

Impedance Spectra Characteristics of Fe-Cr Alloys in a Solid K_2SO_4 -KCl Mixture at 600°C and 650°C

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The low temperature hot corrosion characteristics of Fe-10Cr and Fe-20Cr alloys is studied in solid 0.5K₂SO₄-0.5KCl mixture in air at 600°C and 650°C. A two-electrode system is arranged for electrochemical measurement, which has been proved effective in the study of solid- and molten-salt corrosion. EIS analysis discloses corrosion of Fe-Cr alloys goes through several different reaction stages during extended exposure, such as incubation, acceleration and catastrophic period. Additionally, all these stages are fitted by corresponding equivalent circuits and electrochemical elements, and simulation data of these models generally fits experimental data well. Different Cr content in Fe-based alloys has been investigated involving the active/oxidation process of metal Cr in solid 0.5K₂SO₄-0.5KCl mixture. Corrosion products in above-mentioned different stages are analyzed by scanning electron microscopy. The formation and depletion of protective scale in mixed salt is monitored. Corrosion rate and corrosion mechanism of Fe-10Cr and Fe-20Cr alloys are discussed, too.

Keywords: Electrochemical impedance; Fe-Cr; solid salt; two-electrode system

1. INTRODUCTION

When a part of deposited KCl increasingly react with flue SO₂ to form K₂SO₄, metals will face serious corrosion by their combined effect[1-4], such as KCl-K₂SO₄ mixture will attack metal surfaces of the superheaters and lead to the damage of boilers. The material with a high-corrosion resistance in the combustion has been advanced to prevent corrosion of deposited chloride and sulfate [5-8]. High-Cr ferritic and austenitic steels (Cr content is not less than 18 wt.%) are widely used as high-temperature components and protective chromia scales formed on these alloys surfaces make an

immediate impact in corrosion resistance during high-temperature exposure. Hot-corrosion behavior of Ni and Ni-Cr alloys[9] disclosed that alloys were attacked severely by chlorides and chloride-induced hot corrosion. Although the melting point of KCl-K₂SO₄ mixture is about 694°C, accelerated corrosion of high-Cr alloys at low temperature was observed. Corrosion behavior of thermally sprayed Ni-Cr and Fe-Cr coatings in a KCl-K₂SO₄ mixture at 550°C and 600°C for 168 h[10] showed interlamellar corrosion found at 600°C in some cases due to the penetration of Cl and the depletion of Cr in the coating.

Plenty of studies have proved that it is an effective technique in investigating reaction mechanisms and kinetics in aqueous solution. EIS has also received special attentions to study the corrosion behavior induced by molten salt [3,11-13]. In order to investigate reaction mechanisms, suitable models need be established for fitting the impedance spectra besides impedance measurements. The key factor for application of electrochemical measurements in molten salt is test-cell design. Zeng[14,15] disclosed that a two-electrode system can be prepared conveniently, and was also suitable for simple EIS measurements. The two-electrode system[16] were fulfilled to model the corrosion of pure Al coating on 310S stainless steel in molten (0.62Li+0.38K)₂CO₃ at 650°C. The diffusion impedance was discussed as Warburg impedance, and the surface and porosity of scales were indicated by the values of dispersant coefficient and charge transfer resistance. Two-electrode system was also used to study the initial-stage corrosion of stainless steel at 650°C with thin film of molten carbonates and the corrosion rate is calculated by polarization resistance[17]. Additionally, a two-electrode system was used to analyze corrosion of alloys in the presence of a solid Na₂SO₄ at 800°C[14]. In initial stage, the sulfate deposit was solid. An incubation oxidation produced on the surface of alloys which results in relatively large impedance and medium resistance. With increasing time, solid sulfate was mixed with corrosion product to form molten Na₂SO₄-Na₂MoO₄-MoO₃, which is synchronously reflected in the measured impedance spectroscopy.

Based on above, EIS technology is appropriate to monitor the solid corrosion process. In this study, low temperature hot corrosion behavior of Fe-Cr alloys is investigated by electrochemical impedance spectroscopy using a two-electrode system in a solid 0.5K₂SO₄-0.5KCl mixture at 600°C and 650°C in air. The evolution of impedance spectra and corrosion product is simultaneously detected. Corrosion rate, transfer resistance of ions through the scale and charge transfer resistance are discussed in detail according to EIS.

2. EXPERIMENTAL

Fe-10Cr and Fe-20Cr alloys (wt.%) are employed in the present study. The alloys are prepared by repeated argon arc melting, and then annealing at 1000°C for 24 h. Alloy ingots are cut into pieces in the size of 10 mm×5mm×1 mm. The surface of coupons is ground up to 800-grit and degreased with acetone before use.

The EIS measurements are conducted in the mixed 0.5K₂SO₄-0.5KCl salt (mole fraction) in air at 600°C and 650°C, respectively. K₂SO₄ and KCl are mixed well and then put into an alumina crucible. Before use the mixed salt is dried at 400°C for 48h and then heated to reaction temperature.

During the experiment, specimens are totally buried under the mixed salt for about 25mm, and extracted at selected intervals for morphology analysis with the residual potassium salts.

A two-electrode (two working electrodes) system is used for EIS measurements. Fe–Cr wires are spot-welded with one end of every specimen for electrical contact. Two specimens parallel to each other and are sealed in an alumina tube by a high-temperature insulated cement, with one side uncovered, as shown in Fig. 1a. The vertical distance of two electrodes is about 1mm in order to reduce electrolyte resistance between the gap. Alumina tube with specimens and high-temperature cement is dried for several days at room temperature. It is further solidified at 100°C for 24 h and then 350°C for 10 h. The size of each working electrode is about 5mm×5mm×1mm and they are degreased again before test. The experimental system is shown in Fig. 1b. Corrosion chamber is treated to eliminate the effect of electric and magnetic fields[18], and the temperature of reaction area is calibrated by the standard platinum-rhodium thermocouple with the deviation of $\pm 1^\circ\text{C}$.

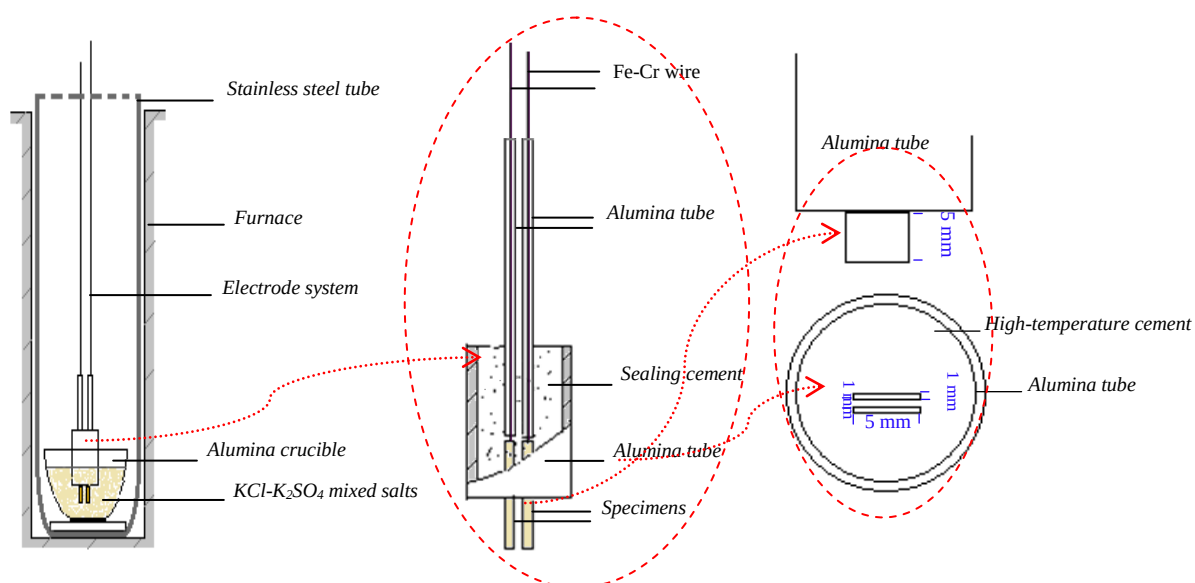


Figure 1. Two-electrode arrangement for electrochemical impedance measurements

Parstat 2273 of Princeton Applied Research is used for EIS measurements which is performed at the open circuit potential between 1×10^{-2} Hz and 1×10^4 Hz. The amplitude of input sine-wave voltage is 10 mV. Each Fe–Cr system is measured for at least three times at each temperature, and two groups of samples are measured together every time. A commercial software Zsimpwin is employed to fit the impedance spectra. Cross section of specimens were analyzed by scanning electron microscopy coupled with EDAX.

3. RESULTS AND DISCUSSION

3.1 Electrochemical impedance measurements

The reaction temperatures 600°C and 650°C are a little lower than the melt point of 0.5K₂SO₄-0.5KCl mixture (694°C). Fig.2 shows impedance spectra of Fe-10Cr alloy corroded in the mixed salt at

600°C for different time. Corrosion of Fe-10Cr goes through two stages during the test period. In initial stage, the Nyquist plots are composed of a large capacitive loop at all frequencies and its center deviates the real axis because of dispersion (Fig.2a and Fig.2b). The total impedance values and salt resistance tend to decrease with exposure time. After about 88h, the Nyquist plots become a small capacitive loop and a line which indicates a diffusion-controlled feature (Fig.2c), and corrosion resistance becomes very small after the long time.

