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Effect of oxide ion donors on the corrosion and dechromization of stainless steels in KCl–NaCl–$BaCl_2$ melt

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Abstract

The corrosion behaviour of several austenitic and ferritic stainless steels was studied in the KCl–NaCl–$BaCl_2$ melt (molar ratio 1 : 1 : 1) at 600 °C in the absence and presence of 0.1 molal sodium salts with different oxyanions, namely, Na_2CO_3, Na_2O_2, Na_2SO_3, Na_2SO_4, Na_3PO_4 and $Na_4P_2O_7$. The corrosion rate, determined from analysis of the melt by atomic absorption, was found to agree well with that determined from anodic polarization and decreased with increasing percentage Cr in the alloy. The presence of the oxyanions led to a decrease in the corrosion rate in the order: $P_2O_7^{4-} < PO_4^{3-} < SO_3^{2-} < SO_4^{2-} < O_2^{2-} < CO_3^{2-}$ which runs parallel to the order of increasing ability of O^{2-} ion donation and indicates that the inhibition process involves the formation of a passivating film on the surface. All stainless steels were found to suffer a significant selective leaching of chromium and among all the oxyanions tested, only CO_3^{2-} anions suppressed the dechromization in the KCl–NaCl–$BaCl_2$ melt significantly.

1. Introduction

Chloride melts are of special interest for the electrolytic production of metals like Li [1–3], In [4, 5] and rare earth elements [6, 7] and as quenching media in metallurgical processes [8]. The corrosion of several grades of stainless steel in different chloride melts have been investigated [9–19] and the most serious problem seems to be the dechromization of the alloys in this melt [20]. In the present study, the dechromization of several austenitic and ferritic stainless steels in the KCl–NaCl–$BaCl_2$ melt (molar ratio 1 : 1 : 1) and the role of small additions of sodium salts with oxyanions on suppression of the corrosion and the selective leaching of chromium is studied. The KCl–NaCl–$BaCl_2$ melt allowed us to conduct corrosion studies on stainless steels at lower temperatures than that possible in binary chloride melts such as KCl–NaCl and KCl–$MgCl_2$.

2. Experimental details

The electrodes were cut from sheets (about 1 mm thick) of the tested stainless steels with the compositions given in Table 1. The electrodes were 1 cm × 1 cm with a side arm of about 20 cm long and 0.2 cm width, used for electrical connection. Before immersion in the melt, the electrode surface was polished with emery papers down to 4/0 grade and degreased with ether. The KCl–NaCl–$BaCl_2$ melt (m.p. 540 °C) was prepared by mixing 1 : 1 : 1 (molar ratio) of the anhydrous salts (analytical grades, Merck), melting them at 600 °C for several hours to eliminate traces of water, cooling the melt and storing in dry atmosphere. The electrolytic cell, the electric furnace and the rest of the experimental details were essentially those described elsewhere [21]. The reference electrode was a Ag/AgCl electrode in the KCl–NaCl–$BaCl_2$ melt in a separate Pyrex glass tube.

The auxiliary electrode consisted of two identical large Pt sheets about 2 cm × 1 cm (each in a Pyrex glass tube with a medium porosity sintered glass disc and was placed at one side of the working electrode. The following analytical grade salts were added to the melt without further treatment: Na_2CO_3, Na_2O_2, Na_2SO_3, Na_2SO_4 and $Na_4P_2O_7$. Analytical grade Na_3PO_4 12 H_2O was used after heating at 150 °C for several hours. Before immersing the electrodes in the electrolytic cell, the melt, with or without the additive, was kept at 600 °C for 2 h to ensure the complete dehydration of the melt. A stream of nitrogen gas was allowed to pass over the melt surface during the corrosion experiment.

