Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Influence of Al_2O_3 on the oxidation resistance of SiC ceramic: First-principle study and experiment

Chunyu Cheng, Hejun Li*, Qiangang Fu*, Lu Li, Liping Guo

State Key Laboratory of Solidification Processing, Shaanxi Key Laboratory of Fiber Reinforced Light Composite Materials Northwestern Polytechnical University, Xi'an, 710072, China

ARTICLE INFO

Keywords:
Al_2O_3
SiO_2
Oxidation
First principle

ABSTRACT

The influence of Al_2O_3 on the oxidation resistance of SiC was studied by first-principle calculation and oxidation test. The oxidation process of the Al_2O_3-doped SiC ceramic divides into three stages. At first, Al atom diffuses into the generated SiO_2 and substitutes Si atom to form −Al−O−Si− ring. Then, the ring is damaged due to the reaction between the O atom in Al−O bond and CO molecule, causing a CO_2 molecule and an O vacancy formation. Finally, once O_2 or another CO molecule approaches O vacancy, −Al−O−O−Si− or −Al−O−C−Si− ring will be formed to recover the network structure of SiO_2.

1. Introduction

Owing to the excellent mechanical properties, such as low coefficient of thermal expansion, high thermal conductivity, excellent thermal stability and oxidation resistance, SiC is widely used in many fields, especially in harsh environments [1–3]. Recently, it is widely investigated to utilize SiC as the protective coating material for applications in high-temperature oxygen-containing environment [4–6]. For example, Chu et al. reported that SiC coated C/C composites exhibited good oxidation resistant property at 1773 K [7]. Many techniques can be used to prepare SiC coatings, such as plasma spray [8], pack cementation [7], slurry [9] and chemical vapor deposition [10]. Among them, pack cementation can create gradient coating with a strong interface bonding between coating and substrate. The raw materials of pack cementation for preparing SiC coating include Si, graphite and Al_2O_3. It is expected that Al_2O_3 was used as sintering aid [11]. Up to now, the effect of Al_2O_3 on the oxidation resistance of SiC is rarely reported.

During the oxidation process of Al_2O_3-doped SiC, self-healed SiO_2 glass layer and gaseous CO and CO_2 form [12], and Al impurities might diffuse into the SiO_2. Lægsgaard and Wang et al. [13–16] found that the Al atom would substitute a Si atom in SiO_2, causing the SiO_2 structure disorder. However, the interaction between the Al−O bond and the generated CO gas remains unclear.

In the present work, the role of Al_2O_3 on the oxidation resistance of SiC was studied by first-principle calculation and isothermal oxidation test. The local chemistry governing CO or O_2 molecule diffusing to an Al-doped SiO_2 was investigated, which was verified qualitatively by the oxidation behavior of SiC ceramic with/without Al_2O_3.

2. Procedures

2.1. Model

The first-principle calculation based on density functional theory (DFT) by CASTEP code was used to evaluate the influence of the introduced Al_2O_3 on the properties of SiO_2. The CA-PZ local density approximation (LDA) method, Broyden-Fletcher-Goldfarb-Shanno (BFGS) and ultrasoft pseudopotentials were employed [17]. The energy cut-off for the basis set was 400 eV, which was sufficient for the total energy and geometry of SiO_2 and Al-doped SiO_2 (cited as "Al-SiO_2" in the following) structure. To investigate the behavior of CO molecule in SiO_2 or Al-SiO_2, a model with 108 atoms of α-quartz was built. Geometry within the unit cell was optimized to the absolute value of force on each unconstrained atom < 0.001 eV/Å. Mulliken bond population in the optimized structure was investigated to express the bond strength. The distance cut-off for bond populations was 3.0 Å.

The solution energy of an interstitial CO or O_2 molecule in SiO_2/Al-SiO_2 was written as following [18]:

* Corresponding authors.
E-mail addresses: lihejun@nwpu.edu.cn (H. Li), fuqiangang@nwpu.edu.cn (Q. Fu).

https://doi.org/10.1016/j.corsci.2018.02.009
Received 24 February 2017; Received in revised form 26 January 2018; Accepted 8 February 2018

Table 1
Mulliken bond populations and lengths of Al—O bonds in Al_2SiO_5 and Al-SiO_2.

	Bond population (bond length/Å)	
	Al_2SiO_5	Al-SiO_2
Al-O	0.27–0.47 (1.760–1.988)	0.42 (1.722) 0.40 (1.741)

$$E^{s}_{CO/O_2} = E_{system+CO/O_2} - E_{system} - E_{CO/O_2}, \quad (1)$$

where $E_{system+CO/O_2}$and E_{system} are the energy of the SiO_2/Al-SiO_2 system with an interstitial CO or O_2 molecule and the separate SiO_2/Al-SiO_2 system, respectively. E_{CO/O_2} denotes the molecule chemical potential of CO or O_2 molecule.

