

Mechanism of formation of corrosion layers on nickel and nickel-based alloys in melts containing oxyanions—a review

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Abstract

A review of the corrosion of Ni and Ni-based alloys in melts containing oxyanions (nitrate, sulphate, hydroxide and carbonate) is presented, emphasising the mechanism of growth, the composition and structure of the passivating oxide films formed on the material in such conditions. First, the thermodynamical background involving solubility and point defect chemistry calculations for oxides formed on Ni, Cr and Ni–Cr alloys in molten salt media is briefly commented. The main passivation product on the Ni surface has been reported to be cubic NiO. In the transition stage, further oxidation of the compact NiO layer has been shown to take place in which Ni(III) ions and nickel cation vacancies are formed. Transport of nickel cation vacancies has been proposed to neutralise the charges of the excess oxide ions formed in the further oxidation reaction. Ex situ analysis studies reported in the literature indicated the possible formation of Ni₂O₃ phase in the anodic layer. During the third stage of oxidation, a survey of the published data indicated that oxygen evolution from oxyanion melts is the predominant reaction taking place on the Ni/NiO electrode. This has been supposed to lead to a further accumulation of oxygen ions in the oxide lattice presumably as oxygen interstitials, and a NiO₂ phase formation has been also suggested. Literature data on the composition of the oxide film on industrial Ni-based alloys and superalloys in melts containing oxyanions are also presented and discussed. Special attention is paid to the effect of the composition of the alloy, the molten salt mixture and the gas atmosphere on the stability and protective ability of corrosion layers.

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Keywords: Molten salt; Corrosion; Ni; Ni–Cr alloy; Passive film

1. Introduction

Corrosion problems in molten salts involve a variety of industrial processes, such as waste incineration treatments, corrosion of recovery boilers in the pulp and paper industry, “hot corrosion” of materials in gas turbines, high-temperature descaling and electromachining processes, and corrosion of current collector materials in molten carbonate fuel cells. These corrosion phenomena are electrochemical in nature, involving the oxidation/dissolution of metal cations from the material, reduction of oxidant species, formation of continuous or porous corrosion films and their fluxing when contacted by the aggressive molten salt mixtures. A few years ago, we made an attempt to review systematically the corrosion of Fe, Ni, Co and their alloys in molten salt electrolytes [1]. However, the growth mechanism, the nature, composition and structure

of the passive films on Ni-based alloys remained largely unexplored within the frames of that work. In that connection, the main purposes of the present paper are as follows:

- To review concisely the thermodynamic predictions for solubilities and point defect chemistries of the relevant oxides in molten salt mixtures and thus define a framework for the description of the nature of oxide films formed on Ni-based engineering materials in such media.
- To summarise the information gained over the recent years on the nature, chemical composition, chemical and crystallographic structure and electrochemical properties of oxide and related passive films formed on Ni-based alloys (including both model, experimental and industrial materials) as depending on the melt and gas phase composition, as well as the presence and amount of alloying elements on the protective ability of the corrosion layers.

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2. Thermodynamical background

The regions of immunity, corrosion and passivation of a metal in aqueous solutions can be assessed from the so-called Pourbaix diagram (potential–pH diagram). Bearing in mind that the oxygen anion was the most likely to be reduced during the partial cathodic reaction, potential– $p_{O^{2-}}$ diagrams were devised in analogy to this treatment for a range of metals in molten salt electrolytes to define the zones of corrosion and passivation. Some representative examples are given below.

2.1. Nickel

Potential– $p_{O^{2-}}$ diagrams for Ni in molten carbonates [2,3], nitrates [4,5], nitrides [6] and sulphates [7–10] have been calculated. In extending Pourbaix's method to cover molten salts it is necessary to define a function analogous to pH which expresses the acidity of the system. It is known that the dissociation of oxygen-containing anions gives rise to well-defined acid–base behaviour (Lux–Flood equilibria). In accordance with the Lux–Flood theory, oxygen-containing anions such as SO_4^{2-} , NO_3^- , CO_3^{2-} or OH^- act as a base in the supply of oxide anions and the corresponding gas oxides are their conjugate acids. From the above equilibria it follows that the acidity of the melt may be expressed either by $p_{O^{2-}}$ or by $-\log p_{\text{gas}}$. Accordingly, the E – $p_{O^{2-}}$ diagram provides a suitable framework for the electrochemical behaviour of different metals. Such a diagram for Ni in fused Na_2SO_4 at 973 K proposed by Gribaudo and Rameau [9] is presented in Fig. 1. The assumption that the occurrence

