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The critical issues of SiC materials for future nuclear systems

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ABSTRACT

SiC ceramic and SiC-based composites are promising structural materials for nuclear applications. This paper gives a viewpoint of the basic characterization and research-highlights of SiC-based composites with respect to applications in future nuclear systems. In particular, the following aspects are considered: 1) SiC fiber, 2) interphase, 3) SiC matrix, and 4) SiC joining. Furthermore, remaining challenges and specific technical issues of SiC-based composites for nuclear applications are discussed, and some suggestions to overcome these are proposed.

1. Introduction

Silicon carbide (SiC) is a covalent compound with low density (3.2 g/cm^3), high strength, good thermal stability, and high theoretical thermal conductivity (490 W/m K) [1,2]. Stoichiometric and crystalline SiC has good irradiation resistance and low induced-activation [3,4]. Therefore, SiC ceramic and SiC-based composites, especially continuous SiC fiber-reinforced SiC matrix composites (SiC/SiC), are promising candidates as nuclear structural materials.

Since the Fukushima nuclear accident in 2011, the need to develop SiC-based composites as the accident tolerant fuel (ATF) cladding has become very urgent. For the in-service light-water reactor (LWR), SiC/SiC composites are expected to substitute Zirconium alloy as fuel cladding. For the next generation reactor, e.g., high-temperature gas-cooled reactors (HTGR's), fluoride-salt-cooled high-temperature reactors (FHR's), and gas-cooled fast reactors (GFR's), SiC/SiC composites are considered as fuel and in-vessel components [3]. Although nuclear power has a negative reputation in Europe and the United States, China still has great interest in developing nuclear power because of the fast increasing energy demand. In 2011, China has started a Strategic Priority Research Program named Future Advanced Nuclear Fission Energy. This program includes two parts: the Accelerator Driven Sub-critical (ADS) Transmutation System and the Thorium molten salt reactor nuclear energy system (TMSR). The ADS Transmutation System has proposed SiC/SiC composites as the cladding materials for the Generation IV reactor. With respect to TMSR, one candidate for the structure material and heat exchanger is Ni-based alloy and Hastelloy, which only permits an outlet temperature maximum of ~700 °C [5]. A more promising choice is SiC/SiC composites, which permit an outlet temperature maximum of ~1000 °C.

SiC/SiC composites also appear to be very promising options for use in future fusion power plants. Several future fusion reactor design concepts, including the TAURO blanket of the European Union, the ARIES-AS concept of the US, and the DREAM concept of Japan, consider SiC/SiC as potential structural materials [6].

2. SiC fiber

SiC fiber is the "skeleton" of SiC/SiC composites, which carries the most of loading. Since SiC fiber was first fabricated by Yajima in 1970s, commercial available SiC fiber has been rapidly improved, and SiC fiber is now classified into three generations. The Generation I SiC fiber was represented by Nicalon (Nipon Carbon Ltd., Japan), which has a characteristic high C/SiC ratio (1.31), a high oxygen mass content (11.7%), and low crystallization of SiC. The Generation II SiC fiber was represented by Hi-Nicalon, whose C/SiC ratio was decreased to 1.05, the oxygen mass content was decreased to 0.2%, and the crystallization of SiC was improved. The Generation III SiC fiber consists of near-stoichiometric beta-SiC with a large grain size. Generation III SiC fiber is represented by Hi-Nicalon Type S (Nipon Carbon Ltd., Japan), Tyranno SA3 (Ube Industries LTD., Japan), and Sylramic (Dow Corning-ATK COI Ceramics Inc., USA). The generation III SiC fiber shows excellent overall performance, including high tensile strength (even at 1800 °C), a high Young modulus, and high thermal conductivity. With regard to nuclear applications, the generation III SiC fiber shows little swelling or any

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other substantial changes under irradiation [7]. However, the presence of impurities or additive elements, e.g., free carbon in Hi-Nicalon Type S, oxygen in Tyranno SA3, and boron in Sylramic, remain uncertainties that affect its longevity. Because fabricating SiC fiber is a complicated task and a great challenge, it is difficult to achieve significant improvements in a short time and many details will not be discussed in this paper.