2.2. Experiment

SiC ceramics were prepared by hot pressing. Firstly, Si (purity: 99.90%) and graphite (purity: 99.99%) powders were mixed with the mass ratio of 4:1. The mixed powders were heated up to 2273 K at a rate of 6–9 °C/min and maintained at this temperature for 2 h. Subsequently, the obtained powders were taken out and milled for more than 4 h before they were pressed at a pressure of 40 MPa at 2143 K for 30 min. The SiC ceramic with Al_2O_3 (cited as "Al-SiC" in the following) was prepared by the same heat treatment and hot pressing. The content of Al_2O_3 (purity: 99.0%) in the initial mixture powders was 5 wt.% with the same mass ratio of Si and graphite. The oxidation test of the ceramic samples was conducted in a corundum tube furnace in air. When the temperature was up to 1773 K, the ceramic samples were put into the furnace for a designated period, and then were taken out of the furnace and naturally cooled to room temperature. Subsequently, they were put directly into the furnace again for the next oxidation period. During the oxidation test, the mass of the ceramic samples was measured by electronic balance with a sensitivity of ± 0.1 mg. Mass change percentages (ΔM%) of the ceramic samples were calculated by the following equation:

$$\Delta M\,\% = (m_0 - m_1)/m_0 \times 100\%, \quad (2)$$

where m_0 and m_1 are the mass of the ceramic samples before and after oxidation, respectively.

Microstructures of the ceramic samples before and after oxidation were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) at an accelerating voltage of 300 kV.

Table 2
Mulliken bond populations and lengths of C—O and Al—O bonds in SiO_2 and Al-SiO_2 with an interstitial CO molecule.

	Bond population(bond length/Å)	
	SiO_2	Al-SiO_2
C—O2	1.19(1.15)	1.11(1.20)
C—O1	−0.04(2.71)	0.52 (1.39)
Al—O	–	0.46(1.68)
	–	0.47(1.68)
	–	0.45(1.71)
Al—O1	–	0.1(2.01)

3. Results and discussion

3.1. The stability of Al in Al_2SiO_5 and Al-doped SiO_2

The substitutional Al atom was initially put in the place of a Si atom in SiO_2, then the structure was allowed to relax. To investigate the stability of Al in Al-SiO_2 and $xAl_2O_3{\cdot}ySiO_2$ formed by reaction (3), Mulliken bond population was employed to evaluate the relative strength of the Al—O bond. A high positive Mulliken bond population value implies a high degree of covalency of the bond. A value close to zero indicates that there is no significant interaction between the electronic populations of the two atoms [19]. Considering the strength and energy of Al—O bond in $xAl_2O_3{\cdot}ySiO_2$ are similar to those in Al_2SiO_5 [20], only the crystal Al_2SiO_5 was calculated.

$$xAl_2O_3(s) + ySiO_2(l) \rightarrow xAl_2O_3{\cdot}ySiO_2(s). \quad (3)$$

Mulliken bond populations and lengths of the Al—O bonds in Al_2SiO_5 are summarized in Table 1. After geometry optimization, the Al—O bond lengths in Al_2SiO_5 were calculated to be 1.760 and 1.988 Å, while those in Al-SiO_2 are 1.722 and 1.741 Å. In addition, the overlap populations between Al atom and O atom in Al_2SiO_5 range from 0.27 to 0.47, while those in Al-SiO_2 are 0.40 and 0.42. These indicate that the Al—O bond in Al-SiO_2 is stable, but parts of the Al—O bonds in Al_2SiO_5 are weak, which results in the escape of Al atom from the Al_2SiO_5.

3.2. The influence of CO molecule on the Al-SiO_2

As CO molecule diffused into the interstitial site near Al atom (Fig. 1(b)), it might have some influences on the Al-SiO_2. For comparison, the SiO_2 with an interstitial CO molecule was calculated (Fig. 1(a)). The calculated solution energies concerning CO molecule in SiO_2 and Al-SiO_2 are 9.56 and 1.59 eV, respectively. The larger positive solution energy means that CO molecule presents in the form of

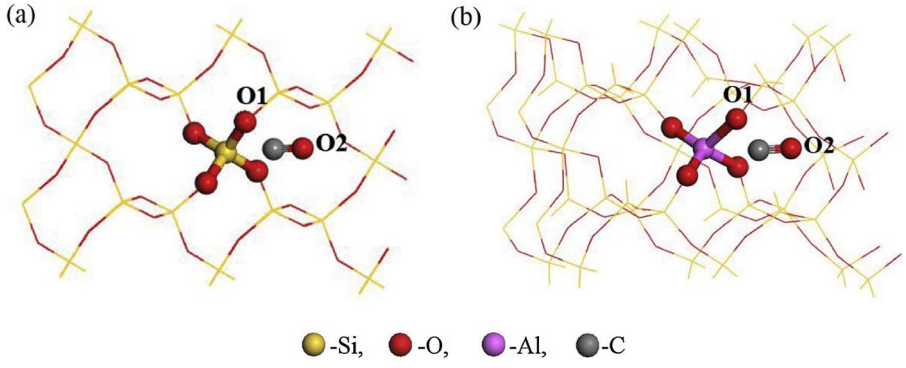

Fig. 1. Bulk structures of (a) SiO_2 and (b) Al-SiO_2 with an interstitial CO molecule.