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Ultra-high temperature steam corrosion of complex silicates for nuclear applications: A computational study

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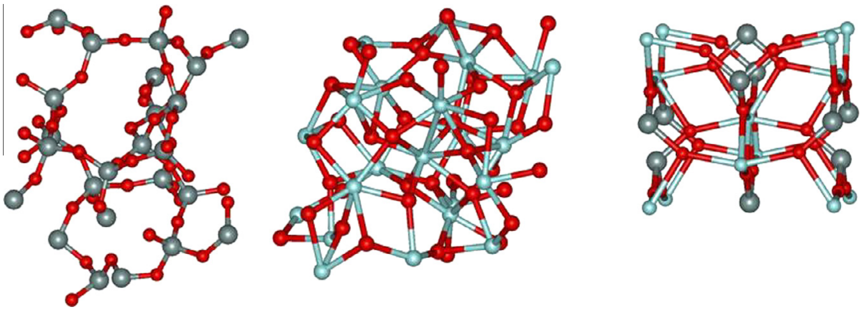
GRAPHICAL ABSTRACT

Schematics of atomic structure for: (a) amorphous SiO_2; (b) amorphous ZrO_2; (c) regular stoichiometric zircon $ZrSiO_4$. Zirconium is shown in cyan, Si – in grey; O – in red.



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ABSTRACT

Stability of materials under extreme conditions is an important issue for safety of nuclear reactors. Presently, silicon carbide (SiC) is being studied as a cladding material candidate for fuel rods in boiling-water and pressurized water-cooled reactors (BWRs and PWRs) that would substitute or modify traditional zircaloy materials. The rate of corrosion of the SiC ceramics in hot vapor environment (up to 2200 °C) simulating emergency conditions of light water reactor (LWR) depends on many environmental factors such as pressure, temperature, viscosity, and surface quality. Using the paralinear oxidation theory developed for ceramics in the combustion reactor environment, we estimated the corrosion rate of SiC ceramics under the conditions representing a significant power excursion in a LWR. It was established that a significant time – at least 100 h – is required for a typical SiC braiding to significantly degrade even in the most aggressive vapor environment (with temperatures up to 2200 °C) which is possible in a LWR at emergency condition. This provides evidence in favor of using the SiC coatings/braidings for additional protection of nuclear reactor rods against off-normal material degradation during power excursions or LOCA incidents. Additionally, we discuss possibilities of using other silica based ceramics in order to find materials with even higher corrosion resistance than SiC. In particular, we found that zircon ($ZrSiO_4$) is also a very promising material for nuclear applications. Thermodynamic and first-principles atomic-scale calculations provide evidence of zircon thermodynamic stability in aggressive environments at least up to 1535 °C.

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1. Introduction

Nuclear fuel rods in water reactors are contained in sealed tubes (cladding) made of zircaloy-2 (BWRs) and zircaloy-4 (BWRs and PWRs). In a recent accident at the Fukushima nuclear plant, during the LOCA accident, the fuel rods inside the reactors overheated due to the release of decay heat. The heat generated steam inside the core increasing the reactor pressure. While zirconium reacts with water vapor even at ambient temperature, this process becomes significantly accelerated at ~800 °C and higher, resulting in the formation zirconium oxides, hydroxides, and hydrogen, – an explosive gas. In turn, the mixture of overheated steam with hydrogen exploded when it came into contact with air. These explosions caused serious damage to the reactor buildings at the Fukushima nuclear plant.

To avoid such accidents in the future, research work is in progress to develop a suitable coating or replace zirconium alloys altogether with ceramic materials in nuclear reactors. In particular, silicon carbide (SiC) is being studied as a cladding material candidate for fuel rods in water-cooled reactors. Silicon carbide is a refractory ceramic with the numerous commercial applications. It has excellent strength, significantly lower chemical reactivity, very low neutron absorption, and resistance to radiation damage. The material's combination of high strength and hardness, chemical inertness, and attractive thermal properties (high conductivity, low thermal expansion, and thermal shock resistance) makes it useful for a variety of applications such as abrasives and wear components, high temperature semiconductors, armor, and reinforcement in composites.

As it follows from the Si–C phase diagram constructed using ThermoCalc, Fig. 1, silicon carbide melts incongruently, according to the peritectic reaction: SiC + Graphite → Liquid at 1404 °C, Cupid and Seifert [1].

Therefore, the SiC has potentially better properties as a cladding material than zircaloy(s), which will start reacting with water vapor producing appreciable amounts of hydrogen around 800 °C. Unlike most ceramic materials, it also performs well in a nuclear reactor environment as it exhibits excellent radiation stability, is composed of low activation elements, and retains its strength and shape even after a long period of irradiation in a nuclear reactor [2,3].

