TOPICAL REVIEW

Corrosion resistance of Si–Al-bearing ultrafine-grained weathering steel

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Abstract

In the Ultra-steel project at the National Institute for Materials Science (NIMS), which run from 1996 to 2005, high-Si–Al-content ultrafine-grained (UFG) weathering steel was developed by grain refinement and weathering guidance. It was found that this steel has excellent strength, toughness and corrosion resistance. Samples were prepared by multi pass warm rolling at temperatures between 773 and 873 K. The grain size of steel rolled at 873 K was about 1 μm, and the tensile strength (TS) and elongation (EL) had excellent values of 800 MPa and 20%, respectively. In general, steels with high Si and Al contents exhibit inferior toughness to carbon steel (SM); however, the toughness of the developed sample was markedly improved by grain refinement. Cyclic corrosion tests in the presence of chloride ions confirmed that the developed steel exhibited excellent corrosion resistance, superior to that of SM. Electron probe microanalysis (EPMA) and transmission electron microscopy (TEM) analyses showed that Si and Al mainly exist in the inner rust layer. Si and Al were identified as existing in the Si$^{2+}$ and Al$^{3+}$ states in the nanoscale complex oxides constituting the inner rust layer. Electrochemical impedance spectroscopy (EIS) measurement showed that the corrosion reaction resistance ($R_t$) of the developed steel was much greater than that of SM. In the developed steel, the nanoscale complex oxides were formed in the inner rust layer, which increased $R_t$, and resulted in the excellent corrosion resistance.

Keywords: corrosion, weathering steel, ultrafine grain, rust, aluminum, silicon

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

It is very important to use weathering steel to reduce the maintenance cost of infrastructure facilities in the world [1, 2]. Weathering steel can form a durable protective rust on the surface under mild conditions; however, as there are many steel structures in coastal areas, it is necessary to use highly resistant weathering steels to protect against corrosion caused by airborne salt particles. Thus, Ni-bearing weathering steels that can be used in coastal environments have been proposed [3]. However, since Ni is a rare metal and prevents the recycling of steels, it may be more difficult to utilize in the future. Therefore, to establish a guiding principle for obtaining weathering steels which are durably protective against corrosion and do not contain a rare metal, the thermodynamic stability of various rusts (Fe-X systems) was investigated using binary-phase potential-pH diagrams in the 1st Ultra-steel project at NIMS [4]. Our results indicated that Si and Al had the potential to form stable complex oxides with iron. Si and Al do not prevent the recycling of steels, which is necessary to take into consideration in life cycle assessment (LCA).
On the other hand, the principle of increasing the strength of steels by grain refinement was demonstrated in the 1st Ultra-steel project [5]. At the next step, in the 2nd project, we attempted to create high-strength and high-corrosion-resistant steel (Factor 4 steel) without a rare metal by the incorporation of Si and Al and using the grain refinement method. Factor 4 steel is ultrafine-grained (UFG) weathering steel that contains only high Si and Al to increase the corrosion resistance [6].

Although there have been many analyses of rust formed on weathering steels in mild environments [7–14], there are many problems that remain unsolved regarding the basic mechanisms of rust formation [15] and the effect of alloy elements [16–18] in saline environments. In contrast, there have been few reports on the effect of Si and Al on the atmospheric corrosion of steels in saline environments [19–21]. In this paper, the formation process and electrochemical behavior of the rust formed by Si–Al-bearing UFG steels under a cyclic wet/dry condition are described. Particular importance is placed on the structure of the rust formed by the developed steel, which is obtained by electron probe microanalysis (EPMA) and transmission electron microscopy (TEM), and on the electrochemical behavior of the rust, investigated by electrochemical impedance spectroscopy (EIS) after being subjected to a wet/dry cyclic corrosion test in the presence of chloride ions. Finally, the corrosion mechanism is explained by indicating the relation between the formation and the electrochemical behavior of the rust of Si–Al-bearing UFG steel.

