Compatibility of SiC- and MAX phase-based ceramics with a KNO₃-NaNO₃ molten solar salt

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Keywords: molten salt corrosion, concentrated solar power, SiC, MAX phases

Abstract

In this work, several ceramic materials were exposed together with two reference structural materials (i.e., 316L stainless steel and Inconel 600) to a molten solar salt (40 wt% KNO₃ and 60 wt% NaNO₃) for 1000 h at 600°C to investigate the compatibility for their use in concentrated solar power (CSP) applications. The exposed ceramics included different SiC grades (solid state-sintered, liquid phase-sintered, and silicon-infiltrated) and MAX phase-based materials (Maxthal® 211 & 312 (nominally, Ti₂AlC & Ti₃SiC₂, respectively), Cr₂AlC, Nb₄AlC₃, (Nb,Zr)₄AlC₃, and a cermet comprising 40 vol% Fe and 60 vol% (Nb,Zr)₄AlC₃). All SiC grades were chemically stable in the molten salt, whereas all Nb-containing MAX phase ceramics were severely oxidized. Comparing the two Maxthal® grades showed that the 312 was chemically more stable than the 211, and both grades formed a Na-based oxide scale. Interestingly, Cr₂AlC showed practically no interaction with the molten salt during the performed exposure and formed a submicrometer stable Cr₃C₇ layer. Hence, it may be considered as promising structural (coating) material candidate for the targeted CSP application.

1 Introduction

Solar radiation is one of the most important sources of sustainable energy production and is, therefore, of great importance for society. Concentrated solar power (CSP) technologies exploit this natural energy source and convert the heat of the sun into electric power. Mirrors are used to focus the solar radiation on a heat transfer fluid (HTF) and heating it up [1]. The HTF transfers the heat to a heat exchanger, converting water into steam and producing electricity by means of a power generator [2]. For smaller scale applications with lower electricity requirements, lower temperature parabolic trough concentrators using organic Rankine cycles is more optimal [3], where organic compounds are used instead of water. More recent technologies make use of supercritical CO₂ Brayton power cycles for the electricity conversion [4]. One of the additional advantages of CSP is the ability to store thermal energy and use it for electricity production when no sunlight is available [1]. A key factor in the whole thermal energy storage process is the correct choice of HTF [5].

The basic HTF property requirements combine a high specific heat capacity for efficient storage and transport with a low viscosity [1]. Very common HTFs are mineral or synthetic oils. However, to expand the service temperature range, molten salts are considered, since they have higher degradation temperatures than oils [6]. Salt mixtures are typically used, mainly nitrates mixed

with nitrites. The most popular nitrate-based salt is a mixture made of 60 wt% NaNO_3 and 40 wt% KNO_3 , also known as ‘solar salt’, while other commonly used salts are Hitec® and Hitec XL® [1,7].

Despite their appealing properties, the use of molten salts in CSP systems has certain drawbacks, the most important of which is the degradation of structural materials in contact with these corrosive fluids. Therefore, the selection of suitable structural materials for the HTF tubing and storage tanks is of major practical importance. Steels would be a straightforward option, as they are commonly used in the chemical and energy industry. A prior investigation by Soleimani Dorcheh et al. [8] reported that low-chromium ferritic steels are prone to corrosion at a temperature of 600°C, but stainless steels (AISI 316 and 347) are better candidates, although they might suffer from sensitization. The need for materials that are compatible with molten solar salts leads to the consideration of ceramic materials, such as silicon carbide (SiC) and ternary carbides (MAX phases).

In general, SiC is known for its chemical stability in Na-containing salt environments (Na_2SO_4 , Na_2CO_3 , NaNO_3 and Na_2S) [9] and high thermal conductivity. In oxidative environments, it forms a Si-based oxide scale that can be protective [10]. Depending on the temperature and the system’s oxygen partial pressure, SiC either forms solid SiO_2 upon its passive oxidation or volatile SiO upon its active oxidation [11]. Ternary nanolaminated carbides belonging to the family of the MAX phases are also proposed as solar receiver materials in CSP systems, due to their high-temperature stability [7]. The MAX phases are a family of ternary carbides and nitrides that combine properties characteristic of metals with properties characteristic of ceramics. M is an early transition metal, A is a group A element and X is either C or N. The MAX phases have a layered crystal structure, where M_6X layers alternate with an A-element layer [12,13]. It is known that members of the MAX phase family perform well in contact with corrosive heavy liquid metals, such as lead (Pb) and lead-bismuth eutectic (LBE) [14]. Heinzel et al. investigated Ti_2AlC [15] and Ti_3SiC_2 [16], reporting that Ti_3SiC_2 remained stable at least up to 750°C for 10000 h in contact with coolants (Pb, LBE) intended for heavy liquid metal-cooled nuclear systems, whereas the Ti_2AlC material suffered from dissolution attack and was less stable due to the secondary phases present and the high solubility of Al in LBE.