SiC exhibits polymorphism, and more than 250 polytypes have been identified. One crystal stacking arrangement results in the cubic 3C-SiC (β) structure. All hexagonal stacking arrangements (2H, 4H, 6H, etc.) are grouped together as α-SiC with the 6H polytype being the most prevalent [4,5]. Different technical solutions may be proposed for developing the SiC ceramic fuel cladding. Recently, it was proposed at the INL to strengthen and protect the underlying zircaloy cladding tubing with braided fiber outer wrap [6,7]. The method provides for an additional layer of protection, thereby avoiding the direct contact of the cooling water with a zircaloy tube. At least in principle, this technical solution might have helped to avoid the Fukushima catastrophe had it been in place at the time of the LOCA accident.

In this work, we present our modeling/simulation results for the corrosion rate of SiC in a very high temperature water vapor environment. Our goal was to understand how fast different SiC based reactor components will degrade in such condition and how long time it will take for the ceramic-modified reactor core to melt. Such estimates are important for the Light Water Reactor Sustainability (LWRS) program.

The paper is organized as follows. Section 2 contains the main equations related to the two-step SiC oxidation in water vapor environment and relation of the main parameters of the theory on the change of the environmental conditions (pressure, temperature, viscosity, surface quality, etc). Using this theory (originally developed for the process of combustion), we provide estimates of the corrosion rate of SiC ceramics in Section 3. We found that it would take a significant time for a typical SiC fiber (which contains ~50,000 individual filaments of 5–10 μm in diameter) to completely degrade even in the vapor environment with temperatures up to 2200 °C imitating emergency LWR conditions. In Section 4 we discuss possibilities for using other silica based ceramics in order to find materials with even higher water resistance than SiC. Section 5 contains a general discussion of the specifics of ceramics used in nuclear applications and special requirements that are needed to be satisfied. In particular, we found that zircon ($ZrSiO_4$) is a very promising material for nuclear applications. Section 6 contains atomic-scale arguments based on the first-principles calculations explaining why zircon is extremely water resistant at high temperatures. Our conclusions are presented in Section 7.

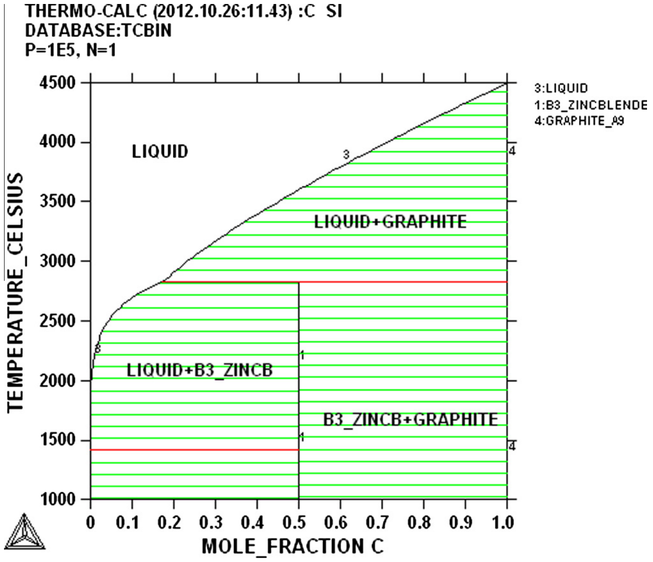

Fig. 1. The Si–C phase diagram calculated using ThermoCalc software and the TCBIN database. Only the 2H-polytype (α-SiC) relevant for our study is presented in this diagram.

2. Paralinear SiC oxidation in water vapor environment

Silicon carbide based composites were developed for use in heat engines. Currently, this material is actively studied as a potential replacement/liner of the existing zircaloy-2 and zircaloy-4 alloys used for manufacturing reactor rods. In both cases, water vapor is a major component of the environments of interest. In particular, it was calculated that the products of combustion contain at least 10% water vapor independent of the fuel-to-air ratio [8]. Simple thermodynamic calculations conducted in 1997 indicated that in an environment containing water vapor, the primary reaction which occurs for the oxidation of SiC is [9]:

$$SiC + 3H_2O = SiO_2 + 3H_2(g) + CO(g), \qquad (1)$$

the symbol 'g' means a gas phase. Our thermodynamic calculations (see Fig. 4) generally confirm this statement. However, the ratio of CO to CO_2 in the mixture will depend upon temperature and the initial conditions in the mixture, see Fig. 2. In the oxygen-enriched environment, corresponding to a combustion process, the following reaction has to be considered [8]:

$$SiC + \frac{3}{2}O_2 = SiO_2 + CO(g), \qquad (2)$$