2. Experimental

A new rolling process characterized by multi pass reduction under a warm slab condition was conducted to obtain low alloy steels with a UFG structure. Slabs of high-Si–Al content steel were quenched from 1373 K and then subjected to multi pass warm rolling. Bi-axial reduction was applied at a temperature between 773 and 873 K to form steel plates with a thickness of 15 mm, a width of 800 mm and a length of 2000 mm. The accumulated area of the reduction was 95%. The chemical composition of the low-alloy steel discussed in this paper was 0.17C-0.8Si-1.5Mn-0.01P-0.003S-0.8Al-0.003N-0.002O-Fe.

The cyclic corrosion test consisted of (1) wetting sample surfaces with 0.4 litre m$^{-2}$ of 0.5 mass% NaCl solution and (2) drying the specimen in a chamber maintained at 25°C and 60% relative humidity (RH) for 12h. Immediately before dropping a solution, the sample was washed in distilled water and dried to prevent progressive salt accumulation.

EPMA and TEM were used for the analysis of the rust. EPMA was carried out at an acceleration voltage of 15 kV, using a beam with a current of $1 \times 10^{-7}$ A, and a diameter of 1 µm. A cross-section of the rusted steel was examined. The distributions of Si, Al, Fe and oxygen in the rust were measured to identify their locations. Moreover, the chemical states of Si and Al in the rust were measured by using K$_{α}$ and K$_{β}$ characteristic x-rays. This new method is advantageous for investigating the chemical states of elements in a local area of under 1 µm diameter using an electron beam source. For the TEM observation, the rust was cut from the inner rust layer by using a focused ion beam (FIB). Energy dispersive spectroscopy (EDS) analysis was carried out to identify the chemical composition of the rust and to select the Si–Al-rich iron oxides from the rust layer.

Electrodes were fabricated on the samples after corrosion test, and EIS measurements were carried out in 0.1 mol Na$_2$SO$_4$ solution under the following conditions: a two-electrode system, a measurement frequency range of 20 kHz to 0.3 mHz and an applied voltage of 10 mV.

3. Results and discussion

3.1. Corrosion prediction using binary-phase potential-pH diagrams

The thermodynamic stability of various rusts (Fe–X systems) was investigated using binary-phase potential-pH diagrams. Figure 1 shows the binary-phase potential-pH diagrams of (1) Fe–Ni and (2) Fe–Al. In the Fe–Ni potential-pH diagram, the complex iron oxide NiFe$_2$O$_4$ was shown to stably exist. As Ni is known to be the effective element that increases the corrosion resistance of the weathering steel, this complex oxide was understood to prevent the corrosion. In the Fe–Al potential-pH diagram, the complex iron oxide FeAl$_2$O$_4$ was shown to stably exist. As FeAl$_2$O$_4$ is the same type of iron oxide as NiFe$_2$O$_4$, Al is expected to increase the corrosion resistance. Moreover, as the complex iron oxide Fe$_2$SiO$_4$ was shown to stably exist in the Fe–Si potential-pH diagram, Si is thought to be the effective element preventing corrosion. Thus, instead of the rare metal Ni, we decided to use Al and Si as the corrosion-resistant elements. Thus, P was not used in this work. Thus, we attempted to create a high-performance steel (Factor 4 steel) without a rare metal by using Si and Al.

3.2. Mechanical properties of S–Al-bearing UFG steel

UFG structures composed of ferrite and cementite were obtained by bi-axial warm rolling (figure 2). The ferrite grain sizes were approximately 0.7 and 1.0 µm at rolling temperatures of 773 and 873 K, respectively.

The strain–stress (S–S) curves of the steel rolled at 873 K are shown in figure 3 The curves of in the L- and C-directions are almost the same. The tensile strength (TS) and elongation (EL) were 800 MPa and 20%, respectively. The yield strength (YS) was increased to 130 MPa by the solid–solution hardening of Si and Al, which was higher than that of SM. Moreover, a yield ratio (YR) of 92% was achieved by work hardening of the second phase of cementite.