In this work, screening exposures of several SiC and MAX phase ceramic material grades to molten solar salt were performed in order to assess their potential as structural materials for CSP applications. Common structural materials, i.e., the AISI 316L austenitic stainless steel and the Inconel 600 Ni-based alloy, were tested as reference materials. Three SiC grades were tested, along with six MAX phase-based materials.

The testing temperature was chosen as 600°C. However, it should be mentioned that the molten salt mixture becomes unstable around 580°C, where it starts to degrade by forming nitrites, according to the following reactions [17–19]:

These reactions produce molecular oxygen influencing the actual available oxygen in the melt, since the solubility limit in nitrites will be different [17–19]. These reactions should be taken into account when discussing the interaction behaviour of the materials with the salt. The formation of the nitrites at the temperature of 600°C, above the salt stability limit, might have influenced the corrosion.

2 Materials and Methods

2.1 Materials synthesis

The materials tested in this work were either commercially available or synthesized in the lab via a powder metallurgical route. Inconel 600 (Flowell International) and AISI 316L (ArcelorMittal) were used as reference materials. The processing parameters for the ceramic grades fabricated in the lab are summarized in Table 2.

Three types of SiC were investigated, i.e., a solid state-sintered (SS SiC), a liquid phase-assisted sintered (LP SiC) and a silicon-infiltrated SiC (SiSiC). The SS and LP SiC grades were produced by spark plasma sintering (SPS, HP D25, FCT Systeme). For the LP SiC, Al_2O_3 and Y_2O_3 were added in an $\text{Al}_2\text{O}_3:\text{Y}_2\text{O}_3$ molar ratio of 5:2. In total, 10.8 wt% Al_2O_3 and 9.6 wt% Y_2O_3 were added to the SiC grade. The SiSiC was 3D-printed and Si-infiltrated, as described in detail elsewhere [20]. More information on the used starting powders and the sintering conditions is provided in Table 2.

The commercially available MAX phase ceramics, i.e., Maxthal® 312 (nominally 90 wt% Ti_3SiC_2 , 10 wt% TiC) and Maxthal® 211 (nominally 55 wt% Ti_2AlC , 38 wt% Ti_3AlC_2 , 7 wt% TiAl_3), were supplied by Kanthal AB, Sweden. The Cr_2AlC , Nb_4AlC_3 and $(\text{Nb,Zr})_4\text{AlC}_3$ were produced by reactive hot pressing (HP). The Nb-based materials, Nb_4AlC_3 and $(\text{Nb,Zr})_4\text{AlC}_3$ were hot pressed at 1700°C for 30 min; more details are provided elsewhere [21]. Cr_2AlC was produced by reactive hot pressing from a mixture of Cr, Al and C powders at 1300°C. Moreover, a MAX phase-based cermet with 60 vol% $(\text{Nb,Zr})_4\text{AlC}_3$ and 40 vol% of a Fe metallic binder was densified in a hot isostatic press (HIP) at 950°C and 200 MPa, for 1 h. The fabrication of a cermet aimed at further increasing the fracture toughness ($K_{\text{IC}} \approx 10.1 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$ [16]) of the $(\text{Nb,Zr})_4\text{AlC}_3$ MAX phase by combining it with a more ductile (metallic) constituent to make a novel, corrosion-resistant composite structural material.

Table 1. Summary of the processing parameters used to produce the ceramics tested in this work.

Sample (Abbreviation)	Phase	Additive	Raw powders	Sintering technique	Sintering temperature (°C)	Sintering pressure (MPa)	Sintering time (min)
Solid state SiC (SS SiC)	β -SiC	B ₄ C	Superior graphite HSC-059s	SPS	1900	50	5
Liquid phase SiC (LP SiC)	α -SiC	- Y ₂ O ₃ Al ₂ O ₃	H.C. Starck UF 25 AEE YT-603 Baikowski SM8	SPS	1750	50	5
Nb ₄ AlC ₃	Nb Al C		CBMM AEE Al-100 Asbury –Micro 250	HP	1700	30	30
(Nb,Zr) ₄ AlC ₃	Nb ZrH ₂ Al C		CBMM Chemetall AEE Al-100 Asbury – Micro 250	HP	1700	30	30
Cr ₂ AlC	Cr Al C		US Research nanomaterials AEE Al-100 Asbury – Micro 250	HP	1300	30	30
Cermet	Fe Nb ZrH ₂ Al C		BASF Carbonyl CBMM Chemetall AEE Al-100 Asbury – Micro 250	HIP	950	200	60