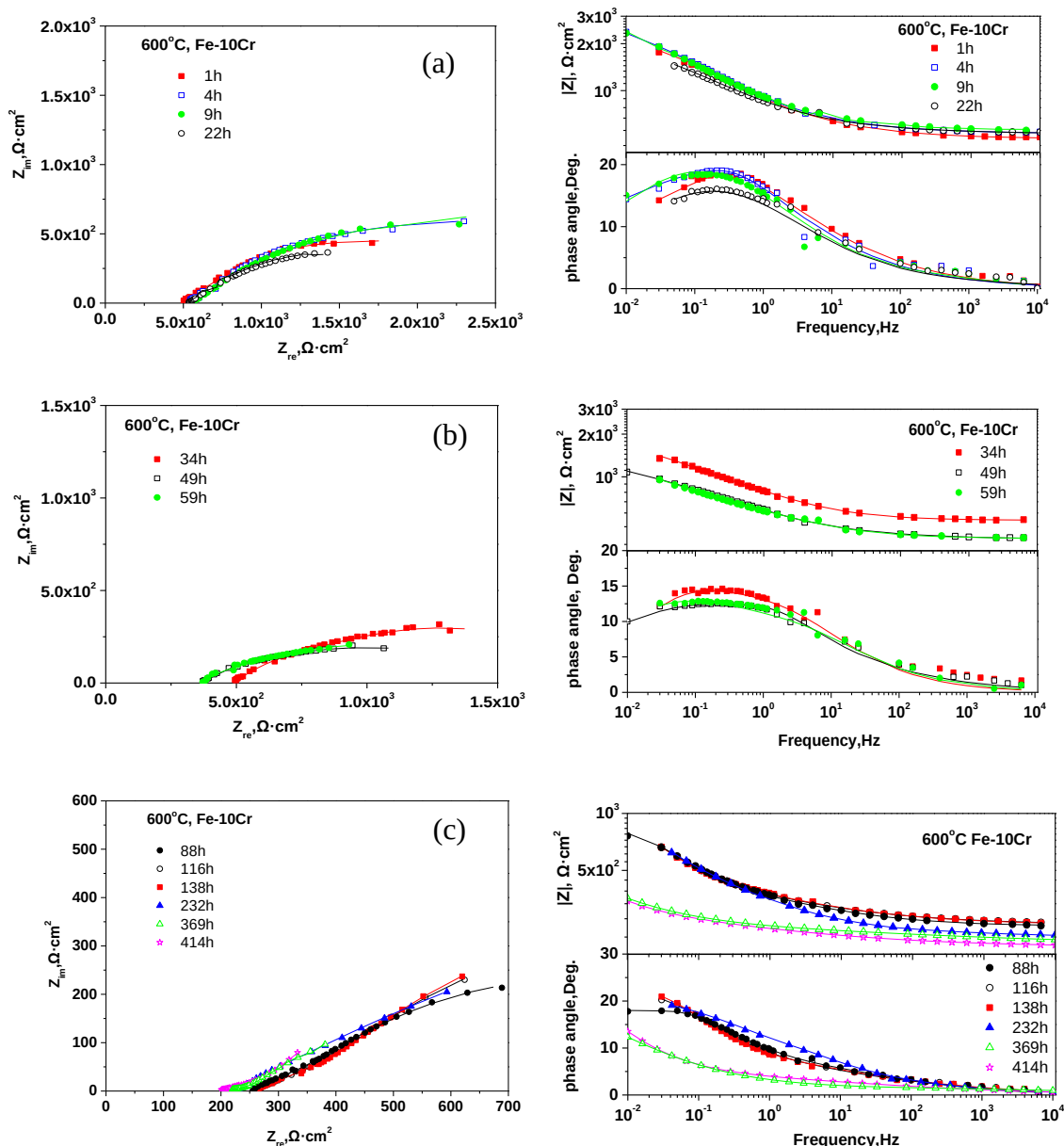


Figure 2. Nyquist and Bode plots for Fe-10Cr alloy buried in K_2SO_4 -KCl mixtures at 600°C in air after different exposure times. Symbol: experimental data; line: simulation data

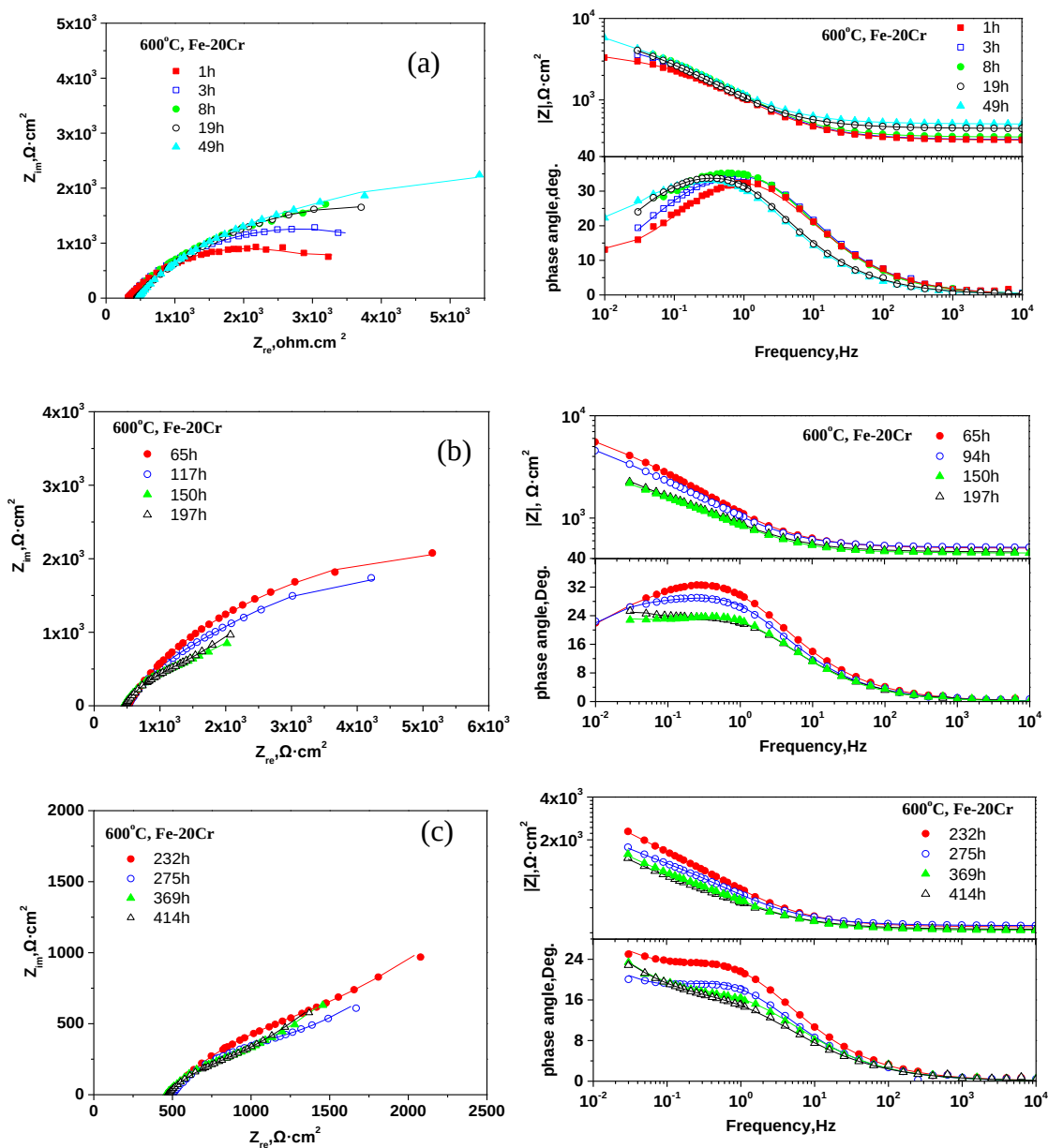


Figure 3. Nyquist and Bode plots for Fe-20Cr alloy buried in K₂SO₄-KCl mixtures at 600°C in air after different exposure times. Symbol: experimental data; line: simulation data

Fig.3 shows impedance spectra of Fe-20Cr corroded in the mixed salt at 600°C for different time (Fig.3a and Fig.3b). The Nyquist and Bode plots show that it is a large capacitive loop at all frequencies between 1h and 117h (Fig.3b), and the diffusion-controlled reaction clearly develops after electrodes corroded for 232h (Fig.3c). The modulus of impedance of Fe-20Cr at 600°C is much larger than that of Fe-10Cr.

