Microstructure and Corrosion Resistance of Fe-Cr-Si Alloys

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Abstract. Fe-Cr-Si alloys material has good abrasion resistance, corrosion resistance and high-temperature oxidation resistance, especially the introduction of Si element can further improve its corrosion resistance. In this work, two Fe-Cr-Si alloys with different Si (10wt. % and 12wt. %) contents were designed and prepared by an arc furnace process. The microstructure and corrosion resistance of Fe-Cr-Si alloys were investigated. Results has shown that the Fe-Cr-Si alloys are composed of primary dendrite and interdendrite matrix, and metal silicide Fe₃Si formed in the microstructure. Fe-Cr-Si alloys have a wider passivation interval than 2Cr13 stainless steel and the corrosion resistance of the Fe-Cr-Si alloys increased by more than 20 times in 10%HCl solution compare to 2Cr13 stainless steel.

Keywords. Fe-Cr-Si alloy, microstructure, intermetallic compounds, corrosion.

1. Introduction

Traditional metal materials inevitably have problems such as corrosion resistance insufficient performance under severe working conditions. In order to improve the service life of materials, researchers have done a lot of work to obtain materials with good corrosion resistance. Compared with traditional metal materials with a wide range of applications, Fe₃Si, Cr₃Si and other intermetallic compounds show more excellent comprehensive properties. It means to possess good strengths at high temperatures, oxidation resistance, corrosion resistance in particular [1, 2]. In the fields of aviation, steel-making, machinery, material surface modification and processing, metallic silicides has a broad prospect in the high-temperature structural material, accident tolerant fuel cladding and Coating materials for hydraulic machines and components etc. [3, 4].

At present, the research direction of metal silicide mainly focuses on its friction and wear and high temperature oxidation resistance [5]. There are few reports on the materials in acidic corrosive media, effective development and use of intermetallic compounds are lacking to some extent. Due to the potential of these materials as corrosion-resisting alloy [6], researching its corrosion behavior in acidic solution is essential. In this paper, Fe-Cr-Si alloys ingot were prepared by arc melting process, and the electrochemical corrosion resistance and behavior of the material in HCl solution were studied, so as to provide a basis for the improvement of the performance of the alloy system and the expansion of application fields.

2. Experimental Procedures

The raw materials to prepare alloys—Fe, Cr, Si, Ni and C (purity of all 99.99%), each had an average particle size of ~80 mesh) were prepared at a current of 300A in an arc furnace. The furnace was firstly pumped to a high vacuum, under a high purity Ar atmosphere, each Fe-Cr-Si alloys sample were smelted in a water-cooled copper crucible. To ensure good homogeneity, each sample was remelted at least four times. The compositions of Fe-Cr-Si alloys in this work are shown in table 1.
Table 1. Nominal chemical composition of two designed Fe-Cr-Si alloys (wt. %).

| Sample     | Fe  | Cr  | Si  | Ni | C  |
|------------|-----|-----|-----|----|----|
| Fe20Cr10Si | 65  | 20  | 10  | 4  | 1  |
| Fe20Cr12Si | 63  | 20  | 12  | 4  | 1  |

The Fe-Cr-Si alloys samples were cut into initial cubical samples of 10 mm×10 mm×3 mm by wire-cutting for the preparation of samples for microstructural analysis and property evaluation, and then polished to a 2000-grit finish and polished to 2.5 μm using diamond spray polishing compounds. Samples were all ultrasonically cleaned in ethanol before the reaction. The phase composition of the alloy was identified by a Smartlab-9KW X-ray diffractometer with a voltage of 40kV, a current of 30mA, and a scan range from 20° to 90°. Preparing metallographic specimens of the Fe-Cr-Si alloys samples according to the method of standard metallographic samples, then etched by a solution of HCl: HNO₃ = 3:1. The microstructure of the alloy was characterized using a scanning electron microscopy (SEM) and a Nova NanoSEM430 instrument. To analyzing Chemical compositions of the phase constituents, electron diffraction spectroscopy (EDS) on the TESCAN LYRA3 microscope were used.

The polarization curves of the advanced action potential of Fe-Cr-Si alloys and 2Cr13 stainless steel were measured with CHI660E. Reference electrode saturated calomel electrode (SCE), reference electrode Pt electrode, working electrode Fe-Cr-Si alloy sample and 2Cr13 stainless steel sample, the electrolyte is 0.5mol/L HCl solution. Before the test, the sample was immersed at the open circuit potential for 30 min to make the corrosion potential stable before the test. The polarization curve measures the scanning rate of 2 mV/s and the scanning range -1.0~1.5 V.

