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Review paper

ISSN 0351-9465, E-ISSN 2466-2585

<https://doi.org/10.62638/ZasMat1128>



Zastita Materijala 65 (2)

202 - 212 (2024)

## Overview of corrosion behaviour of ceramic materials in molten salt environments

### ABSTRACT

*This study reviewed previous studies between the years 2015 and 2021 on how ceramic materials degraded in the presence of molten salt environments. The processes of corrosion resistance of various ceramic compositions subjected to various molten salt compositions and temperatures were also scrutinized. The results offer important new insights into the variables affecting ceramics' corrosion behaviour and the production of corrosion products. The reported result reveals that the ceramic material with the composition  $(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$  performed better than that of  $Sm_2Zr_2O_7$  in terms of hot corrosion resistance in molten salt ( $V_2O_5 + Na_2SO_4$ ). It has also been reported that corrosion behaviour is influenced by particle size. Notably, zirconia (n-YSZ) with nanoscale grain sizes was more susceptible to hot corrosion, which was explained by increased specific surface areas. On the other hand, sintering and additives have been found to enhance corrosion resistance. The  $Y-Y_2Si_2O_7$  ceramic's resistance to corrosion in ( $V_2O_5 + Na_2SO_4$ ) molten salt was enhanced by the addition of alumina. The results of these investigations help us understand how corrosion works and what influences ceramic materials' susceptibility to deterioration in molten salt environment. This information can direct the development of more corrosive-resistant ceramic materials for use in high-temperature environments or molten salt-based energy systems, among other corrosive uses.*

**Keywords:** hot corrosion, alumina, heat exchangers, nitrides, zirconia

### 1. INTRODUCTION

A process called "hot corrosion" occurs when molten salts attack a material's surface at the same time that they interact with the oxide layer that has formed there, often at a high temperature [1]. Hot corrosion is typically considered an accelerated deteriorating process that involves the deposition of corrosive species (like sulphates) from the environment (like combustion gas) to the surface of hot components, followed by the subsequent disintegration of the protective oxide scale [2]. Consequently, corrosive species are created that can enter the material and cause a variety of degradation processes, such as oxide spalling, grain boundary assault, and material embrittlement. Hot corrosion may dramatically lower a material's mechanical strength and lifespan, impairing the functionality and dependability of crucial parts [3].

In general, the menace of corrosion refers to the degradation of materials occasioned by electrochemical or chemical reactions. Unlike ceramics, metals tend to degrade in acidic environments and previous studies have shown that the corrosion of metals can be deterred in various acidic media using different plant extracts and pastes [4–13]. When exposed to acidic conditions, ceramics display improved corrosion resistance in comparison with metals [14]. In places where ceramics are used, such as heat engines and heat exchangers, molten salt deposits are significant corrodents and it has been reported that the  $Na_2SO_4$ -induced corrosion can be quite serious [15].

Ceramics, including structural ceramics, are renowned for having extraordinary qualities including resistance to chemical reactivity, wear, and high temperature [16]. In the commercial world, these ceramics are utilized in a wide range of products, including gas turbine components, welding nozzles, heat exchangers, heat pipes, valves, cutting tools, turbochargers, crucibles, dental work, bone, and joint replacement prostheses [17]. In addition, these promising

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Paper received: 08. 08. 2023.

Paper accepted: 22. 09. 2023.

Paper is available on the website: [www.idk.org.rs/journal](http://www.idk.org.rs/journal)

qualities make ceramics desirable for a wide range of applications, including heat barrier coatings, refractories, and catalytic supports [18]. However, the hot corrosive behaviour of ceramics in hostile conditions, such as molten salts, might restrict their performance and durability [19]. Designing and creating ceramic materials with better resistance to corrosive conditions, therefore, requires an understanding of the ability to characterize the hot corrosion behaviour of ceramics [20].

The extremely corrosive conditions of molten salts may seriously degrade materials [21]. They are made up of a combination of cations and anions, which can react with ceramic surfaces to cause corrosion [22]. Temperature, composition, and the presence of impurities are all factors that affect the corrosive attack in molten salts [23]. Various corrosive species, including chlorides, sulphates, and fluorides, can be introduced into the molten salt environment and speed up the deterioration of ceramics [24]. Further enhancing the corrosive assault may be the presence of impurities or strong gases.

Over a few decades, studies were done on hot corrosion of  $\text{Na}_2\text{SO}_4$ -coated  $\text{Ti}_3\text{AlC}_2$  in the air at 700–1000 °C [25]. No protective scales were reportedly seen, which led to significant hot corrosion of  $\text{Ti}_3\text{AlC}_2$  by fused  $\text{Na}_2\text{SO}_4$  at 900 and 1000 °C. The hot corrosion attack was minimal below the melting point of  $\text{Na}_2\text{SO}_4$ , whereas  $\text{Ti}_3\text{AlC}_2$  experienced a strong hot corrosion attack from fused sodium sulphate above the melting point of  $\text{Na}_2\text{SO}_4$ . Another study examined the hot corrosion of  $\text{Na}_2\text{SO}_4$ -coated and  $\text{Ti}_3\text{SiC}_2$ -based ceramics at 900 and 1000 °C in air [26]. According to reports, the  $\text{Ti}_3\text{SiC}_2$  ceramics covered with roughly 2 mg/cm<sup>2</sup>  $\text{Na}_2\text{SO}_4$  experienced substantial damage.

