

Silicon Carbide and Carbon Molten-Salt Compatibility

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Abstract. Silicon Carbide (SiC) and Carbon (C) in all their polymorphs have a long and interesting history as refractory ceramics and materials applications for Nuclear Fission / Fusion, particularly for high-temperature reactors where molten salts are considered as working fluids. The excellent structural properties of SiC and carbon, combined with their low neutron-capture cross sections (0.171 and 0.0035 barns for Si and C, respectively), make these materials appear ideal. However, historical as well as recent investigations regarding the chemical interaction of SiC and C with other materials typically employed in molten salt loops force researchers to question their use. This review highlights the somewhat sparse number of assessments that focus on the chemistry of SiC- and carbon-based components with molten salt components and structural alloys used to contain them. Since all the initial species found in-situ are known, several facile reaction pathways that result in grain-boundary attack on SiC and carbon-based components (irrespective of irradiation effects) are presented. Finally, some possible chemical and material alternatives are offered that retain the desirable neutronics of SiC and carbon, while still offering robust resistance to significant structural grain-boundary damage due to undesirable bath chemistry.

Keywords: molten salts, silicon carbide, Pebble-Bed Modular Reactor, 235U-enriched nuclear fuels.

INTRODUCTION

Researchers have studied Silicon Carbide (SiC) in its various and surprisingly complex forms for well over a century since Acheson first published a systematic study in 1892, although it was very likely synthesized prior to that^{1,2}. The high tensile strength of SiC, its low neutron-capture cross section, facility of binding with other composite materials and chemical resistance for a variety of fluids have historically made it attractive to both fusion and fission energy systems^{3,4,5,6}.

In parallel fashion over the past 15 years, renewed interest in molten salts as coolants, heat-storage media and as solvents and carriers of fuels and products has emerged in various types of energy systems. This is in addition to the use of molten salts as reactor fluids where the fissile material makes up a substantial part of the molten bath^{10,11}. Recent usage of molten salts include solar thermal applications in Spain, a flurry of interest in room-temperature ionic liquids, as well as advanced research in their use in Advanced High-temperature Reactors^{6,7,8,9}.

As a structural material in high-temperature, high-neutron-flux environments, SiC serves extremely well as the refractory material it is designed to be. Although rare, some reporting has intermittently occurred (which will be covered in the Reactivity section of this paper) however, that SiC in the presence of molten salts or other related

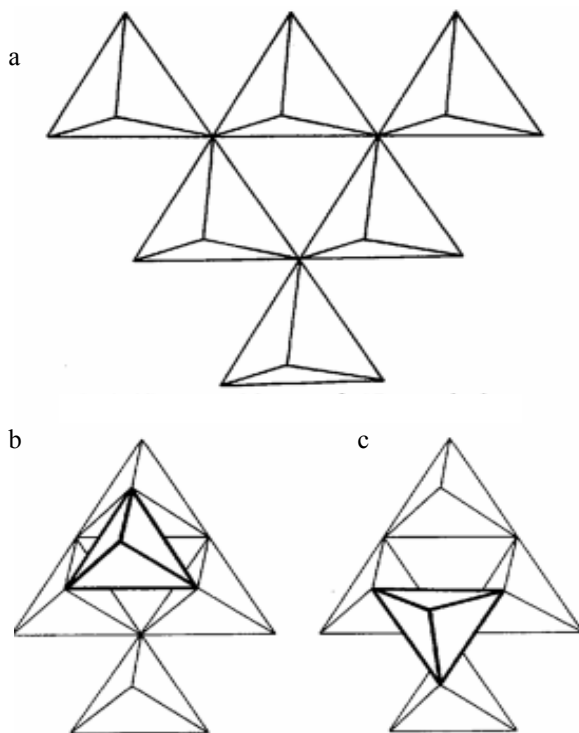
compounds at elevated temperatures results in reactivity in the form of solubilized silicon. This is despite the fact that the some speculation had been raised regarding the underlying reasons for such reactivity, due to the vast number of versions in which SiC can present.

