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The adjustment of microstructure and properties of TiC/Ni–Cr composites by Mo addition applied for intermediate-temperature solid oxide fuel cell interconnects

Qian Qi [a, b, *], Yan Liu [a, **], Hui Zhang [a], Jing Zhao [a], Zhengren Huang [a, ***]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
[b] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

The TiC/Ni–Cr composites, potential candidates for intermediate-temperature solid oxide fuel cell (IT-SOFC) interconnects, were fabricated by pressureless infiltration process and the adjustment of their microstructure and properties by Mo addition was investigated in this work. The results show that the core-rim structure, concave surfaces and coalescence of the particles were observed in the microstructure, which was resulted from the "dissolution-reprecipitation" process and coherent strain energy. The addition of Mo significantly changes the microstructure by refining the particles size and increasing the contiguity. Meanwhile the properties of composites with similar metal volume fraction could be adjusted by altering the microstructure. The large particle size and high contiguity is beneficial to decline the thermal expansion and electrical resistivity; the Vickers hardness increases as the particle size decreases, while the small particle size and high contiguity is detrimental to the flexure strength. The optimized content of Mo was 11 wt% for TiC/Ni–Cr composites.

1. Introduction

Ni-based alloys are considered as the candidates for IT-SOFC interconnects, which requires the comparable thermal expansion to the YSZ electrolyte (10.5×10^{-6} °C^{-1}), high electrical conductivity (≥1S cm) and thermal conductivity, good oxidation and corrosion resistance [1–6]. However, the high coefficient of thermal expansion (CTE) ($14.0–19.0 \times 10^{-6}$ °C^{-1}) of Ni-based alloys restricts their applications in SOFC, though they possess excellent high temperature mechanical strength and oxidation resistance [4–6]. Generally speaking, the CTE of Ni-based alloy can be modified by alloying, such as decreasing the Cr content (Haynes 242). However, this method would result in reduction of oxidation resistance and non-linearity of thermal expansion [5,6].

As we known, the metal matrix composites (MMCs), with excellent mechanical properties, oxidation resistance and lower CTE than pure metal have been widely used in the field of electronic packaging and aerospace [7–9]. Moreover, TiC-based cermets with excellent electrical conductivity (3.3×10^6 S m^{-1}), low CTE (7.4×10^{-6} °C^{-1}), good oxidation resistance and mechanical properties are considered as available SOFC interconnects [10]. Therefore, the TiC/Ni–Cr composites are promising materials with suitable CTE to replace the Ni-base alloys for the application of IT-SOFC interconnects, which has been proven by the author's previous work [11].

According to others' research, some factors, such as the reinforcement nature, volume fraction, morphology (particle size, shape and contiguity) and the interface determine the properties of MMC [7–9,12–21]. Among them, the reinforcement morphology has an important influence on the properties, such as the CTE, electrical resistivity and mechanical property. For example, small particles, which exhibit weaker restriction on the metal matrix than large particles, lead to high CTE, and high contiguity would result in low CTE, because of the additional constraint of partial continuous brittle phase to the metal matrix [13,16]. Meanwhile, the small particles increase the interfacial area and dislocation

* Corresponding author. State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.
** Corresponding author.
*** Corresponding author.
E-mail addresses: qiqian@student.sic.ac.cn (Q. Qi), stony2000@mail.sic.ac.cn (Y. Liu), zhrhuang@mail.sic.ac.cn (Z. Huang).

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density, which scatters the electron and decrease the electrical conductivity. On the contrary, high contiguity of electric ceramic phase contributes to the formation of conducting pathway for the transmission of electron and results in a high electrical conductivity [15,17]. However, the adjustment of reinforcement morphology usually simultaneously leads to the change of the volume fraction. For example, in order to increase the contiguity, the grain composition, increase of compact pressure and preforms pre-sintering are carried out, which would change the volume fraction of metal matrix due to the decrease of porosity of preforms [7,9,12,13]. The change of volume fraction would alter the CTE of composites on a large scale, which would make it inappropriate for the IT-SOFC interconnects. Except for above methods, the addition of minor elements and alteration of process parameters can also be applied to change the morphology, such as in the TiC/Ni–Mo and TiC/Ti composites [20,21]. Especially, these methods can modify the reinforcement morphology without changing the volume fraction obviously. Thus the minor element can be adopted to adjust the microstructure and properties of TiC/Ni–Cr composites to obtain the proper CTE and low electrical resistivity.

In the present study, the element Mo was adopted to adjust the microstructure and properties of the TiC/Ni–Cr composites. The pressureless infiltration process was applied based on the good wettability of liquid Ni–Cr alloy on TiC [22,23]. The Ni–Cr alloy was chosen as the metal matrix due to its wide application in SOFC interconnects [5]. In addition, the microstructure evolution during the fabrication process and the variation characteristics of microstructure with different Mo content were studied. Furthermore, the variation trend of properties (CTE, electrical resistivity, Vickers hardness and flexure strength) of the composites with various microstructures was also analyzed.

