

Corrosion of two kinds of cast steels containing chromium in hot concentrated alkaline

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Abstract: A typical hot concentrated alkaline corrosion environment exists in alumina metallurgical industry, so that steel materials with outstanding alkaline corrosion resistance are strongly demanded for its processing equipment. In this paper, the corrosion resistance of two kinds of martensitic cast steels containing chromium in static 303g/L NaOH alkaline solution at 85 °C was studied through polarization and potential-time curves, corrosion weight loss and corrosion morphology analysis. Experimental results showed that protection effect by passive film of cast steel containing Cr was temporary. The low carbon steel without Cr content also exhibited chemical passivity in the same solution. The corrosion mode of the tested Cr-containing cast steel was composed of active dissolving corrosion and caustic embrittlement cracking. Dissolving corrosion was the primary mechanism for the induced weight loss, while severe caustic embrittlement cracking was secondary. With the increase of chromium content in the cast steel, the tendency of the caustic embrittlement cracking decreased, while the active dissolving corrosion increased.

Key words: cast steel containing Cr; caustic embrittlement cracking; alkaline corrosion

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Cast steels containing Cr, a passive element, are commonly used as corrosion-resistant materials in acid, neutral and diluted alkaline solutions. The function of the Cr element in the hot concentrated alkaline medium is interesting, but reports on the corrosion behavior of Cr-containing cast steels in such conditions were limited. Studies showed that anode dissolving corrosion could easily occur on iron and steel materials in hot concentrated alkaline at a temperature above 80 °C [1-3], and corrosion rates accelerated with the increasing of temperature and/or concentration of alkali [4,5]. Contrary opinions existed over the effects of Cr content on the weight loss of cast iron and steel in the hot concentrated alkaline corrosion. Some research [6] reported the potential of Cr in the hot concentrated alkaline corrosion was more positive than that of Fe, while other studies [7] reported the stability of Cr in alkaline solution is worse than that of Fe. Caustic embrittlement cracking is a typical phenomenon in the hot concentrated alkaline irons and steels for corrosion. Although some achievements have been obtained on the caustic embrittlement cracking of ferritic and austenitic steels, the effects of Cr on the caustic embrittlement cracking need further

investigation. It has been reported that the Cr addition reduces the sensitivity of the caustic embrittlement cracking for low carbon ferritic steel [8], and enhances fracture resistance of caustic embrittlement cracking for austenitic stainless steel [9]. However, no literature could be found on the study of caustic embrittlement cracking of martensitic cast steels in hot concentrated alkaline solutions, especially the effect of Cr content on caustic embrittlement cracking of high strength martensitic alloys. This is just the background of the present research.

The typical hot concentrated alkaline environment can be found in alumina metallurgical processing where metals encounter both corrosion and erosion. The key problem for investigation is whether the martensitic cast steels containing Cr can resist the environmental attack, and can be used as corrosion resistant materials for contacting the solution. To obtain useful data, corrosive environment of the alumina production process under Bayer method was referred in this paper. Several types of Cr-containing martensitic cast steels were immersed in the hot concentrated alkaline solution to evaluate their corrosion behaviors/performances. In particular, the effect of Cr content on weight loss and caustic embrittlement cracking was investigated and discussed.

1 Experimental condition and method

The chemical compositions of three kinds of steels used in the study are shown in Table 1. The specimens of cast steel 20Cr5

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and 20Cr11 were taken from Y-block castings and then heat treated to obtain martensitic matrix. The samples in steel 10 (or 10# steel) were cut from a rolled plate. The same preparation process was used for the specimens containing Cr, so that their stress condition could be controlled to the same or similar level. Microstructure and macro hardness of these specimens are listed in Table 2.

