Corrosion

Alfred Rahmel

1. General Remarks

Molten salts play a significant role in modern research and development projects and their application will extend in the future. As will be apparent from the other chapters in this book, molten salt technology covers areas such as heat transfer, thermal energy storage, batteries, and fuel cells, as well as chemical, electrochemical, and metallurgical processes.

Any handling of a molten salt needs a "container" of a metallic or non-metallic material. Consequently, typical corrosion systems material–molten salt, or more general material–environment, exist which can undergo corrosion. Long-term trouble-free operation of a technical installation is only possible if the corrosion problems are solved. In practice corrosion problems very often limit such technical processes.

Modern corrosion science considers the *system* to include material and environment because neither a material is *a priori* resistant or nonresistant nor a molten salt (environment) is *a priori* aggressive or nonagressive. The corrosion behavior depends only on the system material–molten salt and its parameters.

Firstly, it seems desirable to define the term *corrosion* in the present context because different opinions exist as to be what may be implied by this word. The German standard DIN 50 900[1] defines corrosion as follows:

> Reaction of a material with its environment which produces measurable changes in the material and can result in an impairment of the function of a component or a complete system. In most cases this reaction is of an electrochemical nature. In some cases, however, it can be of a (non-electrochemical) chemical or metal-physical nature.

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A similar definition is being discussed for a comparable ISO standard. The DIN 50 900 standard concerns only metallic materials; however, there is a general agreement that this definition is also appropriate for nonmetallic materials. Of course, the reaction in a system with a nonmetallic material is in general of a chemical and not of an electrochemical nature.

It is further meaningful to distinguish between the *type* of corrosion and the *manifestation* of corrosion. The same manifestation of corrosion (corrosion phenomenon), e.g., a transgranular crack, can be the result of different types of corrosion, e.g., stress corrosion cracking or corrosion fatigue. Any decision concerning the type of corrosion needs prior information about the corrosion mechanism.

Numerous types of corrosion are known, e.g., uniform corrosion, shallow pit formation, pitting corrosion, crevice corrosion, selective corrosion, galvanic corrosion, scaling. These corrosion types can occur without mechanical stress. In the presence of mechanical stress corrosion fatigue, stress corrosion cracking, erosion and cavitation corrosion, fretting corrosion can occur. All these types of corrosion can also occur in molten salt systems.

In corrosion by aqueous solutions the pH value plays an important role because the solubility of the corrosion products in the solution depends strongly on the acidic or basic behavior of the medium. The same is valid in molten salts. However, many molten salts do not contain protons, or their concentration is not related to the acid–base behavior of the melt. Therefore other acid–base concepts have been proposed. Often the Lewis concept of acids as electron pair acceptors and bases being electron pair donors can be applied.[2] For melts with oxyanions like CO_3^{2-}, NO_3^-, or SO_4^{2-}, Lux[3] and Flood et al.[4] have proposed the unified concept

$$base = acid + O^{2-} \tag{1}$$

Bases are O^{2-} donors and acids are O^{2-} acceptors. This means that for a carbonate or sulfate melt

$$CO_3^{2-} = CO_2 + O^{2-} \tag{2}$$

or

$$SO_4^{2-} = SO_3 + O^{2-} \tag{3}$$

Because the O^{2-} ions in these melts have a similar meaning to H_3O^+ ions in aqueous solutions a pO^{2-} value

$$pO^{2-} = -\log a_{O^{2-}} \tag{4}$$

is defined by analogy to pH. $a_{O^{2-}}$ is the oxygen ion activity in the melt.

For systems which do not contain oxygen ions, other consideration may be necessary. In melts with a small self-dissociation, the acid–base concept is, in general, deduced from the self-dissociation, e.g.,

$$2AlCl_3 = AlCl_2^+ + AlCl_4^- \tag{5}$$
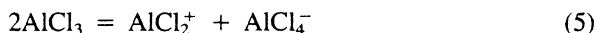
Acids are those substances which release $AlCl_2^+$ ions and bases those which release $AlCl_4^-$ ions. This concept is generally applied to many nonaqueous media.[5]

Only very few data exist concerning the solubility of typical corrosion products, like oxides, in molten salts[6,7] and in particular their acid–base dependence. Recently Rapp *et al.*[8] have investigated the influence of the pO^{2-} value on the solubility of NiO, Co_3O_4, and some ternary oxides in Na_2SO_4 at 1200 K.

The above-mentioned definition indicates that the corrosion of metals is mostly an electrochemical reaction. This relates not only to aqueous solutions but also to molten salts, because most molten salts are excellent ionic conductors. In this respect, there are some similarities between aqueous solutions and molten salts—or more generally nonaqueous media. Thus certain principles valid in aqueous corrosion can be applied to molten salt corrosion systems. One important one is, e.g., that any corrosion caused by metal dissolution comprises two electrochemical partial reactions, anodic metal dissolution, and cathodic reduction of an oxidant. The rates of both partial reactions depend on the electrode potential.