2. Materials and methods

2.1. Material synthesis

TiC powders (99.5% in purity, $d_{50} = 10$ μm, Qinhuangdao Enomaterial Co., Ltd., Hebei, China) and Mo powders (99.9% in purity, 1 μm in diameter, Haotian Nano Technology Co., ltd., Shanghai, China) were used in this study. Ni80Cr20 alloy (Hualong Special Steel Co., Ltd., Jiangsu, China) was selected as the metal matrix. The Mo contents of the composites were set as 9, 10, 11 and 12 wt%. The fabrication process was preformed as follows. First, the TiC and Mo powders were ball-milled in ethanol for 4 h with titanium carbide media (ball to powder ratio, 1:1) in a planetary mill at 300 rpm, and then dried, crushed and sieved. Secondly, the preforms with size of $\Phi 45 \times 8$ mm^2 were prepared by dry-pressing at 20 MPa. Last, the alloy plates ($m_{alloy} = 2\rho_{alloy} \times V_{porosity\ of\ preform}$) were placed on the preforms in the alumina crucibles, and the infiltration was carried out at 1450 °C for 0.5 h in a high temperature graphite resistance furnace with argon atmosphere.

2.2. Microstructure characterization

Phase analysis of the composite was performed by X-ray diffraction (XRD) using a Guinier-Hägg camera (Expectron XDC-1000, Jungner Instrument, Solna, Sweden) with Cu K_α radiation. The microstructure and fracture surfaces of the composites were observed by scanning electron microscopy (SEM, S-4800, HITACHI, Japan) equipped with an energy dispersive spectrometer (EDS). The interfaces structure of composites were observed by a transmission electron microscopy (TEM) using a Tecnai G2 F20 microscope (FEI Co., Hillsboro, OR) working at an accelerating voltage of 200 kV with EDS. The mean particle size was calculated by the mean value of intercept length of about 400 particles, and the contiguity was evaluated from the equation $G = 2N_{ss}/(2N_{ss} + N_{sl})$, where N_{ss} and N_{sl} are the numbers of interceptions of solid/solid and solid/liquid interfaces per unit length of the test line [24].

2.3. Properties tests

The bars for the tests were cut using electro-discharged machine and further ground on a diamond grinding wheel to the final dimensions. The bulk densities of the composites were measured by the Archimedes principle. The flexure strength of the samples was measured under room temperature using an Instron universal testing machine (Model5566) with a span of 30 mm and across-head speed of 0.5 mm/min. Vickers hardness was measured on the polished surfaces by Vickers indentation (Model 2100B; Tukon, Canton, MA) with a load of 2 Kg and an indentation time of 10 s. The CTE of the composites were measured with a NETZSCH Dilatometer 402C in the temperature range from 20 to 450 °C under air atmosphere. The four-probe method in a setup was employed to determine the electrical resistivity using an IM6 Electrochemical Workstation (ZAHNER Germany) at room temperature. The specimens for CTE, flexure strength, Vickers hardness and electrical conductivity test were long bar with size $4 \times 4 \times 20$ mm, $3 \times 4 \times 36$ mm, $\Phi 10 \times 4$ mm and $3 \times 4 \times 36$ mm, respectively.

3. Results and discussion

3.1. Microstructures and phase composition

Fig. 1 presents the microstructure of TiC/Ni–Cr composites with different Mo content. The alloy completely infiltrated into the preforms and no residual pores were found. In addition, the core-rim structure was observed. As shown in Fig. 2a, the EDS analysis of the core-rim structure demonstrates that the dark core mainly contains Ti and C elements. The gray rim consists of Ti, Mo and C elements. This is also confirmed by the XRD patterns of TiC/Ni–Cr composites, as shown in Fig. 2b, which exhibits that the composites with different Mo content consist of the same phases: TiC, C_2MoTi, Cr_2Ni_3 and minor NiTi. In the composites, partial Ti atoms are replaced by Mo atoms and Ti would react with Ni to form the intermetallic NiTi, whose peak intensity becomes stronger with the increase of Mo content. Therefore, it can be affirmed that the core is TiC and the rim is C_2MoTi. The formation of rim can be attributed to the "dissolution–reprecipitation" process, which has been illustrated in the TiC–Mo_2C–Ni cermets [25] and TiC/Fe composite [26]. In this process, the TiC and Mo powders dissolve into the metal liquid, and as Ti, C and Mo solutes become saturated in the liquid, they act as the initial nucleating elements and precipitate on the undissolved TiC particles. The color of the rim varies from gray to white from the outer to the inner due to the higher Mo content in the inner than outer, which is heavier than Ti atoms and shows brighter color. Furthermore, some special microstructures are also found, such as the contact flattening, as the yellow arrows point, and the coalescence of particles, as the red arrows point, which are generally found in liquid phase sintering (LPS) [27]. In the metal matrix composites, when the ceramics with certain solubility in the metal matrix, these phenomena would be observed, such as this system and SiC/Fe–Si composites [28]. The coalescence would results in a high contiguity of TiC phase, which has a significant influence on the properties of the TiC/Ni–Cr composites. Furthermore, as the blue arrow points in Fig. 1b, particles with concave interfaces are observed. The special microstructure is resulted from the coherency strain energy [26,29]. The particle with a pore full of metal, as the white dotted circles in Fig. 1 show, is the same phenomenon because of the two-dimensional sectioning.

Fig. 3 shows the interfacial structure analysis of core-rim