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A novel way to enhance hydrogenation resistance of nano-layered titanium silicon carbide by the doping of aluminium

Chen Chen, Canhui Xu, Fangzhi Li, Yongqiang Tan, Haibin Zhang*, Shuming Peng**

Innovation Research Team for Advanced Ceramics, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, China

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ABSTRACT

The outstanding irradiation and corrosion resistance of nano-layered Ti_3SiC_2 make it suitable for cladding materials in advanced nuclear systems. However, Ti_3SiC_2 shows the relatively poor thermal stability in hydrogen circumstance at high temperature, which is a big obstacle for its nuclear related applications. In this paper, we proposed an effective approach to improve the hydrogenation resistance of Ti_3SiC_2 by the doping of Al. The experimental results demonstrated that compared to pure Ti_3SiC_2, $Ti_3Si_{0.9}Al_{0.1}C_2$ (TSAC) displayed much better hydrogenation resistance. Through first-principles calculation, it was concluded that the introduction of H interstitial atom made the formation energy of Al vacancy much lower, so Al atoms became much easier to remove from TSAC than Si atoms and Ti atoms. The preferable loss of aluminium from TSAC substrate gave rise to the formation of Al_2O_3 layer, which improved the hydrogenation resistance of TSAC by inhibiting further reaction between TSAC and hydrogen.

1. Introduction

The new nano-layered ternary systems with a general formula of $M_{n+1}AX_n$ (n = 1, 2 or 3, referred as MAX phases), where M is a transition metal, A is an A group element and X is C or N, have attracted considerable attentions in recent years owning to their unique combination of metal- and ceramic-like properties. Generally, MAX phases exhibit high thermal and electrical conductivity, good thermal shock resistance, good machinability, low density, high modulus and strength, which enable them to be promising candidates for various applications [1–12]. Ti_3SiC_2 is one representative type of MAX phases with a hexagonal crystal structure and $P6_3/mmc$ space group [13]. Its crystal structure can be depicted as periodic planar stacking of nano-sheets of edge-sharing Ti_6C octahedron and close-packed Si atoms.

Due to their good irradiation [14,15] and corrosion resistance, MAX phases have been considered to be promising cladding materials in nuclear reactors. In order to explore the possibility of TSAC applied in the future Gas Fast nuclear Reactors (GFR), X. M. Liu et al. studied the ion irradiation behaviours of TSAC [16]. It was found that after 74 MeV Kr ion irradiation and 92 MeV Xe ion irradiation with a dose of 10^{19} ions·cm^{-2}, the damage tolerance ability of TSAC well preserved and their basic crystal structure remained stable. In order to study the feasibility of Ti_3SiC_2 serving as pump material of lead-cooled fast reactor, A. Heinzel et al. investigated the corrosion behaviour of Ti_3SiC_2 in liquid Pb [17]. After corrosion at 550 °C in liquid Pb for 4000 h (Oxygen concentration was 10^{-6} wt%), it was found that Ti_3SiC_2 preferentially reacted with oxygen in the corrosion process, and a TiO_2 film was formed on the surface, which played a very good protection role on Ti_3SiC_2, making Ti_3SiC_2 exhibit excellent corrosion resistance in liquid Pb.

Besides irradiation and corrosion, high temperature hydrogenation effect which may remarkably decrease the ductility and result in the failure of materials is also an important factor that should be considered. In the fission reactors, hydrogen can be produced by neutron irradiation of water. Especially, in the case of Loss of Coolant Accident (LOCA), large amount of hydrogen can be generated by reactions between Zr-based clads (zircaloys) and steam water. The existence of hydrogen at high temperature could lead to hydrogen embrittlement of cladding materials and hydrogen explosion. Therefore, hydrogenation behaviour of Ti_3SiC_2 in advanced nuclear energy systems is one key issue that should be resolved. Due to the high diffusivities of fission product surrogates (Ag, Au and Cs) in Ti_3SiC_2, W. L. Jiang et al. suggested some caution

* Corresponding author.
** Corresponding author.
E-mail addresses: hbzhang@caep.cn (H. Zhang), pengshuming@caep.cn (S. Peng).