2.2 The molten salt experiment

Samples of size $10 \times 10 \times 5 \text{ mm}^3$ were ground (cloth: MD Allegro, Struers, $\varnothing = 250 \text{ mm}$) on all sides and one side was polished (cloth: 2TS3, TouchLam, $\varnothing = 300 \text{ mm}$), first with a $3 \text{ }\mu\text{m}$ and then a $1 \text{ }\mu\text{m}$ diamond suspension, to be used as a reference for assessing the extend of interaction without interference of the surface roughness of the materials. As a final step, a colloidal silica suspension was used (cloth: OPS, Struers, $\varnothing = 300 \text{ mm}$) and the samples were cleaned with water and ethanol. The one-side polished samples were placed, with their polished side upwards, in the bottom of alumina crucibles ($\varnothing 16 \text{ mm}$, 30 mm height; Alsint 99.7%, Friatec); the latter were then filled with solar salt (Fig. 1). The salt mixture, known as 'solar salt', was made of 40 wt% KNO_3 and 60 wt% NaNO_3 [1,6]. KNO_3 (Merck, Germany) and NaNO_3 (Merck, Germany) were dry mixed on a multidirectional mixer (Turbula type, WAB) for 24 h. In each crucible, 6 g of the salt mixture were added on top of the polished samples. The setup was covered with an alumina plate to minimize salt loss due to evaporation. The crucibles were put in a chamber furnace and heated in air to 600°C , i.e., close to the salt degradation temperature [17–19]. The ceramic materials were exposed to the molten salt for different times, i.e., 168 h (1 week), 300 h and 1000 h. 4 g of additional salt was added after 500 h in order to ensure that the specimens were at all times in contact with the molten salt. Fig 2 shows the evolution of the salt mass during the first 350 hrs under the used conditions. The goal of our tests was to investigate the compatibility of solar salt with SiC and MAX phases in a first attempt. The tests were performed under static open system conditions whereas in a real CSP system, the salt is flowing through the closed tube system. The one-week experiment was intended as preliminary material screening. Only the materials with a promising corrosion resistance were exposed for longer times, i.e., AISI 316L and Inconel 600 as reference materials, all three types of SiC, Cr_2AlC , Maxthal® 211 and Maxthal® 312. At the end of each test, the molten salt was removed and hot water was poured over the crucibles to dissolve the remaining salt and remove the samples from the alumina crucibles.

Fig. 1. Setup of the molten salt test. The polished ceramics are placed in the alumina crucibles (a), before filling the latter with molten solar salt (b).

Fig. 2. Salt evaporation as a function of time.

2.3 Materials characterization

The exposed polished surfaces were investigated by X-ray diffraction (XRD; Seifert 3003 T/T, GE), using a Cu K_{α} radiation source (operating conditions: 40 kV, 40 mA). The XRD patterns were acquired in the 5° - 75° 2θ range with a step size of 0.02° and a time of 2 s per step. Some samples were analysed by means of a Bruker D2 Phaser (operating conditions: 30 kV, 10 mA) with a Cu K_{α} radiation source; the XRD patterns were acquired in the 5° - 75° 2θ range with a step size of 0.02° and a time of 0.1 or 1 s per step. An additional XRD analysis was performed for some of the ceramics, using a grazing incidence angle of $\omega = 0.1^{\circ}$ in a Seifert 3003 T/T diffractometer. The XRD patterns were analysed using the X-Pert Highscore software. The compositions of the starting materials were determined by Rietveld refinement using the Maud software.

Cross-sections of the exposed materials were obtained by cutting the materials in half with a low-speed diamond containing sawing blade. In order to avoid or limit breakout of reaction layers, the investigated surface was the one in which the saw blade rotation direction was moving into the material, first cutting the reaction layers and then the bulk of the material. Those cross-sections were then polished to a mirror finish (the same procedure as before testing) and studied by scanning electron microscopy (SEM; XL30-FEG & Nova nanoSEM 450, FEI) to assess their interaction with the molten salt and investigate the potentially formed layers. The thickness of the interaction product (typically, oxide scale) was measured by SEM to investigate the kinetics of its formation. In the occasional presence of a crack, the thickness of the interaction product was calculated by subtracting the crack width. For all materials, the thickness of the interaction product was measured on 30 randomly selected points. Qualitative elemental analysis of the different phases and reaction products was done by energy dispersive X-ray spectroscopy (EDS; EDAX). A more detailed investigation of select interaction products was performed by electron probe microanalysis (EPMA; JXA-8530F, JEOL) by means of wavelength dispersive X-ray spectroscopy (WDS; JEOL; operating conditions: 15 kV, 50 nA). The more detailed analysis performed on Cr_2AlC entailed the preparation of a cross-section ($30 \times 5 \mu\text{m}^2$) by focused ion beam milling (FIB; Nova 600 Nanolab, FEI), followed by EDS elemental mapping analysis of the area of interest.

