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High-Temperature Corrosion Behavior of Superalloys in Molten Salts – A Review

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ABSTRACT

The use of molten salts based on fluorides/chlorides/nitrates/sulfates or carbonates is now an accepted practice in energy conversion technologies and many other industrial processes. However, compatibility of molten salts with the structural alloys and materials corrosion has been of real concern at such temperatures (600-900°C). Hence, the material development and corrosion studies turn out to be an essential part of research. The results of recent studies are reviewed to understand the developments that have occurred in the latter part of the last decade. The corrosion kinetics of modern materials in variety of molten salts with focus on reaction mechanisms and corrosion products is investigated by scientists around the globe. Emphasis has also been given on the composition of the oxide films/corrosion products on alloys of interest in wide a range of melts. By and large, molten salt corrosion has been predominantly studied by gravimetric, electrochemical techniques and, morphology and chemical analysis of corrosion products by means of XRD, SEM/ EDX, ICP/AAS, etc. This article gives in-depth insight into the composition of materials, the molten salt mixtures, and various aggressive environments mainly high temperatures and long exposures.

KEYWORDS

Hot corrosion; oxidation; structural materials; oxide scales; molten systems

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1. Introduction

The use of molten salt technology as a working fluid has a proven success in many industrial applications. In fact, molten salts have been proposed for use in many energy conversion technologies mainly due to their potential as heat transfer agents and industrial liquid fuels. Corrosion of materials in molten salt electrolytes for uninterrupted long-term use has been of major concern over the years.

High temperature corrosion investigations began as early as from 1940's for boilers, gas turbines, and industrial waste incinerators. Also with the gaining interest in the nuclear field, materials compatibility, and corrosion behavior in a variety of molten salts was extensively investigated by Oak Ridge National Laboratory (ORNL-USA) from 1950s-1970's. 1-7 Additionally, National Aeronautics and Space Administration (NASA) studied

corrosion resistance of a spectrum of alloys in LiF-19.5CaF₂ and NaF-27CaF₂-36MgF₂ for thermal energy storage applications.8 Since then, it has been a constant rise in corrosion investigations reported in various molten salt environments from both theoretical and experimental viewpoints. However, even today the amount of materials tested in molten salts of interest have been quite limited and not enough to serve as a basis for selection of compatible alloys. The main reason behind this might be the predominant use of immersion (gravimetric weight loss) tests over the electrochemical tests in the past. Immersion testing not only take longer durations but can also show irregularities in the effects of corrosion measured. But with the introduction of electrochemical tests such as free corrosion potential, potentiostatic polarization, scanning polarization, cyclic voltammetry, linear polarization resistance, and electrochemical impedance spectroscopy (EIS) into high temperature molten salt corrosion study has accelerated research efforts and has proved vital in understanding reaction mechanisms and kinetics.9

Due to the growing interest and constantly rising demand for a new generation industrial materials working under extreme conditions, the high temperature corrosion studies of superalloys in different molten salts mixtures have been intensified in the last 10 years or so. The aim of this article is to highlight newly reported corrosion studies of materials/superalloys in various molten salts, with special emphasize on novel approaches employed during the recent investigations. Emphasis has also been given on reaction mechanisms and the composition of the oxide scales on various superalloys in a wide range of melts. Few earlier reviews related to corrosion of materials in molten salts were reported by Tzvetkoff and coauthors first in 1995,10 and then in the decade there after. 11,12 In these reviews, corrosion mechanisms, the growth kinetics, the composition, and structure of the passivating oxide films formed on Ni, Fe, Co, and their alloys were discussed in great detail. Another brief review was reported in 2005 by Sidhu et al.¹³ for hot corrosion of super alloys and role of high-velocity oxy-fuel spray coatings. References selected for this article are concentrated on the last 5-10 years, highlighting the new materials tested and new approach contemplated. Furthermore, this article gives a comprehensive literature overview, with a specific focus on recent publications.

2. General hot corrosion behavior and trends

Superalloy is not immune to corrosion, especially testing in molten salts with extreme accelerated condition of elevated temperatures, propagates probabilities of more profound attack. Meier¹⁴ classified hot corrosion as Type I (high temperature) and Type II (low temperature) corrosion. In Type I or molten salt-induced corrosion, the deposited salt mixture can be a liquid phase by the start of deposition at high temperatures, whereas in type II corrosion, it can be a solid phase in the beginning, and then transform into a liquid phase after its exposure to an alloy at high temperatures. 14,15

Furthermore, the superalloys undergo a two-stage, high-temperature, corrosion degradation: an initiation stage followed by a more attacking propagation stage. 16,17 According to Pettit and Meier, 16 during an initiation stage superalloys degrade at a rate identical to those which would have been obtained in the absence of the deposits. In a propagation stage, the superalloys with deposits significantly affect the protective properties of oxide scales, showing much larger corrosion rates.

At high temperatures, melts transform into conducting liquids, and can accelerate corrosion and an electrochemical process. Mechanisms of corrosion for aqueous solutions also can be applied for corrosion in molten electrolytes. Hence, the corrosion mechanisms which are generally applied to aqueous environments are also applicable to molten salts¹⁸⁻²⁰ and can be in the form of uniform surface corrosion, intergranular corrosion, galvanic corrosion, and pitting.

Corrosion resistance of alloys depends on the content of elements, generally Cr, Al, and Si, which influence the development of passivating oxide layers. But hostility of high temperature molten salts environment when compared to that of aqueous solution, which can render the oxide coating non-protective. That then exposes the underlying alloy to corrosion, which proceeds by attacking the least noble metal constituent in alloys. Efforts have been made to understand this selective removal of elemental constituents from the alloys and that also helped the researchers in proposing corrosion mechanisms. This makes analysis of corrosion products or oxide scales significantly important.

Materials corrosion in these systems is largely driven by thermodynamics of corrosion reactions, presence of impurities, and activity and temperature gradients. However, the corrosion of alloys can also depend on the type of molten salts used, e.g., fluorides, chlorides, nitrates, sulphates, and other salts. Numerous studies are reported in recent years in various mixtures of molten salts, focusing on a variety of parameters and other critical performance-limiting factors. The following part of this article includes a survey of the most recent literature in the area of molten salt corrosion of superalloys.



3. Corrosion in molten salts

3.1. Molten fluoride salts

Molten fluoride salts are of great interest as a heat transfer media because of their exceptional characteristics (i.e., high heat capacity, low viscosity, low vapor pressure, high thermal conductivity, low melting point, high boiling point, relatively good chemical inertness, etc.). In many molten salt systems, passive oxide films are unstable and once the film is vanished, the least noble alloying element is selectively attacked by dissolution. 21,22 These three types of corrosion mechanisms are proposed for materials in static molten fluoride salts: intrinsic corrosion, corrosion by impurities, and galvanic corrosion.²³ Several cases are reported below which will help us understand it better.