Figure 4 shows the Charpy absorbed energy and the crystallinity for the developed steel. In general, steels with high Si and Al contents exhibit inferior toughness to SM; however, the samples showed excellent toughness upon
Figure 1. Binary-phase potential-pH diagrams of (1) Fe–Ni and (2) Fe–Al.

Figure 2. Microstructures of UFG weathering steels rolled at 773–873 K.

Figure 3. Strain–stress curves of developed steel rolled at 873 K in L- and C-directions.

3.3. Analysis of the rust on Si–Al-bearing steel

A corrosion–stress (CS) map of the test samples is shown in figure 5. The corrosion ratios of the samples were estimated by the accelerated corrosion test. Assuming that the amount of corrosion for SM was 100%, then the corrosion ratios of 1%Ni and 3%Ni steels were 84 and 72%, respectively. The corrosion ratios of the test samples were between those of 1%Ni and 3%Ni steel. Thus, the developed steel showed excellent corrosion resistance. The YS of samples was between 700 and 1000 MPa, depending on the rolling temperature. The developed steel has high strength and high corrosion resistance. Few weathering steels have a YS greater than 600 MPa; thus, the developed steel is unique for use as structural steels.
Figure 4. Charpy absorbed energy and crystallinity of developed steel.

Figure 5. Corrosion-yield stress map of UFG weathering steel samples.

The surface layer of rust on a sample of Si–Al-bearing steel was analyzed by EPMA. The distributions of Si, Al, Fe and oxygen in the rust after 20 cycles of the corrosion test are shown in figure 6. Many layers of Al and Si were observed at the same position in the inner rust layer. Thus, they were thought to form a complex oxide with iron.

The chemical state of Si in these concentrated layers was measured by EPMA using Si Kα characteristic x-rays. Figure 7 shows the results of the analysis of a sample subjected to 20 cycles of the corrosion test, and those of the standard reference materials of SiO₂ and metallic silicon (Si). The peak position of the Kα characteristic x-rays for developed steel is different from that of SiO₂ and Si, and appears exactly midway between these two peaks. On the basis of this result, it is suggested that the Si in the rust layer is not metallic but in an oxidized state; however, it is in a...
Figure 8. Characteristic x-ray spectrum of Al K$_\alpha$ obtained by EPMA from rust of developed steel and spectra of standard reference chemicals (Al$_2$O$_3$, Al).

different chemical bonding state from that of SiO$_2$. As the chemical shift is thought to depend mainly on the valence of Si, the silicon is thought to exist in an intermediate oxidized state such as Si$^{2+}$ in the inner rust layer of the developed steel.

Similarly, the results of Al K$_\alpha$ x-ray analyses are shown in figure 8. The Al K$_\alpha$ x-ray spectra of Al$_2$O$_3$ and metallic Al have different peak positions, and the spectrum of the test sample coincides with that of Al$_2$O$_3$. A weak Al K$_\beta$ x-ray spectrum can also be seen in figure 8, and its peak position is the same as that of Al$_2$O$_3$. These facts suggest that Al is in the Al$^{3+}$ oxidized state in the inner rust layer.

X-ray diffraction (XRD) analysis was undertaken of the rust formed on the Si–Al-bearing steel. Using a standard sample of CaF$_2$, the concentration of iron oxide in the sample was quantitatively calculated. The chemical composition of the rust formed on the Si–Al-bearing steel was almost the same as that of carbon steel. No iron oxide was detected in half of the rust, which is because the iron oxide particles in the rust are too fine to be detected by XRD. Thus, to investigate the structure of the inner rust layer, TEM observation was used. The inner rust layer was cut by using FIB. A TEM image of the cut surface of Si–Al-bearing steel is shown in figure 9(A). The existence of the Si and Al in the rust was detected by EDS analysis, as shown in figure 9(B); thus, the rust containing Si and Al could be observed easily. The oxides that contained Si and Al were observed as white particles in the bright-field image shown in figure 9(A). The oxide containing Si, Al and Fe is a complex oxide form of the Fe–Si–Al-type. The size of the oxide particles that contain Si and Al is of the nanometer level, and there are layers with enriched Si and Al; that appear as white particles. From the results of EPMA, Si and Al were identified as existing in the Si$^{2+}$ and Al$^{3+}$ states. Moreover, there were many layers with enriched Si and Al in the inner layer of the rust. As a result, these nanoscale complex oxides (Fe–Si$^{2+}$–Al$^{3+}$–O) increased the corrosion resistance of the developed steel. Thus, we have shown that nanoscale complex oxides are formed in the lower part of the rust layer of developed steel and that they increase the corrosion resistance of the steel.

