Modification of Corrosion Resistance of the Plain Carbon Steels by Pulsed Electric Current

Jun-Yang Gao¹ · Xue-Bing Liu¹ · Hai-Fei Zhou² · Xin-Fang Zhang¹

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Abstract

The fracture of pipelines caused by corrosion cracks and the resulting oil and gas leakage can lead to great environmental pollution and economic losses. These negative effects are due to serious corrosion of the plain carbon steels used for armor of flexible pipe in oil and gas transmission medium. However, corrosion resistance of carbon steel armors has yet to be improved. In this study, the relationship between corrosion resistance and pearlite fraction in the plain carbon steels has been investigated through the application of pulsed electric current. Based on immersion test and electrochemical measurement, pulsed electric current increases the corrosion resistance of the plain carbon steels by reducing the fraction of pearlite phase. Pitting corrosion, which tends to initiate by galvanic corrosion of ferrite and cementite, is therefore inhibited due to the decrease in pearlite fraction (mixture of ferrite and cementite) under electropulsing.

Keywords Corrosion resistance · Pearlite · Pulsed electric current · Plain carbon steel

1 Introduction

With the development of offshore oil to the deeper sea, the corrosion resistance of marine pipelines is increasingly demanding. The carbon steel pipelines commonly used in submarine pipelines cannot meet the needs of the current industry due to poor corrosion resistance. In general, 30MnSi steel (0.3C–0.8Si–1.0Mn), due to its excellent strength, toughness and low cost [1–3], is widely used for armor of flexible pipe in oil and gas transmission medium. Cracks due to corrosion of carbon steel would result in pipe fracture and cause oil and gas leakage, which often caused significant economic losses and environmental pollution. Up to date, corrosion resistance of carbon steel armors has yet to be improved. The conventional way to improve corrosion resistance is to add alloying elements such as Cr

and Ni into steels and thereby changing the microstructure or coating of the steel surface [4, 5]. But these methods increase the production costs while reducing corrosion loss and require many heat treatments.

Pulsed electric current, as an instantaneous high-energy input method with high efficiency and low energy consumption, had been applied to the metallic materials to modify the microstructure and properties in a short time. Solid-state transformations, such as intermetallic compound formation and crystallization of amorphous, can be promoted and induced by pulsed electric current [6]. However, the study of the influence of electropulsing on the corrosion resistance of metallic materials has only just begun. The corrosion resistance of 316L stainless steel can be improved by low-energy high-current pulsed electron beam [7], while the intergranular corrosion of the nickel-based superalloy GH3044 can be retarded by electric field treatment [8]. The pulsed electric current was also used to refine MnS inclusion size during solidification and improve the pitting corrosion resistance of the 304 stainless steel [9]. Moreover, the corrosion resistance of X70 pipeline steel was optimized by grain refinement induced by high-current-density electropulsing [10]. Furthermore, the ultrafine-grained microstructure of low-carbon steel can be induced by high-current-density electropulsing [11], and the fragmentation of the cementite plates in strained

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✉ Xin-Fang Zhang
xfzhang@ustb.edu.cn

¹ School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

² Zhejiang Electric Power Corporation Research Institute, Hangzhou 310014, China

pearlitic steel can be implemented under electropulsing [12]. Therefore, experiments have demonstrated a significant effect of electropulsing on the microstructural evolution in metals and the change in corrosion resistance caused by these evolutions.

Although some interesting and important experimental results have been found, the understanding on the relationship between corrosion resistance and microstructure under external field has still not been clarified yet. It is viable to explain the possibilities and trends for the above experimental phenomena based on thermodynamics, but there are bottlenecks in the understanding of microstructural evolution from the kinetics. Due to the shortage of research data on this relationship, the accumulation of research data under external field becomes important. Based on this urgency, the corrosion resistance for the plain carbon steel used for armor of flexible pipe in oil and gas transmission medium is investigated under pulsed electric

current. The corrosion of the plain carbon steels was inhibited under pulsed electric current by reducing the fraction of pearlite phase. As we all know, carbon steel is poor in corrosion resistance; thereby, this process provides a pathway to inhibit the corrosion of plain carbon steel.

