Effect of Aluminum and Silicon on Atmospheric Corrosion of Low-alloying Steel under Containing NaHSO₃ Wet/dry Environment

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The atmospheric corrosion performance of Al-alloying, Si-alloying and Al-Si-alloying steel were studied by wet/dry cyclic corrosion tests (CCT) at 30 ℃ and 60% relative humidity (RH). The corrosion electrolyte used for CCT was 0.052 wt% NaHSO₃ (pH~4) solution. The result of gravimetry demonstrated that Al-Si-bearing steels showed lower corrosion resistance than other rusted steels. But the rusted 0.7%Si-alloying steel showed a better corrosion resistance than rusted mild steel. Polarization curves demonstrated that Al-/Si-alloying and Al-Si-alloying improved the rest potential of steel at the initial stage; and accelerated the cathodic reduction and anodic dissolution after a rust layer formed on the surfaces of steels. XRD results showed that Al-Si-alloying decreased the volume fraction of Fe₃O₄ and a-FeOOH. The recycle of acid accelerated the corrosion of steel at the initial stage. After the rust layer formed on the steel, the leak of rust destabilized the rust layer due to the dissolution of compound containing Al (such as FeAl₂O₄, (Fe, Si)₂(Fe, Al)O₄). Al-Si-alloying is hence not suitable for improving the anti-corrosion resistance of steel in industrial atmosphere.

Keywords : *Al-alloying, Si-alloying, atmospheric corrosion, electrochemical measurements, physical analysis*

1. Introduction

The excellent anti-corrosion property of weathering steel comes from an adherent and protective rust layer formed on its surface after a long-term atmospheric exposure. However, the price of conventional weathering steel, alloyed by Cu-P-Cr-Ni or other noble elements, is more expensive than that of carbon steel and limits its widely usage.[1]

Al and Si are rich and cheaper elements compared with other alloying elements in conventional weathering steel. So the weathering steel alloyed by Al-/Si-(or Al-Si) has been soaring in recent years. Up to now, previous researches on Al-/Si-alloying weathering steel mainly are focused on its data collection and corrosion performances in saline environment, for example, T Nishimura et al[2,3] clarified the existence of Al as FeAl₂O₄ in rust using a binary-phase potential-pH diagram and physical analyses; our research group found that the corrosion resistance of Al-bearing steel is increased with the increasing Al contents in steel, and Al-Si compound addition to steel presented clear synergistically corrosion resistance.[4] It is still

a lack of research on the corrosion data and corrosion performance of Al-/Si-alloying steel in industry atmosphere containing SO₂.

The purpose of this investigation was to determine the corrosion performance and possible corrosion mechanisms of Al-/Si-alloying steel under containing NaHSO₃ wet/dry cyclic environment from gravimetry, electrochemical measurements and physical analysis.

2. Experimental

The sample materials were in mild steels (0.21C-0.21Si-0.58Mn-0.017P-0.036S-0.02Cu-balance Fe, wt%) containing 0.5%Al, 0.7%Si and 0.5%Al-0.7%Si. The steel sheets were cut into 20 mm×20 mm×2 mm. Then the samples were polished successively down to a 1000 grit SiC paper, cleaned ultrasonically in acetone, rinsed with absolute ethyl alcohol, dried by drier and kept in desiccator for at least 48 hours.

In the corrosion tests, 0.052% NaHSO₃ (pH~4) solution was dropped on the samples' surface at a ratio of 0.4 l-m⁻². Then the samples were put into a CSH-220 constant temperature and humidity testing chamber, dried at 30 ℃ and 60%RH for 12 hours and rinsed by distilled water before dropping the salty solution again in order to avoid pro-

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gressive salt accumulation. The process above was repeated until 120 cycles.

Weight-gain measurements were made after various exposure periods. To investigate how Al-/Si-alloying affects the composition of rust, quantitative analysis of iron rust phases was carried out after 120 cycles, using XRD internal standard method. The rust for XRD was scraped from the corrosion specimens with razor and ground in mortar. XRD was carried out using a Rigaku-D/max 2000 diffractometer employing a Cu Ka target under 50 kV-250 mA and a scanning speed of 2°/min. The standard chemicals used in the measurement were a-FeOOH, analytical rarefied (A.R.) grade; γ-FeOOH, A.R. grade; Fe_3O_4, A.R. grade. Pure fluorite (CaF_2) was used as the solid solvent to prepare a series of standard solid solutions containing the chemicals mentioned above.