Atomic absorption spectroscopy (Perkin–Elmer, model 238) was used for the determination of the concentration of Fe, Cr and Ni cations dissolved in the melt after specific corrosion times. In each experiment, three 0.5 g samples from the solidified melt were analyzed and the average values were taken. The thin

Table 1. Composition of the commercial stainless steels used in the study

Alloy	Composition/wt%									Type*
	Fe	C	Si	Mn	Cr	Ni	P	S	Mo	
1	85.88	0.080	0.627	0.357	12.92	0.31	0.004	0.008	0.026	405
2	83.48	0.062	0.439	0.374	15.03	0.35	0.005	0.010	0.044	429
3	72.74	0.064	0.496	1.38	17.90	7.08	0.005	0.000	0.129	301
4	68.90	0.086	0.489	1.53	19.20	9.49	0.015	0.008	0.109	304
5	69.35	0.053	0.511	0.992	20.45	8.37	0.005	0.000	0.072	304

* The type of stainless steel was determined with reference to the standards given by AISI.

corrosion layers remaining on the alloy surfaces were removed carefully using a plastic knife and analysed.

3. Results and discussion

3.1. *Corrosion in the pure melt*

Two methods were employed to estimate the corrosion of the five stainless steels; a differential method which involved the determination of the main corrosion products, namely, Fe, Cr and Ni ions in the melt or in the scale left after corrosion by atomic absorption and an integral method which involved the determination of the corrosion rate by the anodic polarization characteristics. Figure 1 shows the mass increase of Fe, Cr and Ni in the melt with time of corrosion for the five stainless steels. Except for the initial stage of corrosion at <1 h, the rate of dissolution of either Fe, Cr or Ni from the steel is practically constant over the corrosion period of 6 h. Due to the very low Ni content in the ferritic alloys 1 and 2 (Ni% $\sim$ 0.3%), the Ni analysis for these two alloys was not performed. The corrosion rate, R, was determined from the data given in Fig. 1 by summing the slopes (in $\mu g\,cm^{-2}\,h^{-1}$) for the Fe, Cr and Ni components. The contribution of the thin corrosion layer on the alloy surface was neglected in the calculation of the corrosion rate. Figure 2 shows the anodic polarization curves (Tafel plots) for the five alloys in the melt after the attainment of the steady corrosion potential, E_{corr}. The corrosion current, i_{corr}, was determined from Tafel plots using the relation: $E - E_{corr} = a + b \log i$, where b is the Tafel slope and a is the intercept and equals $-b \log i_{corr}$. Figure 3 shows the dependence of both R and i_{corr} on percentage Cr in the alloy. The quantitative comparison between R and i_{corr} can be made through the application of Faraday's law:

$$R(\mu g\,cm^{-2}\,h^{-1}) = i_{corr}(\mu A\,cm^{-2}) \times A_w \times 60 \times 60/nF$$

where A_w is the atomic weight of the dissolved element, n is the valence of its cation and F is the Faraday constant. Assuming that $A_w = 55.8$ and $n = 2$ (for Fe), $R = 1.04\,i_{corr}$. The quantitative agreement between the corrosion rates determined by the two methods is clear. Generally, the corrosion rate decreases with increasing percentage Cr, although the increase in percentage Cr from 12% to 20% leads to only a 20–30% decrease in the corrosion rate. Compared with other chloride melts like the KCl–NaCl eutectic or the KCl–NaCl–$MgCl_2$ eutectic, the corrosion rate in the KCl–NaCl–$BaCl_2$ melt is higher [21], most probably due to the traces of water which could not be eliminated by heating the melt for several hours before use.

3.2. *Selective leaching of chromium*

The data in Fig. 1 were used to estimate the selective leaching factor, f_{SL}, for each of the main alloy components, namely, Fe, Cr and Ni as follows:

$$f^i_{SL} = \frac{(\text{mass of } i \text{ in the melt}) \times 100}{(\sum_i \text{ mass of } i \text{ in the melt}) \times\ i\% \text{ in the alloy}}$$