2.4 Characterization of pristine materials

2.4.1 SiC-based ceramics

All SiC grades, i.e., the solid state-sintered (SS SiC), liquid phase-sintered (LP SiC) and Si-infiltrated SiC (SiSiC), contained α -SiC. The SS SiC ceramic (Fig. 3a) shows the characteristic α -SiC needle-like crystal habit that originates from the conversion of the β -SiC starting powder during sintering at 1900°C [22]. The dark spots are possibly pores, but could also have originated by particle pull-out during polishing. The crystalline $Y_3Al_5O_{12}$ phase appears in Fig. 3b as the bright phase between the SiC grains in the LP SiC ceramic. This YAG-phase ($Y_3Al_5O_{12}$) formed from the reaction of the Al_2O_3 and Y_2O_3 sintering additives during liquid phase sintering [23,24]. Fig. 3c shows the microstructure of the SiSiC ceramic, where the infiltrated Si and SiC phases can be distinguished based on their atomic number contrast. The brightest phase is the infiltrated Si, the light grey phase is the pristine α -SiC starting powder (Carborex BW, F320, Washington Millings), and the dark grey phase is the in-situ formed β -SiC, which comes from the reaction between carbon from phenolic resin impregnation with the infiltrated Si [20]. The material was fully densified, as a result of liquid Si infiltration, and contained a substantial amount of residual Si (31.8 vol% Si, 68.2 vol% SiC).

Fig. 3. Backscattered electron detector (BSE) images of the SiC-based ceramics tested in this work: (a) SS SiC, (b) LP SiC, and (c) SiSiC.

2.4.2 MAX phase-based ceramics

The microstructures of the pristine MAX phase-based ceramics are shown in Fig. 4. The rather lamellar ternary carbide phase is predominant in all materials. Apart from the MAX phase grains, competing phases (i.e., binary carbides, intermetallics, oxides) may also be observed. The phase assembly of the MAX phase-based ceramics, determined by Rietveld analysis of the XRD patterns, is given in Table 3.

Table 2. Phase assembly of the MAX phase-based ceramics tested in this work.

Material	MAX phase content (wt%)	Other phase content (wt%)
Maxthal® 312	90 Ti_3SiC_2	10 TiC
Maxthal® 211	55 Ti_2AlC 38 Ti_3AlC_2	7 $TiAl_3$
Cr_2AlC	100 Cr_2AlC	-
Nb_4AlC_3	96 Nb_4AlC_3	2 Al_3Nb , 2 Al_2O_3
$(Nb,Zr)_4AlC_3$	95 Nb_4AlC_3	4 $Al_3(Nb,Zr)$, 1 Al_2O_3
Cermet	58 $(Nb,Zr)_4AlC_3$	42 Fe

Fig. 4. BSE images of the pristine MAX phase-based ceramics tested in this work.

2.5 Results of the molten salt experiments

2.5.1 1 week at 600°C

The aim of the 1-week material screening test was to select the best-performing ceramics for the more prolonged test of 1000 h at 600°C. After one week in contact with the solar salt at 600°C, all SiC grades and Cr₂AlC appeared unaffected (Figs. 5a-5c and 5g). On the contrary, the Nb-containing MAX phase ceramics (i.e., Nb₄AlC₃, (Nb,Zr)₄AlC₃ and the Fe/(Nb,Zr)₄AlC₃ cermet) were heavily oxidized, with a bright oxide scale covering the surface of the material fragments (Figs. 5d-5f). Moreover, the commercial Maxthal® 211 and Maxthal® 312 grades developed an oxide scale (Figs. 5h-5i) that was investigated in more detail after their exposure for 1000 h to the solar salt.

Fig. 5. Ceramics after 168 h in molten solar salt: (a) SS SiC, (b) LP SiC, (c) SiSiC, (d) Fe/(Nb,Zr)₄AlC₃ cermet, (e) Nb₄AlC₃, (f) (Nb,Zr)₄AlC₃, (g) Cr₂AlC, (h) Maxthal® 211, and (i) Maxthal® 312.