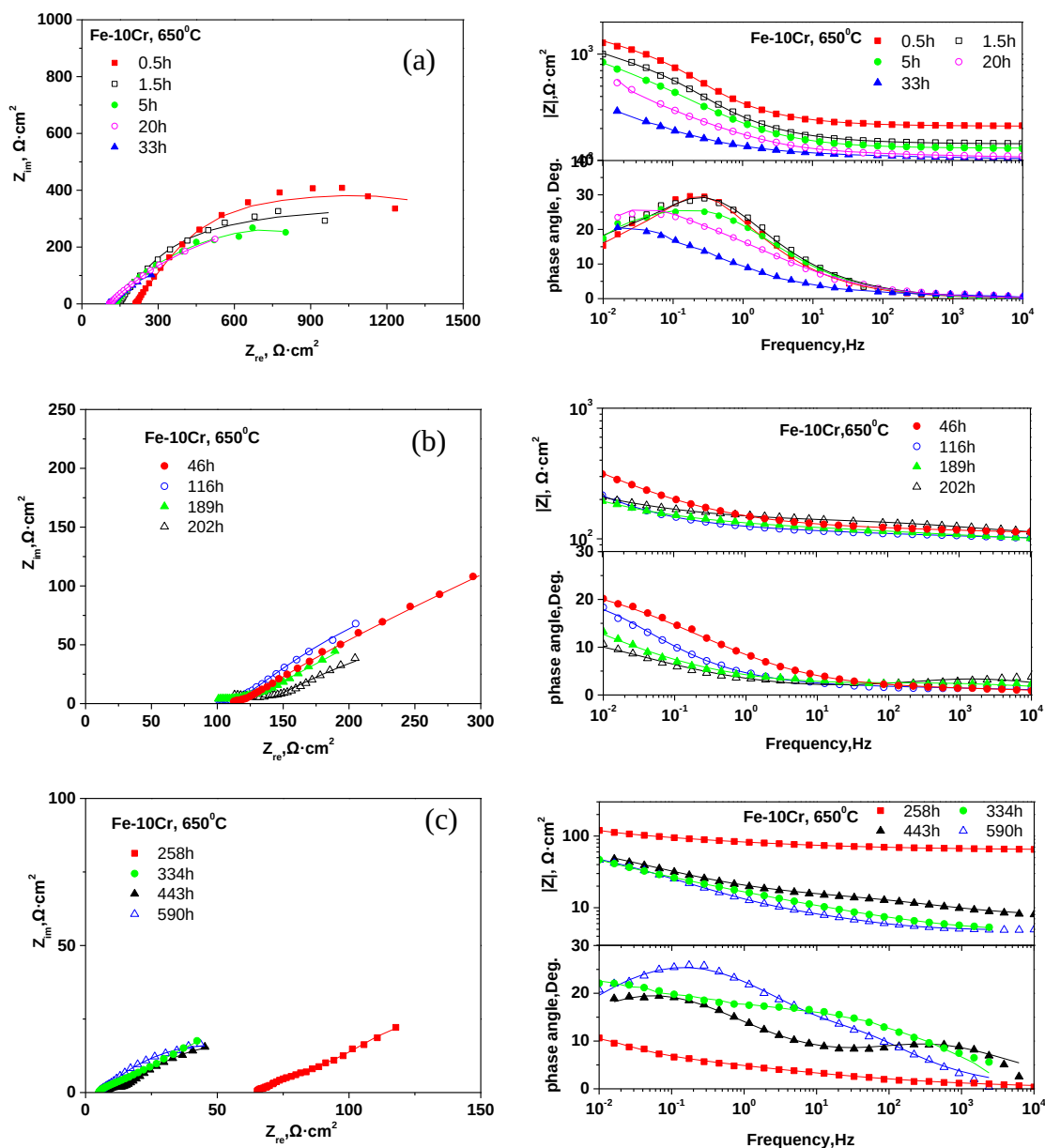


Figure 4. Nyquist and Bode plots for Fe-10Cr alloy buried in K_2SO_4 -KCl mixtures at 650°C in air after different exposure times. symbol: experimental data; line: simulation data

Fig.4 shows EIS of Fe-10Cr corroded in mixed salt at 650°C for a long time. According to impedance spectra, the corrosion process can be divided into three stages. In initial stage, it is a large capacitive loop as before, and the semi-diameter of loop gradually decreases with time. Then the diffusion-controlled reaction (a line at low frequency) develops after electrodes corroded for 20h (Fig.4a). In stage III, both reaction resistance and mixed salt resistance decreases rapidly. The Nyquist plot is composed of two capacitive loops connected by a line. The multiple time constants are found in Bode plots in Fig.4c.

Fig.5 shows EIS of Fe-20Cr alloy corroded in mixed salt at 650°C for 590h. The corrosion process of Fe-20Cr is the same as that of Fe-10Cr. It is also a large capacitive loop in the initial stage for periods of 20h (Fig.5a), and the resistance is much larger than that of Fe-10Cr. In stage II, a line at low frequency emerges (Fig.5b). In stage III, all the resistance is almost as large as the resistance of Fe-10Cr after corrosion for 300h (Fig.5c).

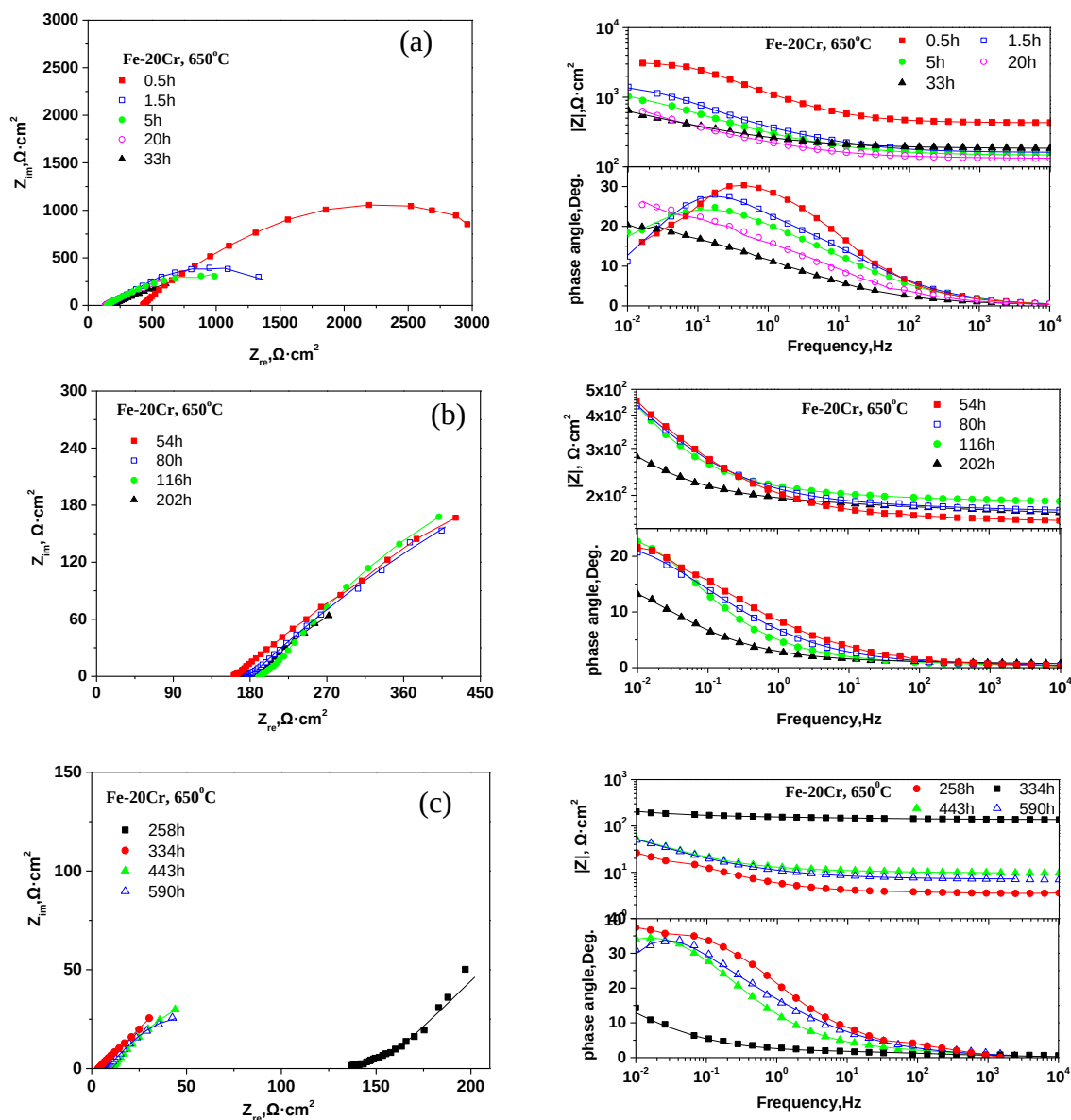


Figure 5. Nyquist and Bode plots for Fe-20Cr alloy buried in K_2SO_4 -KCl mixtures at 650°C in air after different exposure times. symbol: experimental data; line: simulation data

3.2 corrosion products in mixed salt

Fig. 6 shows cross-sectional morphology of Fe-10Cr corroded in mixed salt for 50 h, 120h and 420h. Analysis of EDAX indicates that the outer oxide layer is composed of Fe-rich oxides. Some kali salt is detected in the interface of oxide/metal at 600°C for 120h. With prolongation of exposure time,

the internal oxide, preferential intergranular penetration, is obviously observed for 420h. The aggregate Fe/Cr sulfides and chlorides are found in oxide/metal interface and internal sulfidation/oxidation zone (Table 1). Figs.7 shows that the external oxides of Fe-20Cr corroded for 50 h, 120h and 480h are mainly Fe/Cr oxides, and the oxide layer is much thinner and more compact than that of Fe-10Cr at corresponding time. High temperature corrosion of thermally sprayed Fe-25Cr coating in KCl–K₂SO₄[10] also showed the dense and thick Fe_xO_y layer with Cr_xO_y was developed after 168h at 500°C and 600°C. There is no internal oxidation in Fe-20Cr alloy, but the alloy interface prominently fluctuates after corrosion for 480h. Some sulfides are found in oxide/metal interface (Table 1), too.

