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Short communication

Investigation on the effect of Nb doping on the oxidation mechanism of Ti_3SiC_2

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ABSTRACT

Nb doping substantially changes the oxidation mechanism and significantly enhances its oxidation resistance of Ti_3SiC_2 at 800 °C. After Nb doping, the oxidation of Ti_3SiC_2 is only controlled by the inward diffusion of O, while the outward diffusion of Ti is restrained totally. The oxide layer structure changes from a duplex-layer of TiO_2 outer layer and TiO_2+SiO_2 mixture inner layer to a single TiO_2+SiO_2 mixture layer. It is proposed that Nb doping decreases the concentrations of oxygen vacancies and Ti interstitials in the formed TiO_2, leading to the completely restrained outward diffusion of Ti and the decreased oxidation rate.

1. Introduction

$M_{n+1}AX_n$ phase is a fascinating group of layered ternary ceramics, where M is an early transition metal, A is an IIIA or IVA element, X is C and/or N. They have attracted significant attention due to the combination of merits of both ceramics and metals, such as low density, high modulus and fracture toughness, high electrical and thermal conductivity, easy machinability, good resistance to thermal shock below 1100 °C [1–6]. Among the reported MAX phases, Ti_3SiC_2 is one of the most typical MAXs [7–10]. It is the promising structural ceramic for many high temperature applications, such as heating elements for high-temperature furnaces and components in fuel burning engines for the automobile and aircraft [11–13]. Meanwhile, Ti_3SiC_2 is a promising interconnect material for solid oxide fuel cell [14,15].

It should be noted that no matter for the application of high temperature structure ceramic, or interconnects material of solid oxide fuel cell, the oxidation resistance of Ti_3SiC_2 is very important, which has been widely studied [12,13,16–18]. Unlike the preferential oxidation behavior of Ti_3AlC_2 with formation of a continuous Al_2O_3 scale [19–21], no preferential oxidation happened and no continuous SiO_2 layer formed during the oxidation of Ti_3SiC_2, leading to relative weak oxidation resistance. The oxidation resistance of Ti_3SiC_2 still needs to be improved before practical application [13–15,22,23]. Several methods have been proposed to improve the oxidation resistance of Ti_3SiC_2, such as incorporation of Al_2O_3 and SiC particles [24–28], Si pack cementation [29,30] and Al doping to form $Ti_3(Si_{0.9}Al_{0.1})C_2$ [23]. Our previous studies [13–15] showed that 2–10 at.% Nb doping for Ti_3SiC_2 can also greatly improve the oxidation resistance in the temperature range of 600–1300 °C in air atmosphere. Correspondingly, the oxidation rate constant decreased 1–2 orders of magnitude compared to that of Ti_3SiC_2. Especially, after 2 at.% Nb doping, the oxidation kinetics of Ti_3SiC_2 changed from line to parabolic at 1200–1300 °C in air atmosphere [13]. At 800 °C in air, after 5 at.% Nb doping, the oxide scales layer structure of Ti_3SiC_2 changed from a duplex-layer (TiO_2+SiO_2 inner layer + TiO_2 outer layer) to a single mixture layer (TiO_2+SiO_2) [14,15]. However, the effect of Nb doping on the oxidation mechanism of $(Ti,Nb)_3SiC_2$ is not deeply studied up to now.

In the present work, the marker oxidation experimental is conducted to give an insight into the ions transportation mode and oxide scale growth mechanism of Nb doped and Nb free Ti_3SiC_2 at 800 °C in air. At the same time, based on the defect chemistry theory, the effect of Nb dopant on the native defects concentration in the oxide scale is analyzed. The relationship between defects concentration and the ions transportation mode is discussed. Finally, by summarizing up the above analysis, the fundamental understanding of the effect of Nb doping t on the oxidation mechanism of $(Ti,Nb)_3SiC_2$ is concluded.