HCl corrosion testing was conducted by using specimens of 2Cr13 stainless steel as a reference and Fe-Cr-Si alloys. Corrosion Mass loss used an aggressive medium in 10%HCl solution, which was prepared by diluting analytical grade 37% HCl with ethanol. In order to ensure the reliability of the experimental data, use a new HCl solution for configuration. To reduce the influence of errors, the Fe-Cr-Si alloy samples were polished, cleaned, dried and used before the experiment. Place the sample in a beaker and use an electronic balance with an accuracy of 10⁻⁴g to determine the weight loss of the alloy at 6, 12, 24, 36, 48, 60, 72 h. Combined with the 3D dimensional profilometer to observe the degree and location of the corrosion surface damage, use the Nova Nano SEM430 field emission scanning electron microscope to observe the surface micro morphology of the alloy after corrosion

3. Results
3.1. Microstructure of Fe-Cr-Si Alloys
Figure 1 displays the XRD profiles of two Fe-Cr-Si alloys. The phase composition should be made up of Fe₃Si, solid solution of Fe-Cr, and γ-Fe. Because the intermetallic compound has the coexistence of metal and covalent bonds, it can endow the alloy with higher hardness and strength. At the same time, it also has good corrosion resistance and high temperature oxidation resistance.
Figure 2 reveals the microstructure characteristics of the as-cast solidification microstructure of two Fe-Cr-Si alloys. The as-cast microstructure of two Fe-Cr-Si alloys was mainly composed of metal matrix and typical dendritic phase and the dendritic crystals of alloys are very uniform and compact. Two points were selected from the matrix and dendritic structure as shown in figure 2(a), (b) and the corresponding point analysis result of different regions in microstructure is shown in table 2. The result showed the content of Fe in the dendrite is significantly higher than that in the matrix, while Cr is enriched in the matrix. Si had a relatively uniform distribution both in the dendrite and interdendrite matrix.

![Figure 2. SEM microstructure of two Fe-Cr-Si alloys: (a) Fe20Cr10Si, (b) Fe20Cr12Si.](image)

| Sample       | Area      | Chemical composition (at. %) |
|--------------|-----------|-----------------------------|
|              |           | Fe  | Cr  | Si   |
| Fe20Cr10Si   | Dendrite 1| 58.85 | 12.83 | 20.85 |
|              | Matrix 2  | 40.68 | 30.28 | 15.88 |
| Fe20Cr12Si   | Dendrite 1| 58.20 | 12.78 | 20.10 |
|              | Matrix 2  | 49.09 | 21.34 | 17.87 |

### 3.2. Electrochemical Performance

The Potentiodynamic polarization curve is one of the common electrochemical methods to evaluate the corrosion resistance of materials. The thermodynamic and kinetic parameters of corrosion resistance of materials can be characterized by a polarization curve. Figure 3 shows the potentiodynamic polarization curves of two Fe-Cr-Si alloys and 2Cr13 stainless steel in 0.5mol/ HCl solution. The polarization curves of two Fe-Cr-Si alloys have the same trend, and there is typical passivation interval (The point where the corrosion current density drops sharply in the polarization curve is the beginning of the passivation interval) and pitting breakdown potential (In the polarization curve, the spot where the corrosion current density increases sharply is the pitting breakdown potential). 2Cr13 Stainless steel only has a very small passivation range, with the increase of voltage, the passivation film is quickly broken down (0.05V). The passivation zones of Fe20Cr10Si and Fe20Cr12Si alloys are -0.14 ~ 0.90V and -0.16 ~ 0.92V, respectively. Compared with 2Cr13 stainless steel alloy, the passivation ranges are enlarged, indicating that the passivation films formed by the two alloys can still exist stably with the increase of voltage.

