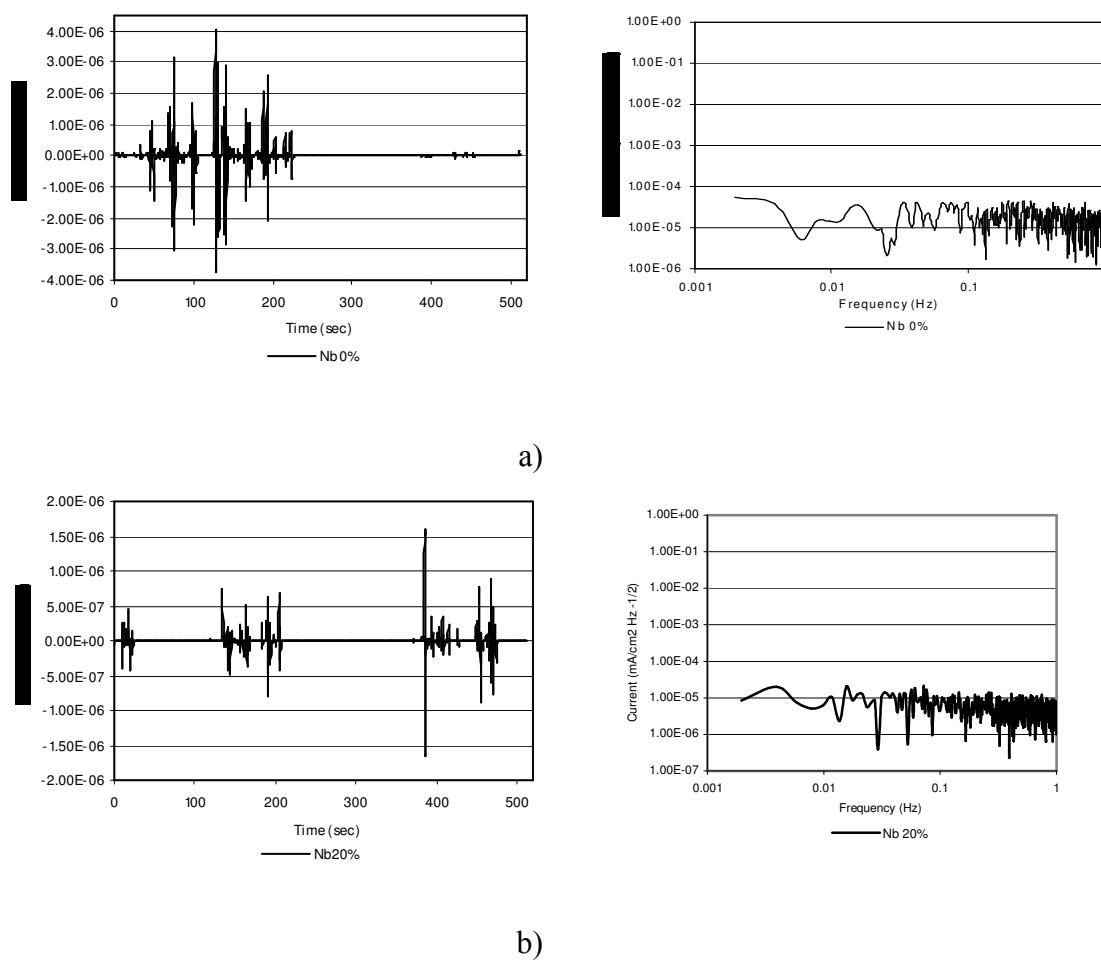


Figure 4. Electrochemical current noise and FFT spectra for a) sample without and b) with 20% niobium addition.

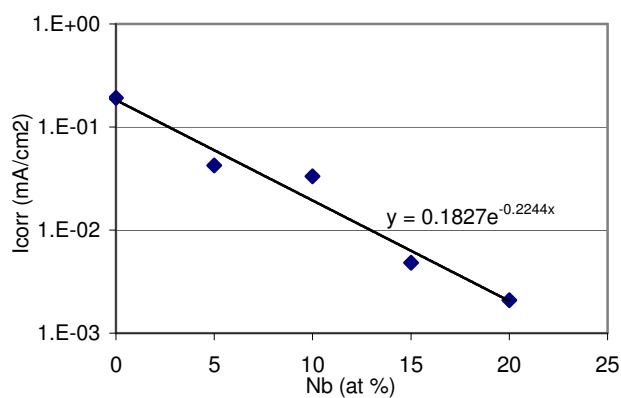


Figure 5. Relation between I_{corr} vs. Nb alloy concentration.

