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Influence of Vanadium on the Corrosion Behavior of High Manganese Steel in 0.5 M H_2SO_4 Solution

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The effect of vanadium on the corrosion behavior of high manganese steel in 0.5 M H_2SO_4 solution has been investigated using scanning electron microscopy, potentiodynamic polarization and impedance spectroscopy. The results have shown that the addition of vanadium to high manganese steel decreases the corrosion current density from 2.1 $\mathrm{mA\,cm^{-2}}$ to 1.29 $\mathrm{mA\,cm^{-2}}$. Impedance diagrams show the existence of a high frequency capacitive loop and a low frequency inductive loop. The addition of vanadium increases charge transfer resistance from 5.18 $\Omega\,\mathrm{cm}^2$ to 12.45 $\Omega\,\mathrm{cm}^2$.

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1. Introduction

The presence of manganese in range of 11 ÷ 19% in austenitic steels gives a good wear resistance to these steels [1]. It also gives the alloy a stable austenitic structure at room temperature. Austenitic manganese steels are widely used for applications requiring high impact and abrasion resistance [2].

The properties of the austenitic manganese steel vary with the variation of the alloying elements. With the increase of carbon content, the ductility decreases. The presence of high content of manganese and aluminum improves the corrosion resistance of manganese steel. The addition of such elements as titanium and vanadium causes a refinement of the grain size, which improves the wear resistance and fatigue strength by the formation of stable and very hard carbides [3].

A. Grajcar et al. [4] have conducted a study on the variation of the corrosion resistance of two manganese steels 26Mn-3Si-3Al-Nb-Ti and 24.5Mn-3.5Si-1.5Al-Nb-Ti, using tests of immersion in two solutions 1 M H_2SO_4 and 3.5% NaCl. They have shown that the corrosion resistance of the two steels in the acid or in NaCl is low. The large mass loss in the solution is due to hydrogen depolarization mechanism. It is a process of reduction of hydrogen ions (from the electrolyte) to the cathode areas by metal electrons.

M. Bobby Kannan et al. [5] have conducted a study on the corrosion behavior of two manganese steels Fe-29Mn-3Al-1.4Si and Fe-0.21Mn-0.42Al-0.02Si in an acid medium (0.1M H_2SO_4). They have shown that in the acidic medium, Fe-29Mn-3Al-1.4Si steel has low corrosion resistance compared to Fe-0.21Mn-0.42Al-0.02Si steel, which is due to the dissolution of manganese and iron in the acid.

2. Materials and equipment

The austenitic manganese steel samples used in the work were produced in the induction furnace of the foundry company ALFET, Tiaret, Algeria. The chemical compositions of two steels are given in Table I.

TABLE I

Chemical compositions of studied steels, Fe-14%Mn-1.2%C (Steel A) and Fe-14%Mn-6%V-1.2%C (Steel B).

Steel	C	Si	Mn	P	S	Cr	Ni	Al	V
(Steel A)	0.91	0.61	11.3	0.035	0.013	1.29	0.34	0.02	0.05
(Steel B)	1.22	1.01	11.7	0.03	0.01	1.29	0.32	0.01	6.07

The tests were performed using the potentiostat-galvanostat type Gamry interface 1000, connected to a PC running the software Gamry Framework. The electrochemical characterization was carried out in a conventional electrochemical cell. The steel (A or B) was connected as the working electrode (ET), platinum was used as counter electrode (CE) and a saturated KCl calomel electrode (SCE) was used as the reference electrode. The 0.5 M sulfuric acid electrolyte was used in the experiments.

The working electrode was polished with abrasive paper of increasingly finer grain size (600, 800, 1200, 2400 and 4000 grade), followed by rinsing with distilled water, and degreasing with acetone. Finally the sample was dried under the air stream. The experiments were performed in static conditions. The solution temperature was 27 °C. The potentiodynamic curves were plotted in the potential range (-800 to 200 mV)/SCE at a scan rate of 1 mV/min. Measurements of the electrochemical impedance spectroscopy (EIS) were performed in the frequency range of 100 kHz to 10 mHz. The applied open circuit potential had 10 mV amplitude.

The microscopic observation was carried out using QUANTA 250 scanning electron microscope.

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3. Results and discussion

The structures of the two steels are presented in the Fig. 1. Both structures are composed of austenitic matrix. The observation of the sample surface shows the presence of two zones having areas of different contrast. Dark areas are enriched in Mn and brighter areas are depleted of Mn [4].