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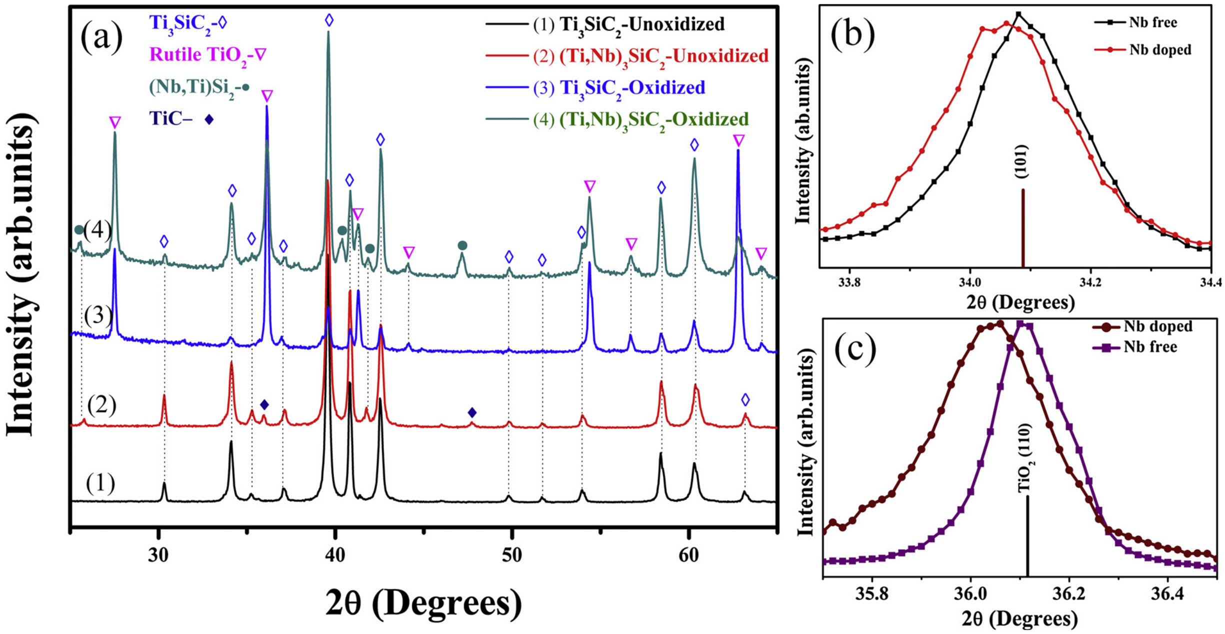

Fig. 1. (a) XRD results of the synthesized and oxidized $(Ti_{0.95}Nb_{0.05})_3SiC_2$ and Ti_3SiC_2; (b) Comparison of (101) peak position of $(Ti,Nb)_3SiC_2$ and Ti_3SiC_2 at 33.7–34.4°; and (c) Comparison of (110) peak of r-TiO_2 formed on $(Ti,Nb)_3SiC_2$ and Ti_3SiC_2.

2. Experimental procedure

Pure and Nb-doped Ti_3SiC_2 solid solution were fabricated by in-situ solid-liquid reaction/hot pressing process. The raw powders included titanium (99%, 300 mesh), niobium (99%, 200 mesh), silicon (99.5%, 400 mesh) and graphite (99%, 200 mesh). The molar ratio of Ti:Nb:Si:C was 2.85:0.15:1:2 and Ti:Si:C was 3:1:2 for $(Ti_{0.95}Nb_{0.05})_3SiC_2$ and Ti_3SiC_2, respectively. The above mixed powders were compacted uniaxially under 5 MPa in a graphite die with a diameter of 50 mm, and then hot pressed at 1550 °C under 30 MPa for 0.5–1 hour in a flowing Ar atmosphere. According to the above procedures, the obtained Ti_3SiC_2 bulk was single phase. For $(Ti_{0.95}Nb_{0.05})_3SiC_2$ bulk, except the main Ti_3SiC_2 phase, a little of TiC and $(Nb,Ti)Si_2$ appeared, as Fig.1(a) showed. $(Ti_{0.95}Nb_{0.05})_3SiC_2$ is noted as $(Ti,Nb)_3SiC_2$ in this work. In addition, Fig.1(b) presented that after Nb doping, the (101) peak of Ti_3SiC_2 shifted to lower angle, which reflected the Nb has been doped into Ti_3SiC_2 lattice.