The metal dissolution reaction is, however, only one step in a whole series of other possible preceding and following reactions. Figure 1 summarizes all possible reactions which can be involved in a corrosion reaction. It illustrates just how complex a corrosion reaction can be.

It is useful to distinguish between the *rate-controlling* reaction and the *corrosion-causing* reaction. The reaction causing the corrosion, e.g., metal dissolution, does not always control the corrosion rate. The rate-controlling reaction must be positively identified because only a change in this reaction step will influence the corrosion rate.

Despite many similarities, there are also important differences between corrosion in aqueous solutions and in molten salts. The preferred rate-controlling step of metal dissolution in aqueous media is the charge transfer reaction. Because of the higher activation energy of charge transfer reactions compared with those of diffusion in liquids, the latter more often become rate controlling in molten salt systems.[9]

Another difference arises from the type of the electrical conductivity. All aqueous media exhibit purely ionic conductivity. Some molten salts, however, also possess electronic conductivity in addition to their ionic component. Examples are the alkali chloride–alkali metal melts,[10] FeO and FeO-rich slags,[11]
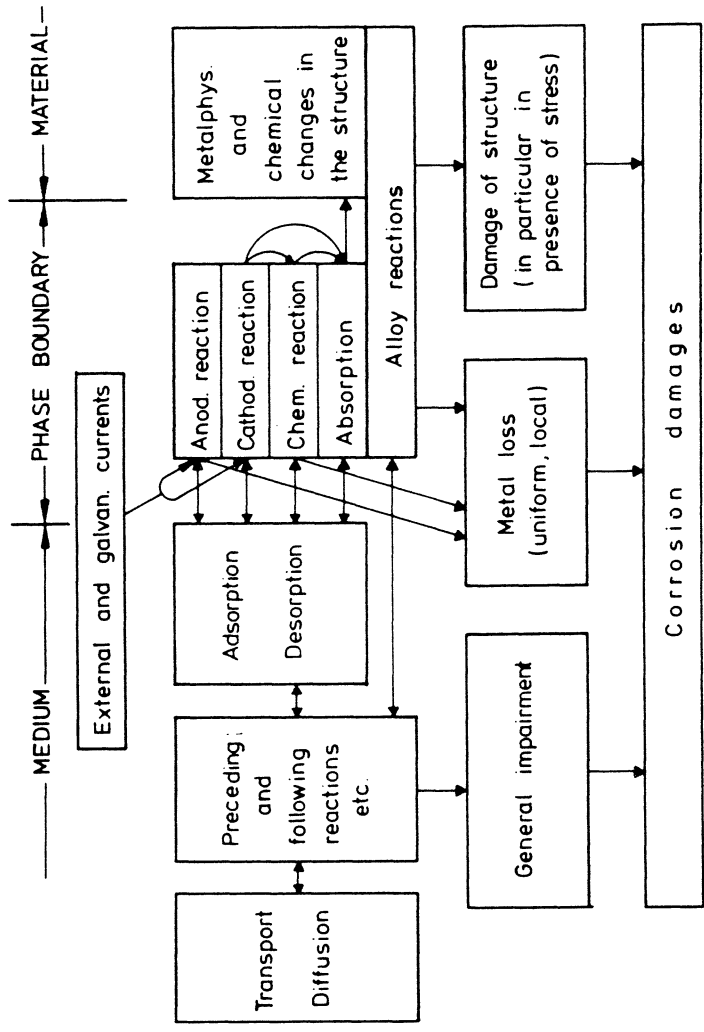
FIGURE 1. Scheme of possible partial reactions during corrosion and kinds of corrosion damage.

V_2O_5,[12-14] iron vanadate,[15] and MoO_3.[16] Electronic conductivity has at least two consequences:

1. Electrochemical polarization measurements are possible only if the electronic partial conductivity is eliminated. This can be done by placing a solid electrolyte between working and counter electrode.[17]

2. The reduction of the oxidant does not occur exclusively at the metal–melt interface but can also take place in the whole melt or at the metal–gas interface.[14] This is an important difference to corrosion in media with pure ionic conductivity. Electronic conductivity considerably enhances the cathodic partial reaction, in particular if the solubility of oxygen—the most important oxidant in corrosion reactions—is low in the melt. Thus the corrosion current density can rise to many A cm^{-2},[17] if no protective surface layer inhibits the metal dissolution rate.