The authors of this paper have several aims. Firstly, a very brief review of the existing literature on SiC and the many forms or *polytypes* of SiC will be discussed, based on historical and modern characterization methods. Secondly, the sparse historical references regarding reported interactions of SiC with molten salts will be highlighted. Third, one possible chemical route resulting in the solubilization of Si stemming from SiC will be presented, with accompanying thermodynamics assertions. Finally, some alternative materials which are related to the binary refractory form of SiC will be discussed, which are similar in deposition methodology, but may offer increased chemical resistance, while maintaining robust structural and neutronic properties.

SiC STRUCTURE

The structural variants of SiC are vast and complex. Soon after Acheson's goniometric studies that described the first two structures of SiC in 1912, Baumhauer described SiC as occurring as *polytypes* (one-dimensional polymorphs). Since then, over 250 polytypes have been described^{12,13,14}. In addition to the polytypism of SiC, it is also capable of syntactic coalescence²². This is a phenomenon where one polytype forms on top of another. Regardless of the polytype exhibited, all crystalline forms of SiC originate as SiC₄ (or CSi₄) tetrahedra. The arrangements of the SiC₄ tetrahedra are what give rise to the multitude of polytypes of SiC, where the tetrahedral stacking along the *c* direction is the one dimensional variant forming the polytypic forms. The tetrahedra are arranged such that all of the atoms comprising the tetrahedra lie in parallel planes of the hexagonal crystal structure²². All forms of SiC can be described as a hexagonal lattice²² of planar SiC tetrahedra (fig.1a), such that the successive layers are either parallel as shown in fig 1b or antiparallel as in fig 1c. The positions that Si can take are either A, B, or C forming the base of the hexagonal cell see Figures 3 and 4 in [23]; reproduced in figure 1 below. If position C projects onto position A, the resultant structure is hexagonal (wurtzite). If A, B, and C do not project onto each other, the cubic (zincblende) system is assumed. The Ramsdell nomenclature is the most widely used to describe polytypes where a capital letter describes the crystal system (C -cubic, H = hexagonal, R = rhombohedral) and the number is the number of repeat units^{15,16}. The most common cubic polytype is 3C-SiC, or β -SiC where an ABCABC pattern is observed. The most common hexagonal polytype found is 6H SiC (α -SiC) with a stacking sequence ABCACB²². Although crystallographically challenging, these polytypes can be readily distinguished, as demonstrated by Guth, et al., using ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS NMR)¹⁷.

2a **FIGURE 1.** The hexagonal plane made from SiC tetrahedra (a); SiC in parallel layers (b); (c) in antiparallel layers²³.



INTERACTIONS WITH MOLTEN SALTS

As mentioned in the Introduction, a resurgence in the use of molten salts in various fields observers has been seen, due to their high thermal conductivity, high specific heats, exceptionally low viscosity in the molten state and high boiling points, with all of these thermodynamic properties measured against water as the benchmark. Table 1, below, provides a broad range of thermodynamic reference data for salts that have been commonly studied for the past four decades.

TABLE 1. Summary of properties for salts commonly studied/reported in the literature. Data adapted and/or converted from [7, 12-17]. †Formula weights represent the weighted molar ratios of the compounds studied. ††Data extrapolated at 587°C.*Data for water are all at 20°C.

<i>Salt/Compound</i>	<i>Weight[†] (g/mol)</i>	<i>Melting Point (°C)</i>	<i>900°C Vapor Pressure (mm Hg)</i>	<i>Density (ρ; g·cm⁻³)</i>	<i>olumetric heat capacity ($\rho \cdot Cp$; cal/(cm³·°C))</i>	<i>Viscosity (ρ; cP)</i>	<i>Thermal conductivity (W/m·K)</i>
LiF-NaF-KF	41.3	454	-0.7	2.02	0.91	2.9	0.92
NaF-ZrF ₄	92.7	500	5	3.14	0.88	5.1	0.49
KF-ZrF ₄	103.9	390	1.2	2.80	0.70	<5.1	0.45
LiF-NaF-ZrF ₄	84.2	436	-5	2.92	0.86	6.9	0.53
LiCl-KCl	55.5	355	5.8	1.52	0.435	1.15	0.42
LiCl-RbCl	75.4	313	n/a	1.88	0.40	1.30	0.36
NaCl-MgCl ₂	73.7	445	<2.5	1.68	0.44	1.36	0.50
KCl-MgCl ₂	81.4	426	<2.0	1.66	0.46	1.40	0.40
NaF-NaBF ₄	104.4	385	9500	1.75	0.63	0.90	0.40
KF-KBF ₄	109.0	460	100	1.7	0.53	0.90	0.38
RbF-RbF ₄	151.3	442	<100	2.21	0.48	0.90	0.28
2LiF·BeF ₂ ^{††}	32.9	459	0.07	1.994	1.03	1.25	1.1
H₂O*	18	0	n/a	1.0	0.44	1.0	0.6