Research has been conducted on the hot corrosion process of composite Alumina/Yttria-stabilized zirconia coating in molten sulphate-vanadate salt [27]. Results demonstrate that when the salt's  $\text{V}_2\text{O}_5$  level was less than around 5 wt%, the  $\text{Al}_2\text{O}_3$  overlay served as a barrier to prevent the molten salt from penetrating the YSZ coating. Due to this,  $\text{ZrO}_2$  instability was greatly mitigated [27]. The hot corrosion behaviour of  $\text{Ti}_3\text{SiC}_2$  in the combination of  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  melts has been investigated [28]. When the concentration of  $\text{Na}_2\text{SO}_4$  was more than 35 wt% at 850 °C, they reported that the  $\text{Ti}_3\text{SiC}_2$  had a significant hot corrosion attack. There were some radial and transverse fissures in the outer and inner layers of the corrosion layer, which exhibited a duplex microstructure. Xie et al. [29] investigated the hot corrosion behaviour of double-ceramic-layer  $\text{LaTi}_2\text{Al}_9\text{O}_{19}$  and yttria-stabilized zirconia thermal

barrier coatings. They reported that the bond coat in the  $\text{LaTi}_2\text{Al}_9\text{O}_{19}$ /yttria-stabilized zirconia thermal barrier coatings significantly contributed to protecting the component against hot corrosion. In addition, the ceramic material,  $\text{LaTi}_2\text{Al}_9\text{O}_{19}$ /yttria-stabilized zirconia was found to show good chemical stability in molten salts of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ . The disintegration of  $\text{LaTi}_2\text{Al}_9\text{O}_{19}$  did not occur even after 1458 hot corrosion cycles at 1373 K, indicating high chemical stability in molten salt of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ , according to further observation [29]. The reason for this behaviour was attributed to the outstanding high-temperature performance and limited heat conductivity of the ceramic material ( $\text{LaTi}_2\text{Al}_9\text{O}_{19}$ ).

The main objectives of this current study are to:

- 1. Review previous studies on the behaviour of ceramic materials in molten salt environments from 2015 to 2021, to better understand how they degrade and how well they can resist corrosion.
- 2. Identify and examine the variables, such as ceramic material composition, particle size, sintering methods, and salt composition, that affect the corrosion behaviour of ceramics in molten salt, and to
- 3. Identify knowledge gaps and potential directions for additional study in the hot corrosion behaviour of ceramics.

## 2. BEHAVIOUR OF CERAMICS IN MOLTEN SALTS

### 2.1. Ceramics attacked by molten salts – Nitrides and carbides

When different molten salts are present, the typically protective layer of  $\text{SiO}_2$  that develops on  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$  can show accelerated corrosion. According to earlier research [30], an acid salt solution did not cause the protective layer to erode. Active corrosion was caused by the production of  $\text{SiO}$  gas at low oxygen pressures. It has been demonstrated that a key factor in the behaviour of molten sodium salts is the activity of  $\text{Na}_2\text{O}$ . The possible reactivity with silica increases as this activity rises [30]. Lin et al. [31] studied the 850–1000 °C hot corrosion behaviour of  $\text{Na}_2\text{SO}_4$ -coated  $\text{Ti}_2\text{AlC}$  in air. Below the melting point of  $\text{Na}_2\text{SO}_4$ , a protective  $\text{Al}_2\text{O}_3$  scale was discovered to slow down further corrosion of the  $\text{Ti}_2\text{AlC}$  substrate. The hot corrosion kinetics were found to be parabolic. Because porous and non-protective scales failed to shield the  $\text{Ti}_2\text{AlC}$  substrate from hot corrosion assaults, severe hot corrosion attacks on  $\text{Ti}_2\text{AlC}$  were reported to occur at 900 and 1000 °C. Notably, it was observed that sulphur separated at the scale/substrate interfaces and chemical

interactions between  $Ti_2AlC$  and the  $Na_2SO_4$  salt dominated the corrosion process. The hot corrosion resistance of  $Ti_2AlC$  can be improved by limiting the penetration of  $Na_2SO_4$  to the  $Ti_2AlC$  substrate, and this was suggested as a practical and effective pre-oxidation treatment [31].

## 2.2. Ceramics' Hot Corrosion Mechanisms

Studies have shown that hot corrosion in ceramics involves several intricate processes that accelerate material deterioration, especially in the presence of sulphate-related salts [32]. On the other hand, yttria-stabilized zirconia's  $LZ_7C_3$  coating was discovered to be flawless and degrading very little [33]. However, certain ceramics have been reported to exhibit relatively low corrosion when exposed to molten  $NaCl-KCl-MgCl_2$  [34]. Designing solutions to reduce hot corrosion and increase the longevity of ceramic components in corrosive environments requires an understanding of the mechanisms behind the hot corrosion of ceramics.