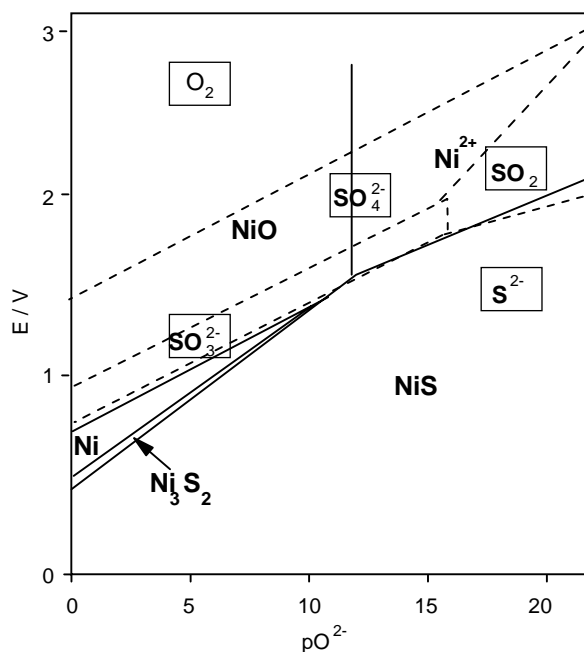


Fig. 1. Potential– $p_{O^{2-}}$ diagram for the Ni–sodium sulphate system at 973 K [9].

of corrosion implies an overall activity of ions $>10^{-6} M$ allows for some predictions. The area of corrosion is distinguished at high potentials and low oxygen ion activity. The passive region comprises the oxide NiO and two sulphides, NiS and Ni_3S_2 , extending over the whole range of $p_{O^{2-}}$. The NiO area extends at potentials above the O_2/O^{2-} line, i.e., passive film breakdown can occur via oxygen discharge (transpassivity). In basic melts the fluxing of the oxide scale by oxide ions can lead to the formation of soluble species (e.g. NiO_2^{2-}) accelerating metal corrosion instead of passivation.

2.2. Chromium

Chromium is one of the main alloying elements ensuring better corrosion resistance of Ni-based alloys of the Inconel or Hastelloy series. In some environments, however, overalloying with Cr can be considered not to lead to any improvement of the corrosion layer stability towards dissolution in the molten salt. The known experimental fact that chromia scales dissolve in molten chlorides can be explained on the basis of the potential– $p_{O^{2-}}$ diagram for Cr (Fig. 2) which is a simplified version of that presented by Ishitsuka and Nose [11] following Takahashi [12]. To allow this diagram to be compared with a classical Pourbaix diagram as drawn in aqueous solutions, the abscissa is reversed. According to the diagram, it is predicted that Cr_2O_3 will be oxidised by oxygen in the atmosphere and dissolve as chromate in molten chlorides when the $p_{O^{2-}}$ of the salt is small. Indeed, molten salts coloured yellow by chromate are usually observed in synthetic chloride ash on steels containing high-amount of Cr in laboratory corrosion tests. On the contrary, Cr_2O_3 is predicted to be stable in molten sulphates that are formed in gas turbines because $p_{O^{2-}}$ of the molten sulphates is high enough to minimise the solubility of Cr_2O_3 [13].

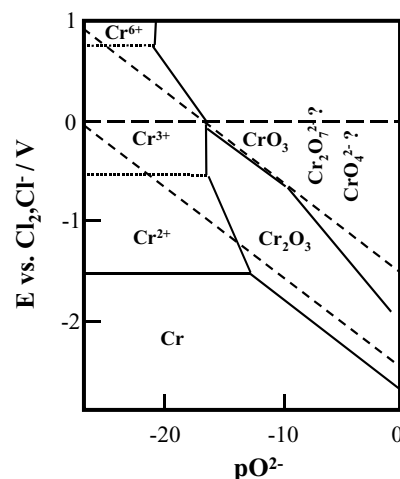


Fig. 2. Potential– $p_{O^{2-}}$ diagram of Cr in molten $NaCl$ – KCl at 1000 K [12].