Corrosion resistance of high-temperature alloys— Hastelloy-N, Hastelloy-X, Haynes-230, Inconel-617, and Incoloy-800 H for their suitability as the heat exchanger—was examined by Olson et al.24 under a molten alkali fluoride salt (FLiNaK) environment at 850°C for 500 h exposure in graphite crucibles. Here, the dissolution of Cr was observed, mostly evident at the grain boundaries of these alloys. The authors also came up with an interesting conclusion that the graphite crucible had accelerated the corrosion rate by forming Cr-carbide. Similar findings were reported by Zheng et al.²⁵ for corrosion behavior of SS 316 L in molten Li₂BeF₄ (FLiBe) at 700°C for 3000 h, in both SS 316 and graphite crucibles. Corrosion attack measured in terms of Cr depletion was almost double for the samples tested in graphite crucibles (17.1 µm/year), compared to results obtained in SS crucibles (31.2 μ m/year). Tested samples from the graphite crucibles showed Cr₇C₃ phases throughout the corrosion scales, confirming the outward diffusion of Cr and inward diffusion of C into the samples.

Ouyang and co-workers^{26,27} investigated long-term corrosion performances of various Ni-based superalloys (Hastelloy-N, Haynes-242, Haynes-263, Hastelloy-B3) under moisture-containing FLiNaK at an ambient temperature of 600-700°C. The effect of moisture content is very well described in these two articles by means of non-purified and purified FLiNaK. Hastelloy-N and Hastelloy-B3 showed fairly superior corrosion protection, while Haynes 263 was found to be the worst performer. They concluded that the effect of temperature becomes more important on the weight loss in the presence of a small amount of H₂O in FLiNaK. They also added that samples in higher moisture-containing FLiNaK were aggressively attacked by intergranular corrosion and pitting. Effect of the oxidants on the corrosion of pure Ni, Fe, and Cr in molten FLiNaK at 700°C was very recently reported by Wang et al.28 and they found out that the

corrosion rates were four times higher in the presence of 2% H₂O. The effect of moisture on high temperature alloys in FLiNaK was further reported by Wang et al.²⁹ for GH3535 supported by electrochemical measurements and Kondo et al.30 for JLF-1 steel (Fe-9Cr-2W-0.1 C) at static and flowing conditions.

Galvanic corrosion among the common alloying constituents can prove detrimental in high temperature environments. Recent research by Wang et al.31 sheds some light on this problem. They reported the galvanic corrosion effects of the couples Ni/Cr, Ni/Fe, and Fe/Cr in eutectic FLiNaK at 700°C. Intense galvanic corrosion took place with the largest galvanic corrosion effect obtained in the order of Ni/Cr, then Fe/Cr, and Ni/Fe, demanding a special attention for future research.

The effect of microstructure on corrosion behavior of superalloys was investigated by studying the monocrystal and polycrystal N5 superalloy in molten FLiNaK salt at 700°C for 100 h.³² The authors reported that the weight loss of the polycrystal alloy was far too high than that of the monocrystal, apparently enhanced due to the existence of grain boundaries, and confirmed by the thicker Al/Cr depleted layer.

A different approach was explored by the addition of trace amounts of elements in corrosion studies in molten salts. Li et al.³³ examined the effect of yttrium additions in Ni-16 Mo-7Cr-4Fe superalloy in molten FLiNaK at 850°C for 620 h. They discovered that the correct amount of yttrium increased the corrosion resistance of the studied alloy by creating the Y-rich film, inhibiting the dissolution of Cr and Fe. But cautioned about excess yttrium's damaging effects. A similar type of investigation was reported by Cheng et al.,34 who evaluated the effect of Zr addition on SS316L and Hastelloy-N at 850°C for 1000 h in static molten FLiNaK. The addition of Zr significantly enhanced the corrosion resistance of both alloys, by forming Zr—Ni intermetallic compound coating, deterring the outward dissolution.

Neutron irradiation may enhance the corrosion of materials in molten salt reactor. Formation of helium and growth of helium bubble is one of the major examples of radiation damage for nuclear materials in molten salt reactor.^{35,36} A group of Australian researchers came up with a relatively fresh perspective on the influence of the presence of helium and helium bubbles on hot corrosion of Ni-based alloys in FLiNaK investigated at 750°C.³⁷. They concluded that the helium ion irradiation significantly accelerated the corrosion of Ni-based alloy in molten fluoride salt, leaving cavities and large corrosion voids.

Other interesting investigations were recently reported by Pavlik et al. on the impact of the addition of CrF₃, FeF₃, FeF₂, and NiF₂ to the molten FLiNaK on Incoloy 800H/HT by static testes;³⁸ Liu et al. for Nibased alloys in molten FLiNaK at 750°C using synchroradiation X-ray microbeam fluorescence techniques;³⁹ Kondo et al. for JLF-1 in FLiBe and FLi-NaK, Hastelloy C-276, Inconel 600 and Inconel 625 static Flibe at 500°C and 600°C for 1000 h; 40,41 and Sellers et al. for Hastelloy N and SS 316L in molten FLiNaK and its interaction with graphite with the aim of studying relevant reactor material combinations.⁴²

The above-reported corrosion studies of superalloys in molten fluoride salts are limited to only a handful of research teams globally and only a few of them involved a varied range of alloys. ^{24,26,27,43,44} Moreover, the data for the corrosion of superalloys in pure FLiNaK are also

Olson²⁴ and Ouyang and co-workers^{26,27} presented a good selection of alloys studied in FLiNaK but the different testing conditions would make the comparisons invalid. For example, Olson et al.²⁴ used graphite crucibles and Ouyang et al.26,27 employed autoclave made of alloy 625 with a pure nickel liner of 30 mm in thickness for carrying out corrosion experiments. The corrosion rates of Cr containing alloys can accelerate significantly if the crucibles are made of reactive metals.45 The similar results have been attained in corrosion of Incoloy 800H in FLiNaK, in which around 20 folds higher corrosion rates were observed in a graphite crucible when compared to Incoloy 800H crucible.^{24,43} This is further confirmed by Kondo et al.40 in the corrosion studies of JLF 1, in the crucible made of JLF 1 and nickel, in which the samples tested in nickel crucibles induced three times higher corrosion rates when compared to JLF 1 crucibles. Hence, the corrosion rates are found to be significantly low in absence of galvanic couple, which needs to be taken into consideration more seriously.²³

Moreover, FLiNaK caused severe intergranular corrosion in most Cr containing alloys, resulting in significant Cr depletion of the grain boundaries. Nevertheless, from the limited data, it can be said that FLiBe caused moderate intergranular corrosion when compared to FLiNaK. Therefore, looking at the severity of fluoride salts and the extent of damage caused by the void formation through intergranular corrosion, only the mass loss might not embody the real picture, although corrosion studies in terms of severity of intergranular attack are limited to the work of only a few authors.²³

Finally, corrosion mechanisms are often ill defined or significantly differ in opinion. This is mainly due to the lack of parametric tests with systematic temperature range and varied contamination concentrations.