### 2.2.1. Degradation owing to chemical processes

One of the main processes causing hot corrosion in ceramics is degradation owing to chemical processes. The ceramic surface may react with molten salts, producing soluble reaction products. The protective oxide layer on the ceramic surface may be removed by these reaction products, exposing the underlying material to more corrosion. The reactivity of the molten salt, the makeup of the ceramic material, and the system temperature all have an impact on the chemical assault process. A study to understand the hot corrosion deterrence of YSZ,  $Gd_2Zr_2O_7$ , and  $Gd_2Zr_2O_7 + YSZ$  composite thermal barrier coatings in  $Na_2SO_4 + V_2O_5$  at  $1050\text{ }^\circ\text{C}$  has been conducted [35]. In heated corrosion testing, the authors observed that a series of linked chemical processes might be classified as the chemical degradation of common YSZ coatings. Additionally, it was discovered that  $NaVO_3$  would occur when  $V_2O_5$  and  $Na_2SO_4$  salt combination were exposed to high heat ( $1050\text{ }^\circ\text{C}$ ).

### 2.2.2. Degradation because of diffusion-controlled processes

Concentration gradients cause the transport of corrosive substances into the ceramic in the diffusion-controlled process of hot corrosion. Corrosive species infiltrate into the ceramic from the surrounding environment, and as they do so, their concentration rises. Temperature, concentration gradients, and material characteristics, such as diffusion coefficients, all affect the diffusion process. Costa-Oliveira and Baxter [36] investigated how salt corrosion affected a hot-pressed silicon nitride in combustion circumstances with various sulphur concentrations. It was reported that

depending on their concentration in the gas phase, pollutants including the salts,  $NaCl$  and  $Na_2SO_4$  frequently found in gas turbine atmospheres were expected to accelerate the corrosion of  $Si_3N_4$  due to their absorption into the scale. This was clarified by assuming that corrosion in sodium-containing environments happened via an ionic diffusion process [36].

Corrosive species can react with the ceramic's components once they get within the material; for instance, if sulphur is present, it may interact with the metal ions in the ceramic lattice to generate sulphides. The creation of new phases like oxides, sulphides, or halides because of the interaction between corrosive species and ceramic elements might harm the material's characteristics. The porosity, grain boundaries, and flaws of the ceramic material can all have an impact on how easily corrosive species diffuse inside it. Corrosive species can enter through porous materials, which speeds up their transportation. They can operate as preferred diffusion channels for the ceramic material's grain boundaries, which are the interfaces between different ceramic grains. Cracks and gaps in materials can act as entrance routes for corrosive species, hastening the deterioration process. Electrochemical techniques have been used to assess the corrosion effect of zirconia addition at 1, 2, and 5 atomic percents (at.%) on the hot corrosion behaviour of  $Mo_3Si$  intermetallic alloy in 60 weight per cent  $NaNO_3$  and 40 weight per cent  $KNO_3$  at  $600\text{ }^\circ\text{C}$  [37]. For the as-cast alloy or when 1 or 2 wt.% Zr was added, and the corrosion process was controlled by charge transfer, but when 5 wt.% Zr was added, and it was controlled by diffusion [37].

### 2.2.3. Degradation by electrochemistry

Electrochemical reactions may occur at the ceramic surface because of molten salts acting as electrolytes. As a result of these interactions, corrosive species are formed by the transfer of ions between the ceramic material and the corrosive environment. The presence of electrochemically active species in the molten salt, the electrical conductivity of the ceramic and the temperature all have an impact on the electrochemical attack process. Li et al. [38] used a molar ratio of 1:1 to study the hot corrosion behaviour of  $Yb_2Zr_2O_7$  ceramic against  $V_2O_5$  and  $Na_2SO_4 + V_2O_5$  at temperatures of  $900-1100\text{ }^\circ\text{C}$  for 2 hours in the air. They noticed that the  $YbVO_4$ , which resulted from the hot corrosion of  $Yb_2Zr_2O_7$  coated in  $V_2O_5$ , was particle-shaped as opposed to rod-like in the  $Yb_2Zr_2O_7$  coated in  $(Na_2SO_4 + V_2O_5)$ . A dissolution-precipitation process-based model was put up to discover how hot corrosion products developed. The model could be used to explain the hot corrosion mechanism. It showed that the larger

driving force in the hot corrosion of  $V_2O_5$ -coated  $Yb_2Zr_2O_7$  contributed to the granular  $YbVO_4$  whilst the relatively smaller driving force in the hot corrosion of  $(Na_2SO_4 + V_2O_5)$ -coated  $Yb_2Zr_2O_7$  resulted in the rod-like  $YbVO_4$  [38].