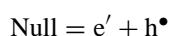
3. Overview of the point defect chemistry of relevant oxides

The solid-state chemical and electrochemical nature of the processes during hot corrosion of engineering metals in contact with thin fused salt layers has been extensively reviewed by Rapp [13,14]. According to this author, the dominant point defects for the nickel oxide, NiO, which has a rock-salt type lattice structure, can be described by the following equilibria [14]:

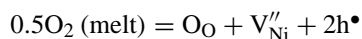
- Native defect equilibrium (formation of Schottky pairs):



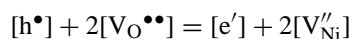
- Intrinsic electronic equilibrium:



- Environmental equilibrium:



- Electroneutrality condition:



The corresponding Kröger–Vink diagram (representing the log–log plot of the concentration of point defects vs. oxygen partial pressure) is shown in Fig. 3 [14]. From this figure, it can be anticipated that at very reducing conditions, NiO with oxygen deficiency and hence electrons as predominant electronic charge carriers (n-type semiconductor) will form. In oxygen-free or mildly oxidising conditions, ionic defect compensation will occur resulting in the formation of a nearly insulating oxide. At higher oxygen partial pressures, the usual form of the NiO with cation deficiency and hence holes as predominant electronic carriers (p-type semiconductor) will be expected.

The substitution of trivalent Cr into NiO, as in the formation of mixed NiO–Cr₂O₃ scales on Ni-based alloys with low Cr content can be treated with the same formalism [14]. In a first approximation, the trivalent Cr dopant is considered to alter the electroneutrality condition only, the equilibrium constants of all the defect equilibria being similar



The resulting Kröger–Vink plot of defect concentrations for a solid solution of NiO and Cr₂O₃ is shown in Fig. 4. The figure demonstrates that the dissolution of trivalent Cr into NiO leads to the increase of cation vacancy concentration in order to achieve electrical compensation. Thus it is expected that Ni–Cr alloys with low Cr content will be oxidised faster than pure Ni, as indeed found in practice [14]. On the other hand, for Cr-rich Ni-based alloys, it can be assumed that the oxide acquires the structure of Cr₂O₃ in which interstitial cations, Cr_i^{•••} (at low oxygen partial pressure) and chromium cation vacancies V_{Cr}^{'''} (at higher oxygen partial pressures) are the predominant ionic current carriers [15]. The introduction of divalent Ni as a dopant in such an oxide will lead to the formation of negatively charged extrinsic defects such as Ni_{Cr}[']. The electroneutrality will then be maintained by an increase in the concentration of interstitial cations at low p_{O_2} and a corresponding decrease in the concentration of cation vacancies at high p_{O_2} .

4. Mechanism of film growth and composition of passive film on Ni and Ni-based alloys in molten salt electrolytes containing oxyanions

4.1. Molten nitrates

The study of anodic dissolution of metals in concentrated ionic solutions at high current densities is relevant in electromachining. The phenomenology of the corresponding

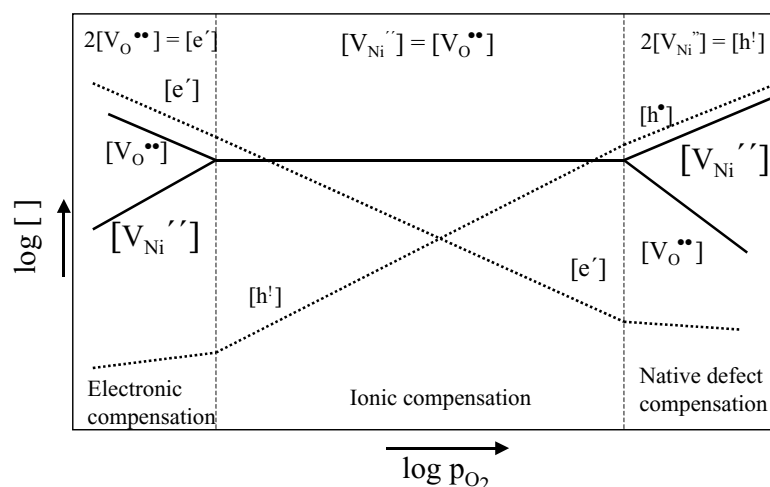


Fig. 3. A Kröger–Vink diagram of the defect chemistry of NiO (after [14]).