For electrochemical tests, a 3-terminal electrochemical cell with a saturated calomel electrode(SCE) as reference electrode, a platinum slice as counter electrode and the steel specimen as working electrode was employed for all electrochemical measurements. EIS instrumentation consisted of a Solartron 1260+1287 system. Potentiodynamic polarization curves were generated using a Solartron 1287 potentiostat. Both EIS and PC of bare and rusted steels were measured in 0.3% NaCl solution. EIS measurements were conducted at the rest potential with a 10 mV perturbation and 6 points/decade. The frequency range covered from 10 kHz to 5 mHz. The experimental results were interpreted on the basis of equivalent circuit using a suitable simulating procedure elaborated by ZSimpWin software. For the measurement of PC, the potential of specimen was swept at a rate of 0.1667 mV/s from the initial potential of -250 mV versus rest potential to the final potential of 250 mV versus rest potential. All the measurements were carried out at room temperature. All the potential values in this paper were set as values versus SCE.

3. Results and discussion

Fig. 1 shows corrosion weight gain as a function of the cyclic number. Generally, weight gain of all steels was increased with time going on. Different steels have various gravimetry: Si-bearing steels showed a lower weight gain than that of mild steel, while 0.5%Al-alloying and 0.5%Al-0.7%Si-alloying steels showed a higher weight gain than that of mild steel. The results above indicated that the effectiveness of Si alloying on corrosion resistance of steel to a certain content, while Al alloying couldn't improve the corrosion resistance of steels in industry atmosphere. In addition, Al-Si-alloying accelerated the corrosion of steel synergistically.
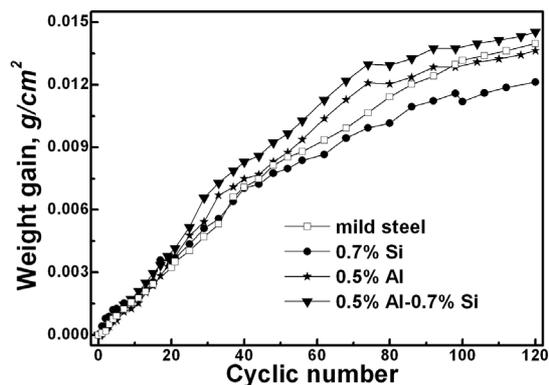

Fig. 1. The weight gain of Al-/Si-alloying steels as a function of cyclic number in 0.052%NaHSO$_3$ solution
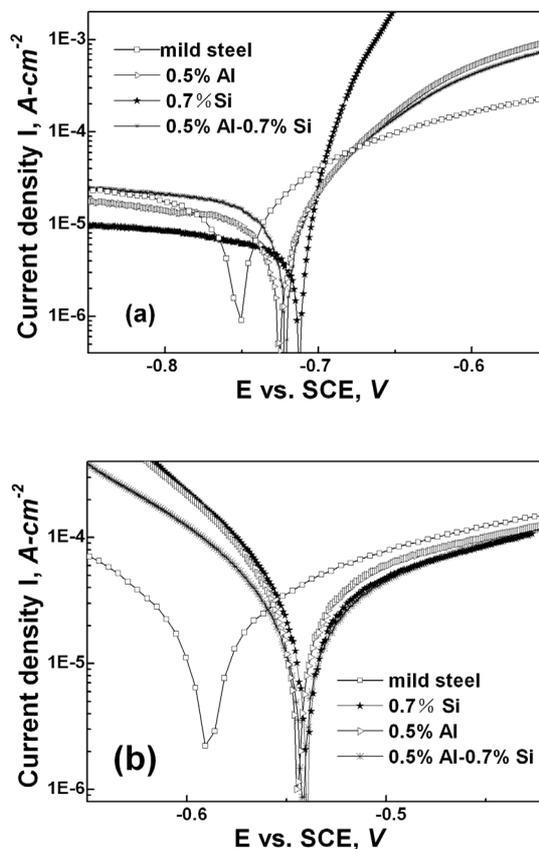

Fig. 2. Polarization curves of Al-/Si-alloying steels: (a) blank steels, (b) rusted steels after 20 wet/dry cycles

Fig. 2 shows the polarization curves of Al-/Si-alloying steels in 0.052% NaHSO$_3$ (pH~4) solution. At the initial stage, alloying increased the rest potential of steels and increased the anodic dissolution current, Si-alloying depressed the cathodic reaction, Al-alloying and Al-Si-alloying didn't clearly affect the cathodic reaction (Fig. 2(a)),

which main reactions are as follows:

$$2Fe+4NaHSO_3+3O_2 \rightarrow 2FeSO_4+2Na_2SO_4+2H_2O \qquad (1)$$

$$FeSO_4+O_2+H_2O \rightarrow FeOOH+H_2SO_4 \qquad (2)$$

Then the renascent sulfuric acid accelerates the corrosion of iron:

$$H_2SO_4+O_2+4Fe \rightarrow FeSO_4+H_2O \qquad (3)$$

The liberated sulfuric acid is regenerated by hydrolysis of fresh $FeSO_4$ again. Thus more acid are produced by the oxidation and hydrolysis of $FeSO_4$ again and again. This kind of phenomenon is called acid regeneration cycle.[5] Due to the preferentially dissolution of Al instead of Fe in Al-bearing steel, the amount of $FeSO_4$ is less than that of mild steel, which could slow the acid circulation.