By analogy with E–pH equilibrium diagrams in aqueous media, which have been particularly developed by Pourbaix,[18] similar equilibrium diagrams—often called E–pO^{2-} diagrams or Littlewood diagrams—have been constructed for different metal–melt systems. An example is given in Figure 2 for nickel in an alkali sulfate melt at 600°C.[19] Such diagrams are based on thermodynamic data and show the ranges of existence of the metal and its compounds as functions
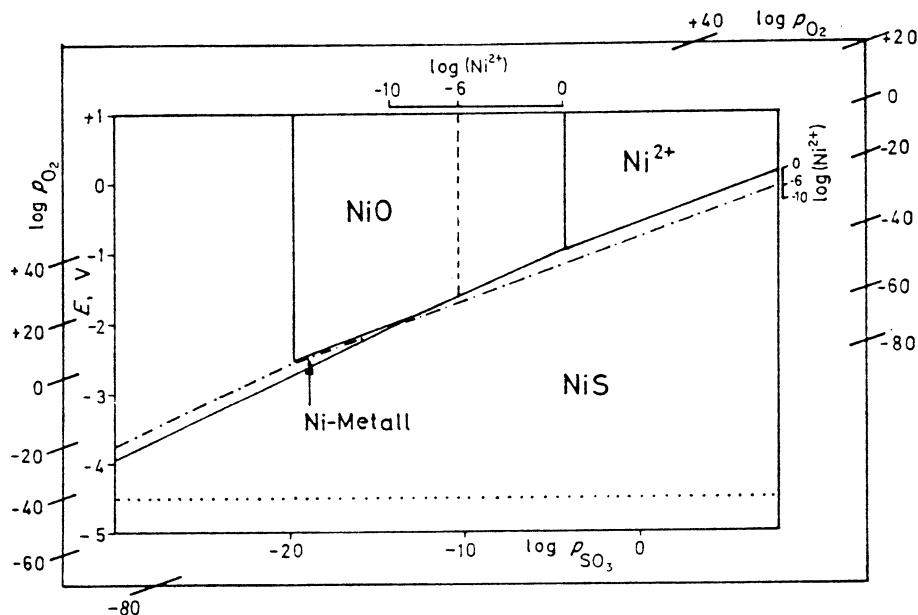

FIGURE 2. E–logp_{SO_3} diagram of nickel in the ternary Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic melt at 873 K (from Reference 19).

of the potential E, the acid–base behavior (pO^{2-} value), and other parameters. The value of such diagrams is rather restricted, for three reasons in particular, viz., (a) the thermodynamic data upon which the diagrams are based contain a lot of uncertainties, (b) the diagrams give no information about the corrosion rate, and (c) O^{2-} ions may be not the only oxide species in the nonaqueous environment but O_2^- and O_2^{2-} ions may also be stable.

2. Corrosion in Different Molten Salts

No attempt will be made in this section to collect and critically review all corrosion data available in the literature. Such an annotated bibliography has recently been published by Janz and Tomkins.[20] That paper is a helpful literature collection with 458 references arranged by anion classification and includes metals, compounds, glasses, and ceramics. Special tables deal with the influence of oxygen, hydrogen ions, and water on the corrosion process.

In this chapter mostly structural materials will be considered and not noble metals like gold, silver, and platinum. The latter group is useful in laboratory investigations but finds only very limited use in industrial applications.

Despite so many publications our knowledge and in particular our industrial experience are very restricted. There are many investigations concerning metal loss, passive film formation, or internal corrosion processes. As stressed in Section 1 corrosion also encompasses other types of attack. Very little information about galvanic corrosion, erosion corrosion, or corrosion fatigue is available. In commercial plants, however, a wide range of different materials are in use which are in contact with metals. Additionally the melt may be flowing, and pumps or other machines may also cause vibration. At high temperatures, all materials undergo creep deformation. The interactions between corrosion and creep deformation have become of increasing interest in recent years[21–23] because the safe operation of high-temperature installations depends on a knowledge of the creep and corrosion behavior of materials in real environments. Creep experiments in molten salts are, however, rather rare.[24,25]

In the following section, the corrosion behavior of materials in melts with different anions will be considered.

2.1. Chloride Melts

Pure chloride melts have found only very limited application, though they have been under consideration for heat transfer and heat storage, batteries, pyrolysis, and metals extraction (see other chapters).
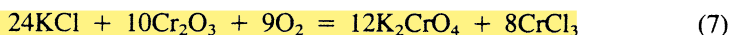
Some E–pO^{2-} equilibrium diagrams have been published by Littlewood *et al.*[26,27]