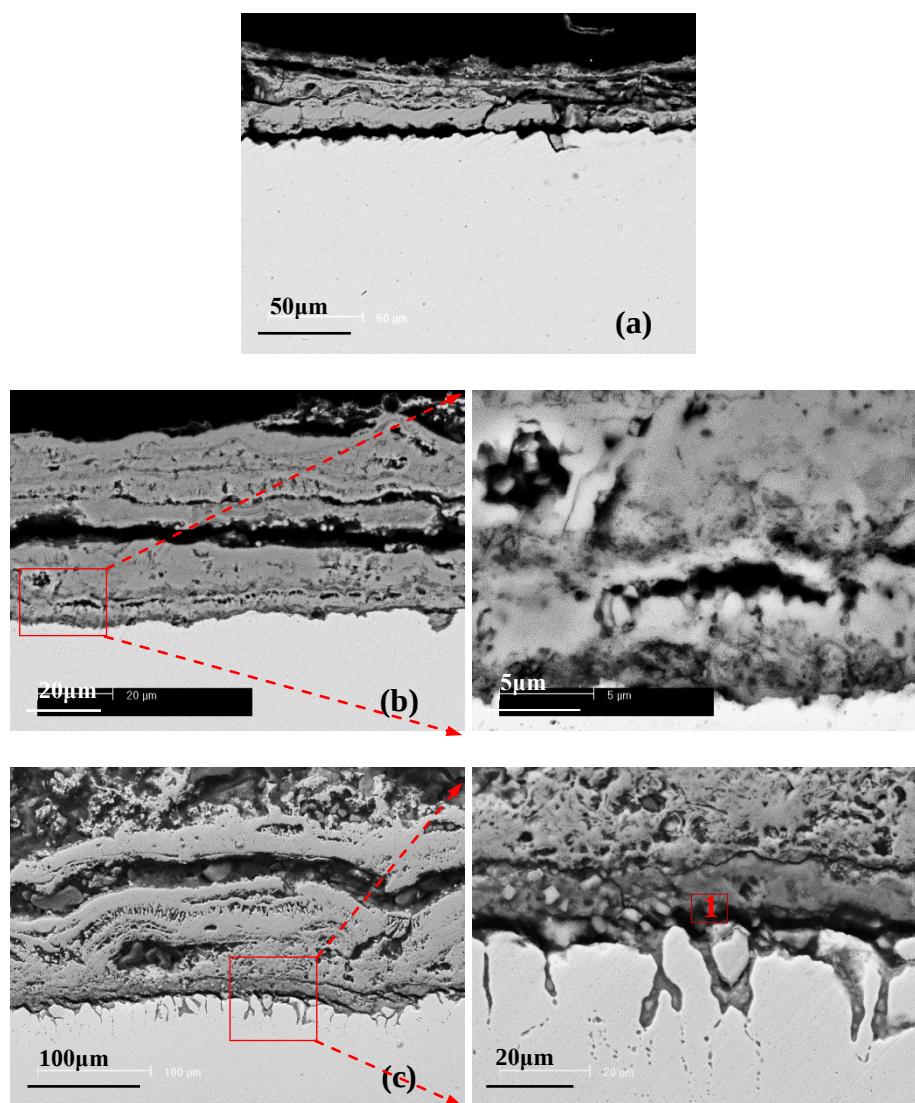


Figure 6. Cross-sectional morphology of Fe-10Cr alloy buried in K₂SO₄-KCl mixtures at 600°C in air after different exposure times (a)50h (b)120h (c)420h

Fig.8 shows cross-sectional morphology of Fe-10Cr alloy buried in K₂SO₄-KCl mixtures at 650°C for 50h, 250h and 590h. It shows that the outer Fe-rich oxides for 50h and 250h are thick and loose. Internal sulfidation/oxidation along grain boundary for 250h is obviously found, and corrosion product in the interface is composed of mixed Fe/Cr sulfides, oxides and salts. When Fe-10Cr corroded

for 590h, a large amount of residual salt is found outside the oxide layer. The light phase is KCl-rich salt, and the grey phase is K_2SO_4 -rich salt. The thickness of oxide layer is much larger than that for 250h, the size of the internal particles markedly increases and some of them are linked together. In addition, the advancing internal oxidation front is basically flat after 590h. The increasing temperature and reaction time lead to the accelerated kinetics and lattice internal oxidation occurs. Table 2 shows S/Cl concentration of oxide layer is high for Fe-10Cr alloy at 650°C, which means vast sulfide/chloride forming and lots of salt permeating. Corrosion of low alloy steel and stainless steel in NaCl-50%Na₂SO₄ at 650°C[19] showed that weight gain is higher in magnitude than in Na₂SO₄-60%V₂O₅, internal attacked was found in low alloy steel. Accelerated corrosion will occur when temperature is higher than the melting point of mixed salt.

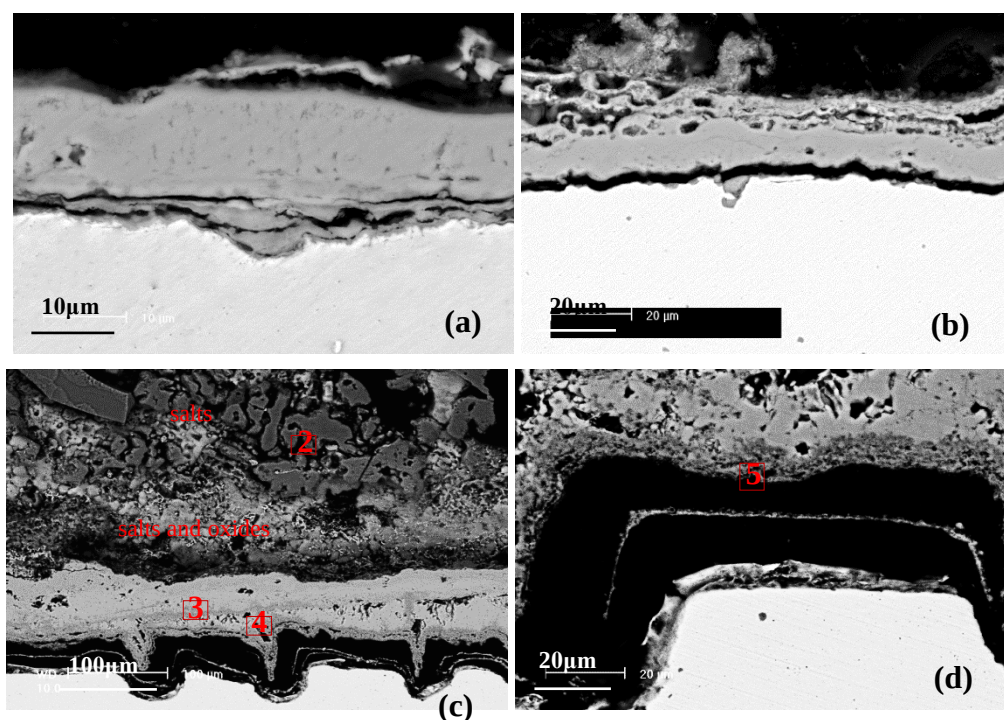


Figure 7. Cross-sectional morphology of Fe-20Cr alloy buried in K_2SO_4 -KCl mixtures at 600°C in air after different exposure times (a)50h (b)120h (c)(d)480h

Table 1. EDAX of corrosion products of Fe-10Cr and Fe-20Cr alloys in K_2SO_4 -KCl mixture at 600°C
EDAX values showed as relative values and qualitative

Marked area, at. %		O	S	Cl	K	Fe	Cr
Fe-10Cr	1	34.8	1.2	2.2	7.6	52.5	1.7
	2	44.8	18.6	-	36.6	-	-
	3	29.7	-	-	-	70.3	-
Fe-20Cr	4	35.0	-	-	-	62.2	2.8
	5	37.7	5.2	-	-	18.1	39.0

Fig.9 shows cross section of Fe-20Cr alloy after corrosion at 650°C for 50h, 250h and 590h. Images of Fe-15Cr and Fe-35Cr corroded beneath KCl at 650°C for 48h[20] showed that a chloride layer is not detected in oxides/substrate interface and the inner layer was separated from the substrate by a gap. The same gap between oxides and substrate is detected and there is no chloride/ sulfide for Fe-10Cr and Fe-20Cr alloys after corrosion at 650°C for 50h. After 250h and 590h, the external oxide layer is thick, some Fe/Cr sulfide precipitates in the outer part, and Fe/Cr chloride concentration near the interface of oxide/alloy remarkably increases (Table 3). There is no internal oxide forming, but the interface becomes more irregular with extended immersion. Corrosion behaviors of Fe-Cr alloys at 450°C for 25h beneath ZnCl_2 -KCl deposits (molten salt)[21] showed that the adherence of corrosion products was worse for higher Cr-containing alloys. Corrosion of Fe-35Cr alloy beneath a NaCl-KCl deposit at 670°C for 48 h[22] showed a thick chromium chloride layer was in the oxides/substrate interface. The chloride layer is not found for both Fe-10Cr and Fe-20Cr alloys and corrosion products of Fe-20Cr alloy still keep good adherence after corrosion in K_2SO_4 -KCl at 650°C for 50h. Corrosion behavior of 310SS in 0.5 K_2SO_4 -0.5KCl at 750°C for 24h[23] showed internal attack was detected and the formation of protective oxide scale was inhibited in the initial stage, which is not found for Fe-20Cr alloy in the initial stage at 650°C.