Regardless of the salt used, all fluoride and chloride salts share the same potential for aggressive attack. Despite select historical usage of fluoride salts such as 2LiF·BeF₂ (also abbreviated FLiBe), more chloride-salt corrosion chemistry as it pertains to interactions with in-situ materials is known, rather than their fluoride counterparts, even though fluoride salts are thermodynamically more stable than their chloride analogs, with respect to their energies of formation^{7,10,18,26,27}. This is highlighted in work such as that by Plambeck or Baes, who charted the galvanic chemistries for select molten salts^{26,27}.

Due to the (electro)chemical potential of inherently conductive media like ionic liquids in general and molten salts in particular, the interplay between such liquids and their containment materials plays a crucial role. Most if not all of the conduit materials historically used to manage these molten-salt flows contain a good portion of Nickel (Ni), such as Hastelloy-N, X Incoloy, Haynes 230 and others. While often viewed as semi-noble, Ni very often plays catalytic roles such as in bis(cyclopentadienyl)Ni(II), Raney's Nickel, Ni(II) Fluoride, K₂NiF₆, or NiO on SiO₂ support, to name but a few. It should be noted that Ni sits atop the Group 10-11 region on the Periodic Table, the so-called Platinum Group Elements or PGEs. These PGEs, as well as Ni, all play a prominent role in catalysis due to the observed energetic similarity of the Xd⁸⁻⁹ and (X+1)s²⁻¹ electrons and correspondingly associated E_g or T_{2g} molecular orbitals (depending on the reagent coordination number). It is therefore logical to speculate that in cases

such as high-nickel alloys which have not been properly passivated or which have surface coatings of Ni compounds in the course of manufacture, the alloys may pose as a reaction medium themselves.

Although very little literature has been found, some evidence for deleterious interaction of molten salts with SiC or SiC-based materials does exist, although the precise chemical mechanism for this has never been proffered. For example, the work by Sabharwall, et al., clearly indicated that the SiC materials were aggressively oxidized by both chloride and fluoride salts when not protected by pyrolytic carbon interphase (this effect was dramatically enhanced by the presence of graphite, due to graphite acting as a de-facto cathode to the anodic alloys)^{7,26}. Additionally, Mazur, et al., demonstrated some simple reactive surface chemistry effects of LiF deposited on single-crystal 6H SiC polytype, where heating to >327°C appeared to elicit contiguous SiC oxidation²⁹. Further, Nishimura, et al., noted the prompt disappearance of, initially, the αSiC (the 6H polytype), followed by the diminishing presence βSiC (the 3C polytype) upon three- and ten-day exposure to FLiBe, the experiment having been conducted in a Ni crucible²⁷. Finally, the experimental evidence of the appearance of Si_xF_y clusters reported by different researchers, yet under fluorinating conditions is consistent with the chemical pathways proposed in this Paper^{7,29}.

The characterization of these events by Nishimura, et al., via XRD is very telling for three reasons. Firstly, also reported in [27] is the concomitant emergence of 2θ reflections consistent with polycrystalline nickel silicide (Ni₃₁Si₁₂), where the authors posit the following possible simple reaction: 31 Ni⁰ + SiC → Ni₃₁Si₁₂ + 12C⁰. It is more likely that the starting material was NiO, given the slow but natural tendency of Ni to oxidize under ambient conditions, as suggested by Katoh, et al.⁸. It is also likely that Nishimura *et al.* apparently produced amorphous carbon (C⁰), which XRD could not detect due to amorphous carbon's lack of long-range periodic ordering²⁷.

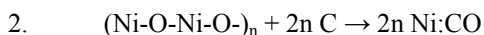
Secondly, the lower crystallographic symmetry of the αSiC polytype, by definition, has a greater number of CSi₄ tetrahedral exposure and a higher likelihood of superlattice defects. See Figure 1 in [28]. The parallel orientation of the CSi₄ tetrahedra in the cubic βSiC polytype leave fewer opportunities for grain-boundary attack. Finally, given the tendency for SiC polytype symmetries to increase with increasing temperature, it is possible that the disappearance of the αSiC polytype results from a combination of in-situ conversion to the more symmetric βSiC polytype, as well as the oxidation of the Si²⁸.