3.2. Molten nitrate salts

Use of molten nitrate salts as heat transfer fluid as well as thermal energy storage material is well documented in Concentrating Solar Power (CSP) plants and for other wide ranges of industrial applications. 46-48 The most used or commercial nitrate salt mixtures are: Solar Salt (60 wt% NaNO₃, 40 wt% KNO₃), HITEC® (40 wt% NaNO₂, 53 wt% KNO₃, 7 wt% NaNO₃) and HITEC® XL (48 wt% Ca(NO₃)₂, 45 wt% KNO₃, 7 wt% NaNO₃).⁴⁹ A number of factors affect the materials corrosion in high temperature environments and looking at the extensive use of these nitrate molten salts, there is a great increase of technological interest in this research area. However, high temperature corrosion behaviors in this promising salt mixtures are not as extensively reported as for fluoride molten salts.

McConohy and Kruizenga⁵⁰ examined the thermophysical property changes and corrosion behavior of nickel-based HA230 and In625 alloys in 60/40% NaNO3/KNO3 molten mixture at temperatures of 600 and 680°C for up to 4000 h. They found that the corrosion rates for both alloys were minimal at 600°C, but increased seriously at 680°C, suggesting the optimum temperature window of about 80°C for containment materials. Their results were also promising as measured thermophysical properties of used molten salt would hardly interfere with the operation of a solar power plant.

Combined efforts of Spanish and Chilean researchers demonstrated a detailed comparison of materials corrosion behavior in molten Solar salt and HITECH XL, in two periodical articles. 51,52 In these articles, stainless steels (AISI 304, 430) and a low-Cr alloy steel (T22) were compared in two types of molten nitrate salt environments at 390 and 550°C for 2000 h. At 390°C, there were no corrosion products obtained for stainless steel samples in both molten salt mixtures. However, T22 steel showed thin layer of corrosion products, measuring 16.2 μ m and 0.88 μ m for Solar salt and HITECH XL, respectively. At 550°C, AISI 304 achieved satisfactory results whereas other alloys suffered severe corrosion. After thorough investigation they concluded that the materials observed low corrosion rates in HITEC XL when compared to Solar salt, giving more choices and increasing the life cycle of modern solar technology. These articles also proved vital in gathering a deep understanding of formation and growth of corrosion and insoluble products.

Dorcheh et al.⁵³ studied the corrosion resistance of P91 and X20CrMoV11-1 (ferritic steels), SS316 and SS347H (austenitic steels), and Ni-based alloy IN625 in the eutectic composition of 40 wt%KNO₃-60 wt%

NaNO₃ at 600°C for up to 5,000 h of immersions. Results showed that both low Cr ferritic steels showed high corrosiveness for longer immersions, whereas stainless steel alloys formed protective oxide scales exhibited slow kinetics in molten nitrate salts. IN625 outperformed the rest by forming a thick NiO layer, confirmed by very linear weight loss rate and low kinetics. However, after comparing the market prices of these alloys, they advocated the use of cheaper stainless steel alloys over the high cost of Ni-based alloys.

Fernandez et al.⁵⁴ carried out investigations on hot corrosion of an alumina-forming austenitic (AFA) stainless steel (OC-4, Fe-25Ni-14Cr-3.5Al-2.5Nb wt% base), relative to 304 stainless steel and T22 steel, in salt mixture of 40 wt% KNO₃-60 wt% NaNO₃ at 390°C by gravimetric analysis and EIS. The AFA OC-4 steel showed excellent corrosion resistance compared to currently used 304 stainless steel and T22, by developing highly protective Al-Cr rich oxide layer. They also carried out salt analysis before and after the experiments for the levels of chloride, sulfates, and nitrites and found similar values to the initial contents proved a limited role in corrosion of AFA OC-4.

The effect of adding Cr on the high-temperature corrosion resistance of Cr-Mo steels in molten LiNO₃-NaNO₃-KNO₃ at 550°C for 250, 500, and 1000 h was well addressed by Cheng et al.55 They found that the weight loss of the steels decreased with the increase in Cr content, also supported by dramatically lower corrosion rates with higher Cr wt%. Microstructure analysis of corrosion products discovered an outer LiFeO2 and an inner (Fe,Cr)₃O₄ layer, which hindered the external diffusion of Fe from the steel substrate.

Chilean nitrate salts are currently used as storage materials in CSP plants in northern Chile. Effects of impurities like Mg, SO4⁻, Cl⁻, and moisture content on the thermal processes and corrosiveness in Chilean solar nitrates were demonstrated by Fernandez et al.⁵⁶ Their other research endeavour reported the high temperature corrosive effects of HITEC mixture on a carbon steel (A516) and low-Cr alloy steels (T11 and T22).⁵⁷

Similar to the fluoride salts, well-controlled and detailed corrosion studies of alloys in molten nitrate and nitrite salts are also inadequate. Although the current research indicates that molten nitrate salt mixtures are relatively less corrosive or benign to alloys, due to the development of protective oxide layer. In addition to that thermal instability of molten nitrate salt making them operable at lower temperatures, therefore common alloys may be used as lower corrosion rates and are observed at such temperatures.

Usually, Fe-based alloys form a passive oxide layer consisting of Fe₃O₄ in molten nitrate salts at around 300°C that oxidize further to Fe₂O₃ at the molten salt interface. These oxide layers are protective up to almost 500°C.58,59 Most work has examined nitrate salt corrosion on stainless steel alloys and only a few have studied Ni-Cr-based alloys for higher temperatures and long exposures. 47,50 These alloys form protective Cr₂O₃ and NiO layers in addition to the iron oxide. The mode of corrosion was general surface corrosion, with the dissolution of chromium oxide into the melt; nickel and iron oxide remain insoluble.⁵⁹

3.3. Molten chloride salts

Molten chloride salts also possess heat transfer characteristics like other molten halide salts and has a lot to offer in high temperature applications.⁶⁰ The abovedocumented molten nitrate salts commercially used in CSP's are stable only up to 500-600°C temperature range.⁶¹ It is essential to develop heat transfer fluids with lower melting points (~200°C) and higher boiling points (>800°C). Moreover, limited global reserves of nitrate salts is another key drawback for the CSP expansion. On the other hand, metal chloride salts, such as NaCl and KCl, are available in large amounts in nature and boil at about 1400°C or more. When these high melting ionic chlorides are mixed with low melting covalent metal halides, i.e., ZnCl2 and AlCl3, a eutectic mixture with dual advantage forms; low melting points and high boiling points. However, corrosion behavior of alloys in these ternary chloride salt mixtures is not extensively reported.62,63

Vignarooban et al.⁶² reported corrosion resistance of commonly used superalloys (Hastelloys C-276, C-22, and N types) in eutectic molten mixtures of various molar concentration of NaCl-KCl-ZnCl2 for up to 500°C using potentiodynamic method and immersion tests. For all molar compositions of the salts studied, Hastelloy C-276 and C-22 types obtained relatively lower corrosion rates but for the type N it remained on the higher side. Hastelloy C-276 showed the lowest corrosion rate 40 μm per year in 13.4NaCl-33.7KCl-52.9ZnCl₂ (mol%) salt at 500°C, the outcomes of the immersion tests also confirmed the results of potentiodynamic method (corrosion rate of 50 μ m per year), promoting its use for CSP applications.