2.5.2 1000 h at 600°C

(a) Reference structural materials AISI 316L and Inconel 600

A multi-layered oxide scale, roughly divided in 3 parts, formed on the AISI 316L material, as shown in the BSE image of the cross-section in Fig. 6a. The outer layer contained no chromium (Cr) and a high iron (Fe) concentration. This layer consisted of Fe₂O₃ (Fig. 6a, points a-b) with a small amount of sodium (Na). This was confirmed by XRD (Fig. 7a) and its Na content was most likely incorporated as NaFeO₂. The intermediate layer was a mixed Fe-Cr oxide (Fig. 6a, points b-c), enriched in Cr. This layer was a mixture of Fe₂O₃ and Cr₂O₃ that was present in a ratio of 1:2 at%, according to EDS. This ratio might correspond to the formation of the spinel phase FeCr₂O₄ [25]. Below the oxide bi-layer, a Cr-depleted, O-enriched inner layer can be distinguished (Fig. 6a, points c-d). This layer appears to result from the outward diffusion of Cr-atoms and the inward diffusion of O-atoms. Moreover, this zone was slightly depleted in Fe. These observations were identified as an internal oxidation zone (IOZ).

Fig. 6. BSE images and corresponding EDS line scans through the interaction products observed on the surface of (a) AISI 316L stainless steel and (b) Inconel 600, after 1000 h in contact with the molten solar salt.

Fig. 7. XRD patterns of the corrosion products found on the surface of the (a) AISI 316L and (b) Inconel 600 reference structural materials, after 1000 h in molten solar salt.

The above findings on AISI 316L were also reported by Soleimani Dorcheh et al. [8] and Bradshaw et al. [26]. They both confirmed the formation of a NaFeO₂ layer on the surface of AISI 316L, followed by a double oxide layer, the upper part of which was an Fe-oxide and the lower part was a mixed Fe/Cr-oxide. Soleimani Dorcheh et al. [25] reported the formation of the FeCr₂O₄ spinel phase, which they claimed to be a passive layer underneath the Na-containing oxide scale NaFeO₂.

The main phase formed was Fe-oxide and that was not protective [27]. Cr prefers to oxidize to Cr(VI) and dissolves in the form of CrO_4^{2-} in basic conditions [28,29], favouring the formation of the Fe-Cr spinel phase under these conditions. The formation of this bi-layer oxide scale is in analogy with the behaviour of stainless steel AISI 316L in LBE (O-concentration around 5 ppm) [30]. Several authors reported the formation of an outer magnetite (Fe_3O_4) layer, an inner FeCr-spinel (FeCr_2O_4) layer at 600°C [31] or $\text{Fe}(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_4$ at 550°C [32], and an IOZ next to the base (unaffected) steel, when in contact with liquid LBE. The thickness of the oxide scale on the steel surface was many times thicker than that forming after the one-week exposure. This reaction-controlled process (see section 3.3) implies that the chemical stability of AISI 316L in contact with the molten solar salt at 600°C is limited.

Fig. 6b shows that the initially polished surface of Inconel 600 was still visible after contact with molten solar salt. The interaction layer consisted of two parts: one growing from the material surface outwards and one growing inwards. The outwards growing part of the interaction layer consisted of a darker, Fe-poor, Na-Ni oxide phase (a-b), and a brighter, Fe-rich, Ni-Fe oxide phase (b-c). The presence of the Fe-oxide phases was confirmed by XRD (Fig. 7b), though no clear Na or Ni phases were detected. On the other hand, the inwards developing interaction zone (c-d) was depleted in Fe, due to the outward Fe diffusion into the surface oxide scale. This zone contained O, due to the inward O diffusion, forming an internal oxidation zone (IOZ) similar to the one observed in the AISI 316L steel. Moreover, some C-precipitates formed at the grain boundaries, suggesting the sensitization of the Ni-based alloy. It should also be noted that the thickness of the bi-layer interaction zone and its two constituents was not uniform. The formation of the bi-layer interaction zone is a clear indication that Inconel 600 will not remain stable in contact with the molten solar salt at 600°C for prolonged exposure times.

(b) SiC-based ceramics

The XRD patterns of the three SiC grades after the 1000 h exposure to the molten solar salt showed negligible differences between the pristine (non-exposed) and exposed materials (Fig. 8).

Fig. 8. XRD patterns of the SiC-based materials before and after their exposure to the molten solar salt for 1000 h at 600°C: (a) SS SiC, (b) LP SiC, and (c) SiSiC.

As shown in Fig. 9, the three SiC grades were not affected much by their exposure to the molten salt and no oxide scale was detected. The originally flat (polished) specimen surface, however, appeared rougher after the molten salt test, suggesting little interaction with the molten salt. The pull-out of some grains in Fig. 9c can be attributed to cutting or polishing. The absence of a Si-based (SiO_2) oxide is in agreement with the findings of Grambalova et al. [33], who reported that

the interaction of K⁺- and Na⁺-based salts with SiO₂ leads to degradation of this oxide. Also Molchanov et al. [34] reported that Na⁺-based solutions dissolve amorphous SiO₂. It is, therefore, reasonable to assume that the possible formation of a SiO₂-based phase has been followed by its dissolution in the molten solar salt.