where i = Fe, Cr or Ni. The variation of f^i_{SL} with time for the alloys is shown in Fig. 4. Naturally $f^i_{SL} < 1$ means surface enrichment with the component, $if^i_{SL} > 1$ means the selective leaching of component i and $f^i_{SL} = 1$ indicates uniform corrosion. Inspection of Fig. 4 indicates selective leaching of Cr from the surface layer for all alloys and surface enrichment with Fe and Ni, as reported previously in other chloride melts [21]. Increasing the percentage Cr in the alloy seems to aid the resistance against dechromization slightly and to a lesser extent the surface enrichment with Ni. The significant loss of Cr from the alloy surface leads to the diffusion of Cr from inside the alloy towards the corroding surface layer to compensate for the depletion of Cr and, consequently, a significant deterioration of the mechanical properties for the surface layer, as well as for the bulk alloy, is expected as a result of corrosion.

The corrosion of the tested alloys in the KCl–NaCl–$BaCl_2$ melt also leads to the formation of loosely adherent scales on the corroding surfaces. The concentration of Fe, Cr and Ni ion in the scales are much higher than in the melt, as can be seen in Table 2, and the f_{SL} values for Cr are slightly lower than in the melt.

3.3. *Effect of addition of oxyanions on corrosion rate*

The addition of 0.1 M sodium salts with different oxyanions, namely, Na_2O_2, Na_2CO_3, Na_2SO_4, Na_2SO_4, Na_3PO_4 and $Na_4P_2O_7$ on both the corrosion rate and the selective leaching of Cr was studied. Figure 5 shows the variation of the steady corrosion potential with