### 3. OVERVIEW OF PREVIOUS STUDIES ON HOT CORROSION BEHAVIOUR OF CERAMICS IN MOLTEN SALT

The summary of the overview of earlier studies on the corrosion behaviour of ceramic materials in molten salts is presented in Table 1. Many scholars have worked on several aspects of the area to arrive at different conclusions. Guo et al. [39]

studied the degradation disposition of some ceramic materials  $(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$  and  $Sm_2Zr_2O_7$  in the presence of molten salt ( $V_2O_5 + Na_2SO_4$ ). They reported that the ceramic material with the composition  $Sm_2Zr_2O_7$  was outperformed by the ceramic with the composition  $(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$  in terms of hot corrosion resistance to  $(V_2O_5 + Na_2SO_4)$  50 wt.% salt. In another study [40], the thermal barrier oxides with stabilized  $ZrO_2$  doped with  $Gd_2O_3$  and  $Yb_2O_3$  were investigated to unravel their corrosion behaviour in  $V_2O_5 + Na_2SO_4$  molten salt. It was observed that the YSZ ceramic material was more susceptible to corrosion in molten salt than GdYb-YSZ ceramic [40].

Table 1. An Overview of previous studies on hot corrosion behaviour of ceramics in molten salts

Tabela 1. Pregled prethodnih studija o ponašanju keramike u toploj koroziji u rastopljenim solima

Ceramic materials	Molten salt composition	Temperature range of study and maximum period of exposure	What to deduce from the study	Ref.
$(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$ & $Sm_2Zr_2O_7$	50 wt.% $V_2O_5$ & 50 wt.% $Na_2SO_4$	700-900 °C/4 h	Compared to $Sm_2Zr_2O_7$ , $(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$ exhibited greater corrosion resistance to $Na_2SO_4+V_2O_5$ salt.	[39]
Thermal barrier oxides with stabilized $ZrO_2$ doped with $Gd_2O_3$ and $Yb_2O_3$	$Gd_2O_3$ (1 mol%) + $Yb_2O_3$ (1 mol%) doped with $Y_2O_3$ (3.5 mol%) stabilized $ZrO_2$ (GdYb-YSZ)	700-1000 °C / 4 h	Despite being vulnerable to molten salt attack, GdYb-YSZ demonstrated greater hot corrosion resistance than YSZ.	[40]
Zirconia with nanostructures	$NaVO_3$	700 °C/24–192 h	The YSZ-based thermal barrier coatings' hot corrosion deterioration was significantly accelerated by microcracks and open holes in the coatings.	[41]
Zirconia stabilized – yttria	$(Na_2SO_4 + V_2O_5)$ 50 wt.%	1000 °C / 4 h	The columnar holes that EB-PVD created contributed to the structure's degeneration brought on by the molten salts that seeped from the top layer, speeding up the rate of destruction.	[42]
Magnesia (Stabilized)	Lithium ( $Li_2O$ & $LiCl$ )	300 – 650 °C/ 360 h	The introduction of lithium gave rise to the initiation of sudden cracks and pores.	[43]
$Y-Y_2Si_2O_7$	$V_2O_5$ & $Na_2SO_4$	20 h	The sample of the ceramic ( $Y-Y_2Si_2O_7$ ) bearing alumina additive was reported to give outstanding resistance to corrosion in the presence of molten salt.	[44]
$(Gd_{0.9}Sc_{0.5})_2Zr_2O_7$	$VO_5$	700°C-1000°C/4h	At varying temperatures between 700-1000°C, the ceramic material $(Gd_{0.9}Sc_{0.5})_2Zr_2O_7$ displayed a potential corrosion resistance coating inhibitor.	[45]
$BaLa_2Ti_3O_{10}$	$V_2O_5, Na_2SO_4+V_2O_5$	900°C/4h	The ceramic material $(BaLa_2Ti_3O_{10})$ having reacted with $V_2O_5$ and $Na_2SO_4+V_2O_5$ appeared to have suitable corrosion resistance in $V_2O_5$ compared to $Na_2SO_4+V_2O_5$ .	[46]

