

Research Article

Hot Corrosion Behavior of High-Chromium, High-Carbon Cast Irons in NaCl-KCl Molten Salts

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A study on the corrosion behavior of a series of experimental high-chromium (18.53–30.48 wt.%), high-carbon (3.82–5.17%) cast irons in NaCl-KCl (1 : 1 M) at 670°C has been evaluated by using weight loss technique and compared with a 304-type stainless steel. It was found that all castings had a higher corrosion rate than conventional 304SS and that the addition of Cr increased the degradation rate of the cast irons. Additionally, corrosion rate increased by increasing the C contents up to 4.29%, but it decreased with a further increase in its contents. Results are discussed in terms of consumption of the Cr₂O₃ layer by the melt.

1. Introduction

The molten salt technology has been widely used in the industrial world because of its physical and chemical characteristics, especially its high electrical conductivity, high processing rate, and high diffusion rate. Recently, it has attracted much attention in the fields of jet engines, fuel cells, catalysts, metal refinement, as well as certain combustion conditions such as waste incinerators, biomass-fired boilers, and power stations [1–5]. Therefore, the studies on the corrosion of structural materials for handling high-temperature molten salts have also been continuously carried out. It is generally realized that Cr is not an effective element for corrosion resistance improvement of Fe-based and Ni-based alloys due to chloride salt attack [6–15]. However, by increasing the Cr contents, the corrosion resistance of Fe-based alloys could be increased. Problems with process equipment resulting from fireside corrosion have been frequently encountered in waste incinerators and biomass-fired boilers. The major problem is the complex nature of the feed (waste) as well as corrosive impurities which form low-melting point compounds with heavy and alkali metal chlorides which prevent the formation of protective oxide scales and then

cause an accelerated degradation of metallic elements [1]. In particular, under reducing conditions such as those typical of the operation of waste gasification plants or even under localized reducing conditions, which frequently arise in the case of incorrect operation of waste incineration systems, it is difficult to form protective oxide scales such as Cr₂O₃, SiO₂, and Al₂O₃ on the surface of structural materials. Thus, the corrosion attack can be further enhanced under reducing atmospheres in the presence of salt deposits [2]. High-chromium, high-carbon cast irons are commonly used in industrial conditions subjected to attrition and wear similar to the environment found in mining or coal cement grinding mills. However, since high chromium alloys are very resistant to hot corrosion by molten salts except where chlorides could be found, the goal of this study was to evaluate the possibility of using these metals in conditions where chlorides are present.

2. Experimental Procedure

Different specimens were prepared, with a chemical composition as shown in Table 1 following different considerations

TABLE 1: Chemical composition of castings (wt.%).

Alloy	1	2	3	4	5	6	7	304SS
C	5.17	5.09	4.65	4.29	4.1	3.93	3.93	0.08
Mn	6.27	5.1	4.8	5.9	5.6	7.42	6.5	2
Si	0.34	0.32	0.32	0.42	0.4	0.32	0.28	1
S	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.03
P	0.15	0.05	0.05	0.05	0.05	0.05	0.17	0.045
Cr	21	21.2	22.52	30.48	29.7	27.7	28.7	19
Ni	1.58	1.8	1.68	1.96	1.94	1.86	1.81	9.5
Mo	2.2	0.92	2.47	3.3	3.25	0.98	1.04	—
V	0.85	0.87	0.615	0.53	1.16	1.14	0.57	—
Ti	0.23	0.24	0.11	0.06	0.21	0.13	0.05	—
C _E	5.31	5.21	4.77	4.45	4.27	4.06	3.97	0.42
Cr _E	23.04	27.63	29.94	38.95	41.3	35.53	33.76	20.5

to vary the microstructure of high chromium, high carbon castings as given elsewhere [16]. It was planned to maintain two levels of the ratio of the equivalent content of chromium (Cr_E) to the equivalent value of carbon (C_E) which were calculated from [17]:

$$C_E = C + \frac{Mo}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Si + Ni + Cu)}{15}, \quad (1)$$

$$Cr_E = Cr + Mo + 1.5Si + 0.5Nb. \quad (2)$$

The experimental levels aimed in the design were 4 and 7 for the Cr/C, 1% and 2.6% for Mo, and 1.2% for the addition of V + Ti. Specimens were melted in air in an induction furnace and poured into metallic ingot moulds approximately 200 mm width, 150 mm height, and 10 mm thick. The working salt consisted of 500 mg/cm² of an eutectic mixture of NaCl-KCl, 1 : 1 M, analytical grade for each test. The testing temperature was 670°C in static air condition during 96 hours. All materials were machined into specimens with dimensions of about 10 mm × 15 mm × 1.5 mm, and, prior to the tests, their surfaces were prepared by the standard technique of grinding with SiC from 240 to 600 grit emery paper, washed with water, and degreased with acetone. For comparison, the same tests were done with a 304-type stainless steel (304SS). Gravimetric corrosion tests were carried out, where the corrosion rate was measured as weight loss, ΔW, in electric furnaces in a static air during 96 hours. Weight loss was calculated as follows:

$$\Delta W = \frac{(m_1 - m_2)}{A}, \quad (3)$$

where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. Three specimens of each alloy were covered by the working salt, but only two were decaled and chemically cleaned according to ASTM G1 81 standard every 24 hours in order to obtain ΔW, whereas the other specimen was mounted in Bakelite in cross-section and polished to analyze the subsurface corrosive attack using a scanning electron microscopy (SEM) aided with energy dispersive

spectroscopy (EDX) to carry out microchemical analysis. Additionally, X-ray analysis was done on the corrosion products taken from corroded specimens.