3.4. Evaluation of the electrochemical behavior of the rust by the EIS measurement

Figure 10 shows the impedance and phase-shift spectra obtained by EIS measurements of the developed steels as a function of the number of cycles of the corrosion test. From the impedance spectra, the resistance at high frequencies can be understood to represent the resistance of the rust ($R_{\text{rust}}$) on the surface of the steel. On the other hand, the resistance at low frequencies corresponds to the corrosion reaction resistance ($R_I$). Figure 11 summarizes the results of EIS.
measurements of the Si–Al-bearing steel and SM conducted after the corrosion test, showing $R_{\text{rust}}$ and $R_t$ against the number of cycles. The developed steel had a higher value of $R_{\text{rust}}$ than SM after each number of cycles. Since $R_{\text{rust}}$ is the resistance of the solution in the pores of the rust, this fact indicates that the rust of the developed steel had a finer structure than that of SM. Both the developed steel and SM showed high initial values of $R_t$, however, they had smaller values of $R_t$ after 8 cycles. This is considered to correspond to the increase in the cathodic reduction of the rust as it was created. $R_t$ showed a constant value for more than 8 cycles because the anodic reaction was suppressed as the surface was covered by the rust. Furthermore, the developed steel had a larger value of $R_t$ than SM after 8 cycles. The main reason for this fact was considered to be that nanoscale complex oxides containing Si and Al are formed in the inner rust layer, which suppressed the anodic reaction. This phenomenon was verified from the measurement of $R_{\text{rust}}$. As the formation of the rust proceeded, the values of $R_{\text{rust}}$ and $R_t$ of the developed steel, which depends on the fineness of the rust, were larger than those of SM.

Figure 12 shows a schematic diagram of the corrosion mechanism of the rusting of the Si–Al-bearing steel. In general, the rust has many micro-defects (pores) through which chloride (Cl) ions can penetrate to the base metal. However, the developed steel forms nanoscale complex oxides containing Si and Al in the inner rust layer at the micro-defects, which increase $R_{\text{rust}}$ and $R_t$ because of the physical protection of the fine rust. In this way, the complex oxides containing Si and Al formed in the inner rust layer prevent the penetration of Cl ions; thus, the developed steel can suppress corrosion in a saline environment.

4. Conclusions

High-Si–Al UFG weathering steel was developed by grain refinement and weathering guidance. It was found that the developed steel had excellent strength, toughness and corrosion resistance. A wet/dry cyclic corrosion test in the presence of Cl ions was performed on the developed steel, and the structure of the rust and its electrochemical behaviors were analyzed. The main results were as follows:

1. In the wet/dry cyclic corrosion test, Si–Al-bearing UFG weathering steel had excellent corrosion resistance compared with carbon steel.
2. EPMA showed that the Si and Al in the rust of the developed steel mostly existed as Si$^{2+}$ and Al$^{3+}$ states in the complex oxides in the inner rust layer. TEM showed that nanoscale complex iron oxides containing high concentrations of Si and Al existed in the inner rust layer of the developed steel.
3. EIS measurement was conducted for the corrosion test samples to determine the rust resistance ($R_{\text{rust}}$) and corrosion reaction resistance ($R_t$) from the impedance spectra. It was found that $R_{\text{rust}}$ and $R_t$ for the Si–Al-bearing steel were much greater than those for SM after the formation of rust. In the Si–Al-bearing steel, nanoscale complex iron oxides containing Si and Al that formed in the inner rust layer increased the value of $R_t$ and suppressed the corrosion.

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