

Mn-ENRICHMENT AT THE PITTING FRONT END IN 27SiMn LOW-ALLOY STEEL

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ABSTRACT This paper conducts an investigation of three different sections of a pit on 27SiMn, finds Mn-enrichment at the pitting front end by means of X-ray diffraction and Electron probe and explains Mn-enrichment phenomenon.

KEY WORDS low-alloy steel, pitting, Mn-enrichment

The masses of experiment data about pitting on steel have been accumulated. The research in pitting growth mechanism adopts a method called “man-made hole model” in many cases. The self-catalytic and acid mechanism of chlorine’s participation has been widely accepted. In this paper, the pitting process on 27SiMn in coal mine is studied by means of Electron probe and X-ray diffraction, and Mn-enrichment at the pitting front end is analyzed.

1. Experiment

Samples: hot-rolling 27SiMn (0.24~0.32% C, 1.10~1.40% Si, 1.10~1.40% Mn), come from failure parts. The process composes of embedding, grinding, polishing and etching.

Condition medium: Mine water is contact liquid phase and its PH level is 7.0 ~ 7.4. Its ion concentration (mg/L): 15~28Cl⁻, 59~190SO₄²⁻, 226~396HCO₃⁻, 18~36K⁺+Na⁺, 18~35Mg²⁺, 65~137Ca²⁺. Contact solid phase is powdered anthracite. These powder or particles come into contact with the samples in mine water. The carbon content of the anthracite is more than 90%. Three different sections of a pit on 27SiMn are analyzed by scanning electron microscopy (JSM-840) and spectrometer (TN-5500).

2. Experiment results and analysis

Fig.1 is a cross section of a rim. Fig.2 is a cross section of the closed zone in the same pit. In Fig.2 the line peaks of chlorine are very obvious at the edge of the pit. According to the environmental condition, the chlorine actually stands for chlorine ions (Cl⁻). This confirms traditional Cl⁻ corrosion mechanism. Fig.3 is a cross section at leading end in the same pit. Fig.4 is X-ray scanning lines in the direction of pit diameter. At the front end of micro-zone, a ring crack is found on the cross section of Fig.3 and Fig.4 shows obviously that Mn-element in low-alloy steel is enriched in the center of cross section on the micro-zone. At the pit front end, Fe atom, comes from crystal lattice, dissolves and oxidizes within the scope of hemisphere and changes into Fe²⁺. The hydrated Fe²⁺ ion moves to the pit rim under the action of inner electric field. Mn enriches in the ring crack on cross sections of the pit front end, and its concentration is rather high in the center pitting, the content of Cl, Ca and S is nearly to zero respectively, and this indicates that there are not Cl⁻, Ca²⁺, SO₄²⁻ and MnS at this position.