To avoid corrosion and maintain structural strength up to 700° C, molten-salt-cooled reactors must make use of high-nickel alloys such as the Hastelloy series or the like. What endows these alloys with their natural corrosion resistance is the passive film of NiO and/or NiF₂ that spontaneously and unavoidably form whenever these alloys get exposed to oxygen, water vapor and/or most fluorinating agents (F₂, NF₃, SeF₄, HF, etc).

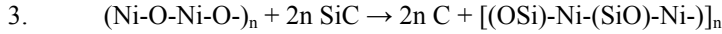
Nickel, nevertheless, is a fairly noble metal, with the d and s orbital electronic configurations as noted above. Thus, when Ni[II] compounds become solubilized by a molten-salt bath, they begin a cascade of redox reactions which become thermodynamically facile at these elevated temperatures and fluorinating conditions. Given copious historical data, known temperature and (Lewis) pH; as well as complete knowledge of the number and type of in-situ species, the following redox cascade is proposed for any fluorinating molten-salt bath, assuming that a nickel oxide (NiO) or fluoride (NiF₂) surface film covers the nickel-rich alloy. Please note that the order of these reactions is largely irrelevant (so the enumeration below is arbitrary), as they will all be in dynamic equilibrium:



Notes: the oligomeric oxide (Ni-O-Ni-O-)_n (similar to the species offered in [31]) is best solvated by the more Lewis-base anions of the salt. The dissolution reaction F⁻(NiF₂)F⁻ → (NiF₄)⁻² proceeds even more readily than for the oxide.

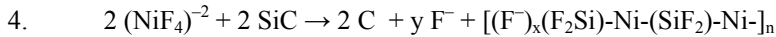


Notes: the Carbon (C) comes from the especially amorphous edges/corners of pyrolytic carbon structures. The lone electron pair (:) belongs to the carbonyl moiety (CO), which along with anions of the salt helps satisfy the need for nickel to be 4- to 6-coordinate (average number depending on anion type and pH).



Notes: It is here that the SiC polytype(s) present and their relative tetrahedral availability are so crucial, given the largely covalent nature of the Si—C sp³ hybridization and the relatively unencumbered access to the σ_u^* antibonding molecular orbitals for the Si species.

The larger oligomeric chain $[(\text{OSi})\text{-Ni-}(\text{SiO})\text{-Ni-}]_n$ is again anion-solvated, further stabilizing these clusters, many of whom will be 5 – 6 Si-coordinated, relative to the less thermodynamically stable species presented by Zhang, et al.³¹.

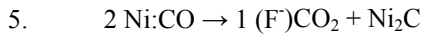


Notes: the presence of Si_xF_y clusters reflects the species reported in [7,29]. Local fluoride anionic variability is unremarkable and common with Lewis-pH dynamics typified in systems like this. The Si:Ni ratio can fall into the 1-2:1, as observed by Nishimura, et al.²⁷

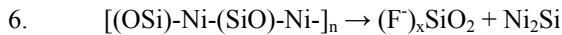
The above reactions result in the formation of vanishingly small clusters of:

- Carbon-monoxide-coordinated Nickel (reaction 2 above)
- Nickel –"Silicon-monoxide" intermetallic (reaction 3)
- Nickel –"Silicon-difluoride" intermetallic (reaction 4)

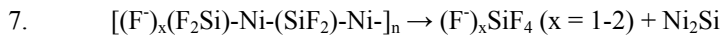
When these small clusters have sufficiently agglomerated, their larger size and liberation will catalyze the following thermodynamically driven "disproportionation" reactions:



Notes: the CO₂F⁻ is a *planar* tetra-atomic anion due to the F⁻ anion, rather than linear O=C=O.



