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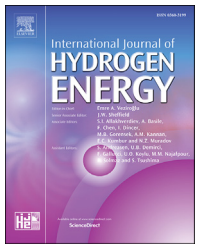

Exploring a novel ceramic $(Ti,W)_3SiC_2$ for interconnect of intermediate temperature solid oxide fuel cell

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ARTICLE INFO

Article history:
Received 3 January 2018
Received in revised form
14 February 2018
Accepted 22 February 2018
Available online 17 March 2018

Keywords:
Ti_3SiC_2
W doping
Interconnect
Oxidation resistance
Area-specific resistance

ABSTRACT

A solid solution $(Ti,W)_3SiC_2$ possessing good oxidation resistance and low area-specific resistance (ASR) after oxidation has been synthesized by an in-situ hot pressing process. The oxidation rate constant at 800 °C in air is 6.29×10^{-14} g^2 cm^{-4} s^{-1} for $(Ti,W)_3SiC_2$. The formed single-layer oxide is composed of W doped rutile TiO_2 and amorphous SiO_2. SiO_2 is evenly inlaid in the communicative body frame of TiO_2. W doped in TiO_2 mainly exists as W^{6+}. W doping not only hinders the outward diffusion of Ti by decreasing the concentration of native Ti interstitials in TiO_2, but also restrains the inward diffusion of oxygen by decreasing the concentration of O vacancies. Furthermore, W dopant in TiO_2 enhances the electrical conductivity of TiO_2 by increasing the concentration of semi-free electron. Therefore, the low ASR of $(Ti,W)_3SiC_2$ after oxidation owes to high electrical conductivity of TiO_2 as well as the reduced thickness of oxide scale. All the results render $(Ti_{1-x}W_x)_3SiC_2$ promising as interconnects for the intermediate temperature solid oxide fuel cell.

Introduction

Solid oxide fuel cells (SOFCs) are promising candidate for future energy conversion equipment due to their advantages of low production of pollutants, fuel flexibility and high efficiency [1–4]. Interconnect is the main component to build up the SOFC-stack, which is located between each individual cell in the cell-stacks. It plays two roles in the stacks, one is acting

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https://doi.org/10.1016/j.ijhydene.2018.02.162
0360-3199/

as bipolar plate electrically connecting adjacent cells in the series; and the other is acting as physical separator of fuels in the anode and air or oxygen in the cathode [5–8]. During operation, interconnect realizes simultaneous dual atmosphere (wet reducing and oxidizing) exposure up to about 800 °C. Therefore, interconnect materials must meet harsh requirements: good electrical conductivity; good oxidation resistance; suitable coefficient of thermal expand (CTE) with other cell components; adequate stability in term of dimension, microstructure, chemistry and phase at operating temperature in oxidizing and reduction environments; gas tight; and no reaction and interdiffusion with adjacent components. Developing a novel interconnect material which can meet all of the requirements is a challenge for the commercialization of SOFC.

When SOFCs operates at the temperature range of 800–1000 °C, $LaCrO_3$ or the doped $LaCrO_3$ are adopted as interconnects material [2]. However, with the development of electrolyte, the operating temperature of SOFC decreases to 600–800 °C, which results in the insufficient electrical conductivity of $LaCrO_3$ or doped $LaCrO_3$ as interconnect. The descending operating temperature [7–9] makes it feasible for metallic interconnects to supplant $LaCrO_3$ materials. Metallic interconnects are Ni-based, Cr-based and Fe-based alloys, which have many advantages, such as high electrical and thermal conductivity, low cost [5,8,10]. However, the oxidation resistance and superior electrical conductivity of these metallic interconnects mainly depend on the formation of Cr_2O_3, which can poison the cathode and cathode/electrolyte interface due to its vaporization, and then cause the performance degradation of SOFC [8,11–13]. Furthermore, the high thermal expansion coefficient of Ni-based and Cr-based alloys restricts their application, and the oxidation resistance of Fe-based alloy needs to be enhanced [14]. To overcome these problems, various kinds of alloys have been investigated [15–22], such as Crofer 22 APU, Hitachi K44M and FeCro. Moreover, many kinds of coatings [23–31] are designed and deposited on interconnect to block the diffusion of volatile Cr (VI) species. Although these efforts have certain effect, it is still a crucial issue for further preventing Cr evaporation, and coating takes the extra cost and complexity for preparation interconnect [14,32].