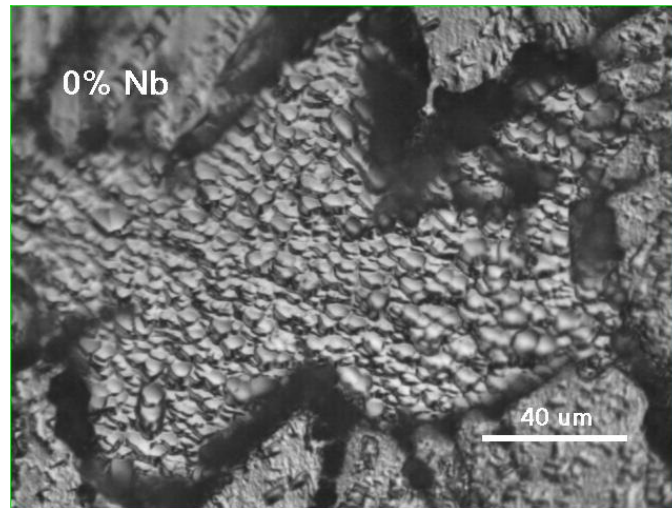


Figure 6. Corrosion attack over the alloy surface without niobium addition.

Fig. 7 shows the dispersive X ray analysis (EDAX) over the surface of the sample revealing the presence of Mo, Si, Nb and oxygen, therefore the presence of an oxide protective film as corrosion product.

Fig. 8 shows the alloy surface morphology with 10 % niobium. Localized corrosion in the form of pitting corrosion is shown and grain boundaries can be also observed. Grain boundaries are clearly visible due to the fact that acid solution effectively dissolves the grain matrix. It is thought that a passive layer is developed, since corrosion products over the surface were not observed. Similar attack was observed for the 5 and 15 % Nb alloy.