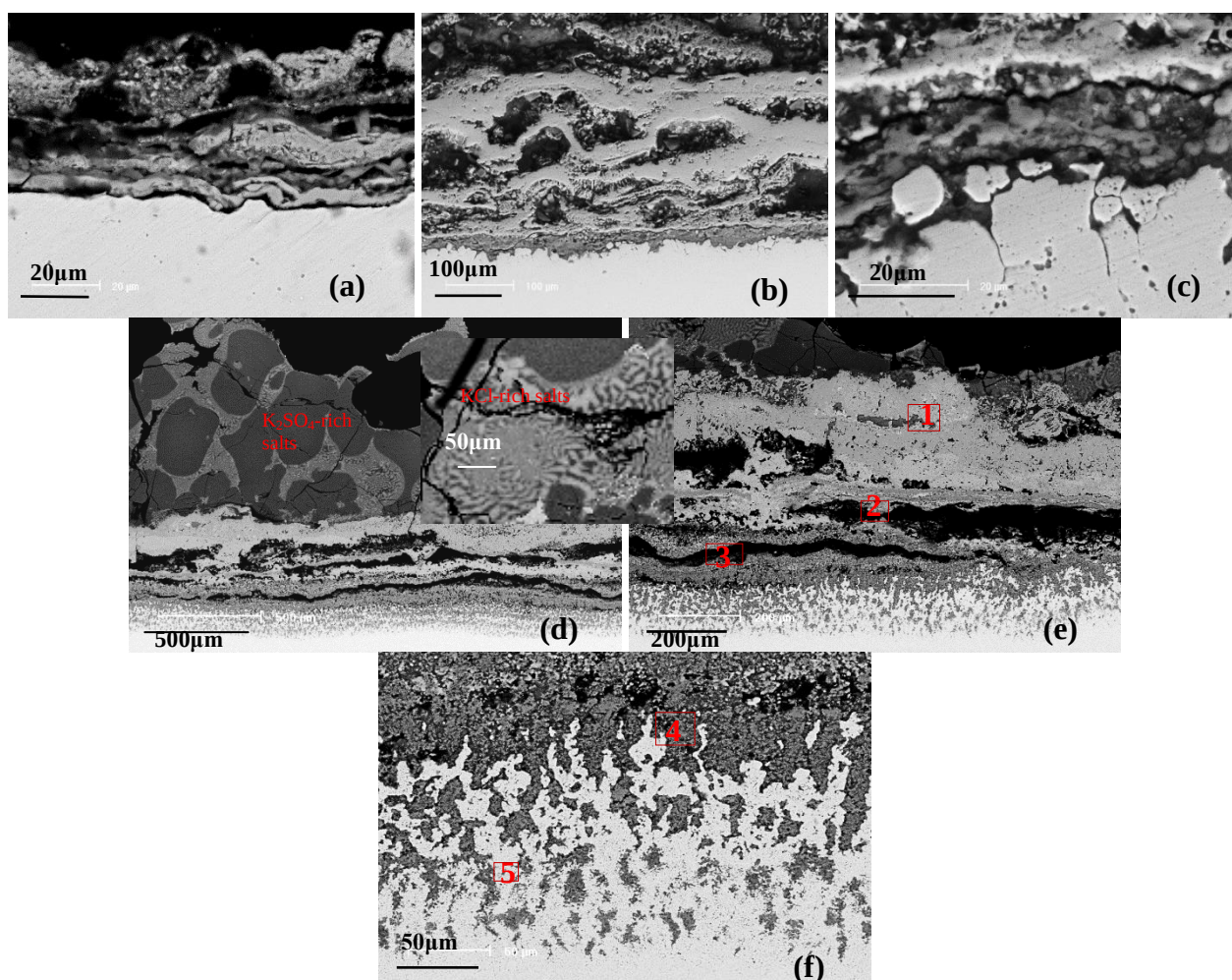


Figure 8. Cross-sectional morphology of Fe-10Cr alloy buried in K_2SO_4 -KCl mixtures at 650°C in air after different exposure times (a)50h (b)(c) 250h (d)(e)(f) 590h

Table 2. EDAX of corrosion products of Fe-10Cr alloys in K_2SO_4 -KCl mixture at 650°C for 590h
EDAX values showed as relative values and qualitative

Marked area, at. %	O	S	Cl	K	Fe	Cr
1	32.0	-	-	-	68.0	-
2	21.8	11	15.6	6.6	31.0	14.0
3	-	25.0	8.5	3.4	42.5	20.6
4	13.4	1.6	31.3	29.7	12.8	11.2
5	27.4	0.7	15.8	13.3	22.3	20.5

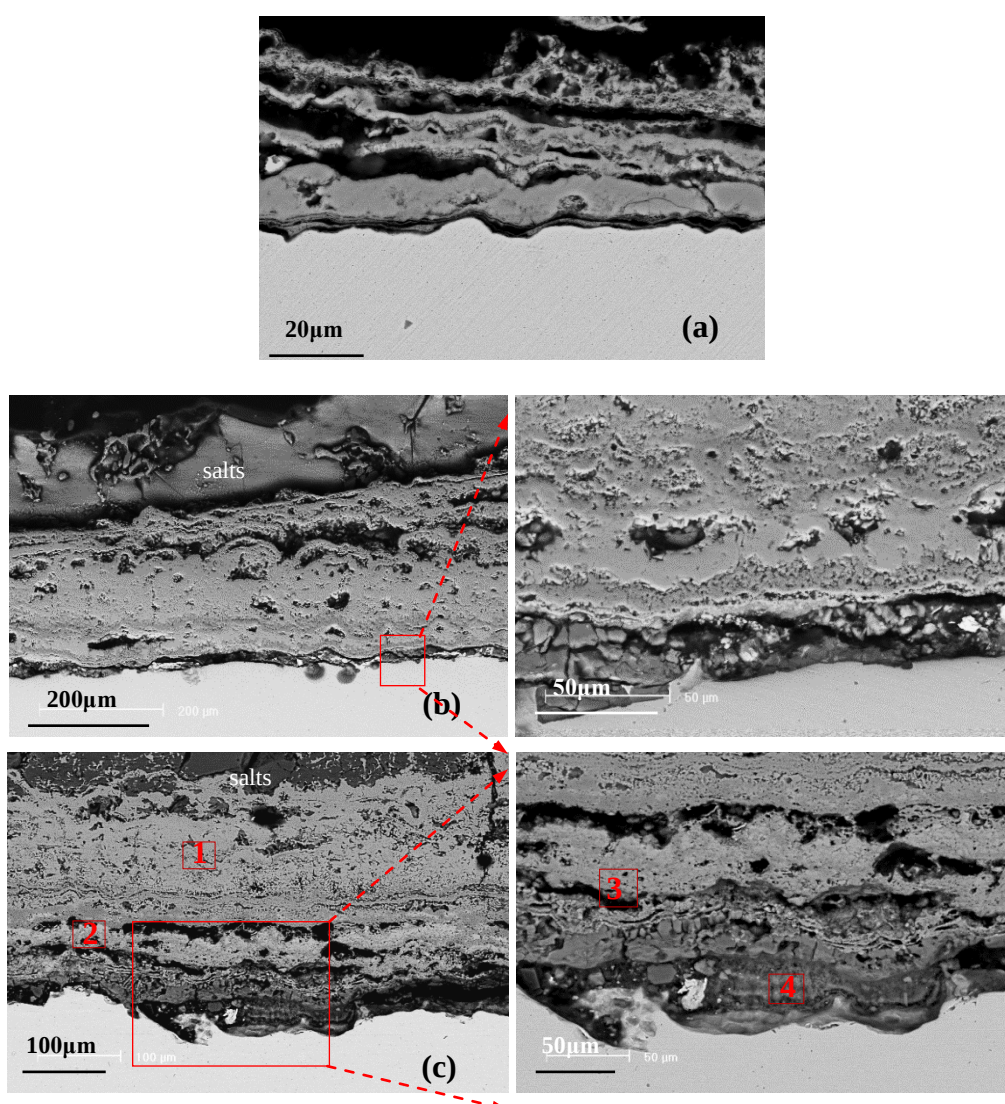
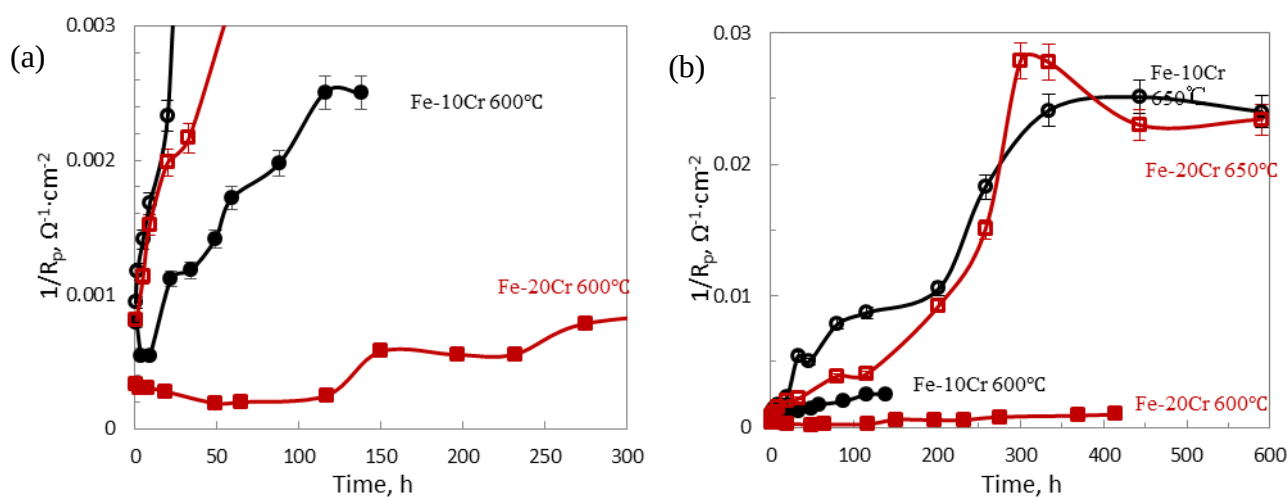