2 Experimental

Commercial warm-rolled 30MnSi steel composed of the following elements (wt%) of 0.30C, 0.8Si, 1.1Mn, 0.025P, 0.025S, 0.025Cu was used for investigation. The dimensions of the sample prepared for wire cutting are presented in Fig. 1a. In order to clarify the effect of the pulsed electric current on the corrosion resistance of the steels, the pulse with a damped oscillation wave detected in situ by a TDS3012 digital storage oscilloscope was applied to the objects. The schematic diagram of experimental arrangement for electropulsing treatment is shown in Fig. 1b. The pulse width is 100 μ s, and the values of maximum current density vary with the discharge voltage. The parameters for pulsed treatment are listed in Table 1. Here, the maximum temperature rise caused by Joule heating is about 150 $^{\circ}$ C, which basically does not have any effect on the microstructure evolution for carbon steels. Thus, the

Fig. 1 a Dimensions of the investigated steels; b schematic diagram of experimental arrangement

Fig. 2 Corrosion rate in immersion test for the untreated and treated 30MnSi steels

Table 1 Parameters of electropulsing treatment

Sample	Discharge voltage in series connection (V)	Discharge current (A)	Current density (A/mm ²)	Width (μ s)
1	—	—	—	—
2	5400	1.2×10^4	1.2×10^3	100
3	6600	1.5×10^4	1.5×10^3	100
4	7200	1.6×10^4	1.6×10^3	100

evolution of microstructure induced by Joule heating is negligible.

After the application of electropulsing, the steels were mechanically ground and polished. The samples were cleaned with absolute ethanol and distilled water. After being blown dried, the samples were weighed with an analytical balance of 0.0001 g accuracy. Prior to the immersion test for corrosion resistance, the other part of the sample was covered with resin, while the middle part was exposed for corrosion testing. The simulated seawater

solution containing heavy metal ions with pH value of 3.0 was prepared for immersion test according to GB T 19746–2005 specification. The samples were immersed in the solution for 72 h at room temperature. After the immersion test, the corrosion product was completely removed with 20% ammonium citrate solution (200 g ammonium citrate was added into distilled water and made 1000 ml solution), cleaned with distilled water, dried and reweighed. Then the average corrosion rate and thickness loss were calculated by the following equations:

$$v = \frac{W_b - W_a}{St}; \quad (1)$$

$$x = \frac{v}{\rho} \times 1000 \times 365 \times 24, \quad (2)$$

where v [g/(mm² h)] is the corrosion rate per hour and per mm², x (mm/y) is the thickness loss per year, W_a (g) and W_b (g) are the weight before and after the corrosion, S is the area of the samples exposed in the solution, t is the time of immersion test, and ρ is the density, which is 7.85 g/cm³.

Similarly, electrochemical tests for the prepared samples were performed using a three-electrode cell system on an electrochemical workstation, where the 30MnSi steel was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum plate as the counter electrode. The potentiodynamic polarization curves were measured in 3.5% NaCl aqueous solution from

Fig. 3 Potentiodynamic polarization curves at various parameters for untreated and treated steels

Table 2 Corrosion potential and corrosion current density of samples

Sample	Corrosion potential (V)	Corrosion current density [log (A/cm ²)]	Corrosion rate (mm/y)
1	− 0.9921	− 3.7205	2.2190
2	− 0.9638	− 4.0590	1.0178
3	−0.9644	−4.0232	1.0432
4	−0.9654	−4.0357	1.0739

Fig. 4 Optical **a** and SEM **b** micrographs for the warm-rolled steel

– 0.5 V (vs SCE) to 0.5 V (vs SCE) at a potential sweeping rate of 10 mV/s.