3. Results and Discussion

Typical microstructures of some of the tested alloys are shown in Figure 1, where it can be seen that basically they consist of big carbides, whose area ranged between 90 and 235 μm² containing different alloying elements such as Fe, Mo, V, and Ti, but the main chemical element was Cr. These carbides were of the type M₇C₃, (M = Cr, Fe, V, Ti, etc.) but in less amount carbides of the types M₃C, M₂C, and MC were present and were surrounded by an austenitic matrix containing mainly Fe, together with Cr, Si, Mo, and Ni [16]. The change in the weight loss with time for the different specimens is shown in Figure 2. It can be seen that 304SS had a much lower weight loss than the rest of alloys for at least one order of magnitude at all times. Among the high-chromium, high-carbon castings, during the first 24 hours, the heats with an equivalent carbon value of 5.21 and 5.31 had the lowest weight loss value, whereas the highest value was for the cast with a C_E value of 4.45. In most of the cases, it can be seen that a linear relationship between the log (ΔW) and time was followed. This was more evident in Figure 2(b), where an expanded of data shown in Figure 2(a), without the results for 304-SS.

It has been shown [5] that in molten salts where chlorides are present, the presence of chromium is detrimental in the corrosion resistance of the alloy. Similarly, it is very well known that stainless steels are very susceptible to sensitization due to the formation of chromium carbides when these steel are exposed to temperatures between 450–800°C; thus, the effect of these two elements, or, better, Cr_E and C_E, has to be made. The variation of the corrosion rate with the C_E values after different exposure times of testing is shown in Figure 3. It can be seen that, with one exception, for C_E values lower than 4.45, the corrosion rate value increases as the C_E value increases; however, for C_E values higher than 4.45 the opposite is true, the corrosion rate decreases

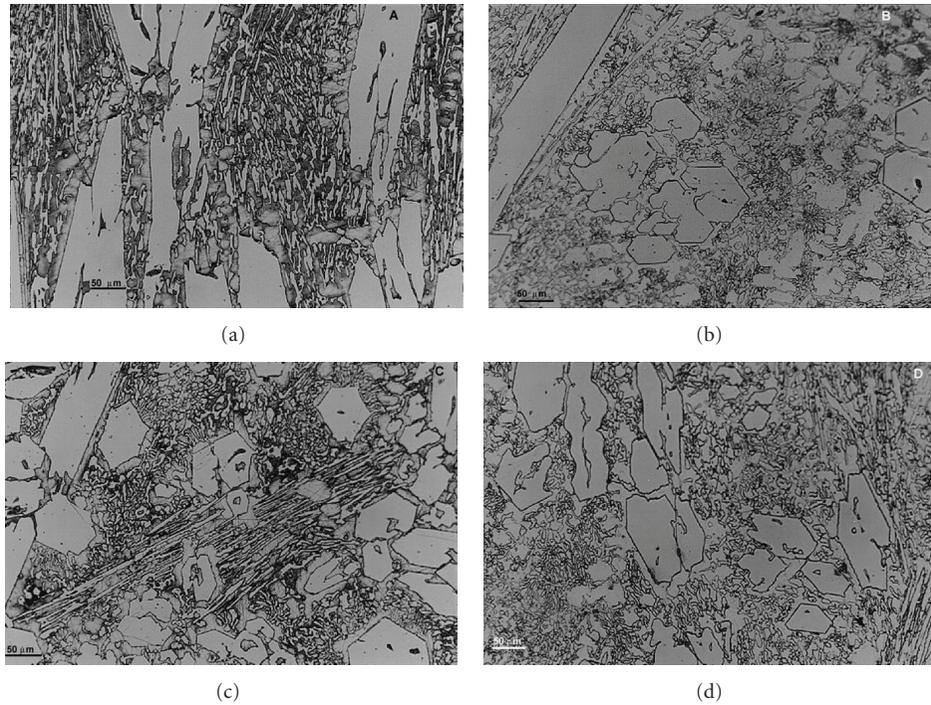


FIGURE 1: Microstructure of castings containing (a) 5.31, (b) 4.77, (c) 5.09, and (d) 4.06 C_E .

