Corrosion properties of high silicon iron-based alloys in nitric acid

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Abstract: The effect of copper and rare-earth elements on corrosion behavior of high silicon iron-based alloys in nitric acid was studied by means of static and loading current corrosion experiments. The anodic polarization curve was also made to discuss the corrosion mechanism. The examination on alloy microstructure and SEM corrosion pattern showed that when silicon content reached 14.5%, the Fe3Si phase appeared and the primary structure of the iron-base alloy was ferrite. When adding 4.57% copper in the iron alloy, its corrosion resistance in static diluted sulfuric acid was improved while its corrosion resistance and electrochemical corrosion properties in the nitric acid were decreased. In contrast, the addition of rare earth elements could improve the corrosion properties in all above conditions including in static diluted sulfuric acid and in nitric acid.

Key Word: polarization curve; corrosion resistance; microstructure; corrosion pattern; iron-based alloys


High silicon iron-based alloys are excellent corrosion resistant materials with advantages of superior corrosion resistant properties, low cost and saving on noble metals such as nickel and chromium. When containing 14.5% or more silicon, the corrosion resistance of these iron-based alloys is better than that of some cast irons containing a significant amount of chromium, nickel and/or molybdenum, and even than that of certain nickel based alloys in some severe corrosion conditions. However, because of its intrinsic properties, the high silicon iron-based alloys have some weaknesses such as low strength and impact toughness, high hardness and brittleness, poor weld ability, low thermal conductivity and high thermal expansion (coefficient), resulting in high tendency for shrinkage/porosity and other casting defects in production, unable to handle thermal shock and high pressure, and poor machine ability. Thus, in some extent, the application and promotion of the high silicon cast iron alloys have been limited only to castings [1-5]. At present the main products of the material in domestic market are pump parts and some small anode castings, while the study about using the material for large castings is very limited due to the poor properties. With the operating requirements on large repair parts of batch descaling in our steelworks (this sort of products are entirely depended on import, the over size is 2 500 mm × 470 mm × 370 mm), the research on the stain resistance of high silicon iron-base alloys in nitric acid was referred, especially the simulation and investigation on their corrosion properties in the electricity added condition. The rare earth high silicon iron-based alloy studied in this article can be used to make the auxiliary anode which worked in the added electricity anode protecting condition, showing a promising application future.

1 Experimental detail
1.1 Sample preparation

The raw materials for experimental alloys include pig iron, premium scrap steel, 75Si-Fe, copper and rare earth, etc. The chemical compositions of the experimental alloys are listed in Table 1. After melted in a 500 kg medium frequency coreless induction furnace, the molten alloy was poured into test cast samples which were then annealed and machined into specimens using a linear cutting machine. The performance measurements were carried out according to requirement/standard.

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Composition, wt.%</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>0.645</td>
</tr>
<tr>
<td>B</td>
<td>0.632</td>
</tr>
<tr>
<td>C</td>
<td>0.549</td>
</tr>
</tbody>
</table>

Note: No. C is a general high silicon iron-base alloy

1.2 Testing procedures

The metallographic and SEM specimens were prepared from the castings into the size of Φ 20 mm × 20 mm, by rough grinding, fine grinding and polishing.

The static corrosion specimen is in the size of Φ 20 mm × 5 mm which was processed with an “electric-spark” (or linear) cutting
Research & Development

November 2007

machine. The specimen was ground to a 120-grit finish, then washed in soap solution, rinsed in distilled water and acetone, dried and weighed. The total surface area of the specimen was then also determined. The specimens were removed periodically from the solution, visually examined, brushed and cleaned thoroughly to remove any loose corrosion products, and weighed to yield a corrosion rate. The specimens were reinserted to determine the effect of exposure time at the corrosion process. The corrosion rates determined in weight loss method \[6, 7\] can be expressed as follows:

\[
\Delta m = \frac{m_0 - m_t}{tS}
\]

where: \(\Delta m\) — corrosion rate, \(g/(m^2 \cdot h)\)

\(m_0\) — weight before corrosion, \(g\)

\(m_t\) — weight after corrosion, \(g\)

\(t\) — exposure time, \(h\)

\(S\) — surface area, \(m^2\)

The specimen used to simulate the field condition (i.e. loading current work condition) was obtained with the linear cutting machine into the size of 5 mm × 20 mm × 100 mm. The specimen was anode which linked to the positive pole of electrical source, and the graphite cathode was in the same size as the anode. The corrosion rate was tested with the weight-loss-method. The result was the average of three experimental values.

In electrochemical tests, high silicon iron-based specimens (10 mm × 10 mm × 5 mm) with different compositions and heat treatments were made with the linear cutting machine. The corrosion testing device used in the experiment contained PS-168B electrochemical measure system (microcomputer controlled), thermostat water bath, dissolving (solution) tank, saturated calomel electrode and auxiliary electrode (platinum electrode) and so on.