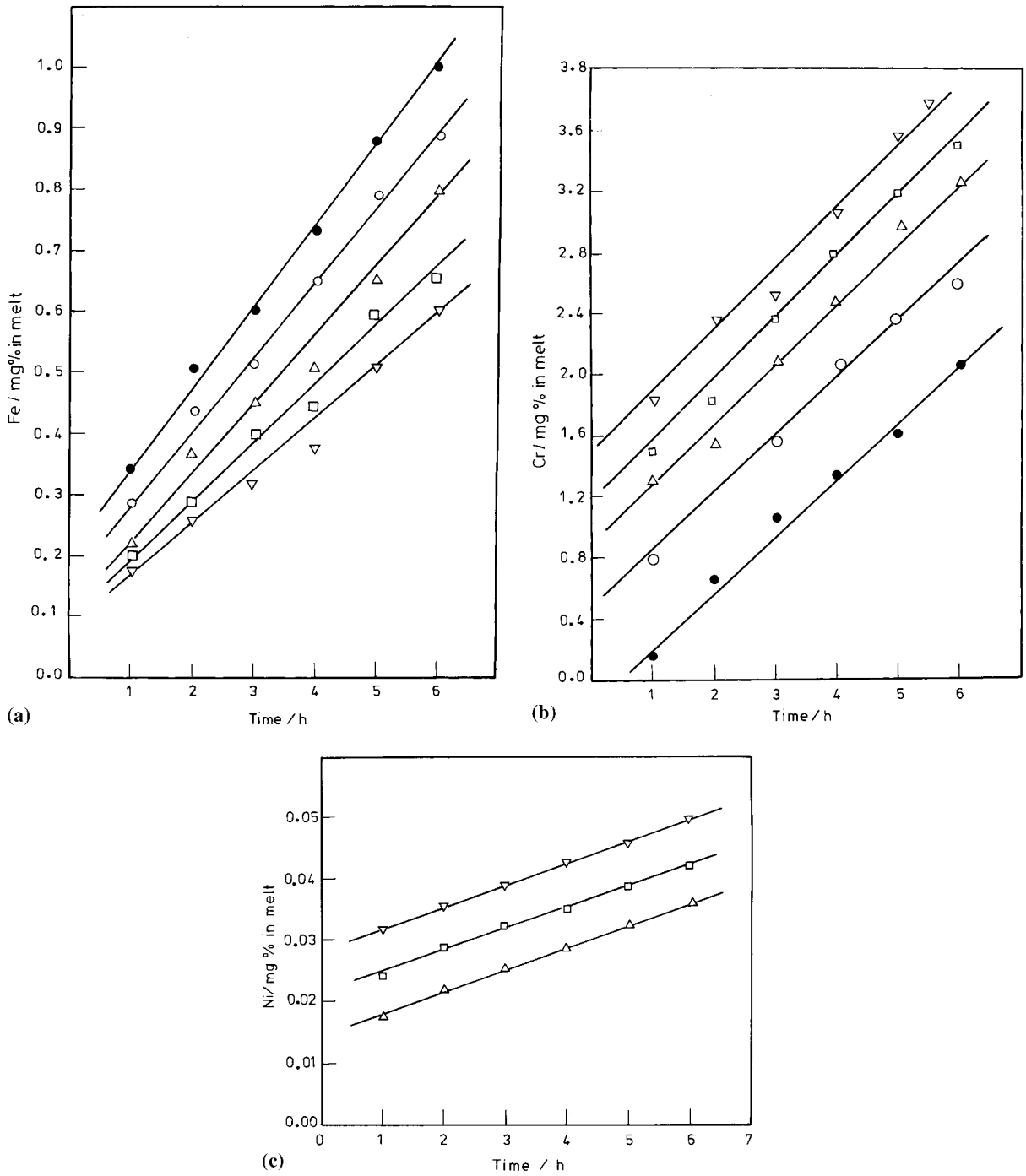

Fig. 1. Mass increase of metal cations in the KCl–NaCl–$BaCl_2$ melt with time during corrosion of stainless steels: (a) Cr, (b) Fe and (c) Ni. Alloy number: (●) 1, (○) 2, (△) 3, (□) 4 and (▽) 5.

percentage Cr in the presence of the various oxyanions. Generally, E_{corr} shifts to more anodic values as percentage Cr increases, regardless of the additive type. The presence of oxyanions leads to an anodic shift in E_{corr} in the order: pure melt $\sim P_2O_7^{4-} < PO_4^{3-} < SO_3^{2-} < SO_4^{2-} < O_2^{2-} \sim CO_3^{2-}$. The order runs almost parallel to the order of the basic character of the oxyanion (i.e., the ability to donate O^{2-} ions) [22]. The anodic shift of E_{corr} with either percentage Cr or the basic character of the anion added is accompanied by a decrease in the corrosion current (Table 3) which indicates that the anodic shift in E_{corr} is attributable to a passivating process which retards the dissolution of the alloy constituents.

Figure 6 is an example of the effect of the oxyanions on the anodic polarization curves of the stainless steels in the KCl–NaCl–$BaCl_2$ melt at 600 °C. Although the curves in Fig. 6 do not exhibit a definite region of passivity, the tendency to develop passivity increases with increasing basic character of the oxyanion. The i_{corr} values estimated from the curves in Fig. 6 are given in Table 3 and clearly show that the oxyanions act as corrosion inhibitors, where the inhibition efficiency