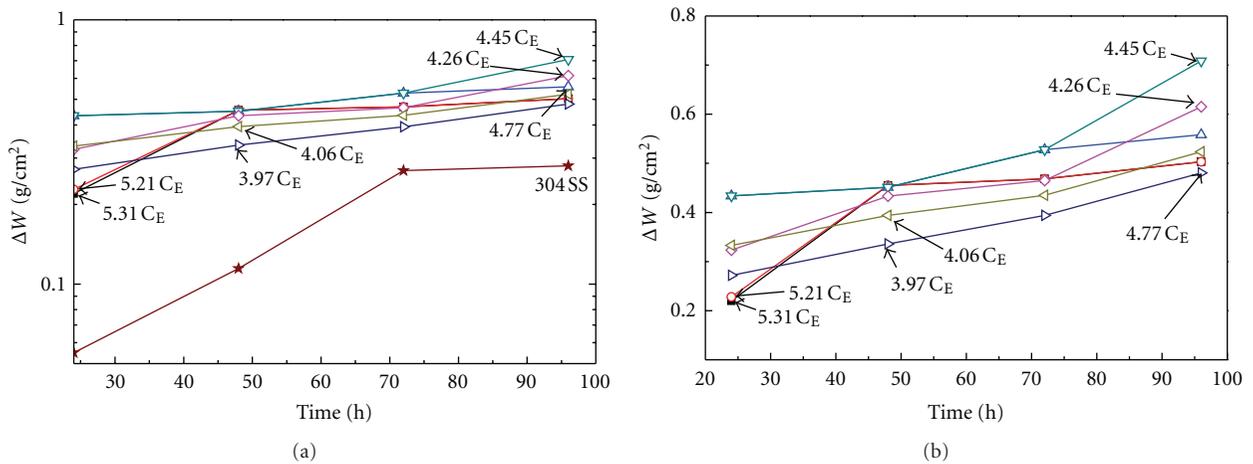


FIGURE 2: (a) Change in the weight loss with time for the different high-chromium, high-carbon cast irons in NaCl-KCl at 670°C, and (b) expanded plot of (a).

with an increase in the C_E . Perhaps this is because, as established above, carbon forms chromium carbides, which decreases the steel corrosion resistance, and, at the same time, it has been held that carbon combines with ten times its own weight of chromium to produce carbides [4], thus, the higher the amount of carbon is, the more chromium will be converted into chromium carbides, decreasing, thus, its corrosion resistance. Additionally, molybdenum seems likely to increase the corrosion resistance due to the refinement of carbides and to the fact that molybdenum displaces some chromium from combination with carbon.

Regarding the equivalent chromium value, Cr_E , Figure 4 shows that, generally speaking, the corrosion rate increases with the addition of this element, that is, the addition of chromium from 20.5% to 41.3% increases the corrosion rate almost three times for high-chromium, high-carbon casts in NaCl-KCl mixtures at 670°C. If we check the Mo contents of these alloys in Table 1, it increases almost in the same fashion as Cr does, so the effect of Mo contents in the corrosion rate is the same as that for Cr. Li and Spiegel [5], working with two Fe-21Cr and Fe-35Cr alloys in NaCl-KCl molten salts at 670°C during 48 h, obtained weight loss values of 0.8 and