Figure 9. Cross-sectional morphology of Fe-20Cr alloy buried in K_2SO_4 -KCl mixtures at 650°C in air after different exposure times (a)50h (b)250h (c) 590h

Table 3. EDAX of corrosion products of Fe-20Cr alloys in K₂SO₄-KCl mixture at 650°C EDAX values showed as relative values and qualitative

Marked area, at. %	O	S	Cl	K	Fe	Cr
1	35.5	-	-	-	60.2	4.3
2	30.0	21.6	-	-	17.6	30.8
3	46.6	-	8.1	3.0	26.2	16.1
4	30.8	-	36.2	1.1	21.8	10.1

**Figure 10.** Corrosion rate in mixed salt at 600°C and 650°C

3.3 corrosion rate

According to Stern-Geary theory[16,24], corrosion rate is given by equation 1.

$$v_t = \frac{k}{R_i - R_h} \quad 1$$

where v_t is the corrosion rate of alloys. k is constant as a function of given metal and electrolyte. R_i and R_h are the resistance at 10 mHz and 10 kHz, respectively. The value of $R_i - R_h$ is named for polarization resistance R_p , and the corrosion rate v_t is proportional to the reciprocal of polarization resistance ($1/R_p$), which is shown in Fig.10.

The magnified view for 600°C is showed in Fig.10a. Corrosion rate of Fe-10Cr rapidly rises during the test period and it is much greater than Fe-20Cr. Corrosion rate of Fe-20Cr is relatively stable within a small range, and the value slightly declines in the initial stage which means the formation of protective scales. Fig.10b shows that values of rate dramatically rise near to 200h for both alloys at 650°C. Corrosion rate of Fe-10Cr is higher than that of Fe-20Cr during the period of 200h, but the values of rate become almost the same after 300h, because corrosion products of both alloys are rather porous and provide little effective protection to matrix[21].

3.4 Electrochemical impedance models

When alloys corroded at 600°C and 650°C, kali salt on the top of alloys is still solid in the initial stage. EIS is assumed to be only the response of oxide scales forming on the surface. Fig.11a shows an equivalent circuit of oxide capacitance parallel with scale resistance which represents the single capacitive loop in the corrosion. R_s is salt resistance, C_{ox} is oxide capacitance and R_{ox} is transfer resistance of ions through the scale. With reaction time increasing, mixed kali salt between two electrodes is sintered and may be the semi-melting status. Fig.11b shows the impedance of a diffusion-controlled reaction, where C_{dl} is double-layer capacitance, R_t is charge transfer resistance, and Z_w is Warburg resistance.

After alloys corroded at 650°C for 300h, the multiple time constants are found in impedance spectra. The impedance in stage III can be represented by the equivalent circuit of Fig.11c. Oxide scales forming on the alloy surface become loose and non-protective. Therefore, the scale is considered as a capacitance parallel with Warburg resistance and double-layer capacitance. Moreover, the center of capacitance loops at high frequency deviates from the real axis, which is called as dispersion effect.

The values of parameters are obtained by fitting the impedance spectra based on the equivalent circuit of Fig.11. In the presence of the solid K_2SO_4 -KCl mixture at 600°C, Fe-Cr alloys undergo a two-stage corrosion behavior during the test period. The corrosion of alloys in the incubation period is mainly formed some oxides, because the salt between electrodes is still solid. The formed oxides may react with K_2SO_4 and KCl to develop composited corrosion product, which results in the melt point of mixture between electrodes slightly decreasing. EIS of B-1900 alloy in a solid Na_2SO_4 [14] showed also B-1900 alloy went through an incubation oxidation in initial stage and then a fast corrosion with the formation of molten mixture. The impedance spectra for 600°C is fitted by the equivalent circuit of Fig.11 a and b, and values are listed in Table 4 and Table 5, respectively.

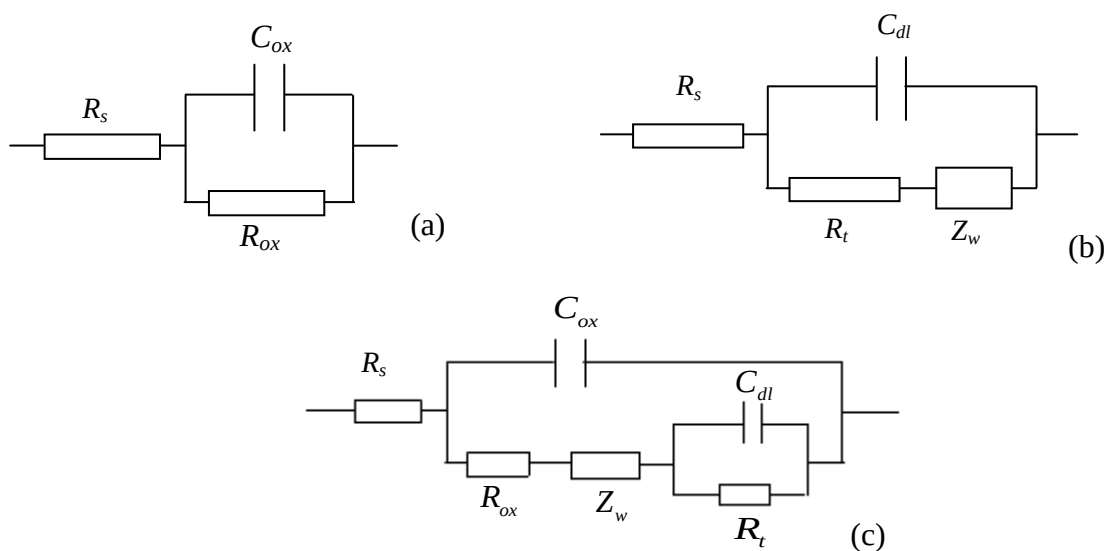


Figure 11. Equivalent circuits for interpretation of EIS

The change of R_s , the resistance of mixed salts between two electrodes, indicates that mixed salts with corrosion product on the surface of electrodes may be partially molten with extended time at 600°C. Fitting results of impedance spectra at 600°C discloses that the incubation period for Fe-10Cr is about 116 h and for Fe-20Cr is about 150 h. Changes of R_{ox} and Y_{ox} with exposure time are shown in Fig.13. The values of R_{ox} and Y_{ox} generally have the opposite variation tendency in EIS analysis, namely when R_{ox} increasing, Y_{ox} will decrease and vice versa. Fig.12a shows that R_{ox} of both alloys at 600°C increases at the beginning and reach a peak value, and then decrease to an appropriate range. The increasing of R_{ox} indicates transfer resistance of ions increasing and the formation of compact corrosion product. Similarly, R_{ox} decreasing indicates that corrosion product becomes loose, which is showed in Fig.6 and Fig.7. Fig.12b shows Y_{ox} of Fe-20Cr decreases at first and then slightly increases with time. The values of Y_{ox} for Fe-10Cr are larger than that for Fe-20Cr. The evolution of Y_{ox} is opposite to transfer resistance of ions through the scale.