Specimens of approximately 1 cm² exposure surface area were used in these electrochemical studies. The specimens were mounted in epoxide resin, ground to a 120 grit finish, washed, polished, rinsed in distilled water and acetone, and then dried. The specimen served as anode was immersed in dissolving tank with 20% HNO₃ solution, and the dissolving tank was placed in thermostat water bath of 65°C to simulating the field application condition. When the electric potential stabilized, the PS-168S scanned the specimen forward at the speed of 1.25 mV/s to check out the E-I anodic polarization curve and to get the corresponding corrosion result \[8, 9\].

2 Results and discussion

2.1 Analysis of metallurgical structure

Microstructures of test samples with different compositions (referred as A, B and C in Table 1) were shown in Fig.1. It can be seen that the matrixes of three different specimens are all high-silicon ferrite. The reason is that when Si reaches 10%, it dramatically decreases the austenitic region, and the austenite tends to disappear. Figure 1 shows that by addition of rare earth the graphite changed to smaller and thinner shapes and later became spotty and short-flake pieces. In sample B, there were a lot of phases containing copper around the grain boundaries. In sample C, the graphite was thin and long type A graphite similar to that in the general grey cast irons. Based on morphology, the graphite is a kind of eutectic phase (graphite) which precipitated during the solidification process.

2.2 Result of X-ray diffraction

In order to observe the phase change in microstructure of these iron-base alloys and the corresponding effect on the corrosion resistance when adding more than 15% Si, X-ray diffraction was conducted on alloy/sample A. The corresponding phase to the identity distance (2.01, 1.42, 1.16) is Fe₃Si according to the X-ray diffraction peak value displayed in the Fig. 2, indicating when Si concentration is up to 15%, the Fe₃Si phase will appear.

2.3 Measurement and analysis of corrosion rates

The corrosion rates of the three alloys submersed in 20% sulfuric acid, 20% nitric acid and 10% nitric acid loading current (1.54 mA/mm²) solutions are given in Table 2. The results showed that, comparing to the general high silicon cast iron, the corrosion rate was reduced by 8 and 1.6 times respectively in the 20%
sulfuric acid (condition I) when adding 4.57% copper and 0.02% rare earth. In the 20% HNO₃ solution (condition II), the alloy A containing 0.02% rare earth exhibited a corrosion rate 1.3 time lower than that of the general high silicon cast iron, while alloy B containing 4.57% copper showed a corrosion rate was 0.5 time higher than that of the general high silicon cast iron. Under loading current conditions, the effect of addition of copper and rare earth on corrosion rate of alloys in 10% HNO₃ was about the same as that in 20% HNO₃, but the corrosion rates were considerably higher than that in the 20% HNO₃ without current.

Table 2 Corrosion rates of alloys in H₂SO₄ and HNO₃

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Corrosion rates, g/(m² · h)</th>
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<tbody>
<tr>
<td>A</td>
<td>0.05472 0.01277 26.99934</td>
</tr>
<tr>
<td>B</td>
<td>0.01073 0.35268 64.91455</td>
</tr>
<tr>
<td>C</td>
<td>0.08584 0.01648 34.08621</td>
</tr>
</tbody>
</table>

Note: I—corrosion rate in 20% H₂SO₄, static uniform corroded for 96 hours; II—corrosion rate in 20% HNO₃, static uniform corroded for 96 hours; III—corrosion rate in 10%HNO₃, loading current with 1.54 mA/mm² current density corroded for 10 hours.

The data showed that the corrosion rate of the high silicon iron-based alloy with 4.57% Cu can be obviously reduced in 20% H₂SO₄. The main reason is that the added copper concentrated under SiO₂ passivation film to enhance the film’s stability, and at the same time, the copper improved the shape and distribution of graphite and refined the microstructure, so that the surface passivation film is more compact and uniform. The other reason is that the copper ions which separated out from metal surface promoted the anode passivation and increased the electrode potential. The formation of a thin but compact copper oxide film at the surface of the high silicon iron-base alloys can also slow down the corrosion progression.

It was found that when rare earth is added, the corrosion rate of high silicon iron-base alloys in sulfuric acid and nitric acid decreased. It is mainly because that the rare earth elements can degas, desulfurize, dehydrogenate and purge the molten iron, reduce slag, improve the shape and distribution of graphite and refine the microstructure, consequently decreasing the quantity of the micro-battery (or cells). Multiple factors were compounded together in function to increase corrosion resistance of the alloy.