Yb <sub>2</sub> O <sub>3</sub> -Gd <sub>2</sub> O <sub>3</sub> -Y <sub>2</sub> O <sub>3</sub>	CaCl <sub>2</sub> -CaF <sub>2</sub> -CaO	1500°C- 1600°C/11h	The ceramic material (Yb <sub>2</sub> O <sub>3</sub> -Gd <sub>2</sub> O <sub>3</sub> -Y <sub>2</sub> O <sub>3</sub> ) sintered at 1500°C for 6h and experienced the highest degradation compared to 1600°C sintered ceramic material (Yb <sub>2</sub> O <sub>3</sub> -Gd <sub>2</sub> O <sub>3</sub> -Y <sub>2</sub> O <sub>3</sub> ) for 11h	[47]
SrHfO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub> & V <sub>2</sub> O <sub>5</sub>	1600°C/10h	A thinner corrosion layer at a higher temperature was observed due to the quick formation of corrosion products (SrV <sub>2</sub> O <sub>6</sub> +m-H <sub>2</sub> O <sub>2(s)</sub> +Na <sub>2</sub> O) which increases as temperature increases.	[48]
LaTi <sub>2</sub> Al <sub>9</sub> O <sub>19</sub>	V <sub>2</sub> O <sub>5</sub>	700°C-950°C/10h	AlVO <sub>4</sub> production was the main reaction seen during a two-hour corrosion session at 700°C but was found to be unstable. It largely dissolved at 800 °C, forming Al <sub>2</sub> O <sub>3</sub> . This shows the dynamic character of the corrosion reactions as well as the propensity of some phases to transform or alter under certain circumstances.	[49]
AlN	LiF-LiCl-LiBr-Li	500°C/300h	High levels of metallic Li (>0.1 weight per cent) were reported to hasten the corrosion of AlN.	[50]
Ba <sub>1-x</sub> SxAx (x=0,0.25,0.5,0.75,1)	Na <sub>2</sub> SO <sub>4</sub>	900°C-1100°C	At elevated temperatures, there was an enhancement in the diffusion of Na into Ba <sub>1-x</sub> SxAx which increased the rate of corrosion significantly.	[51]
La <sub>2</sub> Hf <sub>2</sub> O <sub>7</sub>	Na <sub>2</sub> SO <sub>4</sub> +V <sub>2</sub> O <sub>5</sub> & Na <sub>2</sub> SO <sub>4</sub>	900°C-1200°C/4h	The performance of La <sub>2</sub> Hf <sub>2</sub> O <sub>7</sub> in reaction with Na <sub>2</sub> SO <sub>4</sub> +V <sub>2</sub> O <sub>5</sub> led to a decrease in the thickness of the corrosion product due to an increase in temperature as contact with V <sub>2</sub> O <sub>5</sub> was made.	[52]
Cr <sub>2</sub> AlC max & CoNiCrAlY	Na <sub>2</sub> SO <sub>4</sub> +V <sub>2</sub> O <sub>5</sub>	950°C/30h	It was reported that Cr <sub>2</sub> AlC Max has a better hot corrosion resistance than the CoNiCrAlY sample.	[53]
YSZ, Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> & YSZ/Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	Na <sub>2</sub> SO <sub>4</sub> and V <sub>2</sub> O <sub>5</sub>	1000°C/25h	Double coatings of YSZ/Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> were found to resist hot corrosion than those of single coatings	[54]
Zirconia	NaVO <sub>3</sub> & Na <sub>2</sub> SO <sub>4</sub>	1100°C/ 6h-24h	The formation of a large polyhedron crystal of YVO <sub>4</sub> and m-ZrO <sub>2</sub> as corrosion products was obtained after 6h-24h. Also, the volume fraction of ZrO <sub>2</sub> in 8YSZ ceramics was found to increase after the corrosion test.	[55]
Ba <sub>2</sub> REAl <sub>10</sub> S	Na <sub>2</sub> SO <sub>4</sub> +V <sub>2</sub> O <sub>5</sub>	900°C-1000°C/ 4h	The Lewis acid-base rule, thermodynamics, and phase diagrams were used as the foundation for the postulated hot corrosion mechanisms.	[56]
Yb <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	NaVO <sub>3</sub>	1000°C- 1500°C/2h	YbVO <sub>4</sub> was obtained on a bulk surface at 1000°C-1200°C owing to the acidity of the corrosion medium and a corrosion product (Yb <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ) was obtained.	[57]

Wang et al. [41] investigated how the particle size at the nanoscale can influence the corrosion of zirconia at 700°C in a NaVO<sub>3</sub> corrosive environment. They reported that the samples (n-

YSZ) powders having 30 nm grain sizes were vulnerable to hot corrosion. The reason was attributed to specific surface areas that were larger when compared to those of other specimens. In

another study, the hot corrosion of zirconia stabilized by yttria in ( $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ ) 50 wt.% molten salt at 1000 °C was undertaken [42]. To prevent edge effects, the corrosion salts were said to be applied to the specimen's surfaces at a concentration of 10 mg/cm<sup>2</sup>, about 1.5 mm away from the edge. It was reported that the interface between CoNiAlY bond (metallic) coating and YSZ ceramic coating existed thermally grown oxide layer including surface cracks.

Cho et al. [43] studied the corrosion of magnesia (stabilized) ceramic in molten salt. The molten salt is composed of lithium ( $\text{Li}_2\text{O}$  &  $\text{LiCl}$ ). They reported that although the degradation of the magnesia ceramic occurred at both cyclic and isothermal conditions, the introduction of lithium increased the rate of corrosion to approximately 5 times compared to the initial degradation rate. On the other hand, the impact of sintering on the degradation of  $\text{Y-Y}_2\text{Si}_2\text{O}_7$  ceramics in molten salt ( $\text{V}_2\text{O}_5$  &  $\text{Na}_2\text{SO}_4$ ) has been carried out [44]. The reaction of  $\text{Y-Y}_2\text{Si}_2\text{O}_7$  ceramic with the following additives: Al, Li, and Mg resulted in 2 mol.% of  $\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ , and  $\text{MgO}$ , producing three different samples. The ceramic ( $\text{Y-Y}_2\text{Si}_2\text{O}_7$ ) sample with the alumina addition was said to have exceptional corrosion resistance in the presence of molten salt [44]. Zhang et al. [45] identified the effect of molten salt ( $\text{V}_2\text{O}_5$ ) on ceramic material, bearing the composition,  $\text{Gd}_{0.9}\text{Sc}_{0.5}\text{Zr}_2\text{O}_7$ . They discovered that the corrosion product ( $\text{Sc}_2\text{O}_3$ ), obtained following the interaction between the ceramic material ( $\text{Gd}_{0.9}\text{Sc}_{0.5}\text{Zr}_2\text{O}_7$ ) and the molten salt ( $\text{V}_2\text{O}_5$ ) possessed an outstanding resistance to corrosion due to the molten salt.