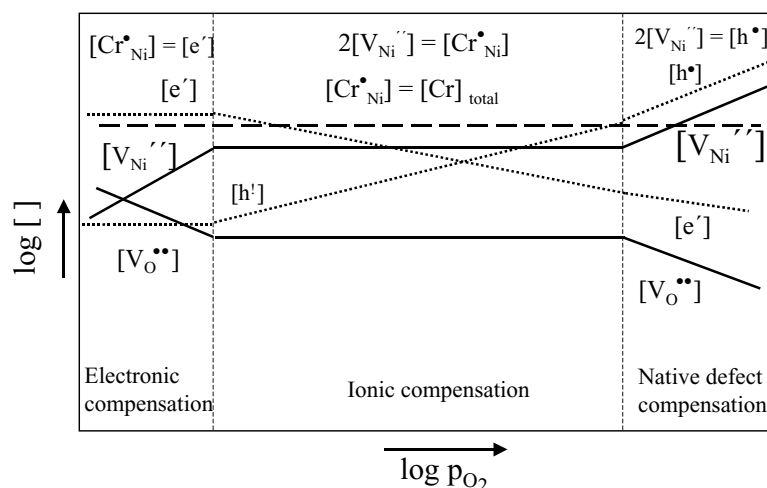


Fig. 4. A Kröger-Vink diagram of the defect chemistry of Cr(III)-doped NiO (after [14]).

processes is closely related to the dissolution of passivated metals through an oxide film. A kinetic model of Ni anodisation in fused nitrate was proposed [16,17] taking into account the formation of the passive film and the electrodisolution of the metal by transport through the passive film. The rate of the passive film formation via two-dimensional nucleation and growth coupled to a diffusional contribution was expressed at a constant potential. The authors concluded that transpassivity is related to the rupture of the passive film resulting in localised corrosion. Solubility studies and thermogravimetric analysis of Ni and Fe species in NaNO_2 –(Na, K) NO_3 mixtures showed that the most stable sparingly soluble oxides are formed under the influence of the nitrite ion as a source of oxygen dianions [18], thus supporting the likelihood of formation of compact barrier-type oxide films in fused nitrates.

4.2. Molten sulphates

The electrochemical behaviour of Ni and its alloys in molten sulphates has been studied in relation to the accelerated oxidation of aircraft gas turbine beneath a thin coating of fused Na_2SO_4 . The extensive work in identifying the electrochemical nature of the “hot corrosion” phenomenon has been very recently reviewed by Rapp [14]. Some of the general aspects of hot corrosion mechanisms have been reviewed also by us [1]. Sequeira and Hocking [19,20] observed nickel passivation via NiO formation in pure molten Na_2SO_4 . The influence of SO_3 (gas) was also studied [19] and a brief summary is given below: (1) The increased SO_3 partial pressure led to the initiation of passivation; (2) the effect is more pronounced for preoxidised nickel samples in an SO_3 atmosphere. Most of the results were confirmed by surface analysis in a subsequent paper [20]—both NiO and a Ni_3S_2 sublayer were identified together with a Ni– Ni_3S_2 eutectic structure. Sulphate oxidation occurred at very positive potentials on the passive Ni surface [19]. Abou-Elenien

[21] established that the corrosion current densities of Ni increased with the SO_2 concentration. The role of SO_2 cannot be separated from that of SO_3 . Both the metal nobility and the formation of a coherent oxide layer affected the corrosion rate in molten sulphates [21].