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in using Ti_3SiC_2 as a fuel cladding material [18]. In our previous work, it was found that Ti_3SiC_2 showed relatively poor high temperature hydrogenation resistance and they tended to dissociate at 1200 °C in hydrogen. The formation of $TiSi_2$ layers that were easily removed from Ti_3SiC_2 was responsible for the dissociation of Ti_3SiC_2 [19]. H. B. Zhang et al. proved that doping with Al to form a continuous protective oxide scale Al_2O_3 was an effective method to enhance the oxidation resistance of Ti_3SiC_2 [20]. In order to enhance the thermal stability of Ti_3SiC_2 in hydrogen, a similar protective layer that was not easy to exfoliate was thought to be essential.

In this work, we intend to explore the hydrogenation behaviour of TSAC as well as its hydrogenation mechanism. TSAC specimens were hydrogenated in the temperature range of 1200–1400 °C, and the related mechanism was clarified by XRD, Raman spectroscopy, SEM and first-principles calculation.

2. Experimental procedure

The bulk TSAC material was fabricated by in situ hot-pressing/solid-liquid reaction method. Commercially available silicon (99.5%, −300 mesh), aluminium (99.5%, −300 mesh), titanium (99.5%, −300 mesh) and graphite (99.5%, −300 mesh) powders were selected as the starting materials to synthesize TSAC with a near stoichiometric ratio. The mixed powders were milled in a polyurethane jar for 18 h. After milling, the powders were cold pressed into a disk with the diameter of 50 mm. The sample was heated to 1500 °C at the rate of 10 °C/min and held for 30 min under a pressure of 30 MPa. Subsequently, it was annealed at 1460 °C for 60 min.

For the hydrogenation experiments, $3 \times 4 \times 5$ mm^3 rectangular bars were cut from TSAC disk using electrical-discharge machining. These bars were ground on 1200 grit SiC papers, polished using diamond paste, chamfered and degreased in acetone. Hydrogenation experiments were conducted in a tungsten furnace under hydrogen atmosphere (Oxygen concentration was 10^{-6} wt%). The samples were heated to 1200–1400 °C and held for 3 h.

The phase distributions of the as-synthesized TSAC sample were identified via X-ray diffraction (XRD, Panalytical, Netherland) with Cu$K\alpha$ radiation ($\lambda = 0.1542$ nm). The surfaces and cross sectional microstructures of the hydrogenated samples were observed via an Ultra 55 scanning electron microscope (SEM, Zeiss, Germany) equipped with an EDS system. The Raman spectra of the sample were detected on LABRAM HR laser Raman (Horiba JY, France). A He–Ne laser (514.5 nm) with an incident power of 20 mW was used as the excitation source, and the spot size was focused to 2 μm.

To understand the influence of hydrogen on the removal behaviour of Al/Si atoms from the TSAC bulk, further investigation was implemented by the first-principles calculation based on the VASP package (Vienna *ab initio* simulation package) with PAW-GGA (PW91) functional. The calculations were performed with a $2 \times 2 \times 1$ supercell, energy cutoff of 500 eV for plane wave basis set and a $9 \times 9 \times 1$ Monkhorst-Pack k-points grid for integration over the Brillouin zone. The total energies were converged up to 10^{-5} eV.