A layer of rust formed on the surface of steels after 20 wet/dry cycles. Then conditions become favorable to

electrochemical changes connected with the interface $Fe|FeSO_4|FeOOH$. At some points iron was dissoluted, while at other points the electrons was used up in the cathodic reduction of the rust to magnetite ($FeOOH+Fe^{2+}+2e \rightarrow 3Fe_3O_4+4H_2O$). Alloying mainly accelerated the cathodic reduction and improved the rest potential of steels (Fig. 2(b)).

Fig. 3 shows the typical results of EIS measurements on Al-/Si-alloying steels after various cycles. Generally, Al-/Si-alloying could increase the polarization resistance (Rp) of steels at the initial stage (as polished, Fig. 3(a)), which could enhance the corrosion resistance of steels. The resistance of rust layer mainly increased with increasing wet/dry cycles (Fig. 3(b) and Fig. 3(c)). The corrosion of steel was uniform corrosion in $NaHSO_3$ solution. The rust layer formed on the steels was loose and porous, too. Therefore, the EIS of steels main existed as the dispersion character of diffusion control (Fig. 3(d)).

Fig. 4 shows the composition of corrosion products on steels after 120 cycles, which was analyzed by XRD. In containing HSO_3^- environment, rust phases were proved
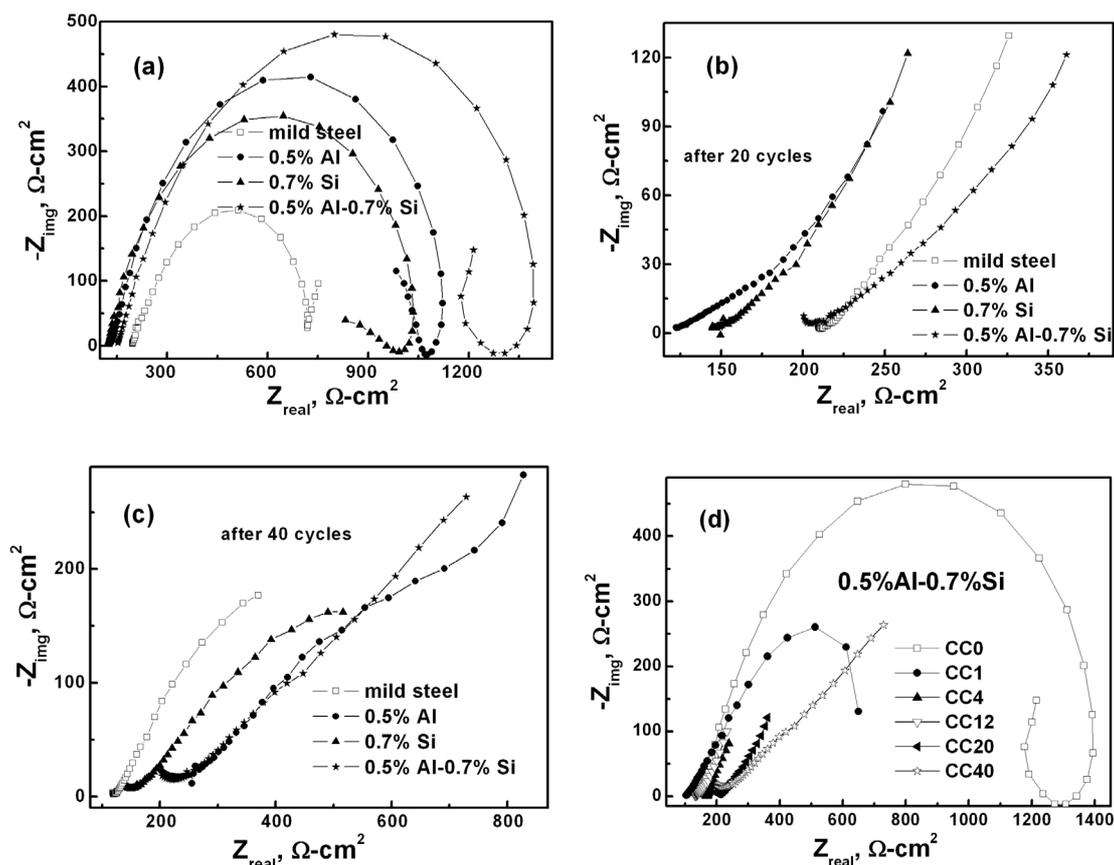