An investigation of corrosion of Ni alloys containing carbides of Ti, Zr, Hf, V, Nb and Ta in molten Na_2SO_4 –NaCl mixtures was carried out by Dmitrieva et al. [22]. HfC and ZrC additives seemed to ensure better corrosion resistance than pure Ni, whereas the other carbides had a negative impact (most pronounced with TiC) [22]. X-ray microanalysis showed that Ni and oxygen were evenly distributed; Ti was mostly in the carbide inclusions. The basic phases determined in the corrosion layer were NiO, Ni_3S_2 in the Ni-containing part, as well as NaTaO_3 , NaNbO_3 , NaVO_3 , VO_x , TiS_x , shaping the cathodic areas [22].

The complex plane plot of the electrochemical impedance for the corrosion of Ni_3Al in molten (Li, Na, K) $_2\text{SO}_4$ was found to be composed of a small semicircle at high frequencies and a line at low frequencies, suggesting a typical charge transfer/diffusion-controlled corrosion reaction [23]. The detection of Warburg impedance may indicate that the alloy corrodes fast due to the formation of a non-protective oxide and that the corrosion is controlled by the diffusional supply of oxidants. The X-ray diffraction and energy-dispersive X-ray absorption of the corrosion products revealed the formation of a non-protective layer composed mainly of uncorroded Ni, Ni_3S_2 , NiO and Al_2O_3 which are dispersively distributed in the corrosion layer. This was thought to agree to a certain extent with the electrochemical impedance measurements [23]. The hot corrosion mechanism of the intermetallic compound Ni_3Al has been very recently described on the basis of the analyses at 600–1000 °C as follows [24]: NiO formation is assumed to consume oxygen in the molten salt film. The consumption of oxygen reduces the partial pressure of O_2 and increases the sulphur partial pressure in the molten salt film. As the increased partial pressure of

S reaches the equilibrium partial pressure of NiS_x and/or AlS_x , these compounds are formed at the salt/alloy interface through sulphidation. The resulting consumption of sulphur will balance out the sulphur and oxygen partial pressures in the molten salt [24], which will cause again a formation of NiO. As the produced sulphides are thermodynamically unstable, with increase in the oxygen potential they are assumed to partly convert to oxides such as NiO, Al_2O_3 or NiAl_2O_4 . Thus two possibilities of the formation of a spinel phase—either through the reaction of Al and Ni with oxygen in the molten salt or through the oxidation of sulphides—have been envisaged by the authors [24].

The corrosion resistance of overalloyed Ni alloys and Ni superalloy coatings of the type NiCoCrAlY has been extensively investigated recently due to the use of these alloys in environments causing catastrophic hot corrosion behaviour (see, e.g. Ref. [25]). Pure Ni shows an active-to-passive transition in a molten sulphate–molten chloride mixture (equimolar Na_2SO_4 – K_2SO_4 – NaCl – KCl at 560°C) [26]. In the case of alloy 625, scanning Auger electron spectroscopy showed that the passive film consisted mainly of Ni oxide with Cr oxide present in the external part of the film. The concentration of Mo is significant in the inner part of the oxide. The internal sulphidation of alloy 625 was thought to be prevented by the presence of MoS_2 in the innermost layer of the oxide film. The lower corrosion rate of Inconel 625 in a Na_2SO_4 – K_2SO_4 – NaCl – KCl synthetic ash at 600°C in comparison to superaustenitic stainless steel was also confirmed by impedance spectroscopic measurements [27]. Exposure experiments carried out at 600°C in a sulphate mixture of 36% CaSO_4 –15% Na_2SO_4 –21% K_2SO_4 –21% PbSO_4 –7% ZnSO_4 showed that Cr-free iron oxides and NiO are reprecipitated as external layer on alloys 602 and 625 [28]. The pits growing into the metal and resulting from insufficient repassivation after fluxing were found to be filled with a layered Cr-rich and Zn-containing oxide with Ni and Fe in a solid solution— $(\text{Zn}, \text{Ni})(\text{Cr}, \text{Fe})_2\text{O}_4$. No Mo was detected in the entire scale for alloy 625. As pyrosulphate is formed in the melt by reaction of sulphates with SO_3 from the gas phase, acidic conditions are established favouring the formation of Cr-rich phases in the pits (the solubility of Cr_2O_3 is low under acidic fluxing). In tests performed in HCl-containing atmosphere more precipitates of NiO and iron oxides are formed together with enhanced growth of Cr-rich corrosion products. On alloy 602CA, the inner oxide layer consists of thin layers of Cr_2O_3 and Fe-rich spinels with dissolved Ni. Some Mo was found in the inner layer on alloy 625 with difference to the studies in the absence of HCl.