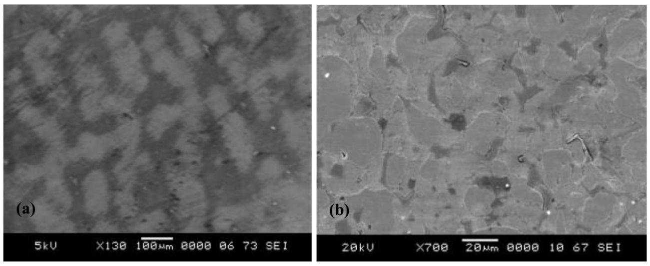

Fig. 1. SEM images of steels, (a) Fe-14%Mn-1.2%C (Steel A), (b) Fe-14%Mn-6%V-1.2%C (Steel B).

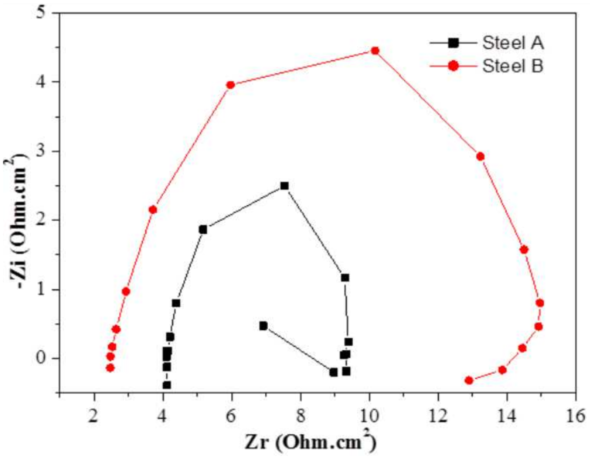

Fig. 2. Nyquist plots of steels: Fe-14%Mn-1.2%C (Steel A), Fe-14%Mn-6%V-1.2%C (Steel B) in 0.5M H_2SO_4.

Figures 2 and 3 show the EIS spectra; Nyquist plots and Bode diagrams of two steels, Fe-14%Mn-1.2%C (Steel A), Fe-14%Mn-6%V-1.2%C (Steel B), in 0.5 M H_2SO_4 electrolyte, at room temperature. The impedance diagram is composed of a capacitive loop at high-frequency and an inductive loop at low-frequency. The capacitive loop is attributed to the charge transfer reaction and time constant of the electric double layer. The inductive loop at low frequency is related to the relaxation process, related with the adsorption species, such as Cl^-_{ads} and H^+_{ads}, on the electrode surface [6]. Adding vanadium increases the modulus (Fig. 3a) and the phase angle shifts (Fig. 3b).

The electrochemical parameters obtained from fitting the experimental data of Nyquist plots by the equivalent circuit model (Fig. 4) are presented in Table II, where R_s is the solution resistance, CPE is constant phase element, R_{ct} is charge transfer resistance, R_L is resistance of the adsorption species and L is the inductance. The addition of vanadium to manganese steel increases the charge transfer resistance R_{ct} and reduces the CPE.

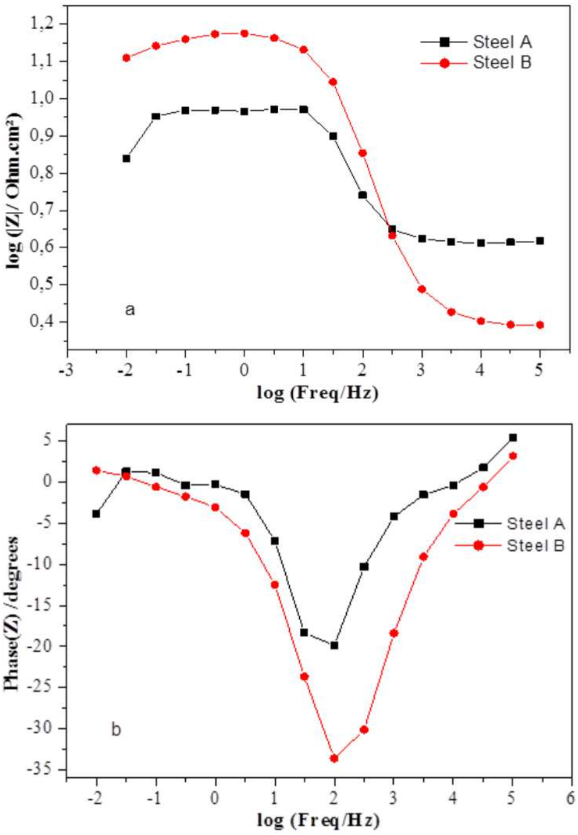

Fig. 3. Bode plots. log Z vs. freq. (a) and phase angle vs. freq. (b) of two steels: Fe-14%Mn-1.2%C (Steel A), Fe-14%Mn-6%V-1.2%C (Steel B) in 0.5M H_2SO_4.