2.1.1. Iron- and Nickel-Based Alloys

Chloride melts attack steels in air rather vigorously.[28,29] Results of corrosion tests in a $NaCl-BaCl_2-MgCl_2$ melt at 500°C and 600°C are shown in Figure 3. The best resistance is evident for steels with high chromium and nickel contents.[29] Al coatings on unalloyed steel have no benefit. FeNiCr alloys with ~20% Cr suffer either serious pore formation in the metal beneath a porous scale or a strong intergranular attack.[29] Pore formation occurs also with pure NiCr alloys with ~20% Cr, while alloys with ~60% Cr reveal preferential grain boundary attack which increases the depth of damage.[30] The resulting melt contains chromate which is probably formed by the reaction

$$2Cr_2O_3 + 5O_2 + 8NaCl = 4Na_2CrO_4 + 4Cl_2 \qquad (6)$$
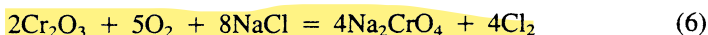
The formation of chromate has also been found in solid $NaCl-Na_2SO_4$ deposits.[31,32] The formation of volatile $CrCl_3$ or $CrOCl$ [32] has also been considered according to

$$24KCl + 10Cr_2O_3 + 9O_2 = 12K_2CrO_4 + 8CrCl_3 \qquad (7)$$

or

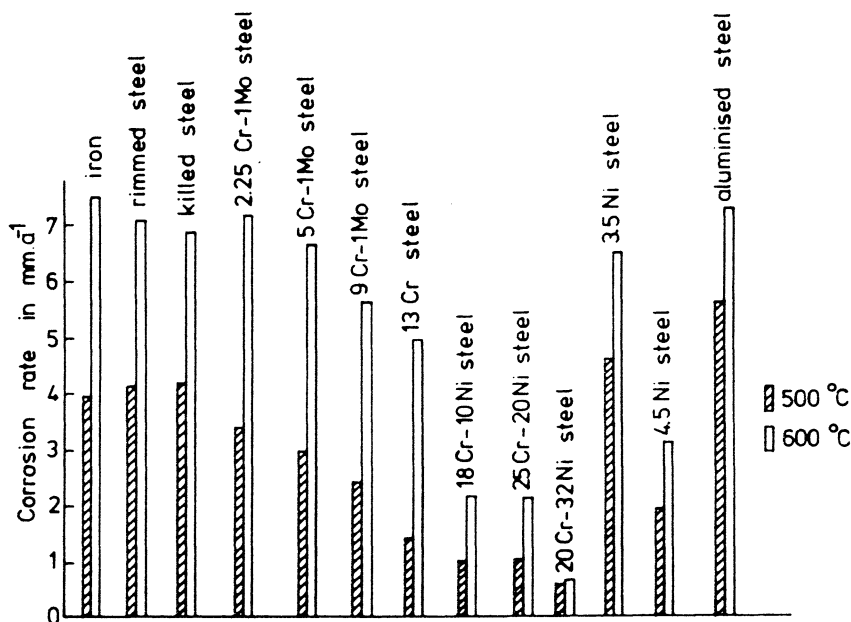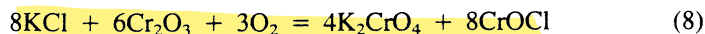$$8KCl + 6Cr_2O_3 + 3O_2 = 4K_2CrO_4 + 8CrOCl \qquad (8)$$

FIGURE 3. Corrosion rate of different materials in a $NaCl-BaCl_2-CaCl_2$ melt (after Reference 29).

The corrosion rate of nickel-based alloys increases with increasing oxygen partial pressure.[33,34] This indicates that oxygen transport to the metal surface is the rate-controlling step. Water vapor also increases the corrosion rate, as has been observed for iron in the KCl–LiCl eutectic.[35] This enhancement is probably caused by hydrogen chloride arising from hydrolysis.

It has been concluded from electrochemical measurements that no protective scale is formed on nickel-based alloys.[33] The diffusion of sodium metal into the alloy has been reported and can impair its mechanical properties.[33]

Various laboratory investigations have been performed to determine the effect of alkali and alkaline-earth chlorides on the corrosion of heat-resistant steels.[31,32,36–42] In air, pure NaCl even causes attack of the metal in the solid state at temperatures above 600°C; a porous scale is formed. Remarkably intergranular corrosion is caused by preferential attack of the carbide $(Cr,Fe)_{23}C_6$. NaBr and NaF cause a similar attack to that observed for NaCl. The surface attack is greatest with NaF and least with NaBr.[31] The corrosion rate of an 18/8-CrNi stainless steel beneath solid chloride deposits increases in the series $CaCl_2$, KCl, NaCl, LiCl.[32]

2.1.2. Other Materials

Mass transport from high to low temperature has been observed with aluminium in $NaCl–KCl–AlCl_3$ melts in the temperature range 170–450°C.[43,44] Very rapid scale growth and severe intergranular attack occur with zircalloy even at 300°C in the eutectic $NaNO_3–KNO_3–NaCl$ melt.[45] The anodic dissolution of platinum can be prevented by oxide ion addition because a passive film is formed.[46] Hydroxide and silicate ions also act similarly.[46]

2.2. Fluoride Melts

Fluoride melts have been considered for cooling, extraction, and reaction media in nuclear reactor technology. Corrosion tests have been performed in the absence of oxygen up to 20,000 hr between 400°C and 700°C with iron- and nickel-based alloy.[47] The salts used were $LiF–BeF_2$ mixtures with varying amounts of UF_4, ThF_4, and ZrF_4 and $NaBF_4–NaF$ mixtures. Nickel-based alloys exhibited better corrosion resistance than iron-based alloys. Material transport occurs in temperature gradients from high to low temperature, in particular with chromium and iron.