3. Results

3.1. Phase identification

Fig. 1 presents the XRD patterns of TSAC samples after hydrogenation treatment. It can be seen that the diffraction peaks of the TSAC phase remains unchanged at 1200–1400 °C without shifting or broadening, demonstrating that the structure of TSAC are quite stable during hydrogenation treatment even at 1400 °C. This is quite different from Ti_3SiC_2 which tended to decompose at 1200 °C

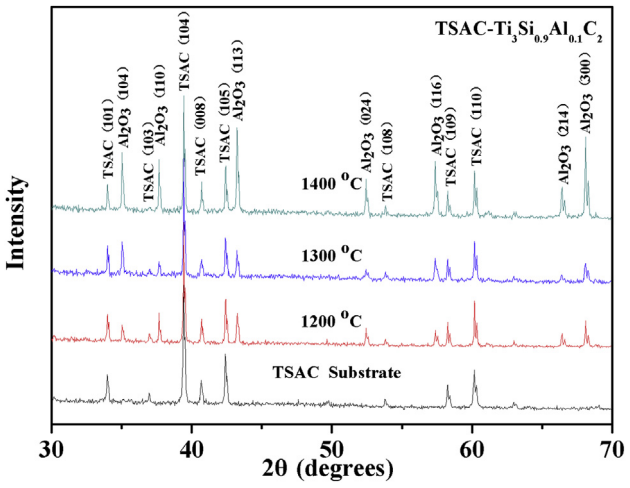

Fig. 1. X-ray diffraction patterns of TSAC samples before and after hydrogenation treatment at 1200 °C–1400 °C for 3 h in flowing hydrogen (TSAC denotes $Ti_3Si_{0.9}Al_{0.1}C_2$).

in hydrogen atmosphere [19](Fig. 2). Besides the main TSAC phase, no diffraction peaks corresponding to hydrides were identified. Al_2O_3 was detected as the only secondary phase after hydrogenation treatment at 1200–1400 °C, and the diffraction peaks of Al_2O_3 became increasingly intensive with increasing hydrogenation temperature. The formation of Al_2O_3 was believed to originate from the reaction between aluminium diffusing outward from TSAC substrate and tiny content of oxygen in the hydrogen atmosphere. While different from the oxidation behaviours of TSAC in air [20], no diffraction peaks corresponding to SiO_2 or TiO_2 were detected. The reason might be that the formation energy of Al_2O_3 was lower than that of SiO_2 and TiO_2 [21,22]. The oxidation product of TSAC in air were identified to be α-Al_2O_3 and TiO_2 at 1000–1100 °C, α-Al_2O_3, TiO_2 and Al_2TiO_5 at 1200–1300 °C, TiO_2 and Al_2TiO_5 at 1350°C[20]. While after thermal treatment at 1200–1400 °C in hydrogen atmosphere, the only reaction product is Al_2O_3. This can be ascribed to the higher affinity to oxygen of aluminium than that of silicon and titanium. Z. J. Feng et al. claimed that the diffusion activity of Al in Ti_2AlC was higher than that of Ti in Ti_2AlC [23]. S. Basu *et al.* stated that a much lower oxygen partial pressure was needed for

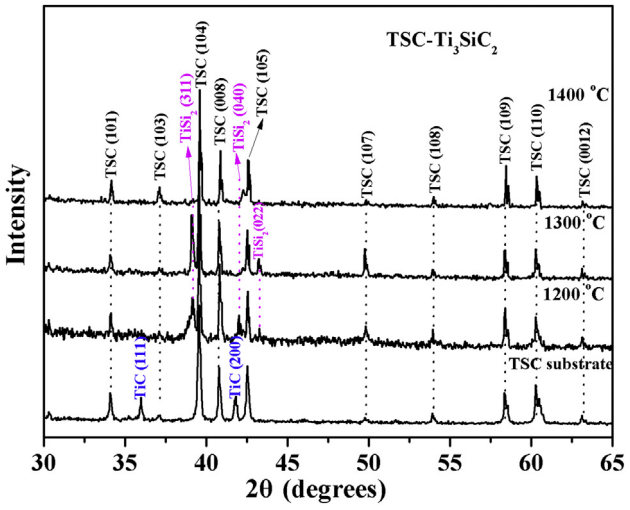

Fig. 2. X-ray diffraction patterns of Ti_3SiC_2 samples before and after hydrogenation treatment at 1200 °C–1400 °C for 3 h in flowing hydrogen (TSC denotes Ti_3SiC_2).