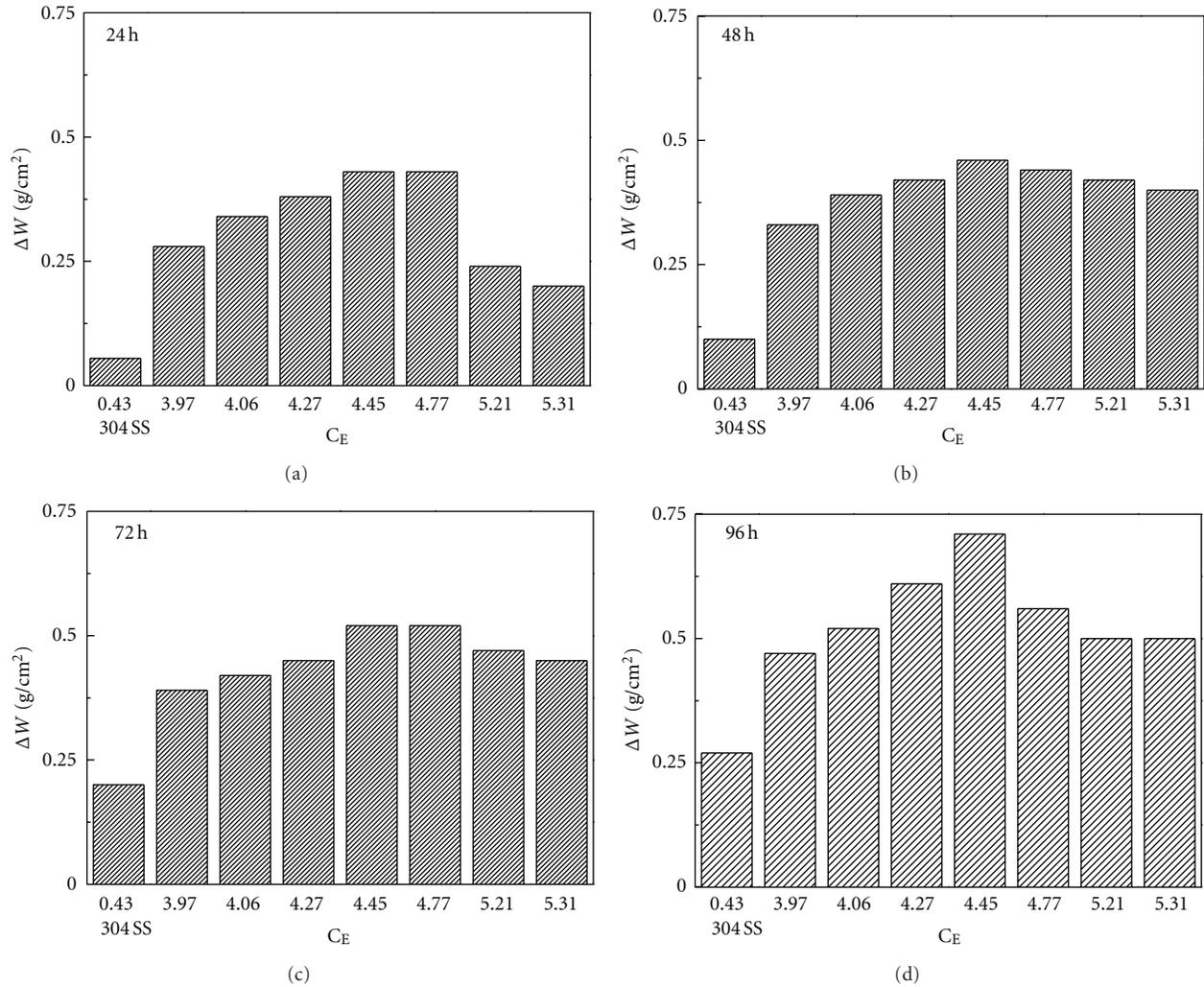


FIGURE 3: Effect of the equivalent carbon contents, C_E , in the weight loss for the different high-chromium, high-carbon cast irons in NaCl-KCl at 670°C after different exposure times.

1 g/cm², respectively. After 48 h of exposure, our specimens had weight loss values between 0.3-0.4 g/cm², lower than the results reported in Li's work. On the other hand, when 10, 20 or 45% Al was added to Fe, the corrosion rates decreased with the increase in the Al contents [5], showing the beneficial effect of Al and the detrimental effect of Cr.

Compounds found in the corrosion products scale of selected samples are shown in Figure 5, where it can be seen that basically they are formed of oxides such as Fe₃O₄, Cr₂O₃, and the salt compounds, that is, NaCl and KCl. Additionally, some peaks corresponding to K₂CrO₄ and Na₂CrO₄ were identified. Figure 6 shows a micrograph of alloy 7 with a C_E value of 3.97 together with X-ray mappings of O, Cr, Fe, and Cl. From these micrographs and the X-ray results, it can be said that not only there are external porous oxides such as Fe₃O₄, and Cr₂O₃, but also some internal degradation occurred since there is evidence of both internal oxides and chlorides. The presence of Cr-rich particles, maybe carbides, was evident from the Cr mapping. For the casting with a

C_E value of 5.31, Figure 7 shows the presence of external porous, detached iron, and chromium oxides together with some chlorides. This time the Cr-rich particles were more severely damaged. Finally, for the cast with a C_E value of 5.21, Figure 8, where it can be clearly seen the presence of a thick, inner iron oxide together with an external thinner, detached chromium oxide layer; this time the presence of internal chlorides was obvious.

The corrosion results described above clearly imply that a high Cr and C contents play a detrimental role in the corrosion resistance against NaCl-KCl melt attack. The corrosion protection of an alloy against salt melt depends on the chemical stability of both the kinds of metal and their compounds such as oxides and chlorides. In fact, a breakdown of the protective oxide readily occurs by dissolution into the melt, and the degradation rate can be especially fast if the oxide has a high solubility [18, 19].

Li and Spiegel [5] have proposed a Cr₂O₃ dissolution mechanism where basically chromium oxide can react with either KCl or NaCl to form chromate (M₂CrO₄) and further