Molten chloride salt mixture of 13.4NaCl-33.7KCl-52.9ZnCl₂ was further studied for Hastelloys C-276 and C-22, and SS 304 in the absence and presence of air from 200-800°C.63 In the absence of air, corrosion rates of all the three tested materials reduced radically, suggesting its use as the container and piping alloys in CSP's. For anaerobic conditions, Hastelloy alloys showed remarkably lower corrosion rates in molten chloride salts even at 800°C, once again proving its suitability for ternary molten chloride salts.

Another ternary eutectic molten chloride salt mixture 50.6 LiCl-22.5 KCl-26.9 CsCl (mol-%) was proposed for liquid salt cooling processes and corrosion resistance of alloys was studied for a low-carbon SS (X2CrNi18-9), Ti-stabilized high-carbon SS (X6CrNiTi18-10) and Nibased superalloy (CMSX-4) by Hofmeister et al.⁶⁴ The low carbon X2CrNi18-9 undergone severe intergranular corrosion while Ti-stabilized high-carbon X6CrNiTi18-10 resisted intergranular corrosion by forming protective Cr₂O₃ layer but only up to temperature of 500°C for shorter immersions. CMSX-4 superalloy exhibited relatively low corrosion rates even at 800°C for 3 h.

Effect of Li and Cu addition on corrosion behavior of Fe-40 at.% Al intermetallic in eutectic molten LiCl-55 wt.% KCl salt was studied for up to 550°C by potentiodynamic polarization techniques. 65 The authors concluded that the intermetallic material showed better corrosion resistance in molten salt mixture with 3 at.% and 5 at.% Cu additions whereas 1 at.% and 3 at.% Li insertion seemed to increase the corrosion rate slightly. The article also gave detailed insight into corrosion reaction mechanism and the formation of oxide layers. Romo et al. further investigated the effect of the inclusion of 3 at% Cr, Co, or Ti on the corrosion performance of Fe40Al intermetallic in molten NaCl-KCl mixture at 750°C by using potentiodynamic polarization and EIS.66 The addition of either Cr, Co, or Ti resulted in fivefold enhanced corrosion resistance due to the formation of a protective Al₂O₃ layer, caused by rapid outward diffusion of Al.

Liu et al.⁶⁷ carried out investigations on high-temperature corrosion of TP347H stainless steel, C22 alloy, and laser-cladded C22 in molten alkali chloride (simulating forestry/ agricultural biomass) salts at 450-750°C, with intervals of 50°C. Coated laser-cladding C22 demonstrated higher corrosion resistance whereas C22 alloy exhibited slight intergranular corrosion, mainly due to the NiO layer. SS-TP347H showed heavy intergranular corrosion leaving Fe-rich oxides as corrosion products.

Abramov et al.⁶⁸ investigated corrosion resistant (Hastelloy N, B-3, G-35, C-2000) and high temperature (Haynes 230, Hastelloy S, and X) alloys in KClmelts in a wide temperature range (450-650°C). They reported that the mechanisms of corrosion of high-temperature alloys and corrosion resistant alloys in KCl-AlCl₃-based melts were found to be different. The authors concluded that high-temperature (Haynes 230, Hastelloy S, and X) alloys with carbide or intermetallic hardening effects, subjected to

intergranular corrosion starting from 550°C. While several corrosion resistant (Hastelloy N, B-3, G-35, C-2000) alloys exhibited good corrosion resistance in KCl-AlCl₃ melts up to 550°C. Although both types of alloys tested cannot be used as structural materials in contact with KCl-AlCl₃ melts at 650°C as the higher temperature lead to severe intergranular corrosion and structural changes in the materials.

Most of the corrosion measurement experiments in molten chloride salts were run in quartz crucibles which do not support the galvanic mechanism. Corrosion of several alloys in KCl-MgCl₂ at 850°C for 100 h in quartz crucibles, plus one test with Incoloy 800 H in a graphite were performed by Sridharan co-workers. 44,69 However, corrosion rates were much higher for Incoloy 800H in KCl-MgCl₂ in quartz crucible when compared to results in graphite crucibles. This may occur due to the reaction of chloride salt with SiO2 in quartz crucibles, resulting in oxidants that can attack alloys.

The studied alloys suffered less intergranular void formation in molten chloride salts than FLiNaK. For example, Inconel 800 H experienced less surface pitting, Cr depletion at the grain boundaries and much less intergranular attack. Intergranular corrosion of Inconel 800H in chloride molten salt was rather shallow in depth (<120 microns) and void production in the grain boundaries was significantly less than in FLiNaK.^{23,44}

As with the FLiNaK, increase in Cr content increased corrosion rate. With the increase of Cr content in the alloys from 10 to 30%, there was a significant increase in the corrosion rate of almost 7-fold, while changes in Ni content have no such noteworthy effect.⁴⁵

3.4. Molten sulphate salts

High-temperature corrosion is also a serious problem in gas turbines for ships and aircraft and in other chemical process systems, e.g., in boilers, internal combustion engines, industrial waste incinerators, etc.⁷⁰ When superalloy-based industrial construction resources come in practical use, a variety of corrosive environments are encountered. Most of these are gases or other reactants but non protective oxide deposits of metallic sulphates and chlorides such as Na₂SO₄ and NaCl may provide extremely aggressive environment and accelerate corrosion. NaCl is present in the marine environment and Vanadium is present in the fuel. These vanadates or sulphate-vanadate mixtures and sulphate-chloride mixtures can further cause the accelerated corrosion conditions.⁷¹ There is a growing consensus that condensed alkali metal salts particularly, Na₂SO₄, are a prerequisite to hot corrosion.⁷² Over the years, the attack of Ni-, Co-, or

Fe-based superalloys by Na₂SO₄ has been used as a model for degradation process in industrial gas turbines and in a number of combustion environments.