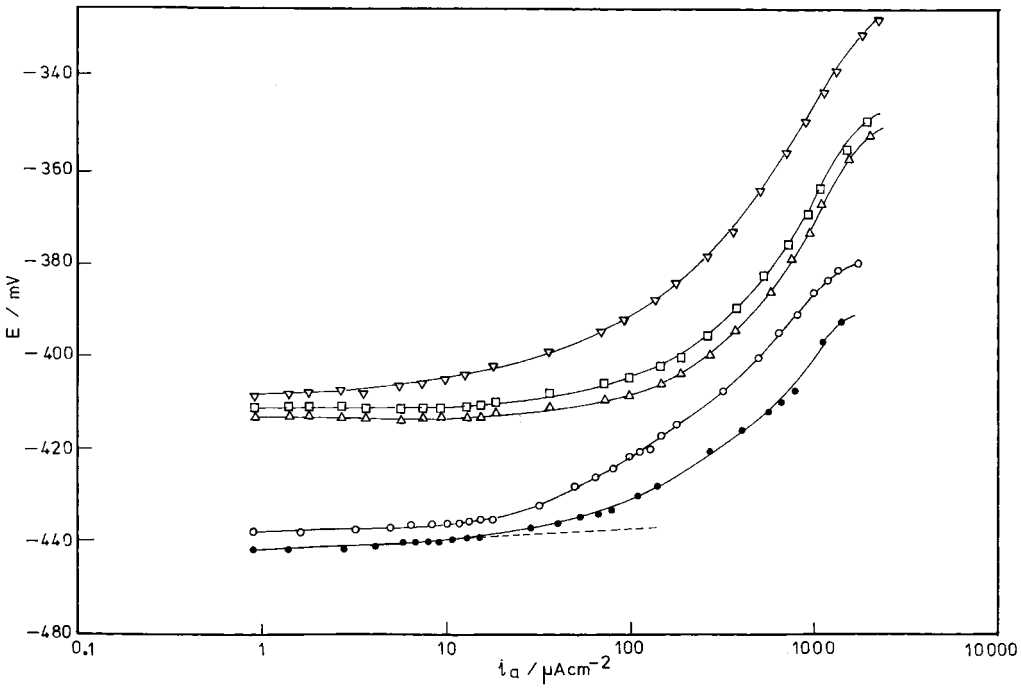

Fig. 2. Anodic polarization curves for stainless steels in the KCl–NaCl–$BaCl_2$ melt at 600 °C. The dashed line refers to the Tafel region used for the determination of corrosion current. Alloy number: (●) 1, (○) 2, (△) 3, (□) 4 and (▽) 5.

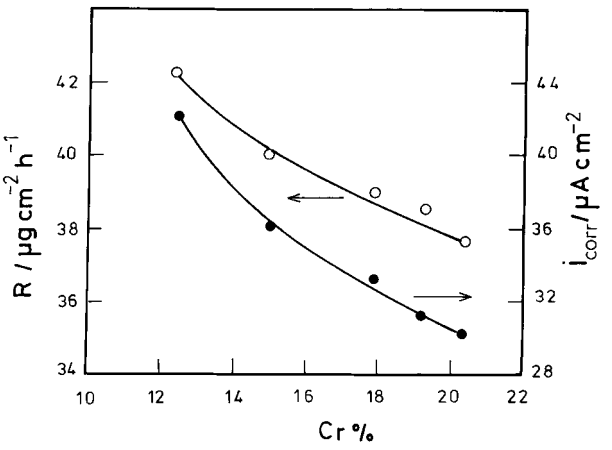

Fig. 3. Dependence of the corrosion rate, R, and the corrosion current, i_{corr}, on the percentage Cr.

Table 2. Concentration of the metal cations* in the scale on alloys after corrosion for 4 h in the KCl–NaCl–$BaCl_2$ melt at 600 °C

Alloy	Concentration of cation/mg% (f_{SL})		
	Fe	Cr	Ni
1	12.46 (0.51)	15.82 (4.50)	–
2	11.05 (0.49)	16.15 (3.95)	–
3	8.49 (0.41)	19.59 (3.82)	0.21 (0.11)
4	7.06 (0.35)	21.85 (3.89)	0.33 (0.12)
5	7.63 (0.35)	23.82 (3.67)	0.27 (0.10)

*The values between parentheses refer to the selective leaching factors, f_{SL}.