Fig. 3. Nyquist diagrams of Al-/Si-alloying steels: blank steels (a), and rusted steels after 20 (b), 40 (c) cycles and 0.5%Al-0.7%Si-bearing steel (d) in 0.052%NaHSO₃ solution, respectively
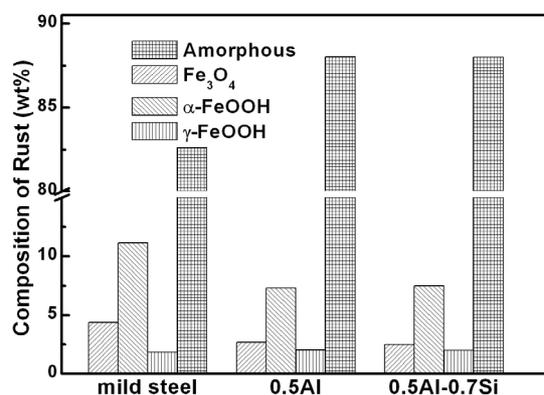
Fig. 4. XRD quantitative analysis of the corrosion production on the steels after 120 cycles in NaHSO$_3$ solutions: 0.5%Al= 0.5%Al-alloying steel, 0.5Al-0.7Si=0.5%Al-0.7%Si-alloying steel

to be a-FeOOH, γ-FeOOH, Fe$_3$O$_4$. Those phases that cannot be identified in quantitative analysis of the iron rust are called amorphous conventionally. Therefore, the main corrosion products formed on Al-/Si-alloying steels were still composed of a-FeOOH, γ-FeOOH, Fe$_3$O$_4$ and amorphous in industrial environment. Both Al-alloying and Al-Si-alloying decreased the volume fraction of Fe$_3$O$_4$ and a-FeOOH, sharply increased the volume fraction of amorphous. Previous studies showed that both Fe$_3$O$_4$ and a-FeOOH are stable corrosion products in atmosphere. The results above indicated that stable rust was difficult in forming on Al-alloying and Al-Si-alloying steels. Considering the pH value of NaHSO$_3$ solution was less than 4 because of acidification (2SO$_3^{2-}$ +O$_2\rightarrow$2SO$_4^{2-}$). The change of rust composition can be interpreted in terms of the dissolution of Fe$_3$O$_4$ and FeAl$_2$O$_4$ based on the thermodynamic stability of the oxide rust:

$$8H^+ + FeAl_2O_4 \rightarrow 4H_2O + 2Al^{3+} + Fe^{2+} \qquad (4)$$

$$8H^+ + Fe_3O_4 \rightarrow 4H_2O + 3Fe^{3+} \qquad (5)$$
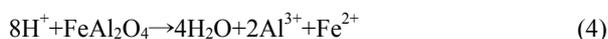
The dissolution of compound (Fe$_3$O$_4$ and FeAl$_2$O$_4$ or (Fe, Si)$_2$(Fe, Al)O$_4$) loosened the rust layer, which made the transmission of O$_2$ easier and accelerated the oxidation of Fe^{2+}:

$$2Fe^{2+} + O_2 + H_2O \rightarrow 2FeOOH \qquad (6)$$

Al-alloying or Al-Si-alloying also depressed the transformation of FeOOH to a-FeOOH under the lower pH value condition, which caused the following reaction was accelerated:

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+} \qquad (7)$$

Therefore, the corrosion of Al-alloying and Al-Si-alloying steels was accelerated.

4. Conclusions

The acid regenerated circulation was main reaction at the initial wet/dry stage under 0.052%NaHSO$_3$ solution (pH~4). For rusted Al-alloying and Al-Si-alloying steels, Al-alloying destabilized the rust layer due to the dissolution of compound containing Al (such as FeAl$_2$O$_4$, (Fe, Si)$_2$(Fe, Al)O$_4$), which loosened the rust layer and accelerated the corrosion of the steels. Thus Al-alloying and Al-Si-alloying are not suitable for improving the anti-corrosion resistance of steel in industrial atmosphere.

References

1. J. H. Dong, X. H. Chen, E. H. Han, and W. Ke, *Proc. Of the 3rd International Conference on Advanced Structural Steels*, p.332, Shanghai (2004).
2. T. Nishimura and T. Kodama, *Corrosion Science*, **45**, 1073 (2003).
3. T. Nishimura and T. Kodama, *13th Asian-Pacific corrosion control conference*, A-16, Osaka (2003).
4. X. H. Chen, J. H. Dong, E. H. Han, and W. Ke, *Corrosion Engineering, Science and Technology*, **42** (2007)
5. U. R. Evans, *Corrosion Science*, **9**, 813 (1969).