Moreover, it should be noted that SiSiC undergoes a transformation towards more α-SiC, indicating a partial β-SiC to α-SiC during thermal treatment. However, this polymorph conversion was not affecting the stability, since both forms of SiC remained stable in contact with the molten salt.

Fig. 9. BSE images of the SiC-based ceramics after their exposure to the molten solar salt for 1000 h at 600°C: (a) SS SiC, (b) LP SiC, and (c) SiSiC.

(c) MAX phase-based ceramics

The interaction of Maxthal® 211, Maxthal® 312 and Cr₂AlC with the molten solar salt is shown in Fig. 10, whereas the XRD patterns of the surface layer are presented in Fig. 11. Maxthal® 211 and Maxthal® 312 formed a porous and rather brittle oxide scale that was easily fragmented during the preparation of metallographic cross-sections (Figs. 10a-10b); on the other hand, the interaction between Cr₂AlC and molten salt was minimal (Fig. 10c).

The XRD pattern of the exposed Maxthal® 211 surface showed the presence of Ti₂AlC, along with the presence of small amounts of anatase (TiO₂) and NaTiO₃ (Fig. 11a). The chemical composition of the Maxthal® 211 oxide scale is shown in the EDS elemental maps of Fig. 12. The elongated Ti₂AlC MAX phase grains reacted with the molten salt, forming a Ti-based oxide (TiO₂), which readily reacted with the Na⁺ in the molten salt to form the Na-containing Na₂TiO₃, as shown by XRD and EDS (Figs. 11a and 12). The Na₂TiO₃ layer appears to have a non-uniform thickness, is highly defective and, by extension, non-protective. The initially polished surface is no longer detectable after exposure. The TiAl intermetallic phase is also affected, but this process is slower. Barsoum et al. [13] reported the formation of a non-protective oxide scale composed of TiO₂ and Al₂O₃ as result of the exposure of Ti_{n+1}AlC_n in air at 1100°C, as follows:

Note that Maxthal® 211 contained both Ti₂AlC (55 wt%) and Ti₃AlC₂ (38 wt%) and both phases form TiO₂ and Al₂O₃. In the present case, however, no alumina (Al₂O₃) was found, which could tentatively be attributed to the dissolution of alumina in caustic Na₂O. As the salt degrades at temperatures above 600°C according to reaction (4), Na₂O can be formed, as follows [35]:

Fig. 10. BSE images of the MAX phase-based materials after 1000 h in molten solar salt: (a) Maxthal® 211, (b) Maxthal® 312, and (c) Cr₂AlC.

Na₂O typically forms Na₂O·Al₂O₃, which implies that alumina dissolves in the molten solar salt. Similar to SiO₂, Grambalova et al. [33] reported that K⁺- and Na⁺-based molten salts interact chemically with Al₂O₃. Treatment of Al₂O₃ with a CaCl₂-NaCl containing electrolyte leads to the electrochemical reduction of Al₂O₃, which becomes stronger at higher concentrations of NaCl [36]. Lee et al. [37] reported that the native aluminium oxide film on Al dissolves faster in contact with more basic solutions that contain more Na⁺ salts. All of these authors claimed that aluminium oxide is not stable in Na⁺-salts. As discussed by Barker et al. [38], the interaction between Na₂O and Al₂O₃ forms Na₅AlO₄, according to the following reaction:

Fig. 11. XRD patterns of the MAX phase-based materials after their exposure to molten solar salt at 600°C for 1000 h: (a) Maxthal® 211, (b) Maxthal® 312, and (c) Cr₂AlC. (d) Grazing incidence (incidence angle $\omega = 0.1^\circ$) XRD pattern of Cr₂AlC.

The Maxthal® 312 ceramic is also susceptible to corrosion in the molten solar salt environment, (Fig. 10b). XRD analysis of the interaction surface layer (Fig. 11b) revealed the formation of Na₂(TiSi₅O₁₃), which agrees with the EDS elemental mapping in Fig. 13. The Si content in the oxide layer increases towards the bulk MAX phase material, while the O content is slightly higher closer to the surface. Liu et al. reported the formation of a mixed TiO₂ and SiO₂ scale on Na₂SO₄-coated Ti₃SiC₂ at 900-1000°C [39], as well as in contact with a Na₂SO₄-NaCl melt [40] at 850°C in air. In both cases, Ti, Si, Na and O were present in the corrosion layer. The findings of these authors agree with the findings of the present work. This interaction can be described as follows [39,40]:

The Na₂O can be formed from the decomposition of NaNO₂, as described in reaction (4).