More recently 316-type stainless steels have been tested in a closed loop with a LiF–34 mol % BeF_2 melt at temperatures between 400°C and 650°C up to several thousand hours.[48] The corrosion rate decreases with time and reaches an average value of 8 μm/year between 3000 and 9000 hr at 650°C. Mass loss is caused by selective corrosion of chromium. Addition of beryllium metal to the melt decreases the corrosion rate to 2 μm/year.[48]

2.3. Nitrate and Nitrite Melts

A wealth of technical experience exists with melts of the alkali nitrates or mixtures of nitrates and nitrites, because they are in use for heat treatment baths. Such mixtures are often called "Hitec" or "HTS." Firstly, two reactions should be considered which relate to the thermal stability of these salts. One is the reaction

$$MeNO_3 = MeNO_2 + 1/2O_2 \tag{9}$$
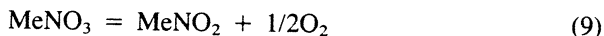
having an equilibrium constant

$$K_9 = \frac{a_{MeNO2} \cdot p_{O2}^{1/2}}{a_{MeNO3}} \tag{10}$$

With increasing temperature, the oxygen partial pressure increases at constant nitrate/nitrite ratio or, what normally occurs in practice, the nitrate/nitrite ratio decreases at constant oxygen pressure. Equilibrium constants have been given for Na and K salts.[49–51] The nitrate ion becomes more stable in the series Li, Na, K. Remarkable amounts of nitrite are in equilibrium with air above ~450°C.

The rate of nitrate dissociation according to equation (9) follows[51–53]

$$-\frac{dc_{MeNO3}}{dt} = k_1 \cdot c_{MeNO3} \tag{11}$$

and the oxidation of nitrite to nitrate

$$-\frac{dc_{MeNO2}}{dt} = k_2 \, c_{MeNO2} \tag{12}$$

Both equations fail to take into account the reverse reaction, so that they will probably only be correct far from equilibrium. The oxidation of nitrite occurs practically only at the melt–gas interface owing to the low oxygen solubility of the melt. Further, it is very slow below ~450°C, so that nitrite can exist over long periods below this temperature.

The other reaction to be considered is the irreversible thermal decomposition of nitrite above ~500°C, which can best be described by the reaction

$$2MeNO_2 = Me_2O + N_2 + 3/2O_2 \tag{13}$$
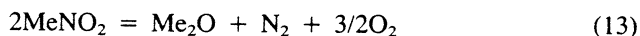
Me_2O can react with water vapor and carbon dioxide from the air to form hydroxide and carbonate, respectively. In particular hydroxide increases the aggressiveness of the melt towards high Cr-containing steels (see Section 2.4).

Unalloyed and low-alloy steels form oxide layers rich in Fe_3O_4 on their surface. In general, these steels can be used up to temperatures of $\sim500°C$, which is within the thermal stability range of nitrate–nitrite melts. However, corrosion resistance increases with the Cr content of the steel.[29,54] Good corrosion resistance has also been reported for type-316 stainless steel.[48] The corrosion rate of unalloyed steel is influenced by its surface treatment. Pickled bright surfaces behave better than preoxidized ones.[55] Acidic additions like $NaPO_3$ or $K_2Cr_2O_7$ increase the corrosion rate of unalloyed steels while basic additions like Na_2O_2 and $NaOH$ inhibit corrosion up to 400°C. At higher temperatures, however, they seem to be detrimental.[56] Nitrite seems to have no significant effect.

The corrosion resistance of copper is inadequate in these media.[54] Equilibrium diagrams for copper–potassium nitrite have been published[57] and iron, cobalt, and nickel in sodium nitrite.[58]

The questions of safety, stability, and prevention of explosion of salt baths containing nitrate has received attention.[54,59] Such mixtures should not be in contact with aluminum, aluminum alloys, cyanides, and organics.

This author feels that rather more technical experience concerning the corrosion resistance of structural material may exist than has been published in the literature.