The investigations of several Ni-based superalloys containing Al and Ta was conducted in molten sulphate mixtures resulting from burning of a synthetic sea salt [29,30]. The initial oxide film on the four new alloys was found to be Al- and Ta-rich. The appearance of sulphides in the alloy indicated that S penetrated the outer part of the oxide film. Other scenarios for the fluxing of the oxide film in-

clude the effect of W (also an alloying element) in changing the molten salt chemistry to produce acidic fluxing, or a breakdown of the Al–Ta initial layer due to internal stresses leading to an entry of the corrosion reactants in the alloys.

The effect of the addition of vanadium oxides to the sulphate melts which induce fast hot corrosion at relatively low temperatures was also recently studied by several groups [31–36]. The exposure of Ni–20% Cr and Ni–20% Cr–4% Al thermal spray coatings in a Na_2SO_4 melt at 900°C after 16 h preoxidation ($10\text{ }\mu\text{m}$ oxide, composition: NiO, Cr_2O_3 and $(\text{Ni}, \text{Cr})_2\text{O}_4$) resulted in fluxing of the oxide by the formed pyrosulphate anion. The X-ray diffraction analysis revealed some NiSO_4 presence in the coating, no sulphides or chromates were detected. The slight corrosion of the sample was presumed to be due to synergistic dissolution of NiO and Cr_2O_3 . The exposure of a Ni–20% Cr–4% Al coatings to the Na_2SO_4 –30% NaVO_3 melt resulted in the formation of a thick layer of corrosion products containing $\text{Ni}_3(\text{VO}_4)_2$, NaVO_3 and traces of V_2O_4 . According to impedance spectroscopic studies of sulphate–vanadate melts [37], the dominant oxidising species is a minority species related to V_2O_5 . The analysis of the oxide film formed on a Ni–10% Cr–10% Co–10% W–6% Al–2% Mo–3% Ti superalloy in a 60% Na_2SO_4 –30% NaVO_3 –10% NaCl at 900 – 975°C [33,34] revealed a thin outer layer of NiO, thick layer of $\text{Ni}_3(\text{VO}_4)_2$ with an inner porous duplex layer of oxides of Ni and Cr and CrS. The metavanadate was thought to cause excessive fluxing of the oxide and sulphate thus to reach the metal/film interface and to form Ni– Ni_3S_2 eutectic layer, which is later transformed to CrS and a series of Ni vanadates. The observed decrease in the corrosion rate was presumably due to the reprecipitation of refractory Ni vanadates such as $\text{Ni}_3\text{V}_2\text{O}_8$ and $\text{Ni}(\text{VO}_3)_2$.

4.3. Molten carbonates

The corrosion and anodic behaviour of a range of metals in molten carbonates were studied in relation to the operation of high-temperature fuel cells. Kim and Devereux [38–41] contributed greatly to the understanding of corrosion and anodic oxidation of nickel in carbonate melts. A numerical procedure for the analysis of complex polarisation curves [40,41] was applied in the study of the corrosion Ni electrode in Na_2CO_3 melt in a CO/CO_2 atmosphere of various compositions. By comparing the environmental dependence of empirical model predictions for the individual reaction with theoretical candidates, a total of four anodic and one cathodic reactions were suggested to run on nickel in carbonate. The existence of NiO and possibly of Ni_2O_3 was confirmed by X-ray diffraction studies [41].