No clear influence of the 10 wt % TiC present in the Maxthal® 312 could be identified with respect to the corrosion resistance of this ceramic to the molten solar salt. Maiya et al. [41] reported TiC coatings on graphite substrates in contact with CaCl₂ at 800°C to be stable, whereas Gu et al. [42] did not observe any significant mass change of TiC in contact with molten FLiNaK at 800°C up to

200 h, confirming the stable behaviour of TiC in molten salt. Moreover, the presence of SiC in SiC-TiC composites improved even the corrosion behaviour in FLiNaK, as observed by Gu et al. [42]. The presence of Si in Maxthal® 312 might have a similar effect as when the Si was added for improving the corrosion of the TiC phase.

Fig. 12. EDS elemental maps of the oxide scale forming on Maxthal® 211, after its exposure to molten solar salt at 600°C for 1000 h.

Cr₂AlC shows very little interaction with the molten solar salt under these exposure conditions. The XRD pattern of the Cr₂AlC interaction layer shows the sole presence of Cr₂AlC (Fig. 11c). However, the WDS elemental mapping in Fig. 14 confirms the presence of elements from the salt on the surface and the ~1 µm-thick continuous layer on the Cr₂AlC surface contains K, Cr and C. This surface layer did not contain O, suggesting that the protective reaction layer is a carbide and not an oxide. The presence of the surface layer is confirmed by the FIB-milled cross-section in Fig. 15, as the darker phase between the Pt layer on top and the Cr₂AlC-based material. EDS point analysis (Table 4) showed that the main elements in this layer are Cr, C and Al although a small amount of O was detected as well but could be neglected, based on the more reliable WDS map.

To identify the sub-micrometre thin layer that formed on the surface (Fig. 10c), a grazing incident angle XRD pattern was obtained (Fig. 11d). The additional peaks observed in the XRD diffraction pattern can be attributed to a Cr-carbide (Cr₇C₃) thin layer. The extra peak formed at 39.6° 2θ, compared to the bulk XRD pattern of Fig. 10c, matches the XRD pattern of Cr₇C₃; the major peak of Cr₇C₃ at 42° 2θ overlaps with a peak of Cr₂AlC. As the specimen surface appeared unaffected after the molten salt experiment, it can be concluded that this carbide layer is stable and protective in contact with the molten solar salt.

Fig. 13. EDS elemental maps of the oxide scale on Maxthal® 312 after its exposure to molten solar salt at 600°C for 1000 h.

Fig. 14. WDS elemental maps of Cr_2AlC after exposure to molten solar salt at 600°C for 1000 h.

Fig. 15. FIB-milled cross-section close to the surface of Cr_2AlC after exposure to molten salt at 600°C for 1000 h. The dots indicate the EDS point analyses summarised in Table 4.

Table 3. EDS elemental composition of the point analyses shown in Fig. 15.

Element	Spot 1 (at%)	Spot 2 (at%)	Spot 3 (at%)	Spot 4 (at%)
C	22.48	23.43	12.66	22.85
O	9.06	11.38		10.71
Ga	1.28	0.96	0.38	1.6
Al	22.49	21.27	22.72	22.80
Pt	1.36	1.39		0.83
Cr	43.33	40.01	64.23	41.21
Mg		1.56		

2.6 Oxidation kinetics

The oxidation kinetics of the materials exposed to the molten solar salt was studied by measuring the thickness of the interaction layer as a function of the exposure time. Fig. 16 is a graphical representation of the obtained results for all materials. Since no interaction layers formed on the SiC grades, their thickness could not be measured. The most stable MAX phase-based material, Cr_2AlC did not show the formation of an oxide scale but is added in this section as a comparison of the stability with the other materials. Cr_2AlC showed a constant interaction layer thickness with time, indicating that the Cr_7C_3 layer is very stable at 600°C and hardly grows within the considered timeframe of 1000 h. The results plotted in Fig. 16 are summarized in Table 5.

Table 4. Information pertaining to Fig. 16; d: layer thickness (μm), t: exposure time (h).

Material	Linear plot	Coefficient of determination
Cr_2AlC	$d = 0.0003 \cdot t + 1.5218$ Starting point (0,0) not included in the linear plot	$R^2 = 0.9976$
AISI 316L	$d = 0.0136 \cdot t$	$R^2 = 0.9878$
Inconel 600	$d = 0.0145 \cdot t$	$R^2 = 0.999$
Maxthal® 312	$d = 0.0298 \cdot t$	$R^2 = 0.9692$
Maxthal® 211	$d = 0.1466 \cdot t$	$R^2 = 0.9312$

Fig. 16. (a) Evolution of the interaction layer thickness as a function of time at 600°C for Cr₂AlC, Inconel 600, AISI 316L, Maxthal® 211 and Maxthal® 312. (b) Oxide scale growth on Maxthal® 211 as a function of the square root of time.