For Fe-Cr-Si alloy, the transformation from activation to passivation occurs in the anode region. When the voltage is -0.48 ~ -0.31V, the current density increases obviously with the corrosion potential, indicating that the material has active dissolution, which is due to FeCr. The formation rate of the passivation film is much lower than the anodic dissolution rate. In the large potential range (-0.10 ~ 1.00V), the alloy is in a stable passivation state, which indicates that the alloy forms a dense and stable passivation film, such as Fe₂O₃, Cr₂O₃, SiO₂, etc. These insoluble passivation films on the sample surface have high thermodynamic stability, which can effectively reduce the concentration of Fe, Cr and other elements on the surface of the alloy. According to the ionic activity formula \(a = rm\) (\(a\) is the ionic activity of the electrolyte, \(r\) is the ionic activity coefficient, and \(m\) is the ionic concentration of the electrolyte), it can be seen that the ionic activity in the
solution is positively correlated with the concentration. When the ionic concentration of the ionized element decreases, the ionic activity is weak and the corrosion rate is low. In the electrochemical experiment of 0.5mol/L HCl solution, with the increase of voltage, the formation rate of passivation film in Fe-Cr-Si alloy is much higher than the anodic dissolution rate, so that the anodic dissolution of the alloy surface is inhibited, and the passivation film shows a good protective effect. In summary, two Fe-Cr-Si alloys materials have a very wide passivation range, so when the alloy is used in mechanical metal components, the material can be artificially passivated to ensure high corrosion resistance.

Figure 3. Potentiodynamic polarization curves of Fe-Cr-Si alloys and 2Cr13 stainless steel in 0.5mol/L HCl solution.

3.3. HCl Corrosion Resistance
The Gravimetric method is the most basic and common method to evaluate the corrosion resistance of Fe-Cr-Si alloy materials, which can accurately and reliably characterize its corrosion resistance. The mass loss curves of the three alloys are shown in figure 4. Before 6h, there was no significant difference between the mass loss of the two Fe-Cr-Si alloys and 2Cr13 stainless steel. With the increase of time, the quality loss of 2Cr13 stainless steel increases, and Fe20Cr10Si and Fe20Cr12Si alloys have no obvious mass change, which is in a stable stage, indicating good corrosion resistance. Therefore, according to the experimental results, it can be inferred that the corrosion resistance of the alloy and the contrast material in 10%HCl solution is 2Cr13, Fe20Cr10Si and Fe20Cr12Si from weak to strong.

Figure 4. Mass loss curves of four Fe-Cr-Si alloys and 2Cr13 stainless steel with time exposing in 10% HCl solution

The 3-dimensional micrograph provides a better understanding of corrosion damage. After soaking, the sample surface presents different morphologies. Figure 5(a) shows the surface damage morphology of 2Cr13 stainless steel, with different degrees of gullies visible, indicating that the stainless steel is corroded seriously in
acid solution. Figure 5(b) and figure 5(c) respectively show the surface damage morphology of Fe20Cr10Si and Fe20Cr12Si alloys, with almost no gullies on the surface which indicating good corrosion resistance.

![Figure 5](image-url)

**Figure 5.** Surface 3D profile of two Fe-Cr-Si alloys and 2Cr13 stainless steel with time exposing in 10% HCl solution: (a) 2Cr13 stainless steel, (b) Fe20Cr10Si, (c) Fe20Cr12Si.

Figure 6 shows the SEM images of the surface morphology of two Fe-Cr-Si alloys and 2Cr13 stainless steel soaked in 10%HCl solution for 72 h. The corrosion of the stainless steel surface is uniformly eroded as a whole, and a large number of penetrating black erosion pits with a diameter of about 30~50 μm can be seen in the severely eroded area. There is no erosion pit on the surface of the Fe20Cr10Si and Fe20Cr12Si alloy, and the surface is similar to the metallographic structure. The reason is that The Fe₃Si metal itself has good corrosion resistance. The second reason is that The Cr and Si element in the alloy plays a solid solution strengthening effect Si element can form a dense oxide film, preventing the direct reaction between metal and solution, and improving the corrosion resistance of alloy in HCl solution.

![Figure 6](image-url)

**Figure 6.** SEM images of the microstructure of four Fe-Cr-Si alloys and 2Cr13 stainless steel exposed to 10% HCl solution for 72 h: (a) 2Cr13 stainless steel, (b) Fe20Cr10Si, (c) Fe20Cr12Si.

4. Conclusion

1. Two Fe-Cr-Si alloys with good quality were prepared by an arc furnace process. The microstructure of Fe-Cr-Si alloys consists of dendrite and interdendrite matrix, and the phase composition is Fe₃Si metal silicide, Fe-Cr solid solution and γ-Fe.

2. The electrochemical properties show that Fe-Cr-Si alloy has a wider passivation range than the contrast sample. The corrosion mechanism is that active dissolution is the main mode in the early stage of anodic polarization, followed by passivation film protection.

3. The chemical corrosion tests show that the Fe-Cr-Si alloys have good corrosion resistance due to the formation of Fe₃Si silicide phase and the solution strengthening of Cr and Si element.

References

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