Liu et al. [46] discovered the influence of molten salts ( $\text{Na}_2\text{SO}_4$ , and  $\text{V}_2\text{O}_5$ ) on the ceramic material ( $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ ). According to the results of this investigation,  $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$  ceramic, a potential candidate for Thermal Barrier Coating, exhibits greater resistance to  $\text{V}_2\text{O}_5$  salt corrosion despite having strong resistance to both salts. On the other hand, the effect of molten salt ( $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ ) on ceramic material ( $\text{Yb}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Y}_2\text{O}_3$ ) was carried out by Kim et al. [47]. They reported that the exposure time could act as a driving force for the penetration of the molten salt ( $\text{CaCl}_2\text{-CaF}_2\text{-CaO}$ ) which further shows a higher degradation rate of the sample ( $\text{Yb}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Y}_2\text{O}_3$ ) sintered at 120h compared to the sample sintered at approximately 6h-11h.

Gu et al. [48] studied the influence of molten salts ( $\text{Na}_2\text{SO}_4$ ,  $\text{V}_2\text{O}_5$  and the combination of  $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$  (in the molar proportion of 1:1) on the microstructure of the ceramic material ( $\text{SrHfO}_3$ ). A schematic illustration of what subsequently occurred and the nature of the corrosion product

can be found in Fig. 1. The authors reported that while the thickness of the corrosion scale increased in mixed molten salt, the thickness of the corrosion layer reduced as the temperature increased in contact with  $\text{V}_2\text{O}_5$  [48]. A thinner corrosion layer at a higher temperature was observed due to the quick formation of corrosion products ( $\text{SrV}_2\text{O}_6 + m\text{-HfO}_2(\text{s}) + \text{Na}_2\text{O}$ ) which increases as temperature increases.

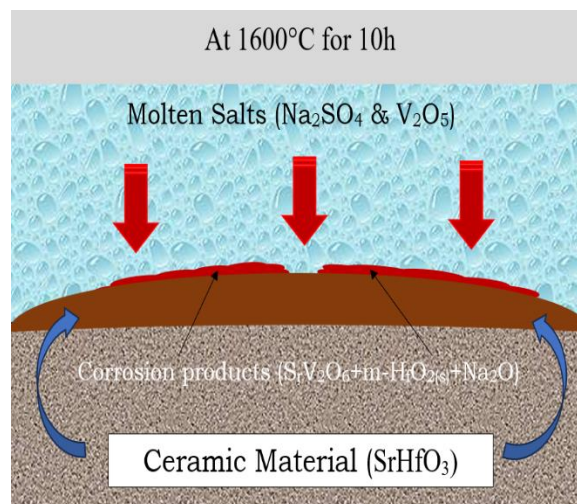


Figure 1. Formation of corrosion products ( $\text{SrV}_2\text{O}_6 + m\text{-HfO}_2(\text{s}) + \text{Na}_2\text{O}$ ) by the exposure of  $\text{SrHfO}_3$  in  $\text{Na}_2\text{SO}_4$  &  $\text{V}_2\text{O}_5$

Slika 1. Formiranje produkata korozije ( $\text{SrV}_2\text{O}_6 + m\text{-HfO}_2(\text{s}) + \text{Na}_2\text{O}$ ) izlaganjem  $\text{SrHfO}_3$  u  $\text{Na}_2\text{SO}_4$  i  $\text{V}_2\text{O}_5$

Evaluation of molten salt ( $\text{V}_2\text{O}_5$ ) on ceramic material ( $\text{LaTi}_2\text{Al}_9\text{O}_{19}$ ) has been carried out [49]. It was reported that the temperature and length of the corrosion process were found to dictate the nature of the corrosion products and microstructures of the  $\text{LaTi}_2\text{Al}_9\text{O}_{19}$  ceramic. Variable reactions and phase formations were produced by altering temperatures and periods. In another interesting study, the AlN ceramics' corrosion behaviour in 500 °C  $\text{LiF-LiCl-LiBr-Li}$  molten salt [50]. The researchers observed that high levels of metallic Li (>0.1 weight per cent) increased the corrosion of AlN. The interaction between Li and the YAG (yttrium aluminium garnet) found in AlN was reported to cause the observed accelerated corrosion. This implies that the existence of high Li concentrations encourages a corrosive environment, which damages AlN [50]. In a molten  $\text{Na}_2\text{SO}_4$  environment, Jiang et al. [51] investigated the hot corrosion behaviour of barium-strontium aluminosilicates. They reported that the diffusion reaction of the Ba/Sr and Na cations had an impact on the hot corrosion behaviour of  $\text{B}_{1-x}\text{S}_x\text{AS}$  compounds in a molten  $\text{Na}_2\text{SO}_4$  environment. This mechanism greatly aided the degradation process. Additionally, the order of cation migration during