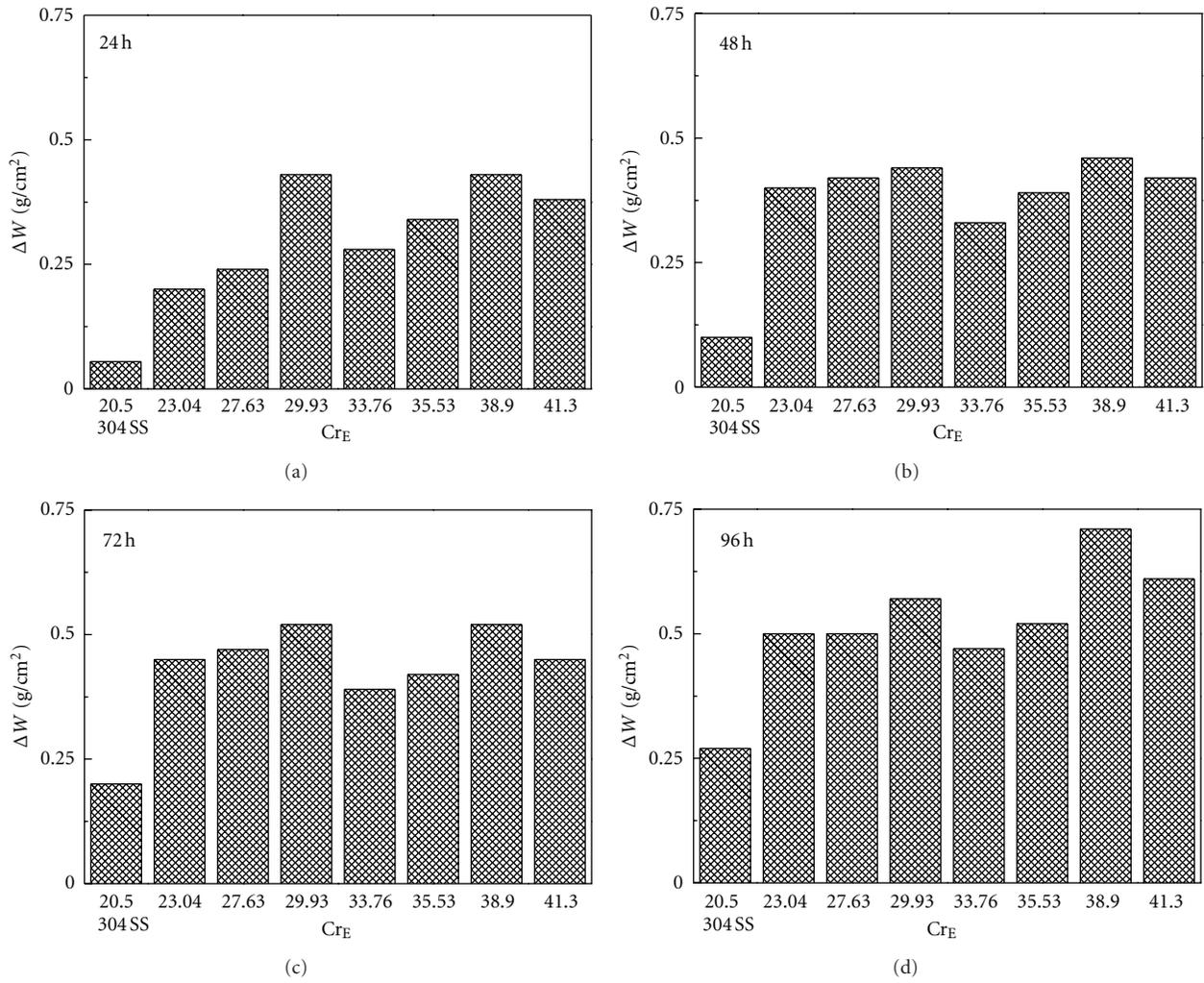


FIGURE 4: Effect of the equivalent chromium contents, Cr_E , in the weight loss for the different high-chromium, high-carbon cast irons in NaCl-KCl at 670°C after different exposure times.

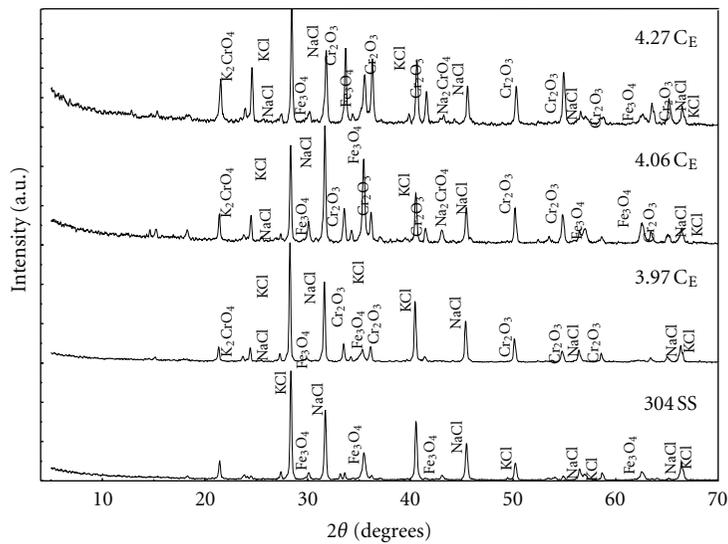


FIGURE 5: X-ray patterns of corrosion products formed on cast irons containing 4.27, 4.06, 3.97 Cr_E and on 304-type stainless steel exposed to NaCl-KCl at 670°C during 96 h.