High-temperature corrosion behavior and its mechanism of a relatively new AFA stainless steel were investigated and compared with the Ni-based K438, K417, and SS 316L in molten sodium sulphate by Yan et al.⁷³ They found that the AFA stainless steel showed superior corrosion resistance compared to super alloy K417 and SS 316L. The main reason behind that was the subsequent formation of dense Al₂O₃ and Cr₂O₃ corrosion scale on its surface, which inhibited the sulphur diffusion into the alloy matrix efficiently and improved corrosion resistance.

During their corrosion study of 20MnMoNi55 and AISI 304 steel in 75 wt. % $Na_2SO_4 + 25$ wt. % K_2SO_4 at 900° C, Kumar and Arora⁷⁴ observed that AISI 304 was more resistant to corrosion than 20MnMoNi55 steel. Better corrosion resistance of AISI 304 was attributed to the formation of more protective oxide scale-contained Fe_2O_3 , Cr_2O_3 , and $NiCr_2O_4$, and less penetration of oxygen.

A single-phase $Cr_{13}Ni_5Si_2$ -based ternary metal silicide alloy was tested in molten $Na_2SO_4 + 25$ wt.% K_2SO_4 at $900^{\circ}C$ and $Na_2SO_4 + 25$ wt.% NaCl at $850^{\circ}C$ and the results were compared for both molten salt mixtures. ⁷⁵ It was established that the $Cr_{13}Ni_5Si_2$ alloy exhibited high corrosion resistance in molten mixture of $Na_2SO_4 + 25$ wt.% K_2SO_4 due to formation of protective Cr_2O_3 as reported in previous cases. But with the addition of NaCl into Na_2SO_4 , Cr_2O_3 layer became more porous and vulnerable, leading to the sulphide build up beneath the oxide scale and hence accelerated the corrosion significantly.

Identical aggressive environment of molten mixture of 75 wt.%Na₂SO₄ + 25 wt.% NaCl was employed for hot corrosion studies of Ni-based M38G superalloy,⁶⁹ Ni-16Cr-xAl-based alloys, 77 Ni-based Rene95, 78 and Ni-20Cr-18W superalloy⁷⁹ in the temperature range of 600-900°C. The results showed that the alloys suffered through high corrosion rates in this molten salt mixture. Effect of pre-oxidation on the degradation of samples was examined and the mechanisms were proposed by Liu et al. 76,77 They concluded that in most cases pre-oxidized samples exhibited higher corrosion resistance compared to the as-cast specimens, mainly due to the formation of protective oxide scale after pre-oxidation. The hot corrosion mechanism of oxidation and sulfuration for Ni-based Rene95 and Ni-20Cr-18W superalloy was also suggested by Zeng et al.⁷⁸ and Zang et al.,⁷⁹ respectively. Both the alloys formed the corrosion layers on the surface mainly composed of Cr₂O₃, NiO, and Ni₃S₂, and

sever spallation of corrosion scales at higher temperatures with increase in penetration of S was observed.

Hot corrosion study of weldments is equally important for industrial components used in corrosive environments, for extended service lifespan. Arivazhagan et al.80 carried out investigations to estimate hot corrosion performance of friction welded AISI 304 and AISI 4140 alloys in air as well as eutectic mixture of Na₂SO₄-60%V₂O₅ and NaCl-50%Na₂SO₄ at 650°C under cyclic conditions. Their careful observation of salt-coated weldment specimens showed that oxide scale was more porous and disintegrated, susceptible to heavy diffusion. Moreover, weldments were found to be more prone to corrosion than their parent metals in corrosive molten environment. Mixture of NaCl with molten alkali sulphate provided highly accelerated corrosive environment and order of the highest corrosion rates was NaCl- $50\%Na_2SO_4 > Na_2SO_4 - 60\%V_2O_5 > air.$

Kamal et al.⁸¹ reported the hot corrosion studies on superalloy Superfer 800 H in two different molten salt environments $Na_2SO_4 + 60\%$ V_2O_5 and $Na_2SO_4 + 60\%$ $V_2O_5 + NaCl$ at 900° C for up to 50 cycles. They concluded that NiO, Cr_2O_3 , and $NiCr_2O_4$ oxide scale formation provide reasonable resistance to corrosion but in presence of NaCl, chloride penetrated through the oxide scales, left them with pits, voids, and cracks. Similarly, various molten mixtures of sulphates, vanadates, and chlorides were also investigated for IN718 by EIS⁸² and salt coating (gravimetric)⁸³ at high temperatures.

Efforts have also been made to counter the hot corrosion associated with these non-protective oxide deposits on alloys by introducing inhibitors and fuel additives. Effect of addition of ZrO₂, 84 SnO₂, 85 CaO, 86 and CeO287 were examined for various Ni-, Co-, or Fe-based superalloys in molten mixture $Na_2SO_4 + 60\% V_2O_5$ at 900°C for 50 cycles. Among Superfer 800H, Superco 605, and Superni 75 alloys examined with ZrO₂, 84 SnO₂, 85 and CeO₂ 87 additives, the Ni-based Superni 75 was most resistant to attack by $Na_2SO_4 + 60\% V_2O_5$ in all the three cases, mainly due to the formation of Cr-rich oxide layer and refractory Ni(VO₃)₂. Whereas Co-based Superco 605 was found to have the lowest protection and Fe-based Superfer 800 H showed marginal resistance to corrosion. In the case of the addition of CaO,86 three Nibased superalloys (Superni 75, Superni 718, and Superni 601) were investigated for a same aggressive environment. CaO inhibitor showed effective protection to the alloys, where Superni 75 provide the best resistance, and Superni 601 and 718 gave lesser inhibition, sequentially.

The susceptibility to hot corrosion of alloys in molten sulphate salts was found to be correlated to the type of



scale produced during initial oxidation. The corrosion rate was the lowest when the Cr content of the alloy was highest, however Mo and Cu content found to increase the corrosion rate. Alloys containing Mo, W, or V undergoes self-sustaining rapid oxidation because solution of oxides of these elements with Na₂SO₄ decrease the oxide ion activity of molten salts, producing melts which are acidic fluxes for oxide scales.^{88,89}

For Fe-, Ni-, and Co-based alloys, the main corrosion products formed were NiO and Cr₂O₃. Scale morphology consisting of inner scales of Cr₂O₃ acting as a protective oxide film and external scales of NiO. Alloys forming an Al₂O₃ were found to be more susceptible to Na₂SO₄ deposits, independent of their Cr content. But in the presence of Na₂SO₄ and NaCl separately, the Cr₂O₃ formers got attacked more aggressively by NaCl than Na₂SO₄. Al₂O₃ formers and NiO formers were more resistant to NaCl attack than Cr₂O₃ formers.⁹⁰ The interaction of metal oxides such as NiO, CoO₃, Al₂O₃, Cr₂O₃, Fe₂O₃, and SiO₂ with molten Na2SO4 were studied in details by Malik and Mobin. 91 Similar to the NaCl additions, V₂O₅ additions to Na₂SO₄ also changed the corrosion kinetics significantly and modified scale structure.⁹²