hot corrosion was impacted by the difference in atomic radius between strontium (Sr) and barium (Ba). It was discovered that strontium cations diffused out of the  $B_{1-x}S_xAS$  structure before barium cations, suggesting that strontium should exit the structure first. A study to determine the performance of  $La_2Hf_2O_7$  ceramic when exposed to the molten salt (sulphate-vanadate) at  $900^\circ\text{C}$ - $1200^\circ\text{C}$  has been carried out [52]. They discovered nanoparticles (non-needle-like) were present and the corrosion rate was directly proportional to the increment in the temperature accompanied by  $LaVO_4$  crystalline grain growing noticeably. Furthermore, the thickness of the corroded layer was reported to increase with an increase in corrosion temperature. A study on the behaviour of the  $Cr_2AlC$  max compound in the presence of  $V_2O_5$  &  $Na_2SO_4$  molten salts has been carried out [53]. The researchers discovered that under the test circumstances, the  $Cr_2AlC$  MAX-phase samples demonstrated greater hot corrosion resistance than the  $CoNiCrAlY$  samples.

Ozgurluk et al. [54] experimented with the reaction of  $YSZ/Gd_2Zr_2O_7$  when exposed to vanadate salt ( $V_2O_5$ ) at  $1000^\circ\text{C}$ . They reported that after the conclusion of the experiment (25h) within 5h cycles at  $1000^\circ\text{C}$ , significant deterioration and spillage on the YSZ coatings was observed. On the other hand, a study on the effect of the presence of  $NaVO_3+Na_2SO_4$  on Zirconia ceramics at  $1100^\circ\text{C}$  has been conducted [55].

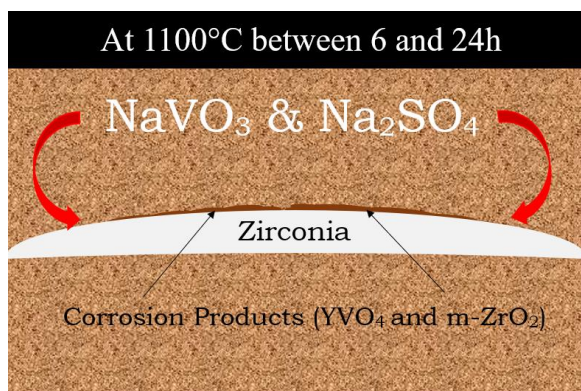


Figure 2. Effect of the presence of  $NaVO_3+Na_2SO_4$  on Zirconia ceramics at  $1100^\circ\text{C}$

Slika 2. Uticaj prisustva  $NaVO_3+Na_2SO_4$  na cirkonijum keramiku na  $1100^\circ\text{C}$

It was observed that  $Na_2SO_4$  was a promoting factor of chemical reactions which increased the rate of corrosion. The process yielded Yttrium orthovanadate ( $YVO_4$ ) and monoclinic zirconia dioxide ( $m\text{-ZrO}_2$ ) as the corrosion products. Another study to evaluate the hot corrosion mechanisms of  $Ba_2REAlO_5$  when exposed to  $Na_2SO_4+V_2O_5$  was successfully carried out [56].

According to the study,  $Ba_2REAlO_5$  formed a reaction layer with a thickness of around  $80\ \mu\text{m}$  after being exposed to a temperature of  $1000^\circ\text{C}$  for 4 hours. This implies that at this higher temperature, the material is more prone to corrosion. Finally, Zhang et al. [57] undertook a study to determine the behaviour of  $Yb_2Si_2O_7$  ceramics when exposed to molten salt ( $NaVO_3$ ) at  $1000^\circ\text{C}$ - $1500^\circ\text{C}$ . They observed that the reaction between  $Yb_2Si_2O_7$  and  $NaVO_3$  produced rod-shaped  $YbVO_4$  (ytterbium vanadate) grains at temperatures between  $1000$  and  $1200^\circ\text{C}$ . As the temperature increased,  $YbVO_4$  concentration fell until it vanished at  $1300^\circ\text{C}$ . The hot corrosion product,  $Yb_2SiO_5$  (ytterbium silicate), showed a polyhedral form at temperatures of  $1300^\circ\text{C}$  or higher. With an increase in temperature, the corrosion products contained more  $Yb_2SiO_5$ .

#### 4. CONCLUSION

From the present study on the overview of how ceramic materials behave when exposed to molten salt environments, the following conclusions may be drawn:

- The composition of ceramics has a big impact on corrosion resistance. In the presence of molten salt ( $V_2O_5 + Na_2SO_4$ ), studies have shown that the ceramic material  $(Sm_{0.5}Sc_{0.5})_2Zr_2O_7$  performed better than  $Sm_2Zr_2O_7$  in terms of hot corrosion resistance. This emphasizes how crucial it is to choose ceramic compositions carefully to increase corrosion resistance in particular situations.
- The size of the particles affects corrosion behaviour. In a  $NaVO_3$  corrosive environment, it was reported that zirconia ceramics with smaller particle sizes ( $30\ \text{nm}$  grain sizes) were more susceptible to heat corrosion. This shows that certain surface areas, affected by particle size, contribute to the susceptibility of ceramic materials to corrosion.
- Additives can improve corrosion resistance. Studies have shown that using alumina ( $Al_2O_3$ ) as an additive to  $Y\text{-}Y_2Si_2O_7$  ceramics produced remarkable resistance to corrosion in molten salt ( $V_2O_5$  &  $Na_2SO_4$ ). This suggests that adding carefully chosen additives might enhance the corrosion resistance of ceramic materials.
- The alumina layer has been found to exhibit resistance to corrosion. The identification of an alumina layer (corrosion product) with exceptional corrosion resistance in a variety of molten salt conditions raises the possibility that this layer may play a significant role in determining how quickly ceramic materials

corrode. An alumina layer can serve as a barrier of defence against further deterioration.