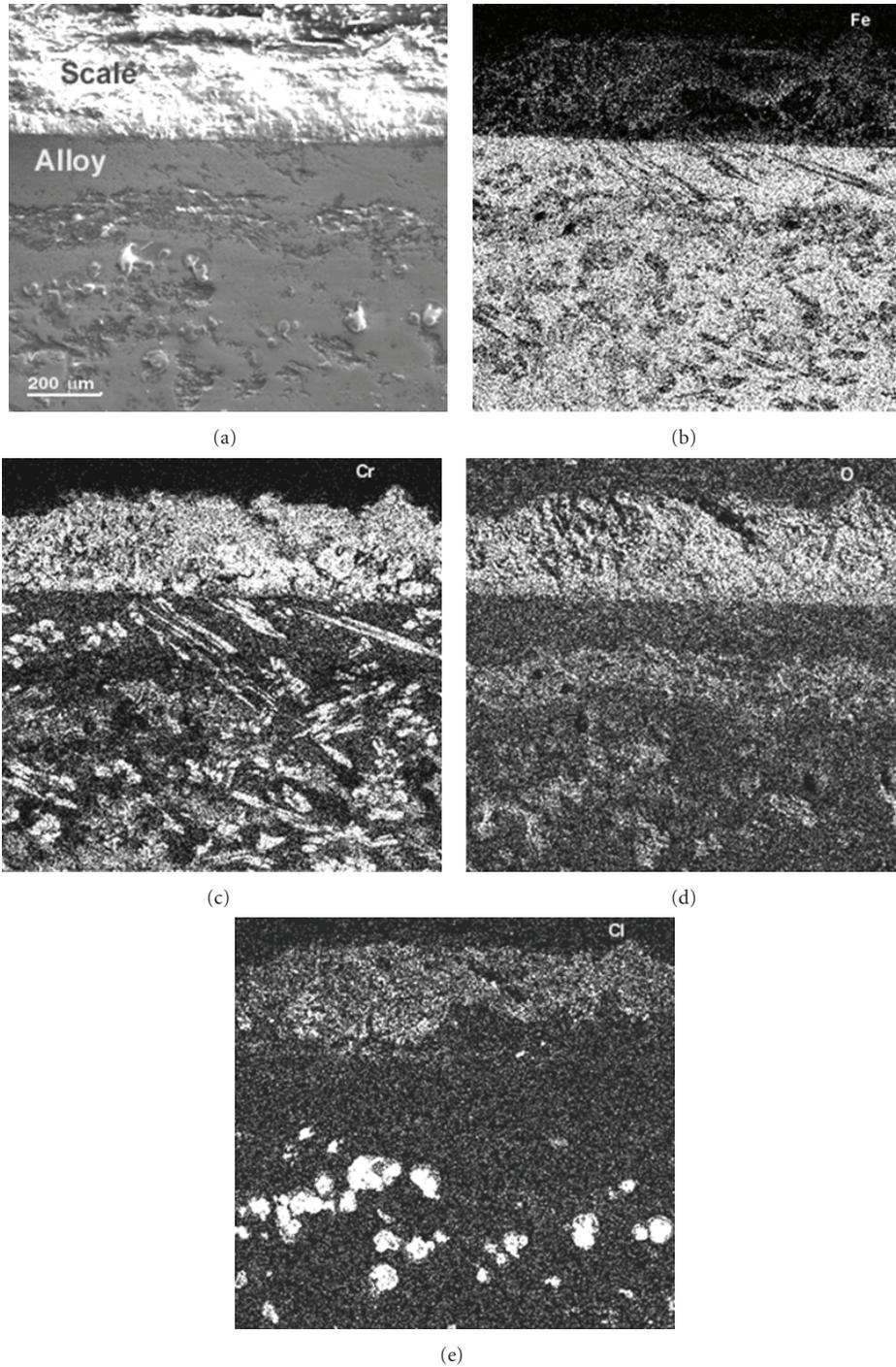
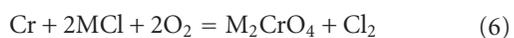
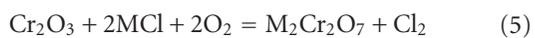
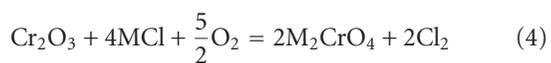
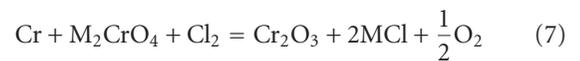


FIGURE 6: Micrograph of cast iron containing 3.97 C_E-corroded NaCl-KCl at 670°C during 96 h together with X-ray mappings of Fe, Cr, O, and Cl.

combine these chloride salts to cause a continued liquid phase-enhanced hot corrosion following the next reactions:



where M is Na or K. Further, these chromates and chlorine act as oxidants



while Cr can be selectively oxidized into its chloride by the following reaction:



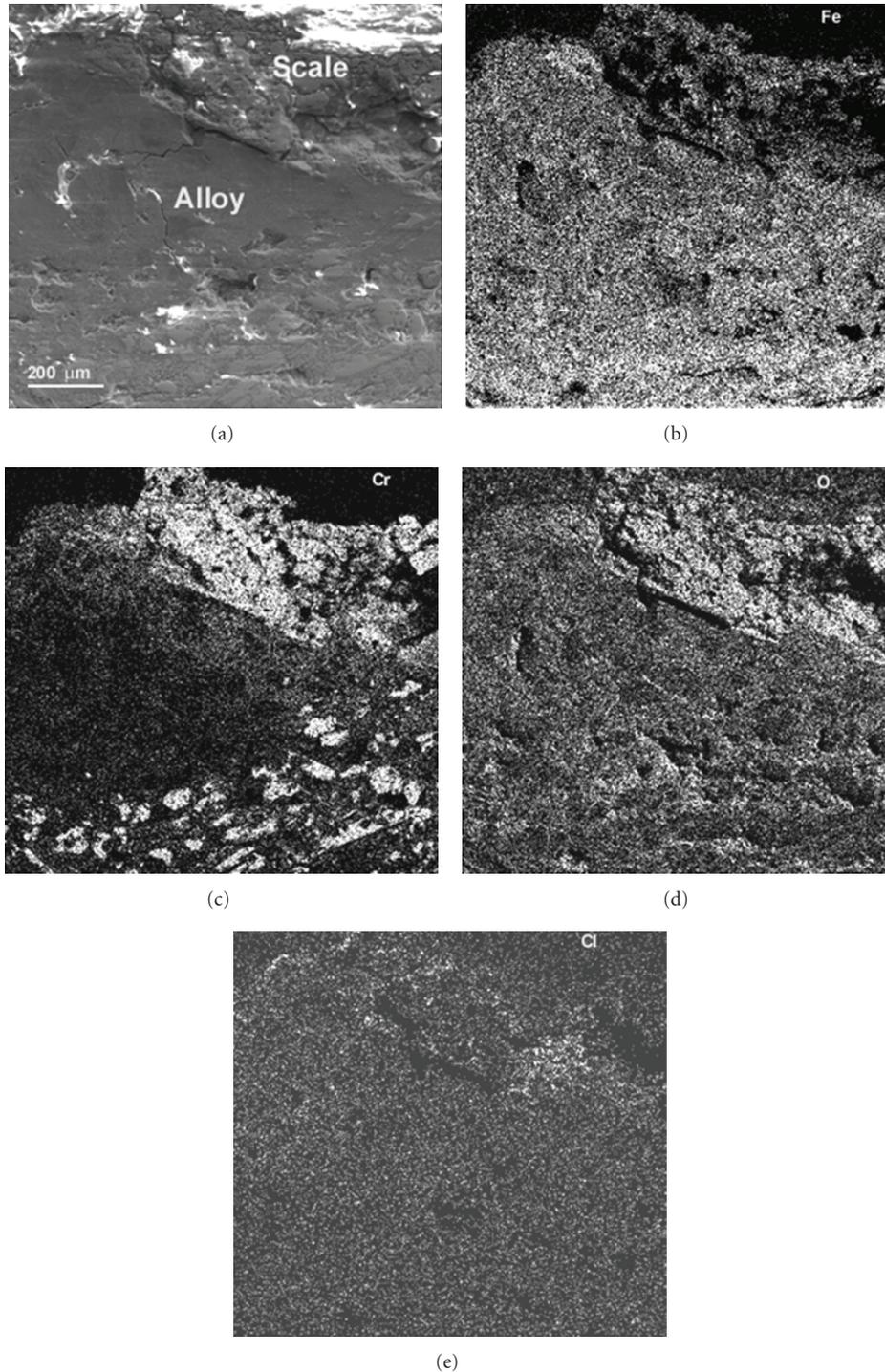


FIGURE 7: Micrograph of cast iron containing 5.31 C_E -corroded NaCl-KCl at 670°C during 96 h together with X-ray mappings of Fe, Cr, O, and Cl.

Although X-ray results did not show the presence of $CrCl_2$, (Figure 5) X-ray mappings in Figure 6 shows both Cr and Cl together, supporting this assumption. However, the outward diffusion of $CrCl_2$ is extremely unlikely due to its large molecular volume. Moreover, in the absence of porosity, the transport of matter through the scale occurs

by movement of ions, not of molecules. Moreover, $CrCl_2$ may transform locally into oxide without diffusing outwards when the local oxygen potential (which will increase with time at a fixed position in the scale) becomes sufficiently large without implying the participation of molecular oxygen, for instance, by reacting with chromates. Due to a gradient in