3. Interphase

The interphase between fiber and matrix, which is the "ligament" of the composites, provides chemical protection of fibers, transfers the load between matrix and fiber, and controls the crack deflection [8]. Both the composition and structure of the interphase have important effects on the mechanical, thermal physical, oxidation resistance, and irradiation resistance properties of SiC/SiC composites.

For SiC/SiC composites, the interphase of pyrolytic carbon (PyC), boron nitride (BN), and multilayer $(PyC/SiC)_n$ or $(BN/SiC)_n$ are commonly used as fiber surface coatings. Both PyC and BN have a layered structure, thus, they are beneficial to avoid cracks and improve the toughness of the composites. Generally, PyC interphase composites have outstanding mechanical properties, but they lack oxidation resistance. BN interphase composites show slightly poorer mechanical properties but improved oxidation resistance. Multilayer interphase composites usually combine the advantages of composites with monolayer interphases. For example, composites with PyC/SiC multilayer interphase show a similar fracture behavior as monolayer PyC interphase composites but they exhibit better neutron irradiation stability [9].

With regard to nuclear applications, one challenge the SiC/SiC composites face is the uncertain long-term irradiation-stability. Although the challenge is mainly attributed to the damage of SiC fiber under irradiation, the instability of the interphase still contributes [8]. PyC is known to undergo moderate changes of contraction-swelling-amorphization in irradiation environments [10], which would decrease both reliability and service life of the composites with PyC or PyC-contained interphases. With regard to the BN interphase, the rapid transmutation of ^{10}B under neutron irradiation also renders it unsuitable for nuclear applications [3]. In the past years, the effect of irradiation on the structural, mechanical, and thermal properties of SiC/SiC composites has been investigated extensively. Newsome et al. investigated the effects of fast neutron irradiation on SiC and SiC/SiC composites [11]. The results show that swelling is seen for both monolithic CVD SiC and SiC/SiC composites. The swelling magnitude of CVD SiC is approximately 1.9%, 1.1%, and 0.7% at the irradiation temperature of 300, 500, and 800 °C, respectively. The elastic modulus of CVD SiC is not greatly influenced by irradiation and the flexure strength is increased. SiC/SiC composites reinforced with Hi-Nicalon Type S fibers and Hi-Nicalon fibers show similar swelling behavior to that of CVD SiC. Significant irradiation effects on mechanical properties are not seen in the composites. However, the proportional limit stress (PLS) of the composites is slightly decreased, which is attributed to fiber/matrix interphase degradation and/or elastic modulus reduction following irradiation. Some of the investigations indicate that the poorer properties of SiC/SiC composites after irradiation are due to structural changes of the interphase. Katoh et al. investigated the effect of neutron irradiation for a damage level > 70 dpa on the Hi-Nicalon Type S SiC/SiC composites at temperatures ranging from 300 to 800 °C [12,13]. Their results show that sever cracking and degradation occur at the multilayer PyC/SiC interphase at 300 °C. The Young modulus decreased significantly at 40 to 70 dpa for the samples irradiated below 500 °C, which involves partial debonding caused by interphase damage. Nozawa et al. investigated the effect of neutron irradiation on the interphase of Hi-Nicalon Type S SiC composites with a PyC interphase and a PyC/SiC multilayer interphase [9]. The results show that both interfacial debond shear-strength (IDSS) and interfacial-friction stress (IFS) first decrease for increasing neutron doses and then approach a constant value for low dose (~10 dpa) irradiation.