3.5. Other molten mixtures

3.5.1 Lithium molten salts

LiCl-Li₂O molten lithium salts are not extensively employed for studying corrosion behaviors of superalloys like molten fluorides, chlorides, or sulphates, but the group of Korean researchers reported quite a few periodical articles lately, predominantly for Ni-based superalloys. 93-98 Cho et al. investigated high-temperature corrosion behavior of Inconel 713LC, Nimonic 80A, and Nimonic 90,93 Inconel 713LC-based superalloys N1, N2, and N3,94 Inconel 713LC-based N101/101H and 102/ 102H,95 Ni-based N07263, N06600, and N06625,96 and N06230, N07263, and N0662597 in molten LiCl-Li2O at temperatures ranging from 650-850°C for extended period of time. The authors tried to study electrolytic reduction after exposure to the oxidative LiCl-Li₂O molten salt environment under an oxidizing and inert atmosphere. They concluded that the alloys which formed continuous, thick, and adherent protective oxide layers exhibited superior corrosion resistance. Thick and continuous Cr-rich oxide layer and a Ni-rich layer inhibited the corrosion, while Fe-rich oxide scale accelerated corrosion by allowing oxygen diffusion. Similarly, effect of higher Cr and Fe contents in the alloys, on the corrosion performance in LiCl-Li₂O molten system was studied by Lim and Jung⁹⁸ by employing Ni-based Inconel alloys (Inconel 600, 601, and 690) and Fe-based Incoloy 800H alloy. They concluded that Inconel 600 with lowest Cr

and Fe percentage performed the best and other alloys with higher Cr and Fe content showed higher corrosion rates. They concluded that too much Cr and Fe content proved detrimental for corrosion resistance.

Although the corrosion studies of superalloys in molten lithium salts are limited to only a few research teams, the reported articles above provide reasonable clarity and useful information's. However, the conclusions drawn by Cho et al. 93,94,96,97 lead us to an ambiguous state over the Cr content in respective alloys. In Cho et al., ^{93,94} alloys with least Cr content performed the best and the authors concluded that an excess Cr causes deleterious effects on the corrosion resistance of alloys while with Cho et al. 96,97 reported that the dense and continuous Cr-rich oxide layer retarded the progress of the corrosion process. Results might have contradicted due to the presence of higher Fe content in the alloys in Cho et al. 96,97 and at the same time advocated an optimum Cr and Fe content in the alloys.

3.5.2. Molten carbonate salts

Molten lithium/potassium carbonate or lithium/sodium carbonate are used as an electrolyte for molten carbonate fuel cells (MCFC). MCFC's operates at about 650°C and metallic parts in these systems often suffer from hightemperature corrosion. Molten carbonate electrolyte in contact with metallic components causes various forms of hot corrosion attacks, such as oxidation, carburization, and fluxing reactions.⁹⁹ A handful of studies reported about hot corrosion behavior of anodic and cathodic metallic part of the cell in molten carbonate mixtures. 100-104 Randstorm et al. 100 investigated corrosion of some anode current collector materials in molten (Li_{0.62}K_{0.38})₂CO₃ salts. Most of the samples tested formed non-protective oxide layers and suffered carburization in studied molten salt environment. Further, Liu et al. 101 examined the effect of rare earth element dysprosium on corrosion of potential cathode NiO/Ni in molten (Li_{0.62}K_{0.38})₂CO₃ mixture at 650°C. They found that addition of dysprosium into NiO/Ni reduced its passive anodic current and inhibited the outward diffusion of nickel, thus increased the corrosion resistance.

The effect of Li addition on the corrosion behavior of Ni₃Al alloy in molten (Li_{0.62}K_{0.38})₂CO₃ salts at 650°C has been studied by using electrochemical techniques including EIS. 102 The results showed that for short exposure times the alloys was under diffusion control mechanism but with longer immersions, protective oxide scales can be dissolved by molten salt, putting the alloys at a risk of heavy pitting corrosion. Frangini and Loreti 103 also studied effect of alkaline earth additives (Mg, Ca, and Ba) on molten carbonate corrosion of SS 316L. They observed that trace amounts of additives (1.5 mol %) of Mg, Ca

and Ba did not interfere with corrosion mechanism. But with increase in concentration of Mg and Ca, corrosion resistance of SS 316L increased, due to the formation of protective (Mg or Ca)-doped lithium ferrite layer. On the contrary, further Ba additions did not affect the corrosion mechanism, because it did not react with growing oxide scale.

At times, corrosion process can cause over 20% loss of electrolyte by forming corrosion products containing Li and K. Ni et al. 104 carried out the initial-stage corrosion of SS 310S in molten (Li_{0.62}K_{0.38})₂CO₃ mixture at 650°C also by using EIS. The results were emphasized on loss of molten salt and lithiation process. This study confirmed that larger amount of molten salt caused harsh lithiation process causing twisted diffusion paths, resulting in intense degradation of the oxide films. Furthermore, critical issues and short literature survey was reported for corrosion of metallic stack components of MCFC in molten carbonates by Frangini. 105 It focused principally on materials commonly used as the cathode side separator plate in MCFC's (SS 316L and SS 310S) and promising alternatives available for improved corrosion resistance and high electrical conductivity.

3.5.3 Unconventional molten salts

Among the wide array of superalloys usage as the high temperature materials, construction of high temperature and high pressure vessels, industrial waste incinerators, and KIVCET flash smelter boilers used in pyro-metallurgical method of lead, zinc, and black liquor recovery boilers are typical. Despite the presence of heavy metals such as lead, zinc, and iron, together with chlorine, oxygen, and sulphur in molten salt medium, high temperature corrosion performance in such mediums are seldom reported. 106-109 Zahrani and Alfantazi investigated corrosion resistance of Inconel 625 in presence of heavy metals by employing mixture of 47PbSO₄-23ZnO-13Pb3O₄- $10Fe_2O_3-7PbCl_2$ (wt.%)¹⁰⁷ and $47PbSO_4-13Pb_3O_4-$ 7PbCl₂-23ZnO-10CdO (wt.%)¹⁰⁸ at 600, 700, and 800°C by using electrochemical and gravimetric techniques. The alloy proved susceptible with an increase in temperatures; porous and non-protective oxide layer only supported corrosion attack by internal oxidation and sulfidation. Inconel 625 suffered uniform corrosion, intergranular corrosion, and extensive pitting corrosion. Likewise, molten salt-induced corrosion and degradation mechanisms of Inconel 625 weld overlay in 47PbSO₄-13Pb₃O₄-7PbCl₂-23ZnO-10CdO (wt.%) at 600, 700, and 800°C was also reported comprehensively. 109

Another uncommon molten salt mixture was tested by Usami et al.110 who used multi-component molybdate

and simple Na₂MoO₄-MoO₃ molybdate mixtures to study corrosion behavior of SS 304L for the temperatures of up to 1000°C. For multi-component molybdates, no substantial reaction was observed between molybdates and SS 304L samples at 700°C for shorter exposures. Reaction rate of SS 304L with multi-component molybdates increased with increase in temperature, but still the reaction occurred only up to 300 μ m depth even at 1000°C. In the simple Na₂MoO₄-MoO₃ molybdate, concentration of MoO₃ was directly proportional to the attained reaction rate.