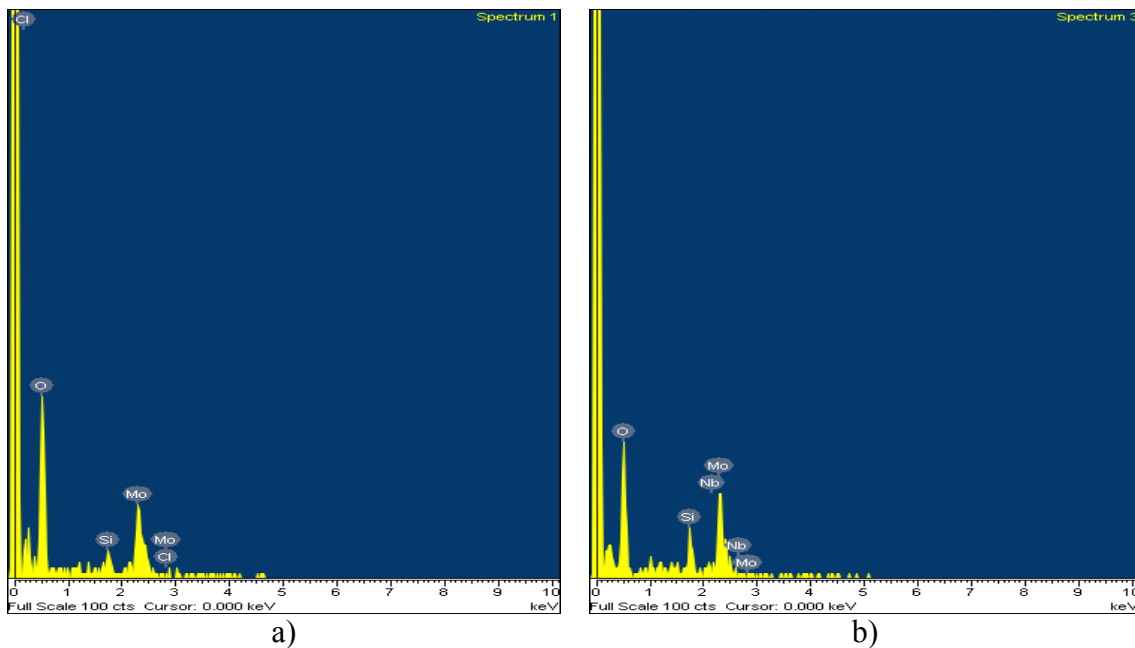


Figure 7. EDAX for sample (a) without Nb, and (b) with 20% Nb.

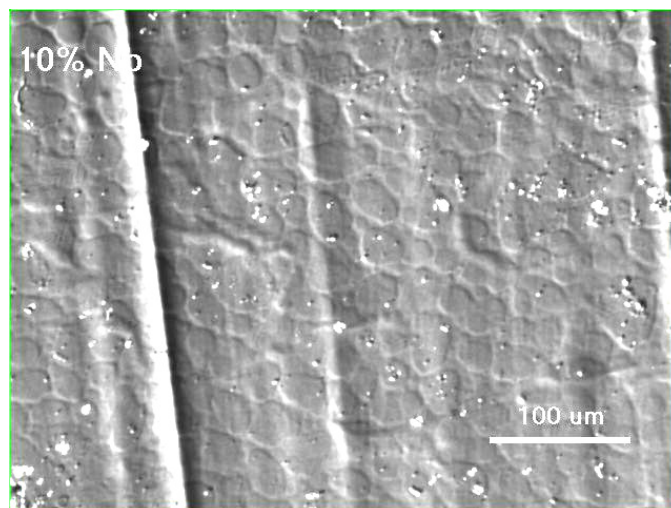


Figure 8. Corrosion attack over the alloy surface with 10% niobium addition.

In Fig. 9 some irregularities likely produced during preparation were observed over the surface of the specimen with 20% Nb. The surface is free of corrosion products and only some shallow pits were observed. Therefore, it appears that the use of the maximum percentage of Nb seems to be the optimal concentration to resist corrosion at least under the experimental conditions of the present work. These observations correlate well with the electrochemical measurement results obtained.

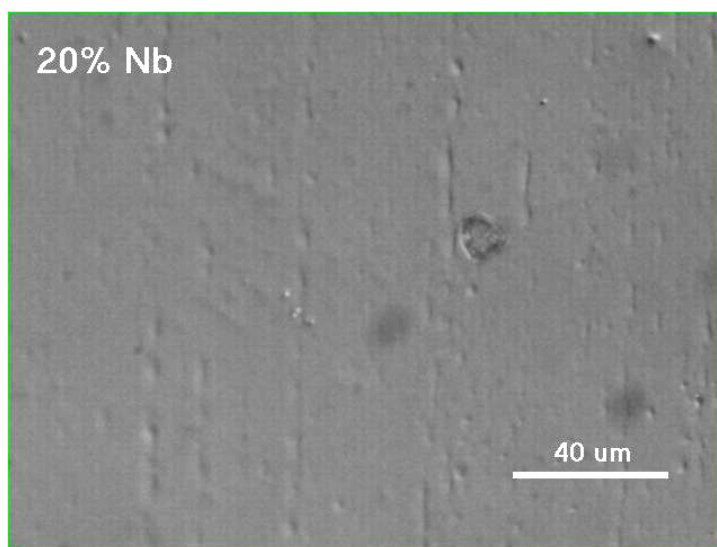


Figure 9. Corrosion attack over the alloy surface with 20% niobium addition.

Conclusions

For the experimental conditions tested, the following conclusions can be drawn from the electrochemical measurements made:

The addition of niobium to molybdenum silicide samples contributes to the reduction of the corrosion attack. As the niobium concentration increases, the overall corrosion rate decreases and the passive current diminished. Also the

pitting potential became more positive, being localized corrosion its main form of attack in the presence of a more stable passive or protective layer formed in the alloys with niobium additions.

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