Table 4. Fitting results of impedance spectra for Fe-10Cr buried in K₂SO₄-KCl mixture at 600°C in air for different exposure times

Fe-10Cr	R_s $\Omega.cm^2$	Y_{ox} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{ox}	R_{ox} $\Omega.cm^2$	Y_{dl} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{dl}	R_t $\Omega.cm^2$	A_w $\Omega.cm^2.S^{-n}$	α
1h	497.4	8.22×10^{-4}	0.47	2415	-	-	-	-	-
2h	522.6	8.31×10^{-4}	0.49	2530	-	-	-	-	-
4h	537.5	8.73×10^{-4}	0.47	2773	-	-	-	-	-
6h	544.4	9.43×10^{-4}	0.46	3043	-	-	-	-	-
9h	557.7	9.66×10^{-4}	0.46	3147	-	-	-	-	-
22h	533.2	1.07×10^{-3}	0.44	2226	-	-	-	-	-
34h	484.3	1.09×10^{-3}	0.44	1617	-	-	-	-	-
49h	362.0	1.59×10^{-3}	0.41	1084	-	-	-	-	-
59h	359.6	1.74×10^{-3}	0.39	1191	-	-	-	-	-
71h	335.9	1.64×10^{-3}	0.40	1120	-	-	-	-	-
88h	275.5	4.57×10^{-3}	0.40	1069	-	-	-	-	-
116h	262.3	-	-	-	9.80×10^{-4}	0.50	67.31	232.39	-0.40
138h	260.6	-	-	-	6.00×10^{-4}	0.53	65.00	303.85	-0.43
232h	247.2	-	-	-	1.64×10^{-4}	0.50	57.4	321.7	-0.38
369h	240.1	-	-	-	5.49×10^{-3}	0.51	40.02	300.8	-0.39
414h	204.4	-	-	-	6.19×10^{-3}	0.46	36.96	194.4	-0.44

The impedance spectra at 650°C is fitted by the equivalent circuit of Fig.11a, Fig.11b and Fig.11c, and values are listed in Table 6 and Table 7, respectively. The corrosion undergoes three stages during the period of 590 h at 650°C. The first two stages are similar with the corrosion process at 600°C, but the third stage turns into the fast corrosion process of alloys and Cr content have little influence on the corrosion resistance in this stage. The incubation period of Fe-Cr alloys at 650°C is prominently reduced than that at 600°C. In Stage II, R_t and A_w of Fe-20Cr are larger than Fe-10Cr, but the values of R_t rapidly reduce with reaction time. Corrosion rate of both alloys increases in the catastrophic stages (stage III), thus the electrochemical transfer resistance, ions transfer resistance and Warburg resistance all decrease. Semi-melting compounds between electrodes, which is composed of

K₂SO₄-KCl mixture and some corrosion products such as K₂O, K₂Fe₂O₄, FeCl₂ and CrCl₂, can give rise to fast corrosion of alloys with much smaller impedance.

Table 5. Fitting results of impedance spectra for Fe-20Cr buried in K₂SO₄-KCl mixture at 600°C in air for different exposure times

Fe-20Cr	R_s $\Omega.cm^2$	Y_{ox} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{ox}	R_{ox} $\Omega.cm^2$	Y_{dl} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{dl}	R_t $\Omega.cm^2$	A_w $\Omega.cm^2.S^{-n}$	α
1h	319.1	3.53×10^{-4}	0.62	3459	-	-	-	-	-
3h	323.3	3.40×10^{-4}	0.62	4731	-	-	-	-	-
8h	345.6	3.44×10^{-4}	0.61	5999	-	-	-	-	-
19h	444.5	4.13×10^{-4}	0.61	6122	-	-	-	-	-
28h	352.1	5.48×10^{-4}	0.60	5809	-	-	-	-	-
49h	501.6	4.06×10^{-4}	0.60	6861	-	-	-	-	-
65h	503.5	4.23×10^{-4}	0.59	6723	-	-	-	-	-
94h	504.8	4.92×10^{-4}	0.58	5700	-	-	-	-	-
117h	509.5	5.16×10^{-4}	0.57	5465	-	-	-	-	-
137h	448.7	6.96×10^{-4}	0.57	3241	-	-	-	-	-
150h	456.3	-	-	-	4.53×10^{-4}	0.67	983.2	704.2	-0.38
197h	469.2	-	-	-	3.98×10^{-4}	0.68	735.4	909.1	-0.35
232h	490.6	-	-	-	3.93×10^{-4}	0.68	607.6	900.1	-0.33
275h	499.6	-	-	-	5.30×10^{-4}	0.66	623.4	607.5	-0.32
369h	465.6	-	-	-	5.17×10^{-4}	0.68	456.1	488.4	-0.41
414h	472.8	-	-	-	6.08×10^{-4}	0.66	397.3	491.9	-0.39

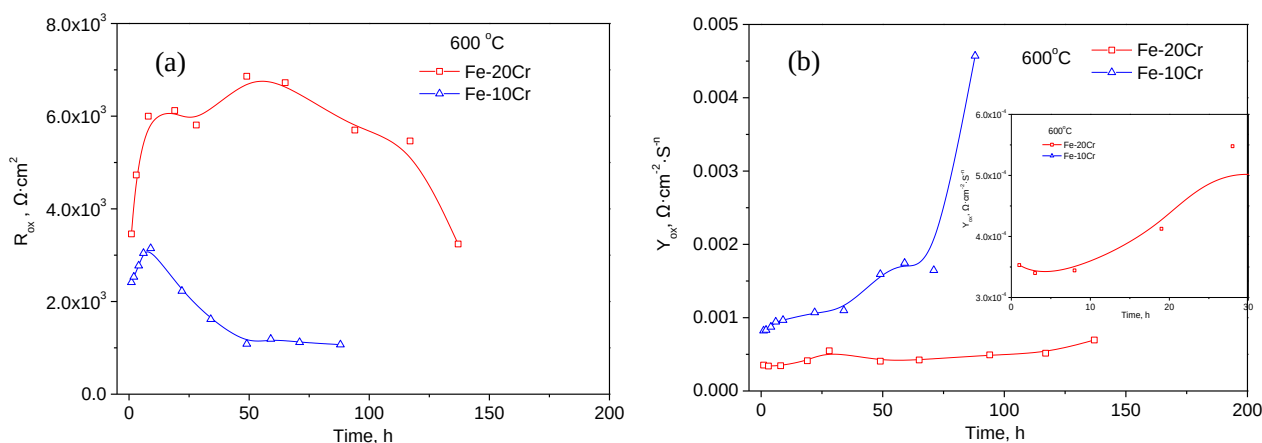


Figure 12. Changes of R_{ox} (a) and Y_{ox} (b) with exposure time in K₂SO₄-KCl mixture at 600°C

Table 6. Fitting results of impedance spectra for Fe-10Cr buried in K₂SO₄-KCl mixture at 650°C in air for different exposure times

Fe-10Cr Time,h	R_s $\Omega.cm^2$	Y_{ox} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{ox}	R_{ox} $\Omega.cm^2$	Y_{dl} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{dl}	R_t $\Omega.cm^2$	A_w $\Omega.cm^2.S^{-n}$	α
0.5	212.2	1.68×10^{-3}	0.63	1454	-	-	-	-	-

1.5	144.6	2.20×10^{-3}	0.60	1222	-	-	-	-	-
5	130.0	3.09×10^{-3}	0.55	1125	-	-	-	-	-
9	123.2	3.10×10^{-3}	0.52	1027	-	-	-	-	-
20	111.6	4.91×10^{-3}	0.53	944.9	-	-	-	-	-
33	104.7	-	-	-	2.86×10^{-3}	0.64	31.31	308.3	-0.33
54	103.2	-	-	-	1.05×10^{-3}	0.40	13.45	152.4	-0.38
80	88.7	-	-	-	5.55×10^{-4}	0.42	17.18	145.3	-0.39
116	97.92	-	-	-	1.89×10^{-3}	0.37	17.94	149.8	-0.41
141	98.53	-	-	-	1.74×10^{-3}	0.35	23.45	138.6	-0.41
189	94.31	-	-	-	1.85×10^{-2}	0.36	29.43	133.1	-0.35
214	71.65	-	-	-	1.12×10^{-2}	0.39	9.52	115.5	-0.31
258	65.39	-	-	-	1.64×10^{-2}	0.33	32.14	27.75	-0.30
300	4.96	-	-	-	7.63×10^{-3}	0.57	5.44	14.18	-0.36
334	5.21	2.48×10^{-4}	0.96	1.53	8.24×10^{-3}	0.62	4.29	16.73	-0.30
443	7.52	1.13×10^{-2}	0.98	0.41	4.65×10^{-3}	0.48	10.6	17.16	-0.31
590	4.77	4.86×10^{-2}	0.94	0.46	4.12×10^{-3}	0.46	5.3	14.80	-0.30

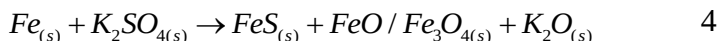
Table 7. Fitting results of impedance spectra for Fe-20Cr buried in K₂SO₄-KCl mixture at 650°C in air for different exposure times