Molten NaCl is a strong corrosive for materials at high temperatures and most of the corrosion studies available are primarily focused on mixed salts with NaCl as the part of the corrosive mixture. 62,63,75-79 However, testing of pure NaCl as the sole corrosive medium has not been investigated extensively. Yang et al.111 carried out high temperature corrosion studies of Fe-, Cr-, Ni-based alloys in pure molten NaCl at 800°C for 192 h. The results showed that order of corrosion rates of the alloys can be attributed to the reactions between Cr and NaCl; Cr base > Ni base > Fe base. Cr-based alloy showed worst resistance and accelerated corrosion process, and loss of Cr was the main reason for increase in corrosion rate for all the three alloys tested.

4. Concluding remarks

Molten salt technology has been used for many years and corrosion studies of materials in high temperature melts is an area of growing interest but still in a developing phase. The corrosion kinetics of modern materials in a variety of molten salts with focus on reaction mechanisms and corrosion products is investigated with great intent in recent years. With this article, we have tried to summarize our understanding of high-temperature corrosion behavior of superalloys in molten salts by a thorough literature survey of the most recent publications.

The corrosion mechanism of metals/alloys in molten salt is complicated to that of in aqueous solution. Efforts have been made to propose detailed corrosion mechanisms, however it lacks consistency and clarification in several cases. Moreover, majority of the work reported preferred gravimetric method over electrochemical tests. However, weight loss measurements might not exemplify genuine extent of corrosion, because intergranular corrosion can cause premature failures even at low weight loss values. In addition, because of the complexity of corrosion mechanisms, many generalized conclusions may not be a fair assumption as resulted mechanism can be a



mixture of more than one reactions. EIS seemed to provide better clues in elucidating the reaction kinetics and formation of corrosion products, although limited electro impedance models are available for fitting the impedance spectra. Detailed experimental and theoretical investigations are required to establish electrochemical impedance models along with impedance measurements. Even today, there is not enough data available for the number of alloys tested in molten salts of interest, to serve as a basis for selection of compatible alloys. Furthermore, existing corrosion data also lacks parametric study of corrosion, as a function of impurity type, impurity concentration, galvanic potential, and temperature.

On the other hand, these results reviewed in this paper provide significant base and rich promise for the future trends of investigation in this field. It has to be said that continuous and determined attempts have been made by some authors to overcome drawbacks, despite tough challenges. It is obvious that cautious interpretation of these results will lead the way in development of new alloys and their compatibility in harsh molten salt environments. To support a quick view of the article Appendix 1 has been provided.