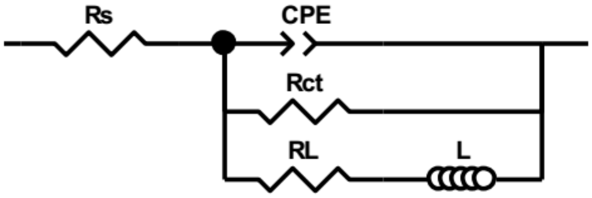

Fig. 4. Electrical equivalent circuit used to fit the impedance.

TABLE II

Data from electrochemical impedance measurements of steels: Fe-14%Mn-1.2%C (Steel A), Fe-14%Mn-6%V-1.2%C (Steel B) in 0.5 M H_2SO_4.

Steel	R_s [Ω cm^2]	R_{ct} [Ω cm^2]	CPE [μF cm^{-2}]	n	R_L [Ω cm^2]	L [H cm^2]
Steel A	4.135	5.187	824.4	0.964	10.64	61.03
Steel B	2.47	12.45	791.8	0.793	81.8	374.6

Figure 5 shows the polarization curves, potentiodynamic cathodic and anodic, of austenitic manganese steel without and with addition of 6% vanadium, in 0.5 M H_2SO_4, at room temperature. In Table III, the data related to the corrosion potential E_{corr} and corrosion current density I_{corr} obtained from these curves, are presented. The general form of $\log I = f(E)$ curves of the two steels is substantially identical. The calculated corrosion potential E_{corr} in the case of steel A is -474 mV with current associated with corrosion of $I_{\mathrm{corr}} = 2.1$ mA cm^{-2}. The corresponding values for steel B are -515 mV and 1.29 mA cm^{-2}, respectively. Comparison of values E_{corr} and I_{corr} shows that the addition of vanadium to the austenitic manganese steel decreases the corrosion current density.

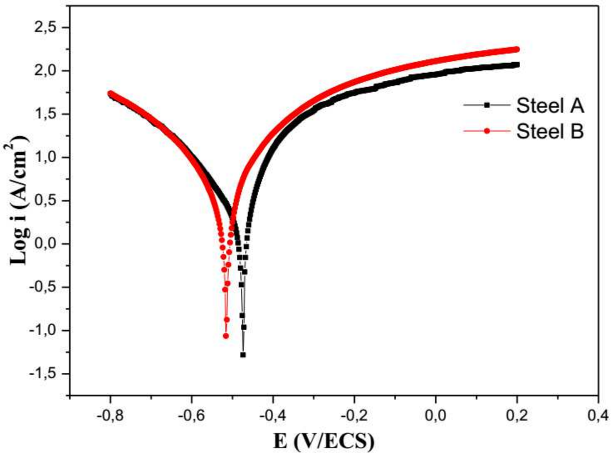

Fig. 5. Potentiodynamic polarization curves of steels: Fe-14%Mn-1.2%C (Steel A) and Fe-14%Mn-6%V-1.2%C (Steel B) in 0.5 M H_2SO_4.

TABLE III

Electrochemical parameters obtained from potentiodynamic polarization curves of two steels: Fe-14%Mn-1.2%C (Steel A) and Fe-14%Mn-6%V-1.2%C (Steel B) in 0.5 M H_2SO_4.

Steel	E_{corr} [mV vs. SCE]	I_{corr} [mA/cm^2]	B_a (mV/dec)	B_c (mV/dec)
Steel A	-474	2. 101	94.3	184.0
Steel B	-515	1. 295	63.5	82.1

4. Conclusions

The influence of vanadium on the electrochemical behavior of austenitic manganese steel Fe-14%Mn-1.2%C has been studied. The results of polarization curves show that the addition of vanadium to manganese-steel decreases the corrosion current from 2.1 mA cm^{-2} to 1.29 mA cm^{-2}. EIS measurements show that with the addition of vanadium, the charge transfer resistance increases, which increases the corrosion resistance of the steel.

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