Fe-20Cr Time,h	R_s $\Omega.cm^2$	Y_{ox} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{ox}	R_{ox} $\Omega.cm^2$	Y_{dl} $\Omega^{-1}.cm^{-2}.S^{-n}$	n_{dl}	R_t $\Omega.cm^2$	A_w $\Omega.cm^2.S^n$	α
1.5	155.1	1.55×10^{-3}	0.49	2085	-	-	-	-	-
5	141.3	2.22×10^{-3}	0.46	1645	-	-	-	-	-
9	146.1	2.93×10^{-3}	0.47	1575	-	-	-	-	-
20	146.4	-	-	-	1.72×10^{-3}	0.56	103.6	972.66	-0.34
33	157.0	-	-	-	3.01×10^{-3}	0.54	96.89	786.90	-0.31
46	160.1	-	-	-	3.03×10^{-3}	0.51	33.36	690.68	-0.30
54	157.4	-	-	-	4.53×10^{-3}	0.50	6.19	586.92	-0.31
80	166.9	-	-	-	6.11×10^{-3}	0.58	4.43	592.59	-0.41
116	185.9	-	-	-	3.02×10^{-3}	0.56	7.28	484.75	-0.46
141	182.7	-	-	-	2.19×10^{-3}	0.50	14.66	372.72	-0.43
189	139.1	-	-	-	2.00×10^{-3}	0.51	9.81	368.79	-0.39
202	141.4	-	-	-	3.05×10^{-3}	0.49	6.95	260.75	-0.38
258	134.2	-	-	-	4.33×10^{-3}	0.53	15.94	152.14	-0.45
300	3.54	-	-	-	8.85×10^{-2}	0.54	47.35	24.87	-0.49
334	3.46	1.55×10^{-2}	0.98	3.47	4.35×10^{-2}	0.65	2.59	13.07	-0.44
443	8.68	9.62×10^{-2}	0.92	7.32	4.14×10^{-2}	0.56	1.97	11.23	-0.43
590	6.63	3.69×10^{-1}	0.86	17.14	1.10×10^{-2}	0.55	0.62	10.20	-0.43

3.5 Corrosion mechanism

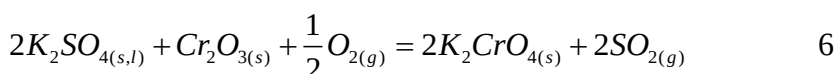
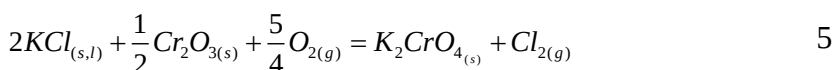
Mohanty[22] disclosed that K₂SO₄ deposits increased corrosion rate of Fe–Cr–Ni alloy by about 200 times than air oxidation, and K₂SO₄-KCl increased the rate by about 20,000 times. The

corrosion of Fe-Cr alloys involves complicated reaction stages including the incubation period and acceleration period. At the initial stage, solid Na_2SO_4 contacts and reacts with Fe-Cr alloy to produce sulfide and oxide[25,26].

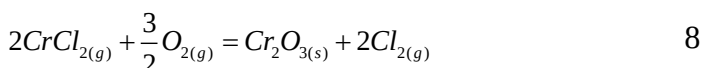
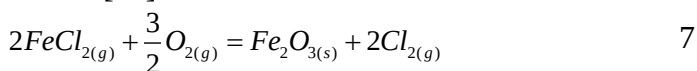


In the meantime, iron and chromium are also directly oxidized forming additional oxides at the salt/alloy interface. During this reaction process, the partial pressure of oxygen below solid kali salt is relatively high, corresponding to the partial pressure needed for oxide formation, and medium resistance between two electrodes is large in EIS analysis. High partial pressure of oxygen leads to formation of external oxides without internal oxides in this stage for Fe-10Cr alloy. Additionally, the increasing of Cr content in Fe-based alloys is beneficial to the formation of external protective oxides, which makes transfer resistance R_{ox} through the oxide layer is much larger for Fe-20Cr than Fe-10Cr.

In the next reaction process, the K_2SO_4 -KCl mixture will readily react with the Fe oxides and Cr oxides in the oxide/salt interface.



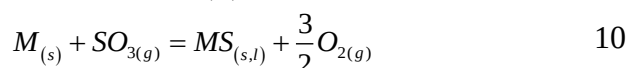
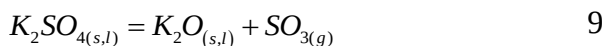
The large amount of chlorine forming will evidently increase chlorine partial pressure and simultaneously decrease oxygen partial pressure. The gaseous chlorine gradually diffuses through cracks and pores of the scale into oxide/alloy interface[27], and directly reacts with alloys to form the solid FeCl_2 and CrCl_2 , respectively. This solid species have a high vapor pressure over 500°C and then volatilizes[28].



When the partial pressure of chloride is enough high in oxide/alloy interface, the gaseous chloride will diffuse back into the oxide/salt interface. And then Fe and Cr oxides will again precipitate on the zone of high oxygen partial pressure. The precipitating oxide scale is rather porous and the corrosion rate will be significantly enhanced. The active/oxidation process results that the external oxide layer is an expanded and layered structure especially for alloys corroded for a long time, and its thickness will remarkably increase by this way. This morphology is obviously detected when Fe-Cr alloys are corroded at 650°C for 590h showed in Figs.8 and 9. Corrosion behaviour of Fe-Cr and Fe-Al alloys in NaCl-KCl showed corrosion resistance of Fe-Al alloys was improved with increasing Al content, but the increasing of Cr content in Fe-Cr alloys exhibits an enhanced metal consumption[29]. A mass of above-mentioned corrosion products, such as KCl- K_2CrO_4 , will integrate with kali salt mixture to form low melting eutectic, so medium resistance R_s between electrodes and charge transfer resistance R_t in the semi-melting eutectic become small, especially for 650°C . Meanwhile formation of external oxides on the surface of Fe-10Cr makes chromium-depleted zone develop near the interface of oxide/alloy. Internal oxide occurs in Fe-10Cr alloy in Fig.6 and Fig.8 due to above-mentioned chlorine partial pressure increasing, oxygen partial pressure decreasing and relative low Cr content. Corrosion of Fe-Cr-(Ni) alloys with chloride and sulfate coating[30] showed that few internal attacks

were noted in 430SS (Fe-15.9 wt.%Cr), but internal attack in Fe-Cr-Ni alloys (304SS and 310SS) is very pronounced. Effect of alloying elements revealed uniform-subscale attack of Fe-Cr-(Ni) alloys was enhanced due to the higher reactivity of Cr in chloride and sulfate coating.

Furthermore, the effect of sulfate cannot be neglected and sulfides have more crystal defects and lower negative free energies compared to metal oxides [30]. The sulfate is commonly hard to diffuse through the oxide layer in solid salts. When oxide scale is destroyed by chloride, gaseous sulfide also diffuses into oxide/alloy interface through cracks or pores of oxide scales and then reacts with alloys. Accelerated oxidation will be induced by co-action of gaseous sulfide and chloride, and the formation of sulfide will further accelerate internal oxidation of Fe-10Cr alloy.



Corrosion of thermally sprayed Fe-Cr coatings was tested in 0.5K₂SO₄-0.5KCl mixture at 550°C and 600°C in air for 168h[10]. The degradation of Fe-13Cr coating was extremely strong due to the amount of Cr not enough. Fe-25Cr coating performed very at both 550°C and 600°C and the oxide layer thickness is less than 6µm. The result shows corrosion resistance of thermally sprayed Fe-25Cr coating in 0.5K₂SO₄-0.5KCl mixture at 600°C is better than Fe-20Cr alloy in this study. Additionally, Fe-25Cr coating suffered from heavy depletion of Cr at 600°C in air. Cr concentration was not investigated in this study.

Equilibrium partial pressures of solid Fe and Cr chlorides at 400°C-700°C are discussed in reference[31]. The chlorides evaporate, diffuse towards the salt/scale interface, and react with oxygen to form solid oxides with gaseous chlorine released. Equilibrium partial pressures of solid Cr chlorides are lower than Fe chlorides. Therefore, gaseous $CrCl_2 / CrCl_3$ preferentially diffuses outwards. Equilibrium oxygen partial pressure[31] of the reaction shows that gaseous $CrCl_2 / CrCl_3$ is the lower equilibrium oxygen partial pressure to produce the solid Cr_2O_3 . It is the reason why corrosion rate of Fe-10Cr become almost the same as that of Fe-20Cr after corrosion for 300 h at 650°C.

4. CONCLUSIONS

EIS has been used to synchronously monitor the corrosion of Fe-10Cr and Fe-20Cr in 0.5K₂SO₄-0.5KCl mixture at 600°C and 650°C, respectively. The evolution of resistance between two electrodes discloses mixed salt with corrosion products will be partially melted after 200h at 650°C, not at 600°C. Corrosion rates of alloys increase with increasing temperature and rise fast with mixed salt partially melting down at 650°C. Electrochemical parameters calculated from the equivalent circuit discover R_{ox} and R_t of Fe-20Cr are much greater than Fe-10Cr at the beginning in the range of 600°C and 650°C. Additionally, electrochemical transfer resistance, ions transfer resistance and Warburg resistance all decrease in the catastrophic stages by co-action of gaseous sulfide and chloride. The volatilization and re-deposition of Fe/Cr chlorides leads to corresponding porous and layered corrosion products, especially for 650°C. Two-electrode system is proved effective in investigating reaction mechanisms of Fe-Cr alloys in the presence of a solid K₂SO₄-KCl mixture at 600°C and 650°C.

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