Table 1 Chemical composition of test specimens, wt. %

Materials	C	Cr	Ni	Si	Mn	Mo	P	S
Steel 10 (10# Steel)	0.10	-	-	0.13	0.47	-	0.020	0.010
20Cr5	0.22	4.63	0.82	0.73	0.92	0.26	0.035	0.020
20Cr11	0.22	10.69	0.93	0.75	0.78	0.10	0.030	0.040

Table 2 Microstructure and hardness of test materials

Materials	Micostructure	HRC
Steel 10	F	-
20Cr5	M+Ar	44
20Cr11	M+Ar	44

Note: M-martensite, Ar-retained austenite, F-ferrite

The 303g/L NaOH solution made of chemical grade reagent and deionized water was used in measurements on corrosion rate and electrochemistry properties. The temperature of the solution was maintained at 85 °C by a thermostat water tank. Specimens for the measurement of the static immersion corrosion rate were sized to 20 mm × 20 mm × 8 mm, with all the sample surfaces polished. Three samples of each material were carried/tested, and the specimens from the same material were placed in the same container. The contact between specimens and their glass epoxy supporters was line-contact, and the ratio between the volume of test solution and specimen surface area was 20 mL/cm². Test durations (or immersion periods) were set at 14, 62 and 230 h, respectively. After corrosion test, specimens were wiped with rubber or soft cloth to remove the corrosion products, washed with water and placed into ethanol immediately. After having dried with warm air, the specimens were placed into a drier (storage), and their weights were measured after cooling. The corrosion rate was defined as the average weight loss rate of the three samples.

Cylinder specimens with diameter of 10 mm were used for the measurement of potential-time curve in static immersion. One end of the cylinder specimens was polished to mirror surface-finish and taken as a working electrode. The other end was welded to a copper cable that would act as electrode line. All surfaces except the working (or test) surface were coated with epoxy, and after the resin setting, test specimens were covered with a silicon-rubber tube of diameter of 9 mm, to avoid these surfaces contacting with the alkaline solution. These samples were immersed continually in the testing medium at 85 °C. Their potentials were recorded everyday by using Hg/HgO/NaOH(1N) as the reference electrode. In this paper, all potentials are in reference to this electrode unless otherwise mentioned.

The working and reference electrodes used for anodic polarization curves were the same as that for the potential-time curve test. Graphite counter electrode was used, and the positive sweep (rate=10 mV/min) from rest potential of working electrode started after 20 minutes immersion.

Finally, corrosion morphology of cast steel containing Cr after static immersing test was investigated with scanning electronic microscopy (SEM).

2 Results and discussion

Figure 1 shows anodic polarization curves of 20Cr5, 20Cr11 and steel 10 in the testing solution. The difference in the shape/characteristics of the anodic polarization curves indicated a great influence of Cr content on the corrosion process. The curve of steel 10 was a typical polarization curve of chemical passive system. The rest potential of the steel 10 was about -480 mV, and the current density increased gradually when the rest potential increased to -100 mV, and the current density kept unchanged in the range from -100 mV to 500 mV. This suggested that the corrosion of the steel was controlled by anodic passivity. The behavior of steel 10 could be explained by potential-pH equilibrium diagram for the system of Fe-H₂O^[10]. The pH of the testing solution was between 14 and 15. At this pH value, the stable materials in the system are Fe, HFeO₂⁻ and Fe₂O₃ in order when the potential changes from negative to positive direction. With the potential was more positive, the system turned into over-passivation. In a wide range of the potential from -750 mV to 250 mV (vs. standard hydrogen electrode), the stable material was Fe₂O₃. The RP of steel 10 was -480mV, which was located in the stable range of Fe₂O₃. Fe₂O₃ film was formed on the surface of steel 10 at this potential level. This film resulted in the corrosion resistance of the steel in the testing solution.