The samples for marker oxidation test with dimension of $10 \times 10 \times 2$ mm^3, were grounded down to 2000# SiC paper, polished using 1 μm diamond paste, chamfered, and then degreased in the ethanol and distilled water. The inert markers of Au points were evaporated on the samples surfaces by vacuum evaporator. The evaporation condition was: 9 mA current and 1 kV voltage. Before Au point deposition, the samples were wrapped by Al foil and punched points and lines using needle. Then the samples were put in a tubular resistance furnace and isothermally oxidized at 800 °C in air for 100 h.

The cross-section sample was prepared by embed the oxidized sample in the resin, followed by carefully grounding and polishing. The surface and cross-section morphologies of the formed oxide scale were observed by the SUPRA35 scanning electron microscope (SEM, LEO, Oberkochen, Germany), equipped with an energy-dispersive spectroscopy (EDS, INCA, Oxford Instrument, Oxford, U.K.) system. A thin layer of Au was sputtered on the surface of the oxidized sample before SEM examination. The chemical composition of the oxide scale formed on Nb doped Ti_3SiC_2 was determined by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed on the sample surfaces using a surface analysis system ESCALAB250 equipped with an Mg radiation (Kα = 1253.6 eV). All binding energies used in this study were referenced to the binding energy of the carbon C1s peak at 284.6 eV. The peak fitting was performed using a Gaussian/Lorentzian peak shape after a Shirley background removal with XPSPEAK 4.1 software.

3. Results and discussion

In order to give an insight into the effect of Nb doping on the oxidation mechanism of $(Ti,Nb)_3SiC_2$ solid solution, the marker oxidation experiment for $(Ti,Nb)_3SiC_2$ is conducted at 800 °C in air atmosphere. For comparison, the same marker oxidation experiment is also carried on Ti_3SiC_2. Fig.1(a) exhibits the XRD patterns of $(Ti,Nb)_3SiC_2$ solid solution and Ti_3SiC_2 after marker oxidation. The detected oxide scale on the two materials is only rutile TiO_2. No any of Nb or Si oxide is detected. Fig.1(c) presents the comparison of the (110) peak of rutile TiO_2 formed on $(Ti,Nb)_3SiC_2$ solid solution and Ti_3SiC_2. It can be seen clearly that the (110) peak of rutile TiO_2 formed on $(Ti,Nb)_3SiC_2$ shifts to lower angle compared with that on Ti_3SiC_2, which reflects that the crystal lattice of (110) surface of TiO_2 is enlarged. In addition, no Nb oxide is detected in the oxide scale formed on $(Ti,Nb)_3SiC_2$. Thus, it is indicated that Nb added in Ti_3SiC_2 has doped into rutile TiO_2 lattice after oxidation.

Fig.2(a) and (b) exhibits the surface morphologies of $(Ti,Nb)_3SiC_2$ and Ti_3SiC_2 after the marker oxidation experiment. It can be clearly seen that Au points appears on the top surface of the $(Ti,Nb)_3SiC_2$, but no any Au trail can be found on the top surface of oxidized Ti_3SiC_2. At the same time, it should be noted that the oxide grains formed on the $(Ti,Nb)_3SiC_2$ are much smaller than that of Ti_3SiC_2. The grain shape of $(Ti,Nb)_3SiC_2$ still can be seen from the surface morphology of $(Ti,Nb)_3SiC_2$ after oxidation.

Fig. 2(c) and (d) illustrate the cross-section morphologies of the two samples after marker oxidation test. The oxide scales formed on both the two samples are dense, and no void or local spallation is observed at the oxide/substrate interface. The oxide scale on $(Ti,Nb)_3SiC_2$ is monolithic layer with the thickness of approximate 1.8 μm. Differently, a duplex-layer oxide scale forms on Ti_3SiC_2 with the thickness of about 3 μm. From the EDS line-scanning profiles along the cross-section of the oxidized samples, it can be seen that the oxide scale formed on $(Ti,Nb)_3SiC_2$ is rich in Ti, Si and O elements. Nb is uniformly distributed in the oxide layer. Therefore, by combining the results of XRD and EDS