For the characterization of microstructures, polished followed by etched with 4 vol% nital solution, the microstructure was observed by optical microscopy and field emission scanning electronic microscopy with energy-dispersive spectroscopy (FESEM-EDS). Here, all tests including pulsed treatment and corrosion resistance test are repeated more than three times to ensure the repeatability of the experiment.

3 Results and Discussion

Figure 2 presents the corrosion rate in the simulated seawater solution for the untreated and treated 30MnSi steels. The corrosion rate of non-pulsed steel is 11.2 mm/y, while the minimum corrosion rate is 1.9 mm/y for the pulsed steel. It is amazing that the corrosion resistance of the carbon steel is increased by 5.9 times. Even for the maximum corrosion rate of 5.3 mm/y for the pulse steel, the corrosion rate is also improved by 2.1 times. It is suggested that the pulsed electric current greatly improves the

Fig. 5 SEM images for the pulsed samples: **a, b** for sample 2, **c, d** for sample 3, **e, f** for sample 4

corrosion resistance of plain carbon steel. Moreover, the corrosion resistance of carbon steel is reduced with the increase in current density. This indicates that there is a critical current density value under which the corrosion rate of 30MnSi steel is the lowest.

Figure 3 shows the potentiodynamic polarization curve of 30MnSi steels under various treatments. It is seen that the corrosion potential of samples treated with pulse is higher compared to the untreated samples. According to Tafel curve extrapolation, the corrosion potentials and corrosion current densities were calculated, and the results are shown in Table 2. Similarly, it can be observed that the corrosion potential also becomes smaller and smaller as the applied current density increases. This indicates that the corrosion resistance of the samples under electrochemical test is also related to the applied current density. In other words, for the pulsed sample, the greater the applied pulse current density, the lower the corrosion resistance of the sample. In this study, the corrosion resistance of the pulsed material was still stronger than that of the untreated materials even at the maximum current density.

The thickness loss per year (mm/y) was calculated by the following formula:

$$V = \frac{A \times I_{\text{corr}}}{n \times F \times \rho} \times 87,600, \quad (3)$$

where V is the thickness loss per year, A is atomic weight, I_{corr} is the corrosion current density, n is the valence of metal, F is the Faraday's constant ($F = 26.8 \text{ A h}$), and ρ is the density of metal. As calculated in Table 2, the corrosion rate of untreated steel is 2.219 mm/y, while those of pulsed steel are 1.0178, 1.0432 and 1.0739 mm/y, respectively. In comparison with the untreated steel, the corrosion rate of samples 2, 3 and 4 were reduced by 54.0, 52.9 and 51.6%. Both the immersion test and electrochemical measurement indicate that pulsed electric current significantly increases the corrosion resistance of plain carbon steels.

In order to clarify the mechanism of corrosion resistance under pulsed electric current, the microstructure of the commercial warm-rolled 30MnSi steel (sample 1) was investigated by optical microscope and SEM. The optical image in Fig. 4a shows that the warm-rolled steel is composed of white ferrite and dark pearlite, in which the ferrite is irregular and the pearlite is lumpy. In Fig. 4b, the SEM image clearly shows that the pearlite is a lamellar structure, which is a mechanical mixture of ferrite and cementite (Fe_3C) [13].

After applying the pulsed electric current, the microstructure of the carbon steels had undergone significant changes. For the sample 2 with current density of $1.2 \times 10^3 \text{ A/mm}^2$, the fragmentation of pearlite in Fig. 5b is clearly observed in comparison with that of the warm-

rolled samples. In general, the electrical conductivity of the ferrite is much larger than that of the pearlite consisting of high carbon and low iron [12, 14, 15]. The system free energy ΔG^e can be expressed by the following equation [12, 16]:

$$\Delta G^e = \frac{\mu}{8\pi} \iint \frac{\vec{j}_0(r)\vec{j}_0(r') - \vec{j}_1(r)\vec{j}_1(r')}{|r - r'|} d^3r d^3r', \quad (4)$$

where μ is the magnetic permeability, j is the current density, and r and r' are two different positions inside the system. The current distribution is changed from $\vec{j}_0$ to $\vec{j}_1$ due to the different electrical conductivities of ferrite phase and pearlite phase, which causes the change in free energy ΔG^e . Meanwhile, the dimensions of the matrix and the phases also affect the change in free energy. The experimental and computational results show that the electric current promotes a structural evolution of the material toward an overall lower resistance state. The configuration of the phase in the metal matrix, such as morphology and fraction, should be changed to satisfy the requirement for the minimum resistance in the electric current direction. Therefore, the pearlite in the sample 2 is refined under pulsed electric current to reduce the system resistance.