The result showed that the addition of 4.57% copper can decrease the corrosion rate of high silicon iron-based alloys in H₂SO₄, but increase the corrosion rate in the HNO₃ solution. The main reason is that although copper can increase the potential of alloys, it can react with the diluted HNO₃, which can be proven by the appearance of the corrosion product of blue copper nitrate. The reactive mode is:

\[ 3\text{Cu} + 8\text{HNO}_3 \text{(diluted)} = 3\text{Cu(NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} \quad (2) \]

In the above reaction, the copper reacts and forms copper nitrate which dissolves in solution. The copper at grain boundaries were leached out and created a corrosion channel, causing the continued corrosion. As a result, the corrosion rate was increased in this case.

In the loading current condition, the oxidation film grows accompanied by its dissolution, resulting that the corrosion rate was two orders of magnitude higher than without current. Under certain current and potential, the high silicon iron-based alloys were anodized to form SiO oxide in nitric acid. But under higher electric field, the effective surface oxide film cracked, pits and dots formed on its surface, and the film turned into ineffective. The ineffective surface films dissolved quickly until the underneath effective film exposed in the nitric acid. Gradual dissolution made the “high quality” compact oxide film becomes thinner, increasing the electric field within the film. The oxide film cracked again under the re intensified electric field and the effective surface oxide film became ineffective, and this effective to ineffective transition continued. The process did repeat and led to the corrosion rate increased in current pass [11-14].

2.4 Electrochemical tests

Results of potentiodynamic (1.25 mV/s) anodic polarization in 20% nitric acid solution are shown in Fig.3. Current densities applied on these alloys were same. Anodic polarization curves of the three test alloys showed four regions: the active region, transition region, passivation region and over passivation region. The transition zone of the general high silicon iron-based alloy was not obvious.

![Fig. 3 Potentiodynamic anodic polarization curve of A, B and C in 20% HNO₃](image)

The high silicon cast iron containing 4.57% copper (alloy B) passivated at 260 mV close to the 220 mV for the general high silicon cast iron, while the alloy containing RE (alloy A) passivated only at 5 mV. The alloy containing copper and the general high silicon cast iron were more active and dissolving than the alloys containing RE prior to passivation, resulting in the high corrosion rate in sulfuric solutions. The passive range extended from 250 mV to 1 500 mV on the alloy containing RE, while 400 mV to 1 500 mV on the general high silicon cast iron and 550 mV to 1 550 mV on the alloy containing copper. The wider passive range indicates better corrosion resistance. From +1 500 mV to +1 800 mV, all three alloys exist the over-passivation region [15].

The critical current values on these alloys were quite different. The critical current of the alloy containing RE is one order of magnitude lower than that of general high silicon iron-based alloy, and two to three orders lower than the alloy containing copper. The critical current densities reflect the tendency to passivation, formation of surface films. The results indicated that
the addition of rare earth elements increased the passive current densities which effectively increased the corrosion resistance. This was consistent with obtained corrosion results (Table 2).

Therefore, addition of RE increased the transpassiviation potential, reduced the passive current, enlarged the passivation regions of the alloys and improved corrosion resistance. Although the addition of 4.57% copper increased the transpassiviation potential, it narrowed the passive region, leading to increase corrosion rate of the alloys in the diluted nitric acid solutions.

2.5 Observation of the corrosion pattern of oxide film

The SEM images of the oxide films of alloy-A and alloy-B after corrosion tests with loading current (1.54 mV/mm²) are shown in the Fig.4. These SEM micrographs were obtained by scanning the surface of oxidized layer and its cross-section using a Cambridge S-360 scanning electron microscope (SEM/EDX) equipped with an energy dispersive spectrometer.

![Fig. 4 The SEM images of the oxide films of alloy-A and alloy-B](image)

It can be seen from Fig. 4 that the oxide film thickness of alloy-A is thinner and more compact than that of the alloy-B. There exist a large amount of voids in the oxide film which was likely the leftovers from copper reaction with the nitric acid. Cracks on the surface oxide film are obvious both on alloy-A and alloy-B, which were caused by the function of the electric field. But the cracked degree of alloy-B oxide film was more severe (more extensive and larger in crack size) than that of alloy-A, indicating that the properties of alloy-A oxide film is better than that of alloy-B. Therefore the addition of rare earth is beneficial in improving the quality of oxide film and enhancing the corrosion resistance.

3 Conclusions

(1) With addition of 15% Si, the primary (matrix) structure of high silicon iron-based alloys is high silicon ferrite, and at the same time, the Fe3Si was appeared.

(2) The copper addition decreases the corrosion rate of the alloys in sulfuric acid, but increases the corrosion rate in nitric acid solutions.

(3) The addition of rare earth in the alloys reduces the corrosion rate in sulfuric acid, static diluted nitric acid as well as the nitric acid with loading current.

(4) The anodic polarization curves consist of four regions for the three test alloys: the active region, transition region, passive region and over passivation region. But the transition region for the general high silicon cast iron was not obvious.

(5) The addition of rare earth in high silicon iron-based alloy improves the quality of the oxide film, and more compact and thicker oxide film is effective to enhance the corrosion resistance.

References