These findings show the intricate interactions between the composition of ceramic materials, particle size, additives, molten salt composition, and the production of protective corrosion products that affect how they react to corrosion and how resistant they are to it. The development of corrosion-resistant ceramics for specific applications requires an understanding of these aspects.

## 5. KNOWLEDGE GAPS AND POTENTIAL RESEARCH AREAS

Following the overview of the behaviour of ceramics during hot corrosion in a variety of molten salts, the following areas have been identified as knowledge gaps. Additionally, some recommendations for possible future study areas have been made:

- Although the reviewed papers investigated the hot corrosion behaviour of several ceramics in molten salts, they did not go into detail about the precise corrosion mechanisms at play. It would be beneficial to comprehend the exact mechanisms by which corrosion occurs in various ceramic materials to help produce corrosion-resistant coatings or materials.
- The reviewed papers included the maximum exposure time for each investigation; however, they gave no details on how long the ceramic materials will last in hot corrosion environments. To determine if ceramics are suitable for use in practical applications, it would be crucial to look at the stability and degradation of ceramics, especially in the presence of sulphate-based molten salts over long periods.
- The reviewed studies discussed several ceramic compositions and how resistant they were to heat corrosion. The tuning of composition characteristics, such as dopants, additives, or material processing strategies to improve corrosion resistance, was not covered, nevertheless. Additional investigation is required to determine the composition's effect on hot corrosion behaviour and the best compositions for various applications.
- The major emphasis of many of the reviewed studies was on the temperature and the composition of molten salts as the main determinants of hot corrosion behaviour. The corrosion process, however, can also be impacted by other environmental variables such as gas atmospheres, contaminants, and thermal cycling. A deeper knowledge of the hot corrosion behaviour of ceramics would result

from examining the combined influence of these elements.

- The reviewed studies largely involved qualitative analyses of hot corrosion behaviour, concentrating on the relative resistance or susceptibility of various ceramics. To evaluate the performance of ceramics under hot corrosion circumstances, quantitative measurements of corrosion rates, mass loss, or other degradation characteristics would offer more accurate and comparable information.

It would be easier to create better corrosion-resistant materials if these information gaps were filled, which would lead to a better understanding of hot corrosion behaviour in ceramics.

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## IZVOD

### PREGLED KOROZIONOG PONAŠANJA KERAMIČKIH MATERIJALA U OKRUŽENJIMA RASTOPLJENE SOLI

Ova studija je pregledala prethodne studije između 2015. i 2021. o tome kako su keramički materijali degradirali u prisustvu rastopljene soli. Takođe, ispitani su procesi otpornosti na koroziju različitih keramičkih kompozicija izloženih različitim sastavima rastopljene soli i temperaturama. Rezultati nude važne nove uvide u varijable koje utiču na koroziono ponašanje keramike i proizvodnju proizvoda korozije. Prijavljeni rezultat otkriva da je keramički materijal sastava (Sm<sub>0.5</sub>Sc<sub>0.5</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> imao bolji učinak od Sm<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> u pogledu otpornosti na toplu koroziju u rastopljenoj soli (V<sub>2</sub>O<sub>5</sub> + Na<sub>2</sub>SO<sub>4</sub>). Takođe, prijavljeno je da na ponašanje korozije utiče veličina čestica. Značajno je da je cirkonijum (n-ISZ) sa veličinom zrna na nanoskali bio podložniji vrućoj koroziji, što se objašnjava povećanim specifičnim površinama. S druge strane, utvrđeno je da sinterovanje i aditivi povećavaju otpornost na koroziju. Otpornost I-I<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> keramike na koroziju u (V<sub>2</sub>O<sub>5</sub> + Na<sub>2</sub>SO<sub>4</sub>) rastopljenoj soli je poboljšana dodatkom glinice. Rezultati ovih istraživanja pomažu nam da razumemo kako korozija funkcioniše i šta utiče na podložnost keramičkih materijala propadanju u rastopljenim slanim medijima. Ove informacije mogu da usmere stvaranje keramičkih materijala otpornijih na koroziju za upotrebu u okruženjima sa visokim temperaturama ili energetskim sistemima na bazi rastopljene soli, između ostalih korozivnih upotreba.

**Ključne reči:** vruća korozija, glinica, izmenjivači toplote, nitridi, cirkonijum

*Pregledni rad*

*Rad primljen:* 08.08.2023.

*Rad prihvaćen:* 22.09.2023.

*Rad je dostupan na sajtu:* [www.idk.org.rs/casopis](http://www.idk.org.rs/casopis)