MAX phases are a group of layered ternary compounds with the general formula of $M_{n+1}AX_n$ (M: early transition metal, A: IIIA or IVA element, X: C and/or N). They have attracted significant attention due to the combination of merits of both ceramics and metals. Ti_3SiC_2, one of the most typical MAXs, possesses unique properties, such as high electrical and thermal conductivity, good resistance to thermal shock below 1100 °C, easy machinability, high modulus and fracture toughness [33,34]. More importantly, its thermal expansion coefficient (9.2×10^{-6} K^{-1} (20–1000 °C)) [33] matches with that of yttria stabilized zirconia (YSZ, 10.5×10^{-6} K^{-1}). All of the above aspects meet the requirements of interconnects. Ti_3SiC_2 is a potential material as interconnect for IT-SOFC.

Previous works [35] exhibit that when Ti_3SiC_2 is oxidized at 600–800 °C in air, its oxidation kinetics roughly follows parabolic law, and the formed oxide scales has a duplex structure with an outer layer of rutile-TiO_2 (r-TiO_2) and an inner layer of mixture of r-TiO_2 and amorphous SiO_2 (a-SiO_2). The oxidation rate constant of Ti_3SiC_2 (5.64×10^{-13} g^2/cm^4 s) is higher than that of metallic interconnect, such as crofer 22 APU (1.71×10^{-13} g^2/cm^4 s). What's more, the electrical conductivity of Ti_3SiC_2 after oxidation needs to be improved [35]. To resolve these problems, Nb and Ta doped Ti_3SiC_2 is designed and studied in the previous works [35–38]. The results revealed that Nb and Ta doping into the rutile TiO_2 lattice in the formed oxide scale, and improved both the oxidation resistance and post electrical conductivity of Ti_3SiC_2 after oxidation. It is found that the one more charger of Ta^{5+}, and Nb^{5+} than Ti^{4+} is the key factor to play the doping effect. Therefore, it is inferred that W doping with two more charger of W^{6+} than Ti^{4+} will exhibit better effect than Nb and Ta, leading to the better performance of $(Ti,W)_3SiC_2$ as interconnect of SOFC.

In this paper, the W doped Ti_3SiC_2 solid solution is successfully synthesized by an in-situ hot pressing process. The solid solution exhibits better oxidation resistance than that of the typical metallic interconnect, such as Crofer 22 APU, Ebrite, and Nb and Ta doped Ti_3SiC_2. The electrical conductivity of the W doped Ti_3SiC_2 after oxidation is suitable for the application of interconnect. Furthermore, the effect of W doping on improving oxidation behaviors and electrical property of Ti_3SiC_2 after oxidation is studied. The results reveal that the W doped Ti_3SiC_2 is a promising interconnects for SOFC.

Experimental procedure

2.5 at.% and 5 at.% W doped Ti_3SiC_2 bulk was fabricated by in-situ hot pressing process, with the elements molar ratio of 2.925:0.075:1:2 and 2.85:0.15:1:2 for Ti:W:Si:C, 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 1580 °C under 30 MPa for approximately 1 h in a flowing Ar atmosphere.

The electrical conductivity of the W doped Ti_3SiC_2 bulk was measured by 4-point method, with the sample size of $4 \times 4 \times 36$ mm^3. The thermal conductivity was measured by the United States FlashlineTM-5000 Thermal Properties Analyzer, and Non-steady state method was adopted. The sample size was $\Phi 12.7 \times 2$ mm^3. The coefficient of thermal expansion of $(Ti,W)_3SiC_2$ was tested on the Setsys-24 thermo-mechanical analyzer (Setaram, Caluire, France). The sample size was $\Phi 6 \times 8$ mm^3. The test temperature range was from room temperature to 1273 K.

Oxidation test was carried on tubular resistance furnace at 800 °C in air atmosphere. The test sample of $10 \times 10 \times 2$ mm^3 was cut from the as-synthesized bulks by electrical discharge method. Prior to oxidation, the surfaces of the samples were grounded down to 2000 SiC paper, chamfered, polished using 1 μm diamond paste, and then degreased in ethanol and distilled water. The sample was suspended in a silica crucible, and then heated up with furnace temperature increasing. In the whole oxidation period, after every 100 h isothermal oxidation the samples were cooled down rapidly to room temperature in air, and weighed using a microbalance with the accuracy of 1×10^{-5} g, and then put into the hot furnace