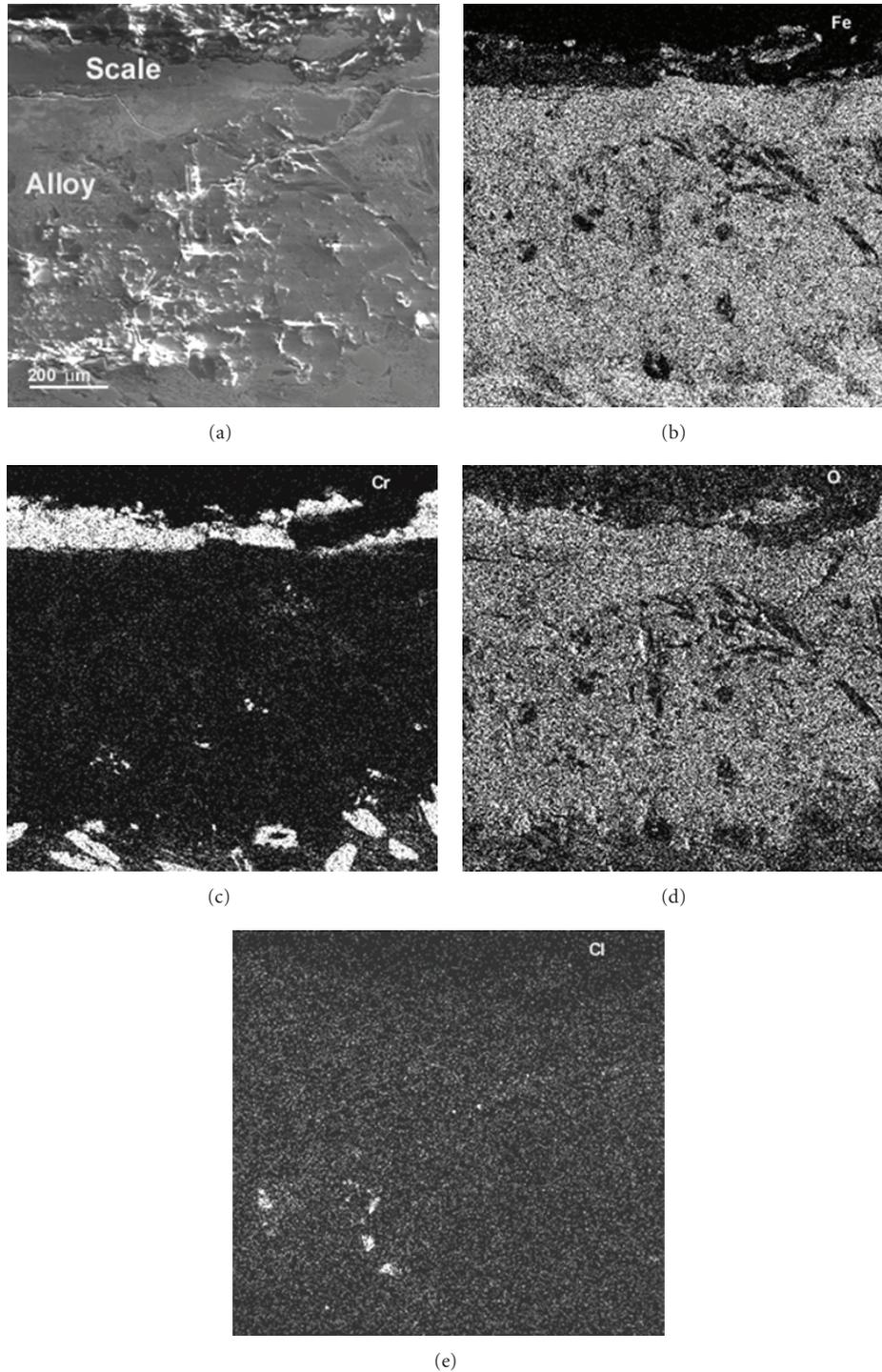
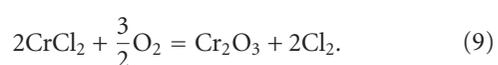


FIGURE 8: Micrograph of cast iron containing 5.21 C_E -corroded NaCl-KCl at 670°C during 96 h together with X-ray mappings of Fe, Cr, O, and Cl.

concentration, $CrCl_2$ will diffuse outwards where there is high oxygen potential and it will be converted to Cr_2O_3 according to



Micrographs shown in Figures 6–8 show the presence of an external Cr_2O_3 layer, while X-ray patterns showed K_2CrO_4 and Na_2CrO_4 which supports this assumption. Some research works have confirmed that Cr_2O_3 has a much higher solubility in NaCl-KCl melt as chromate than do iron oxides [20]. Thus, Cr can cause deterioration of the corrosion

resistance on encountering chloride salts in an oxidizing atmosphere. Previous works have indicated that K- or Na-chromate can be formed on Cr-containing materials involving molten alkali chlorides and transform from preoxidized chromium oxides [21–23]. Many new liquid phases can be formed, and, thus, protective Cr_2O_3 films are difficult to be established under a NaCl-KCl melt, and instead, a liquid phase-assisted hot corrosion can continue for long periods of time.

4. Conclusions

A study on the effect of high Cr, high C on the hot corrosion of cast irons in NaCl-KCl melts at 670°C has been evaluated and compared with that for conventional 304-type stainless steel. It was found that all cast irons had a higher corrosion rate than 304 stainless steel and that this degradation rate increased by increasing the Cr contents. In addition to this, the corrosion rate increased with the increase in the C contents up to 4.29%, but it decreased with a further increase in its contents due to the dissolution by protective Cr_2O_3 layer in the Cl-containing melt.

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