Notes: the SiO₂ species are solubilized by the presence of (F⁻)_x; x = 1-2



Although the CO₂, SiO₂ and SiF₄ (all complexed with F⁻) of Reactions 5 – 7 are non-corrosive to structural metals, their nickel intermetallic byproducts: the reactive NiC and agglomerophilic silicide are in fact corrosive to MSR structures. The most driven reaction for removing carbides and silicides from the salt is their alloying reaction with metal M:

- Ni_xC + M → MC + x Ni + exotherm;
- Ni_xSi + M → MSi + x Ni + exotherm;

where M = Mn, Cr, Mo, Ni, Ti, Zr (listed in order of increasing electropositivity).

The problem with the above is that one or more of these transition metals make up appreciable percentages of typically all structural alloys. The most common metal additive to nickel is chromium, without which one cannot have Hastelloy and the like.

Failure to *a-priori* passivate all such alloys, maintain said passivation, while preventing the dissolution of their passive coating shall engender growth of Cr_xC and Cr_xSi intermetallics on and within Hastelloy or similar high-nickel structures. Such measures simply require active bath management. It is these and similar intermetallics that already have been reported to embrittle grain boundaries of such nickel alloys³².

SiC WITHIN TRISO FUELS

Tri-isotropic (TRISO) coated ^{235}U -enriched nuclear fuels contained within the fluoride-molten-salt bath of a Pebble-Bed Modular Reactor (PBMR) may represent one commercially viable production method for fission energy³³. The facility of molten salts to transfer the heat generated from the fission cycle under pressures of $\sim 1\text{ATM}$ and at significantly higher mean temperatures than water ($500\text{-}800^\circ\text{C}$, depending on the fuels, salts and conditions) make the combination of TRISO and molten salts quite attractive^{7,8,18, 21,23,25, 26,33,34,35}. Integral to the TRISO pebbles are concentric SiC layers, which are sandwiched between layers of pyrolytic carbon.

SiC had been selected as a structural barrier to contain Fission Products (nuclear fragments that result from the fission event), as well as provide tensile support for the MOX cores of the pebbles themselves. The apparent crystallographic shortcomings of both polytypic conversion and syntactic coalescence, however, may be partly responsible for the failure of these materials as reported in other work^{7,8,18,26,27}.

Mokoduwe, et al. report that the primary method for fabricating the SiC layer for TRISO fuels is Chemical Vapor Deposition (CVD) at $\sim 1450^\circ\text{C}$, but that there is a direct correlation between temperature and 3C SiC morphology (both grain size and polytypic changes) upon annealing³⁴. Mokoduwe's findings are corroborated by an INL report published in 2002, which found that CVD done at temperatures less than 1250°C , can create hexagonal and disordered polytypes of SiC³⁵. D. Hélayry, et al., reported that they could not detect any α -SiC with either XRD or Raman microspectrometry with CVD-coated SiC particles, although Hélayry does note that prior results contradicts his XRD findings albeit with different sample preparations^{36,37,38}. However the same group with additional coauthors reported elsewhere that with high resolution transmission electron microscopy, they did find small amounts of α -SiC with sizes less than 50 nm, embedded throughout an 3C-SiC matrix, a probable in-situ example of syntactic coalescence³⁹. In their paper on an EBSD study of CVD SiC, Tan, et al. reflect upon these findings, noting that the α -SiC structures of the sizes D. Hélayry et al report are too small to be resolved by EBSD. Given this fact, as expected, L. Tan et al. did not detect any α -SiC in their EBSD study⁴⁰.

CONCLUSION AND FUTURE WORK

The neutronic and thermodynamic properties of SiC make it an attractive prospect for PBMRs. However the in-situ microscopic and mesoscopic changes these materials undergo from temperature changes and deposition methods (which form inconsistent polytypes), force researchers to reassess the exclusive use of SiC as a refractory coating to retain Fission Products within TRISO fuels. Without surface passivation prior to molten-salt usage within high-nickel alloys where SiC-based materials are deployed, while simultaneously using *active* chemical control of the salt bath, the dissolution of SiC, pyrolytic Carbon, "inert" Graphite, along with the formation of unwanted Silicide & Carbides, premature embrittling all structural alloys will remain continual problems.

Related research employing the more ionic binary refractory carbides such as TiC, HfC, TaC and ZrC, in combination with Carbon-Carbon reinforced fibers and composite materials may offer more robust potential against in-situ chemical reactivity of the more susceptible sp^3 -hybridized covalent bonds which exist between Si and C, given their low electronegativity difference and low ($\sim 13\%$) ionic character^{4,5,41-45}.

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