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Appendix1

Molten Salt Environment	Materials	Procedures	Reference
FLiNaK _(eut)	Incoloy 800, Hastelloy-N, Hastelloy-X, Haynes 230, Inconel 617	SEM-EDS, gravimetry	24
FLiBe	SS 316, graphite crucible	SEM-EDS, XRD, gravimetry	25
FLiNaK _(eut)	Hastelloy-N, Haynes-242, Haynes-263, Hastelloy-	SEM-EDS, gravimetry	26,27
FLiNaK _(eut)	B3 coupons of Ni, Fe, Cr	SEM-EDS, gravimetry, potentiodynamic polarization, electrochemical impedance, OCP	28
FLiNaK _(eut)	GH3535 alloy	SEM-EDX, Potentiodynamic polarization, EIS	29
FLiNaK _(eut)	JLF-1 ferritic martensitic steel	SEM, gravimetry	30
FLiNaK _(eut)	couples Ni/Cr, Ni/Fe and Fe/Cr	SEM-EDX, XRD, electrochemical measurements	31
FLiNaK _(eut)	N5 polycrystal superalloy	SEM, gravimetry	32
FLiNaK _(eut)	Ni–16Mo–7Cr–4Fe superalloy with various yttrium contents	SEM-EDS, XRD, gravimetry	33
FLiNaK(eut) + Zr additions	SS316L, Hastelloy-N	SEM-EDS, XRD, gravimetry	34
FLiNaK _(eut)	GH3535 alloy	TEM, HAADF-STEM modes	37
FLiNaK(eut) + Cr, Fe, Ni additions	Incoloy 800 H/HT	SEM-EDX, XRD, gravimetry	38
FLiNaK _(eut)	Inconel 600, Hastelloy X and Hastelloy C-276	SEM, synchrotron-XRF, synchrotron-XRD	39
FLiBe, FLiNaK _(eut)	JLF-1 ferritic martensitic steel	SEM-EDS	40
FLiBe, FLiNaK _(eut)	Inconel 625, Inconel 600, Hastelloy C-276	SEM, gravimetry	41
NaNO ₃ /KNO ₃ (60/40%)	Haynes 230, Inconel 625	SEM-EDS, XRD, gravimetry, DSC	50
NaNO ₃ /KNO ₃ (60/40%)	SS 304, SS 430, low-Cr alloy steel (T22)	SEM-EDS, XRD, gravimetry, DSC, TG	51
HITEC XL (R)	SS 304, SS 430, low-Cr alloy steel (T22), carbon steel (A1)	SEM-EDS, XRD, gravimetry, DSC, TG	52
NaNO ₃ /KNO ₃ (60/40%)	P91, X20CrMoV11-1, SS 316, SS 347H, Inconel 625	SEM, EPMA, gravimetry	53
NaNO ₃ /KNO ₃ (60/40%)	AFA SS OC-4	EIS, gravimetry, SEM, XRD	54
NaNO ₃ /KNO ₃ (60/40%)	SB450, T22, T5, T9, X20	SEM-BSE/EDS, XRD, gravimetry	55
NaNO ₃ /KNO ₃ (60/40%)	A1 and T22 steels	SEM-EDX, XRD, Volhard procedure, gravimetry, UV–Vis spectroscopy, ICP-OES	56
HITEC (R)	A516, T11, T22	SEM-EDX, XRD, gravimetry	57
NaCl-KCl-ZnCl _{2 (eut)}	Hastelloys C-276, C-22 and N	potentiodynamic method, immersion method	62
NaCl-KCl-ZnCl _{2 (eut)}	Hastelloys C-276 and C-22, and SS 304	Potentiodynamic polarization, Immersion method, SEM	63
LiCI–KCI–CsCl(eut)	SS (X2CrNi18–9), SS (X6CrNiTi18–10), superalloy (CMSX-4)	TGA, XPS, FT-IR, SEM-BSE, optical microscopy	64
LiCl-KCl (eut)	Fe-40 at.% Al with Li and Cu additions	SEM-EDS, electrochemical techniques	65
NaCl-KCl (M 1:1)	Fe-40 at.% Al with addition of Cr, Co, Ti	SEM-EDX, electrochemical techniques	66
KCI-NaCI (wt.% 98.6–1.4 and 95.5–4.5)	SS TP347H, C22 alloy and laser-cladded C22	SEM-EDS, XRD, gravimetry	67
static air, salt-coated samples (Na ₂ SO ₄)	AFA alloy, Ni-based K438, K417 and SS 316L	SEM-EDS, XRD, gravimetry	73
Na ₂ SO ₄ -K ₂ SO ₄ , Na ₂ SO ₄ -NaCl (both wt. % 75– 25)	20MnMoNi55 and AISI 304	FESEM/EDAX, XRD, gravimetry	74
Na ₂ SO ₄ -K ₂ SO ₄ (wt. % 75–25)	Cr ₁₃ Ni ₅ Si ₂	SEM-EDS, XRD, gravimetry	75
Na ₂ SO ₄ -NaCl (wt. % 75–25)	M38G superalloy	SEM-EDS, XRD, gravimetry	76
Na ₂ SO ₄ -NaCl (wt. % 75–25)	Ni–16Cr–xAl	SEM-EDS, XRD, gravimetry	77
Na ₂ SO ₄ -NaCl (wt. % 75–25)	Ni-based Rene95	SEM-EDS, XRD, gravimetry	78
	Ni-20Cr-18W	SEM-EDS, XRD, gravimetry	76 79
Na ₂ SO ₄ -NaCl (wt. % 75–25)		SEM-EDAX, XRD, gravimetry	80
Na ₂ SO ₄ -60%V ₂ O ₅ , NaCl-50%Na ₂ SO ₄	SS 304, SS 4140		
$Na_2SO_4 + 60\% V_2O_5$ and $Na_2SO_4 + 60\% V_2O_5 + NaCl$	Incoloy 800H	SEM-EDAX, XRD, gravimetry	81
Na ₂ SO ₄ , NaVO ₃ , 80 wt%V ₂ O ₅ - 20 wt%Na ₂ SO ₄ , Natural Ash (V ₂ O ₅ , Na ₂ O. V ₂ O ₄ .5V ₂ O ₅ and NaV ₆ O ₁₅)	Inconel 718	EIS, SEM-EDS	82
air, salt-coated samples (100 wt.% NaCl, 75 wt.% Na ₂ SO ₄ + 25 wt.% NaCl, and 90 wt.% Na ₂ SO ₄ + 5 wt.% NaCl + 5 wt.% V ₃ O ₅)	Inconel 718	SEM-EDS, XRD, gravimetry	83
$Na_2SO_4 + 60\% V_2O_5 (+ZrO_2)$	Incoloy 800H, KC20WN/L 605, Nimonic 75	SEM-EDS, EPMA, XRD, gravimetry	84
$Na_2SO_4 + 60\% V_2O_5 (+SnO_2)$	Incoloy 800H, KC20WN/L 605, Nimonic 75	SEM-EDS, EPMA, XRD, gravimetry	85
$Na_2SO_4 + 60\% V_2O_5 (+CaO)$	Nimonic 75, Inconel 718, Ni 601	SEM-EDS, EPMA, XRD, gravimetry	86
$Na_2SO_4 + 60\% V_2O_5 (+CeO_2)$	Incoloy 800H, KC20WN/L 605, Nimonic 75	SEM-EDS, EPMA, XRD, gravimetry	87
LiCI-LiO ₂	Inconel 713LC, Nimonic 80A and Nimonic 90	SEM-EDS, XRD, gravimetry	93
=	•	SEM-EDS, XRD, gravimetry SEM-EDS, XRD, gravimetry	93 94
LiCl-LiO ₂	Inconel 713LC, N2, N3 Ni based alloys	SEM EDC VDD gravimating	
	Inconel 713LC, N101, N102 (modified 713LC)	SEM-EDS, XRD, gravimetry	95
		CENTEDS AND	
LiCl-LiO ₂	N07263, N06600, and N06625 superalloys	SEM-EDS, XRD, gravimetry	96
LiCI-LiO ₂	N07263, N06600, and N06625 superalloys N06230, N07263, N06625 superalloys	SEM-EDS, XRD, gravimetry	97
LiCl-LiO ₂	N07263, N06600, and N06625 superalloys		



Molten Salt Environment	Materials	Procedures	Reference
(Li0.62K0.38) ₂ CO ₃	Ni based Alloys	Electrical resistance, SEM-EDS	100
(Li,K) ₂ CO ₃ (eut)	NiO impregnated with 0.5–3 wt.% Dy 650 °C in $60\% \text{ CO}_2$ – $40\% \text{ O}_2$	dynamic polarization, XRD, XPS	101
(Li0.62K0.38) ₂ CO ₃	$Ni_3AI + 1$, 3 and 5 wt.% Li	electrochemical techniques, SEM-EDX, XRD	102
Li ₂ CO ₃ /Na ₂ CO ₃ (eut) + BaCO ₃ , CaCO ₃ , MgO (0–10mol %)	SS 316L	electrochemical techniques, SEM-EDX, XRD	103
(Li0.62K0.38) ₂ CO ₃	SS 310S	EIS, SEM-EDX	104
carbonate Li/K and Li/Na electrolytes	SS 316L and 310S	electrochemical techniques, gravimetry	105
PbSO ₄ –Pb ₃ O ₄ –PbCl ₂ –Fe ₂ O ₃ –ZnO	Inconel 625	XRD, SEM/EDX, ICP/AAS, OCP, potentiodynamic polarization, EIS, gravimetry	107
$PbSO_4-Pb_3O_4-PbCl_2-ZnO + 10 \text{ wt.}\% \text{ CdO}$	Inconel 626	XRD, SEM/EDX, ICP/AAS, OCP, potentiodynamic polarization, EIS	108
47 PbSO ₄ -23 ZnO-13 Pb ₃ O ₄ -10 CdO-7 PbCl ₂	Inconel 627	SEM/EDX, XRD, DTA, ICP/AAS, elektrochemical methods, gravimetry	109
Na ₂ MoO ₄ -MoO ₃ and mixed molybdates	SS 304L	SEM-EDX, XRD, ICP	110
NaCl	Fe, Cr, Ni-based alloys (wt.% 70–20–30, 10–50–40, 8.86–16.06–75.08)	SEM-EDS, EPMA, XRD	111