The irradiation instability of the traditional interphase materials presents an opportunity for the development of an alternative interphase for SiC/SiC composites. The alternative interphase is expected to have good chemical stability, irradiation resistance, and fracture energy absorption. When referring to the above properties, we naturally think of a series of materials called the "MAX phase". The MAX phase, represented by Ti_3SiC_2 and Ti_3AlC_2, is a group of layered ternary compounds with the general formula $M_{n+1}AX_n$ (M: early transition metal; A: group A element; X: C or N). The MAX phase has a fracture energy absorption mechanism as basal plane slip, grain buckling, kink-band formation, and grain fracture [14], which can play a similar role as PyC and BN in the SiC/SiC composites. The MAX phase combines some properties of the metal and matrix materials, such as good electrical and thermal conductivity, damage tolerance, oxidation resistance, and above all, good irradiation resistance. J.C·Nappe et al. investigated the structural changes induced by heavy-ion irradiation in Ti_3SiC_2 [15]. Their results show that Ti_3SiC_2 swells at room temperature ($2.2 \pm 0.8\%$) after an average irradiation dose of 4.3 dpa. No crack formation has been observed after sample irradiation at 1223 k up to 10^{19} m^{-2}. Maulik et al. investigated the effect of helium irradiation on Ti_3AlC_2 [16]. The results suggest that the MAX phases may be resistant to the formation of large He-bubbles for temperatures as low as 500 °C. Peng song et al. also showed that Ti_3AlC_2 exhibits excellent resistance against He-ion irradiation [17]. When the damage level increased up to 52.2 dpa for room temperature irradiation, neither amorphization nor large cracks appear in Ti_3AlC_2. Tallman et al. investigated the effect of neutron irradiation on Ti_3AlC_2, Ti_2AlC, Ti_3SiC_2, and Ti_2AlN [18]. They indicate Ti_2AlC and Ti_3SiC_2 are quite stable under neutron irradiations at elevated temperatures. They also reveal that Ti_2AlC and Ti_3SiC_2 are more neutron radiation tolerant that TiC and Al_2O_3 [19]. Ang et al. investigated the phase stability, swelling, microstructure and strength of Ti_3SiC_2 ceramics after low dose neutron irradiation [20]. The results show that Ti_3SiC_2 appears to be irradiation tolerant at ~400 °C, and increasingly irradiation resistant at ~630–700 °C.

According to the above analysis, the MAX phase appears to be an ideal candidate for the interphase materials of nuclear-grade SiC/SiC composites. However, the fabrication of the MAX phase coating on SiC fibers still remains a challenge. Until today, there has been no report of a successful fabrication of a MAX phase on SiC fiber. In the past, almost the complete interphase of SiC/SiC composites was fabricated using chemical vapor deposition (CVD). This could enable continuous, uniform, and thickness controllable fiber coating. However, CVD cannot be used to fabricate a MAX phase coating due to the serve reaction condition [21]. Therefore, it is desirable to develop a feasible method to prepare MAX phase coating on a SiC fiber. In our recent work, we have explored the possibility of preparing the MAX phase coating on SiC fiber. A continuous and uniform coating with a dominating phase of Ti_3SiC_2 and TiC was fabricated on SiC fiber via the in-situ reaction of SiC and Ti in a NaCl-KCl eutectic molten salt – see Fig. 1. The results show that the composition and thickness of the coating could be controlled by changing the reaction conditions, e.g., temperature, composition of the starting materials, and reaction time. Our preliminary work provides a feasible way to prepare a MAX phase on SiC fiber. However, two issues remain to be solved. One is the optimization of the reaction condition to obtain a high purity Ti_3SiC_2 coating. The other is that it is not feasible to fabricate the coating via the in-situ reaction on SiC fiber because the reaction would damage the fiber. Therefore, pre-depositing a SiC coating on the fiber by CVD and consuming the CVD-SiC to fabricate the Ti_3SiC_2 coating might be an alternative approach.

4. SiC matrix

SiC matrix represents the "muscle" of the SiC/SiC composites. Generally, the SiC/SiC composites are fabricated by introducing a SiC matrix into the SiC fiber woven preform. During the last few decades, several techniques have been developed to fabricate the SiC matrix. The mainly include chemical vapor infiltration (CVI), nano-infiltration and transient

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