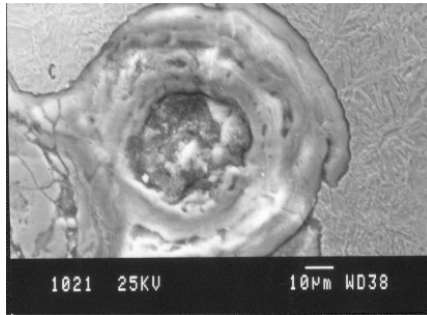


Fig.1 Cross Section of a Rim

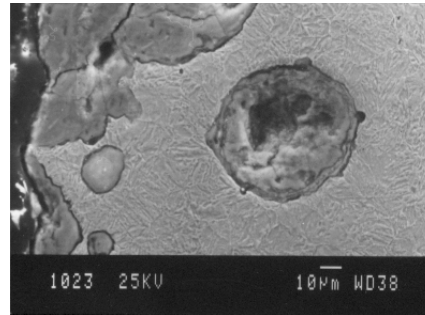


Fig.2 Cross Section of the Closed Zone

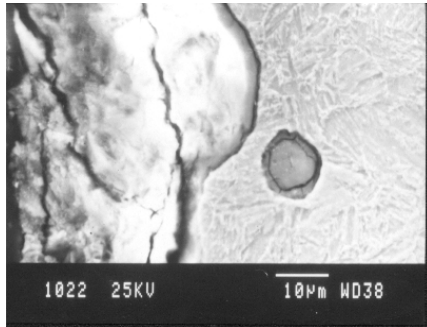


Fig.3 Cross Section at Leading End

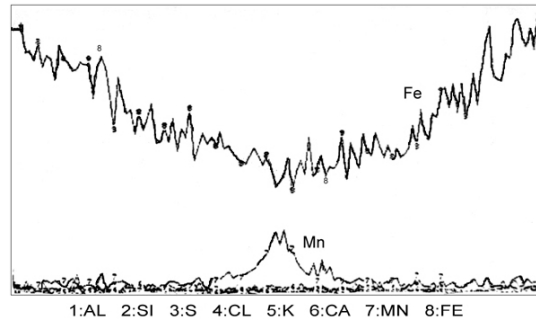


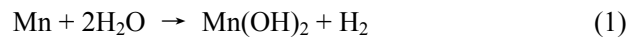
Fig.4 X-ray Scanning Lines in the Direction of Pit Diameter

In addition, it is difficult for O_2 to move to the front end micro-zone. If there were O_2 at the position, the whole micro-zone should be composed of Fe and Mn oxides, and Mn oxides alone should not enrich in the center.

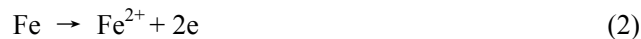
Mn standard electrode potential $\phi_0(Mn^{2+}/Mn)$ is -1.18, Fe standard electrode potential $\phi_0(Fe^{2+}/Fe)$ is -0.44. Mn has the greater trend of anodic dissolution. It is impossible for Mn to exist in the form of Mn atom.

There are strong electric current density, electric intensity and alloy polarization at the front end as a result of great cathode area outside the pit. H_2O has two characters: strong polarity and great dielectric constant. Under the action of external electric field, H_2O produces orientation effect, its positive side orients negative electrode of electric field and its negative one does positive one. The result is that stronger hydrophily exists and therefore H_2O alone concentrates at the pitting front end. There are not Cl^- , Ca^{2+} , SO_4^{2-} hydrated ions to be verified by Electron probe [ZAF] quantitative analysis of micro-zone elements.

The following reaction takes place of a normal atmospheric temperature:

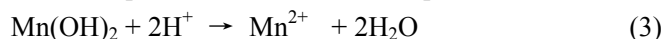


Mn reacts directly with H_2O , and produce $Mn(OH)_2$. But Fe atom can't react directly with H_2O . According to pitting electrochemistry, Fe produces electrochemical oxidation as a result of the H_2O polarity and longitudinal electric field action.



Fe^{2+} hydrates move to the pit rim in the electric field. With being extracted constantly in crystallic lattice and with Fe^{2+} migration, Mn is oxidated, and the $Mn(OH)_2$ product is accumulated and concentrates in the center of micro-zone cross sections. The above analysis shows that in process of pit expansion in 27SiMn, Mn atom reacts directly with H_2O at the pit front end micro-zone and the $Mn(OH)_2$ product enriches in the center of micro-zone cross sections under the action of Fe dissolution and Fe^{2+} migration caused by macrogalvanic cell.

With pit growth, enriched Mn(OH)_2 certainly will reach the closed zone in a pit (Fig.2). According to Cl^- self-catalytic and acid mechanism, there is high H^+ concentration in the closed zone as a result of Cl^- existence. Mn^{2+} is at the lowest point of Gibbs free energy-oxidation state diagram, but Mn(OH)_2 is far higher than Mn^{2+} . This indicates that Mn^{2+} is the most stable oxidation state in acidis solution. The spontaneous reaction takes place as follows:



3. Conclusions

Pits are found on 27SiMn in mine water. There is Mn-Enrichment at the pitting front end. It is certified that Mn reacts directly with H_2O and produces Mn(OH)_2 at the micro-zone by means of electron probe. Mn(OH)_2 enriches in the center of the micro-zone cross sections under the action of continuous Fe^{2+} dissolution and migration. With pit growth, Mn(OH)_2 reacts with H^+ and changes into Mn^{2+} when it reaches the Cl^- closed-zone of a pit.

Preference

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