2.4. Hydroxide Melts

Sodium hydroxide melts are occasionally used in the pickling procedure for high chromium containing alloys.[60–63] The corrosion behavior of metallic materials has been investigated[64–71]; one report[64] seems to be the more extensive. Nickel is more resistant than unalloyed steels and these are again more resistant than high-alloy Cr– and CrNi–stainless steels. The corrosion rate depends significantly on the peroxide content of the melt, which in turn depends on the reaction

$$2NaOH + 1/2O_2 = Na_2O_2 + H_2O \qquad (14)$$
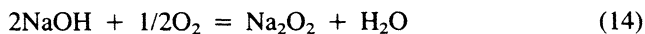
with an equilibrium constant

$$K_{14} = \frac{p_{H2O} \cdot a_{Na2O2}}{p_{O2}^{1/2}} \quad (a_{NaOH} \approx 1) \qquad (15)$$

involving the oxygen and water vapor pressure of the atmosphere.[71] Increasing water vapor and decreasing oxygen pressures reduce the peroxide content of the melt and simultaneously reduce the corrosion rate of nickel, iron, iron oxides, and chromium oxide.[70] One exception is silver, whose corrosion rate is enhanced

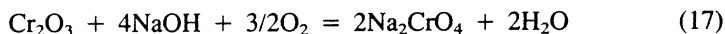by water vapor.[70,72] Considerations about the stability of oxide, peroxide, and superoxide ions have also been published[73] and a suitable acid–base reaction proposed.[74] Apparently, water is the strongest acid and O^{2-} the strongest base.[73]

The poor corrosion resistance of stainless steels with high chromium contents is caused by the high oxidation rate of Cr_2O_3 to chromate in the presence of oxygen or peroxide according to

$$Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O \qquad (16)$$

or

$$Cr_2O_3 + 4NaOH + 3/2O_2 = 2Na_2CrO_4 + 2H_2O \qquad (17)$$
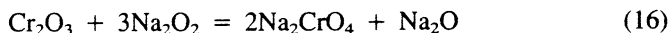
The selective oxidation of chromium often leads to pore formation in the metal beneath the surface or causes intergranular attack.[68]

Equilibrium diagrams for manganese[75] and mercury[76] have been published.

The aggressiveness of hydroxide melts towards nickel, copper, and iron increases in the series LiOH, NaOH, KOH.[65] In the same series, the amounts of peroxide and superoxide, stable in the melt under the same conditions, increase.[72]

Glass, silica, and all high silica- or silicon-containing ceramics and refractories are severely attacked by hydroxide melts. Alumina is much more resistant than glass and silica.

2.5. Carbonate Melts

Equilibrium diagrams (E–pCO_2 diagrams) have been constructed for carbonate melts and for the metals nickel, iron, silver, gold, and platinum in carbonate melts.[77] These diagrams show the significance of p_{CO_2} in relation to their acid–base behavior (see Chapter 1).

Silver corrodes in the presence of oxygen and/or carbon dioxide up to the equilibrium concentration of Ag^+ ions in the melt.[78,79] A small attack was also observed at 600–700°C with a gold–20% palladium alloy resulting in the formation of sodium palladate.[80] Nickel became brittle by intergranular formation of NiO.[80] Type-347 stainless steel exhibited good resistance, probably by formation of a $LiFeO_2$ (or $LiCrO_2$) surface layer.[80]

Extensive experiences with test loops have been reported.[81] At 500°C austenitic stainless steels exhibit satisfactory resistance. At 600°C chromium-containing nickel-based alloys are required; at 700°C high-chromium alloys (~50% Cr) are needed. The corrosion of chromium-containing metals is controlled by the formation of a lithium chromite ($LiCrO_2$) film on the alloy surface. This film

has a chromium oxide structure with the vacant cation interstices filled with lithium ions. At temperatures above 700°C, this film does not reform sufficiently rapidly to prevent pitting corrosion once the film is ruptured and therefore metallic materials cannot be applied above this temperature.

Contamination by sulfur compounds such as sulfate, sulfite, and sulfide increase corrosion rates markedly.[81,82] Sulfates also cause stress corrosion cracking in constant load tests with types-304 and -347 stainless steels and with Inconel 600, but not with Hastelloy G, Incoloy 800, and Carpenter 7 Mo.[81] Thermal gradients do not appear to be a problem but erosion corrosion has been observed at high flow rates of the melt.[81]

Aluminized coatings on metallic substrates also provide an adequate corrosion barrier as long as a sufficient aluminum content is present in the surface to reform the film. Their temperature limit is ~700°C.[81]

At 800°C and above high-purity, high-density α-alumina is required, which forms a melt-insoluble sodium aluminate ($NaAlO_2$) surface film.[81] This surface film is, however, soluble in water. The good resistance of fused-cast alumina has been confirmed.[83] Low-density or amorphous alumina is not resistant.[81] Because all mortars are corroded, brick-lined vessels must be designed so that the thermal gradient across the bricks permits the melt to freeze before the lining is penetrated.[81]

A 77 wt % Cr–23 wt % Al_2O_3 cermet has also shown remarkable corrosion resistance even at 1000°C.[81]

Recent developments associated with the specification of materials for molten carbonate fuel cells are dealt with in Chapter 12 of this volume by Selman and Marianowski, and also by Maru in the companion volume *Molten Salt Techniques*.