The reference structural materials AISI 316L and Inconel 600 showed a linear reaction-controlled oxidation behaviour with comparable reaction rates (Fig. 16a). However, the oxide scale thickness of Inconel 600 was not uniform, in contrast to the oxide scale forming on the AISI 316L steel. The observed linear oxide scale growth on AISI 316L agreed with the findings of Soleimani Dorcheh et al. [25]. They reported that oxidation kinetics up to 1000 h were linear, after which they could change to a parabolic behaviour up to 5000 h, i.e., changing the oxidation kinetics from reaction-controlled to diffusion-controlled, after a certain oxide scale thickness. The observed linear oxidation kinetics implied that the formation of the oxide scales is reaction-controlled and that both materials would corrode further in time. It can, however, not be excluded that the oxidation kinetics will change beyond a certain oxide scale thickness. The herein considered exposure times were not long enough to allow for such observation.

The oxidation behaviour of Maxthal® 211, however, showed clearly that a linear regression was not the best fit (Fig. 16a). It is possible that the oxide scale that formed after the exposure of 1000 h dissolved partly in the salt and that the actual oxide scale thickness was larger than the measured one. The shorter time (up to 300 h) data showed a linear behaviour that implied reaction-controlled kinetics. Moreover, it should be noted that the oxide scale that formed on the sample exposed to the molten salt for 1000 h, did not have a uniform thickness. In some areas, the MAX phase grains were heavily oxidised, while the oxide scale was much thinner on other

locations. This also explains the larger observed data scatter at 1000 h of exposure. Upon the air oxidation of Ti_2AlC , Barsoum et al. [13] reported the formation of a non-protective alumina layer; oxidation obeyed parabolic kinetics and was diffusion-controlled, limited by the interdiffusion of Ti and O forming the TiO_2 scale. However, in the present study, parabolic kinetics did not fit the data, as the thickness did not increase linearly with the square root of time (Fig. 16b). The oxidation kinetics started as reaction-controlled (linear) and levelled off beyond 300 h. The oxidation kinetics of the Maxthal® 312, however, was reaction-controlled up to 1000 h.

Both commercial MAX phase grades, Maxthal® 211 and 312, showed faster oxidation kinetics than reference materials AISI 316L and Inconel 600, indicating that these materials would be a better choice over the commercial Maxthal® grades for the envisaged CSP application. The Cr_2AlC MAX phase, on the other hand, remained stable in the molten solar salt, forming a thin and stable interaction layer. In this sense, Cr_2AlC outperformed both reference structural materials and all other MAX phase-based ceramics.

3 Conclusions

This work exposed two reference structural materials (AISI 316L and Inconel 600) and various SiC-based and MAX phase-based ceramics to a molten solar salt (60 wt% NaNO_3 , 40 wt% KNO_3) for up to 1000 h at 600°C. The main findings of this study would be summarised as follows:

1. AISI 316L and Inconel 600 were not perfectly compatible with the molten solar salt. The AISI 316L steel formed a multi-layered oxide scale, consisting of an Fe_2O_3 outer layer, an $\text{Fe}(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_4$ spinel inner layer, and an internal oxidation zone (IOZ) next to the base steel; the oxidation kinetics was linear in the 1000-h timeframe. Inconel 600 formed a Na-containing, mixed Ni,Fe-oxide, with Cr-carbide grain boundary precipitates presumably leading to the alloy sensitization.
2. The SS SiC, LP YAG-containing SiC, and SiSiC SiC-based ceramics showed negligible interaction and can thus be considered compatible with the molten solar salt.
3. Commercial Maxthal® 211 formed a non-protective anatase (TiO_2) oxide scale, and the Ti_2AlC -grains oxidized progressively in the molten solar salt. The formation of an alumina scale was not observed, while a non-uniform $\text{Na}_2(\text{TiO}_3)$ scale covered the sample surface. This suggests that the molten salt environment was too aggressive for Al_2O_3 formation.
4. Commercial Maxthal® 312 showed a more controlled oxidation behaviour than its 211 counterpart. A $\text{Na}_2(\text{TiSi}_5\text{O}_{13})$ interaction layer of more uniform thickness was observed. This phase might have resulted from the degradation of the molten solar salt into nitrites, which produced Na_2O , followed by the formation of a mixed interaction layer containing Na, O, Si and Ti.
5. Cr_2AlC was the most stable MAX phase-based material, forming a protective, micrometre-thin layer of Cr_7C_3 , in contact with the molten solar salt, on which some salt leftovers were also detected. The formation of Cr_2O_3 or Al_2O_3 was not observed in this study.

Acknowledgements

The authors would like to thank Sebastian Meyers (KU Leuven, Dept. of Mechanical Engineering) for providing the SiSiC specimens and Dr. Jesus Gonzalez-Julian and Dr. Martin Bram from Forschungszentrum Jülich for the HIPing of the cermet sample.

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