However, when the current density increases, the pearlite does not become more refined (Fig. 5d, f). So the question we are concerned with is whether the fraction of pearlite has changed. Based on Fig. 5a, c and e, the pearlite fraction in pulsed samples was counted by the ImageJ software. The fraction of pearlite in untreated sample was also investigated based on Fig. 4a. As shown in Fig. 6, the pearlite fraction for pulsed samples is lower than that without electropulsing. As the current density increases, the pearlite fraction increases, but it is lower than that of the untreated sample. In general, the electrical conductivity of ferrite is greater than that of cementite, but as the

Fig. 6 Fraction of pearlite for the pulsed and untreated samples

temperature increases, the difference in the electrical conductivity between the ferrite and cementite will gradually decrease [14, 17], as shown in Fig. 7. In this study, as the current density increases, the Joule heat also increases, so that the difference in the electrical conductivity between the ferrite and cementite will decrease. The decrease in the difference in the conductivity leads to a decrease in the fraction of ferrite formation, while the fraction of pearlite formation increases slightly. This is why the content of pearlite increases slightly with the increase in current density.

Simultaneously, the corrosion rate of pulsed samples is also lower than that of untreated sample (see Fig. 2 and Table 2). That is, the lower the fraction of pearlite, the slower the corrosion rate of steel in this study. Pitting corrosion tends to initiate by galvanic corrosion of ferrite and Fe_3C [14, 18–20]; at the same time, pearlite is composed of ferrite and cementite. So pulsed electric current

Fig. 7 Electrical conductivity of ferrite and cementite with temperature

can increase the corrosion resistance of the plain carbon steels by decreasing the fraction of pearlite in this study. As shown in Fig. 8, the micro-morphologies of the ferrite-pearlite steel after immersion for 24 h (Fig. 8a) and 72 h (Fig. 8b) in the acidic chloride solution indicate that the lamellar ferrite in the pearlite is preferentially dissolved, resulting in the remaining lamellar cementite Fe_3C on the surface. On the other hand, there are many deep gaps along the lamellar cementite, which indicates that the fraction of residual Fe_3C will increase as the ferrite is corroded. To clarify this assumption, XRD (Fig. 9) was used to detect changes in the volume fraction of the phases. For untreated samples (0 h), only the diffraction peaks of ferrite can be detected, while the peaks of Fe_3C are below the detection level of XRD. When the sample is immersed for 24 h, a weak diffraction peak of Fe_3C can be detected, which indicates that the relative content of Fe_3C increases after

Fig. 9 XRD patterns of the ferrite-pearlite steel after immersion for 0, 24, 48 and 72 h in the acidic chloride solution

Fig. 8 Micro-morphologies of ferrite-pearlite steel after immersion for **a** 24 h and **b** 72 h

etching. With the prolonged corrosion time (48 and 72 h), ferrite is dissolved in a large amount, and the relative content of Fe_3C is getting larger and larger, so the detected signal becomes stronger and stronger.

4 Conclusion

The results of immersion test and electrochemical measurement indicate that pulsed electric current increases the corrosion resistance of the plain carbon steels. Due to the lower electrical conductivity of the pearlite, the resistance in the pulsed samples is reduced by decreasing the pearlite fraction. Therefore, electropulsing technique provides an effective way to increase the corrosion resistance of the plain carbon steels used for armor of flexible pipe in oil and gas transmission medium.

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