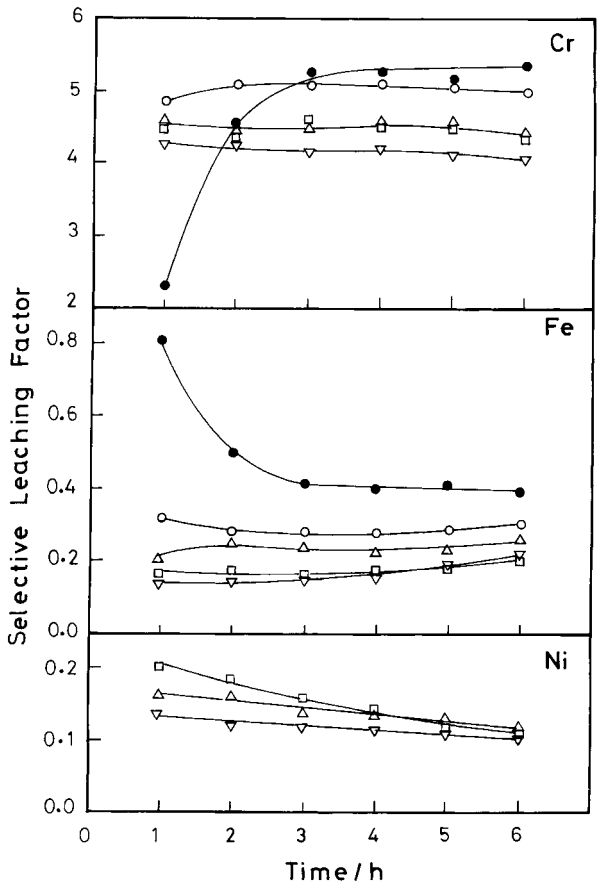

Fig. 4. Variation of the selective leaching factor for Cr, Fe and Ni with time for the stainless steels in the KCl–NaCl–$BaCl_2$ melt at 600 °C. Alloy number: (●) 1, (○) 2, (△) 3, (□) 4 and (▽) 5.

increases generally as the basic character increases: pure melt < Na_3PO_4 < Na_2SO_4 ~ Na_2SO_3 < Na_2O_2 < Na_2CO_3. The corrosion inhibition of the stainless steels in the presence of O^{2-} ion donors is due to the formation of a passivating oxide layer on the alloy surface which

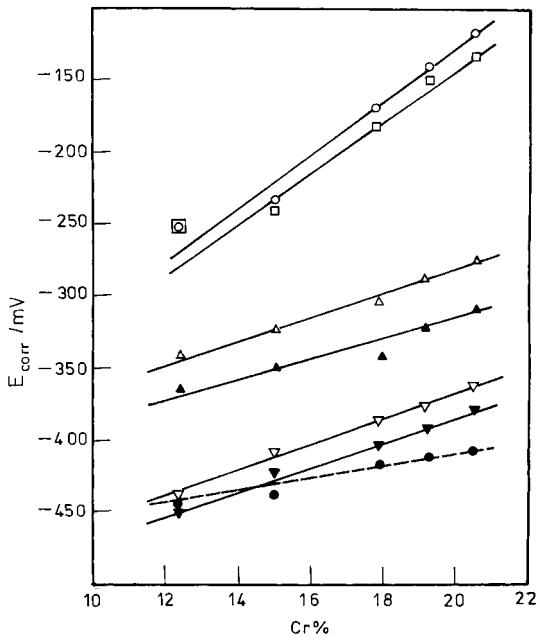

Fig. 5. Dependence of the steady corrosion potential, E_{corr}, on percentage Cr in the stainless steel in the KCl–NaCl–$BaCl_2$ melt containing 0.1 M of sodium salts with different oxyanions: (○) Na_2CO_3, (□) Na_2O_2, (△) Na_2SO_4, (▲) Na_2SO_3, (▽) Na_3PO_4 and (▼) $Na_4P_2O_7$. The dashed line refers to the pure melt. Temperature 600 °C.