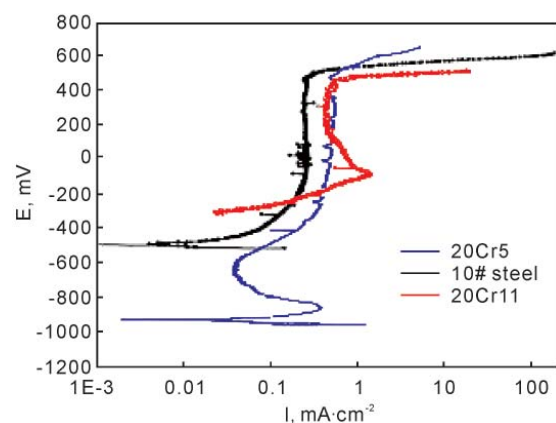


Fig. 1 The anodic polarization curves of 20Cr5, 20Cr11 and steel 10

By a comparison between the Fig. 1 and the previous work of the present author (Fig. 3 in reference [11]), it could be found that the polarization curves of 20Cr11 and Cr26 iron were similar. Thus, the polarization curve of the 20Cr11 may be the polarization curve of film. The potential curve of 20Cr5 was similar to that of like naked metal. Similar to the Cr13 and Cr26 irons^[11], the two types of the cast steel containing Cr exhibited active dissolution by their anodic polarization curves.

This fact showed again that the Cr addition enabled iron-based alloys to appear electrochemical activity in concentrated alkaline solution. Referring to the potential-pH equilibrium diagram for Cr-H₂O^[10], the element Cr actively dissolved forming CrO₃³⁻ ion in high pH area and when the potential was lower than -300 mV (vs. standard hydrogen electrode). This behavior might be induced in the Fe based alloys when Cr was added. The curve shape, especially the characteristic of active dissolution of alloy observed in the experiment should be attributed by the Cr dissolution.

Figure 2 shows the potential-time curves of steel 10, 20Cr5 and 20Cr11. The potential of steel 10 was from -200 mV to -500 mV during the immersion, i.e. the electrode was always in passivity and Fe formed Fe₂O₃. On the other hand, the potentials of 20Cr5 and 20Cr11 varied greatly during the immersion, which means that surfaces of the two electrodes also varied greatly. It should be noted that when potential was located at about -1 000 mV, there existed not only Cr dissolution but also Fe dissolution to form HFeO₂⁻ (referring to potential-pH equilibrium diagram for Fe-H₂O). The potential variation of the steel containing Cr with the immersion time was similar to those two types of the cast iron^[11], and therefore, the corrosion process could also be divided into three stages. The first stage was passive film dissolving. Because of the high Cr content in the steels, passive films were formed in atmosphere and their thickness was related to the Cr content. When the passive film was complete, a relatively high self rest potential of -400mV to -200mV, close to the equilibrium potential of partial cathode reaction, had been reached for the specimens in the hot concentrated alkaline of the present test, leading to that the film dissolved at a low rate and was un-repairable by itself. The steel 20Cr11 with high Cr content had a relatively thick film that required certain time for its dissolution. In this case, the time from which the electrode potential was -400 to -200 mV was near 70 h. The film of steel 20Cr5 was very thin, so that it dissolved in a very short time, with exposition of the metal and decreasing the electrode potential to about -1 000 mV. The second stage was the exposed surface corrosion. In this stage, metal matrix dissolved. The cathodic process was a depolarization of oxygen and water with a high rate, as a result of decreased potential to about -1 000 mV. The difference of time duration in the second stage existed between the two types of cast steels 20Cr11 and 20Cr5. After the samples were covered with the corrosion products to a certain degree, the potential rose from about -1 000 mV to about -400 mV and the corrosion went into the third stage, in which the corrosion occurred under the corrosion products. In this stage, the rest potential of the cast steel fluctuated in a range from -450 mV to -300 mV and the corrosion rate was obviously lower than that of the second stage.

Table 3 shows the weight loss of steel 10, 20Cr5 and 20Cr11 in the testing solution. The weight loss increased with the increase of the Cr content in the three time durations, which was consistent with the results of polarization curve. From Table 3 it can be seen that the weight loss was different in the three time durations, corresponding to the location of the potential curve. If a material in the immersion corrosion testing had a long time when its

potential was located at about -1 000 mV, its weight loss value was large and vice-versa (see Fig. 2). The phenomenon was similar to that for the Cr13 and Cr26 cast irons^[11].