It has been shown via cyclic voltammetric experiments that the behaviour of binary Ni–Fe alloys in molten Li_2CO_3 – K_2CO_3 exhibits a gradual change from Fe-like to Ni-like behaviour [42]. The first oxidation reaction is the oxidation of Fe resulting in a cubic solid solution of FeO and α - LiFeO_2 formation. At a more anodic potential a solid

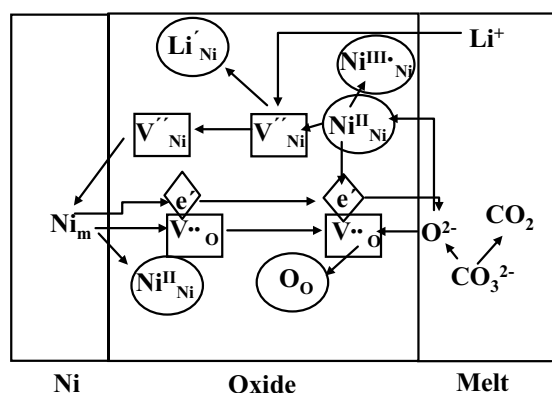
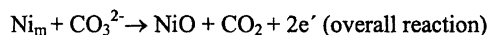
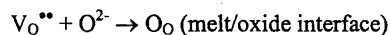
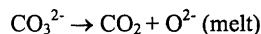
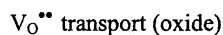
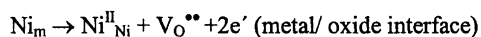


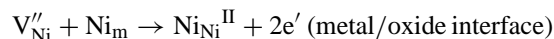
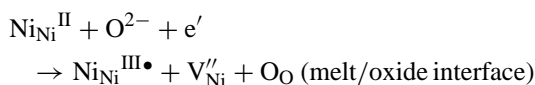
Fig. 5. Solid-state oxidation of metallic Ni in molten carbonate (after [43]).

solution of NiO and α -LiFeO₂ followed by α -LiFe₅O₈ are formed resulting in a dual passive layer on the alloy surface (inner layer of NiO- α -LiFeO₂, outer layer of α -LiFe₅O₈). At high anodic potentials, some α -Fe₂O₃ was detected, forming slowly on the Fe-rich alloys [42].

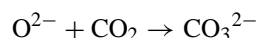
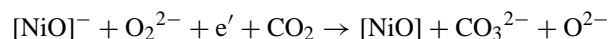
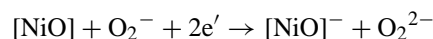
The oxidation of Ni was followed in molten Li₂CO₃-K₂CO₃ (62:38) under standard oxidant gas (15% O₂-30% CO₂) at 650 °C by open circuit potential measurements and optical observations [43]. Comparable results have been obtained more recently by other authors using X-ray diffraction and electrochemical impedance measurements [44,45]. The solid-state reaction scheme for oxidation-lithiation of metallic Ni is shown in Fig. 5. The first stage of the oxidation according to the authors clearly corresponds to the oxidation of Ni to NiO. After the oxide scale has grown continuously, this process is most probably governed by the ingress of oxygen into the scale which can be understood as a transport of oxygen vacancies in the reverse direction



In the transition stage, further oxidation of the compact NiO layer begins at the melt/oxide interface in which Ni(III) ions and nickel cation vacancies are formed. Transport of nickel cation vacancies is assumed to be required to neutralise the charges of the excess oxide ions formed in the further oxidation reaction:



During the third stage of oxidation, the carbonate/oxygen equilibrium is the only reaction taking place on the Ni/NiO electrode. This is supposed to lead to a further accumulation of oxygen ions in the oxide lattice presumably as oxygen interstitials, [NiO]⁻ [43]