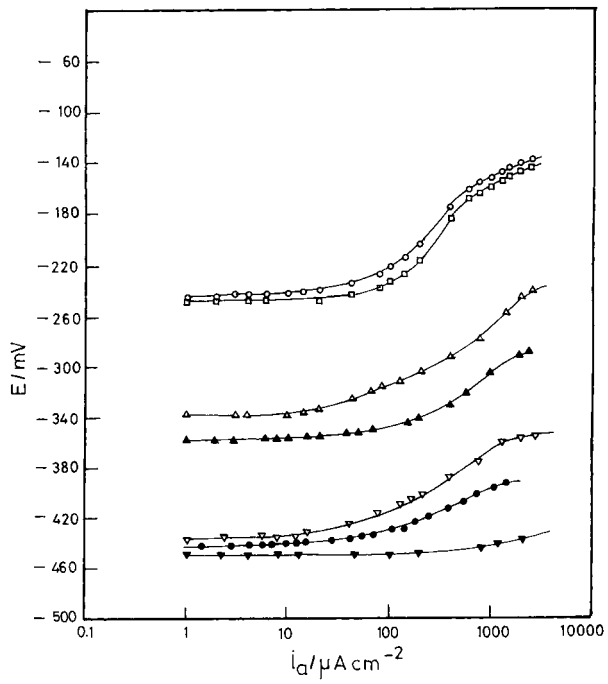

Fig. 6. Anodic polarization curves for the alloy 1 in the KCl–NaCl–$BaCl_2$ melt containing 0.1 M of sodium salts with different oxyanions: (○) Na_2CO_3, (□) Na_2O_2, (△) Na_2SO_4, (▲) Na_2SO_3, (▽) Na_3PO_4 and (▼) $Na_4P_2O_7$. Temperature 600 °C.

Table 3. Corrosion current and inhibition percent* for stainless steels in the KCl–NaCl–$BaCl_2$ melt containing 0.1 molal of sodium salts of different oxyanions at 600 °C

Alloy	Pure melt	Na_2CO_3	Na_2O_2	Na_2SO_4	Na_2SO_3	Na_3PO_4
1	42	18 (57)	22 (48)	26 (38)	32 (23)	34 (19)
2	36	14 (61)	15 (58)	18 (50)	22 (39)	30 (29)
3	33	14 (58)	12 (64)	19 (42)	13 (61)	23 (30)
4	32	9 (17)	10 (68)	20 (37)	18 (43)	26 (17)
5	30	13 (57)	14 (53)	16 (47)	14 (53)	25 (17)

* The i_{corr} values are given in $\mu A\,cm^{-2}$ and the values between parentheses refer to the inhibition percent, $I\% = \{1 - [(i_{corr})_{with\ additive}/(i_{corr})_{pure\ melt}]\} \times 100$.

Table 4. Selective leaching factors for alloy 3 in the KCl–NaCl–$BaCl_2$ melt at 600 °C in the presence of 0.1 molal of sodium salts of different oxyanions after corrosion, for 4 h

Addition	Selective leaching factor, f_{SL}		
	Fe	Cr	Ni
Pure	0.23	4.62	0.12
Na_2CO_3	0.96	1.57	0.31
Na_2O_2	0.66	2.78	0.35
Na_2SO_4	0.35	4.08	0.21
Na_2SO_3	0.23	4.59	0.13
Na_3PO_4	0.23	4.60	0.13
$Na_4P_2O_7$	0.23	4.61	0.13

acts as a physical barrier against dissolution of the alloy components into the melt in the form of soluble cations.

3.4. *Effect of addition of oxyanions on the dechromization*

To study the effect of addition of oxyanions on the selective leaching of Cr, one of the five stainless steels (alloy 3) was immersed in the KCl–NaCl–$BaCl_2$ melt in the presence of 0.1 M of various oxyanions at 600 °C for 4 h. Samples of the melt, after corrosion, were quantitatively analysed by atomic absorption spectrophotometry for Fe, Cr and Ni and the results are given in Table 4. It is most interesting to see that only CO_3^{2-} anions (and to lesser extent O_2^{2-} anions) lead to a significant improvement in the f_{SL} values towards the prevention of such a form of corrosion. The rest of the oxyanions have no significant effect on the selective leaching of percentage Cr. Thus addition of Na_2CO_3 can lead to significant suppression of both the corrosion rate and the selective leaching of Cr from the stainless steel in KCl–NaCl–$BaCl_2$ melt.

4. Conclusion

Austenitic and ferritic stainless steels with 12–20% Cr suffer corrosion with significant selective leaching of chromium in the KCl–NaCl–$BaCl_2$ melt at 600 °C. Small additions of sodium salts with O^{2-} ion donating ability leads to 17–71% suppression of corrosion with

Na_2CO_3 having the greatest effect in suppression of both corrosion and dechromization.

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