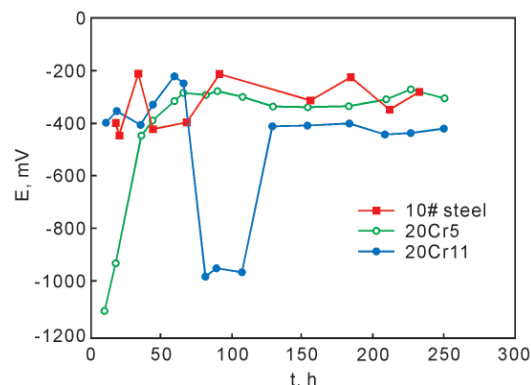


Fig. 2 The electrode potential - time relationship of steel 10, 20Cr5 and 20Cr11

Table 3 The weight loss of steel 10, 20Cr5 and 20Cr11 in the testing solution, g/m² · h

Materials	14 h	62 h	230 h
Steel 10	0.0730	0.0391	0.0316
20 Cr5	0.0843	0.0907	0.0785
20Cr11	0.1290	0.1400	0.1205

Figure 3 and 4 are appearances of the cast steel 20Cr5 and 20Cr11 after the immersion respectively. Two main corrosion characteristics may be seen on the corroded specimens. First, the surfaces of the sample were rough after the corrosion and there were several etching pits on them. Especially on the surface of 20Cr11, etching pits appeared in a fairly large area (see Fig. 4). The corrosion pit damages were resulted from active corrosion during the immersion. Second, caustic embrittlement cracking induced cracks/fracture obviously existed in both steels, indicating that stress corrosion cracking occurred. The cracking

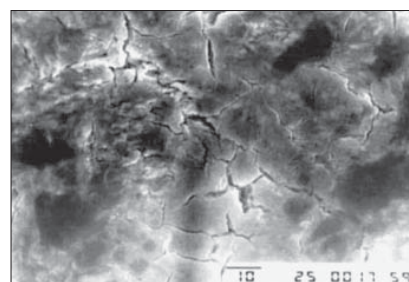


Fig. 3 Morphology of the 20Cr5

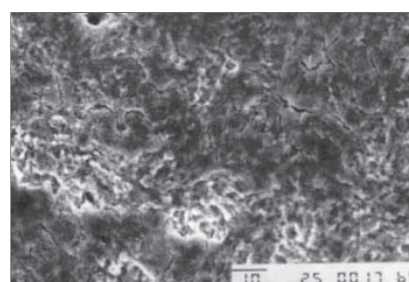


Fig. 4 Morphology of the 20Cr11

tendency of 20Cr11 with higher Cr content was weaker than that of 20Cr5. After immersion corrosion, crack and small etching pits appeared on 20Cr11 surface, while coarse cracks resulted on 20Cr5 surface (see Fig. 3).

Although the tendency of caustic embrittlement cracking of the 20Cr11 was lower than that of the 20Cr5, the corrosion rate of 20Cr11 was high, indicating that the weight loss caused by dissolving corrosion was higher than that by the caustic embrittlement cracking. The findings also indicated that anodic dissolving corrosion was a main cause for weight loss of the steels and the caustic embrittlement cracking extensively fractured the material matrix. With increase of Cr content, weight loss increased but the caustic embrittlement cracking tendency decreased.

3 Conclusions

(1) The protection effect by passive film of martensitic cast steel containing Cr when immersed statically in 85°C, 303g/L NaOH solution was temporary. The low carbon steel without Cr exhibited chemical passivity in the same solution.

(2) The corrosion of the martensitic cast steel in the hot concentrated alkaline included active dissolving corrosion and caustic embrittlement cracking. The active dissolving corrosion was the main cause for the weight loss, and the serious caustic embrittlement cracking fractured the metal matrix.

(3) The effect of Cr content on corrosion of the cast steel in the solution was remarkable. With increasing the Cr content in cast steel, the weight loss by active dissolving corrosion increased, but the caustic embrittlement cracking tendency decreased.

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