The formation of NiO and its further oxidation to form a Ni(III) containing oxide was inferred from cyclic voltammetric measurements by Petrushina et al. [46]. In more acidic molten carbonates such as Na₂CO₃-K₂CO₃ it was proposed that NiO is formed directly via the reaction of the metal with carbonate anion [47], whereas in Li₂CO₃-K₂CO₃ an intermediate compound (e.g. some metastable form of NiCO₃) was suggested. When such an intermediate compound forms and then decomposes to give NiO the final product has a fine structure resulting in a large active area of the electrode; in contrast, the active area of the electrode apparently increases less during the direct oxidation of Ni in Na₂CO₃-K₂CO₃ [47]. The impedance spectra of Ni in Li₂CO₃-K₂CO₃ (62:38) at 650 °C were shown to exhibit typical characteristics of a charge transfer/diffusion-controlled reaction, i.e. a semicircle at the high-frequency part and a line in the low-frequency part [48,49]. Based on the measurement of the diffusion impedance, the diffusion of oxide anion was proposed to be the predominant feature of oxygen reduction. The oxide layer on Ni apparently had sufficient conductivity in order the transport of point defects in it not to be the rate-controlling step in the overall corrosion reaction.

4.4. Molten hydroxides

Nickel corrosion in molten alkali hydroxides was the subject of a series of investigations due to the possible use of the metal as a base material for high-temperature reactors and baths. Budnik et al. [50,51] showed that during Ni corrosion in hydrated NaOH-KOH melts at 200 °C, the frequency dependence of the electrochemical impedance was consistent with the impedance of a film-covered electrode (most probably by NiO). The open circuit evolution of the electrode impedance following anodic polarisation was explained by the oxygen exchange at the electrode surface [50]. A further study of the same authors [51] gave evidence of the formation of a corrosion layer of NiO by X-ray diffraction. Thermogravimetric analysis [51] showed that, besides Na₂NiO₂, higher valency Ni compounds are formed.

The limiting stage of the process appeared to be either the NiO/Ni₂NiO₂ transformation or the nickelate dissolution in the melt. Owing to its higher ability to dissolve oxygen, KOH was proven to be more aggressive towards Ni than NaOH [51].

Nickel corrosion in NaOH was further studied. The films formed on Ni in dry NaOH melt at 700–850 °C were analysed by X-ray diffraction [52]. NiO was identified as the main detectable product. X-ray diffraction and infrared spectroscopy of these products supported the hypothesis of the formation of NaNiO₂. It was speculated that an interaction of NiO with Na₂O₂ formed in the NaOH melt could produce sodium nickelate. Studies of Ni alloys in molten hydroxide are scarce. The good corrosion resistance of Inconel 600 in NaOH at 380 °C was attributed by Tran et al. [53] to the formation of a protective passive film of Ni–Cr spinel-type oxide which prevents the leaching of Cr as chromite and chromate from the alloy.

5. Summary and conclusions

An overview of the literature on the growth kinetics, chemical composition and crystallographic structure of the passive films formed on Ni and Ni-based alloys in molten salt electrolytes containing oxyanions is presented. The following conclusions regarding the correlation between composition, structure and protective ability of the passive films can be drawn from this literature survey:

- Mainly barrier-type films are reported to form on Ni and its alloys in fused nitrates. The kinetics of film formation and the extent of passivation in nitrate (and nitrite) media bears the closest resemblance to the stable oxide film-based passivity in aqueous media.
- Molten sulphate mixtures are shown to be particularly aggressive towards Ni superalloys. Only partial protection by the formation of Cr-rich passive films such as spinel-type oxides has been observed. At the metal/oxide interface, sulphides are detected which do not offer plausible protection except for a possible positive role of MoS₂ formed on Ni alloys containing significant amounts of Mo (it has been found to prevent further internal sulphidation of the material). Acidic oxides such as those of V(V) and Mo(VI) have been found to induce rapid fluxing of the oxide scale and therefore catastrophic hot corrosion. On the other hand, chromates have been reported to be beneficial for the repassivation of the surfaces following fluxing of the oxide scale by the molten salt.
- NiO with some Ni(III) ions and accordingly nickel cation vacancies is suggested to be the main constituent of the corrosion films on Ni in molten carbonates, the amount of Li incorporated in it being significant all over the oxide scale.
- There are comparatively few data on the kinetics of growth, composition and structure of the passive films

formed on Ni and its alloys in molten hydroxides. The most protective oxide is formed on Ni and is based on NiO with possibly some high-valent Ni cations incorporated in it. There are data on the enhanced dissolution of Cr in molten hydroxides, showing certain analogy of the behaviour to that in some molten chloride mixtures.

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