2.6. Sulfate Melts

Sulfate melts play a significant role in technology as undesired deposits, e.g., on heat exchanger surfaces in conventional boiler plants[84,85] and refuse incineration plants[86] and on turbine blades in gas turbines burning fossil fuels.[87] These deposits are molten or semimolten, depending on the operating temperature and the composition of the deposit, and often cause severe corrosion problems. These technical problems triggered numerous investigations into the corrosion behavior of iron, nickel, and cobalt-based alloys in sulfate melts or beneath sulfate deposits. Some interesting results for the potential dependence of this corrosion behavior will now be described briefly.

E–pO^{2-} stability diagrams have been published.[88–90] Irrespective of the uncertainties in such diagrams they do reveal the existance of an E–pO^{2-} area in which metal sulfides are stable (this factor has been neglected in References

89 and 90). This is important because sulfide scales give little or no corrosion protection.

From potentiostatic corrosion tests it follows that the corrosion behavior of all metallic materials depends significantly on the potential; other factors include the compositions of the material and the melt. The metals can be divided into two groups.[91] To the first group belong all active corroding metals like silver and copper. The potential dependence of the anodic partial current of metal dissolution follows a Tafel-like relationship, but the rate-controlling step is not the charge transfer reaction but the diffusion of the metals ions from the convective diffusion boundary layer into the melt.[92] The metals of the second group form protective scales in a particular potential region. All chromium containing high-temperature metallic materials belong to this group. In the eutectic melt of (in mol %) 78% Li_2SO_4, 13.5% K_2SO_4, and 8.5% Na_2SO_4 iron, unalloyed steels, ferritic, and austenitic stainless steels, as well as nickel- and cobalt-based alloys form protective oxide layers below a critical potential.[93,94] The scales formed on steels in this passive potential region consist of Li-containing oxides.[93] Above a critical potential, often called the breakdown potential, external corrosion and internal sulfidation occur, both significantly increasing with increasing potential. Increasing the chromium content of the alloy shifts this breakdown potential to more positive potentials[93] and thus extends the passive potential region. A similar potential dependence has been found with nickel- and cobalt-based alloys in the eutectic melt of (in mol %) 53% Na_2SO_4, 7% $CaSO_4$, and 40% $MgSO_4$ at 1073 and 1173 K.[91,95] In this melt MgO is precipitated on the surface below a critical potential, becomes incorporated into the oxide scale, and thus improves the protection afforded by the scale.[91,95]

The breakdown of the protective oxide scale above a critical potential is caused by a preferential dissolution of the bivalent oxides into the melt. With increasing potential the discharge of SO_4^{2-} ions in the melt according to

$$SO_4^{2-} = SO_3 + 1/2O_2 + 2e^- \qquad (18)$$
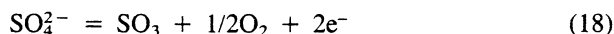
becomes increasingly evident,[95,96] resulting in an increase of the surface acidity with increasing potential. The result is that preferentially bivalent oxides of the protective oxide layer become dissolved according to the reaction

$$MeO + SO_3 = MeSO_4 \qquad (19)$$

because they have a lower thermal SO_3 dissociation pressure than higher valency oxides. This dissolution is often called "acidic fluxing".[97] This selective dissolution can lead at first to an enhanced internal sulfidation, if the chromium content of the alloy is not too low, because the scale becomes "permeable" to sulfur. Alloys with low chromium content immediately suffer a severe external corrosion

and internal sulfidation. However, the high-chromium-containing alloys also experience severe corrosion above a second critical potential because increasing amounts of oxides become dissolved with increasing potential.

In Na_2SO_4–K_2SO_4 melts at 900°C severe corrosion occurs at positive as well as at negative potentials.[98] Protective oxide films are formed only in an intermediate potential region, provided the chromium content is sufficient. For instance, the nickel-based alloys IN 597 and IN 738 LC with chromium contents higher than 15% form protective scales over a potential range of ~1000 mV (Figure 4), while an oxide layer on the nickel-based alloy IN 100 with only 10% Cr is stable in the same potential region only for a period of a few hours.[98] At positive potentials acidic fluxing again occurs, while at negative potentials basic fluxing destroys the oxide film. At negative potentials oxide ions are formed either by the reduction of oxygen according to

$$1/2O_2 + 2e^- = O^{2-} \tag{20}$$

or by the reduction of the SO_4 ions according to the reactions[99]

$$SO_4^{2-} + 2e^- = SO_3^{2-} + O^{2-} \tag{21a}$$

$$SO_4^{2-} + 6e^- = S + 4O^{2-} \tag{21b}$$

$$SO_4^{2-} + 8e^- = S^{2-} + 4O^{2-} \tag{21c}$$
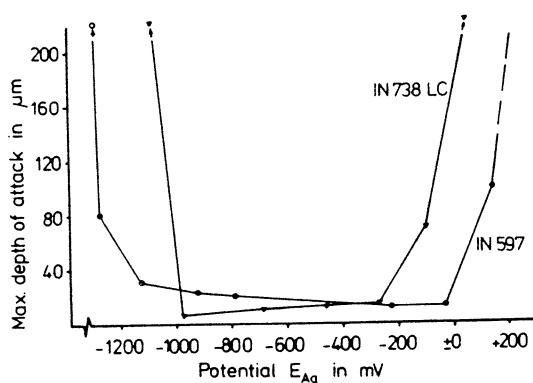
FIGURE 4. Influence of electrode potential on the maximum depth of attack of the nickel-based alloys IN 597 and IN 738 LC in a 90% Na_2SO_4–10% K_2SO_4 melt at 1173 K (after Reference 98). (The potential E_{Ag} refers to a Ag/Ag^+-reference electrode.)

Accordingly, a basic pO^{2-} value appears at the alloy surface which can lead to the dissolution of oxides according to[8]
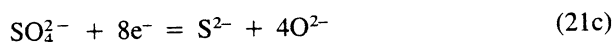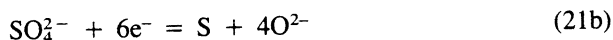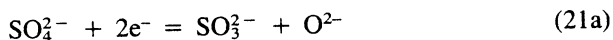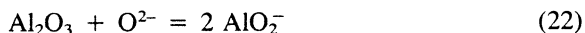
$$Al_2O_3 + O^{2-} = 2\,AlO_2^- \tag{22}$$

or

$$2NiO + 1/2O_2 + O^{2-} = 2NiO_2^- \tag{23}$$

Basic fluxing is avoided in $MgSO_4$-rich melts because MgO is insoluble in basic sulfate melts and becomes precipitated on the alloy surface at low pO^{2-} values.[95]

The corrosion potential and thus the corrosion rate under free corrosion conditions depend upon the presence of "impurities" in the melt (or in the gas phase) which enhance the cathodic partial reaction or make the melt acidic or basic. Such compounds include, e.g., the acids SO_3, V_2O_5, and MoO_3.[100]

There are, at present, some conflicting opinions as to whether sulfates or sulfur compounds lead to the deterioration of the high-temperature mechanical properties of superalloys. Huff and Schreiber[101] reported that a change of the atmosphere from air to combustion gases of low-sulphur-containing JP4 fuel impairs the creep rupture properties. The decrease in lifetime is much greater in the presence of deposits rich in sulfates. The same has been reported by Schmitt-Thomas *et al.*,[102] although this result could not be confirmed by another group.[103] Creep tests on the nickel-based alloys IN 597 and Nimonic 105 in the eutectic Na_2SO_4–$CaSO_4$–$MgSO_4$ melt at 1073 K revealed that the presence of a sulfate melt does not *a priori* impair their mechanical properties. The creep rupture properties are the same as in air if a protective scale is formed on the alloy surface.[104] Internal sulfidation can, however, significantly reduce the time to rupture and the elongation at rupture. Above a "critical" thickness of the internal sulfidation zone, the fracture mechanism can also change from predominantly intergranular to predominantly transgranular.[104] This change in the fracture mechanism is not fully understood. It seems that transgranular cracks are initiated in the internal sulfidation zone, and that the transgranular crack propagation rate is strongly enhanced by the presence of sulfur. That sulfur compounds can enhance the crack propagation rate has also been observed in other experiments.[105]

3. Conclusions

The relevant literature on corrosion in molten salts indicates that the principles of metal dissolution are of an electrochemical nature and are known.

However, only a few systems have been investigated in detail. These are not generally relevant for industrial applications.

Paralleling corrosion behavior in aqueous media, corrosion-resistant metals form protective surface layers in molten salts, also. Some information exists about these surface films but, only very little about their stability as a function of electrode potential and other system parameters.

There is a lack of reliable data on the corrosion behavior of structural materials under industrial conditions. Only a few data exist on the galvanic corrosion of metal couples, on erosion corrosion, stress corrosion cracking, corrosion fatigue, and on the interaction between corrosion and creep deformation in melts.

Such information as is available for many molten salts provides a basis for the preselection of structural materials, which then need to be tested in detail in the laboratory or in a pilot plant under conditions close to the operation conditions. These tests should also include experiments which reveal possible interactions between corrosion and constant or cyclic mechanical stress.

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