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Fabrication of 3D Ni nanosheet array on Crofer22APU interconnect and NiO-YSZ anode support to sinter with small-size Ag nanoparticles for low-temperature sealing SOFCs

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ABSTRACT

A novel low-temperature sealing method was developed to seal solid oxide fuel cells. The 3D Ni nanosheet array was pre-fabricated on faying surfaces of Crofer22APU interconnect and NiO-YSZ anode-support. Then it was covered with Au film without changing its morphology. This special nanostructure improved sintering efficiency between Ag nanoparticles and substrates. A dense joint was obtained at the low-temperature between 250 °C–300 °C. This method effectively avoided the oxidation of interconnect during sealing. When joints were sealed at 300 °C, the shear strength reached 16 MPa. The fracture was mainly located in the central Ag layer, presenting a significant plastic deformation. Due to the effective protection of Ni layer, joints also possessed excellent oxidation resistance in oxidizing atmosphere at 800 °C for 400 h. After high-temperature oxidation, the shear strength was increased to 23 MPa, revealing an increasement of 43.8% compared with the as-sealed condition (16 MPa). This sealing method has great potential in sealing solid oxide fuel cells. It also can be extended to seal other energy-conversion devices.

Introduction

Solid oxide fuel cells (SOFCs), as an electrochemical energy-conversion device, possess many superior features such as high efficiency (over 70% with fuel regeneration), fuel flexibility, quiet operation and low pollutant emission [1–6]. However, the widespread commercial applications have not been realized for many reasons. The sealing process is essential for fabricating a SOFC stack, whether it is a high temperature, intermediate temperature or low temperature SOFC. Because, the sealants will be used to bond the cell stacks, and prevent gas mixing between the anode and cathode compartments, which is of critical importance for the durability and efficiency of stack system [7–10]. In general, the contact position between the ceramic cell support and the steel interconnect is the key area where the tightening seal is required [11–13]. Among all types of supported fuel cells, including anode supported [14], electrolyte supported [15] and metal supported cells [16], the anode supported cell is the

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most widely studied and the most common one. Therefore, this study focused on the sealing process of anode supported fuel cell.

At present, several joining methods have been employed to seal SOFC stacks. Glass or glass-ceramic bonding has been tested in the last years [17–20]. However, the problems like poor resistance to static or dynamic forces have seriously restricted its use [19–21]. The static force mainly comes from the thermal stress caused by the mismatch of thermal expansion coefficient (CTE) among supported cell, interconnect and sealants during service. Besides, the restrain stress arising from the assembly process, as well as the self-weigh of SOFC stacks also increase the static stress [22,23]. As for the dynamic stress, it is mainly caused by the vibration during service, especially when the SOFC stack is used as a mobile power supply [24,25]. The glass sealants can react with metal interconnects both in the sealing and service processes, which leads to the excessive corrosion of metal interconnects [24]. It is detrimental to the long-term performance of SOFC stacks. The crystallization during sintering or operation also easily results in the formation of cracks and the loss of gas-tightness over time [26,27]. Active metal brazing (AMB) has been widely studied for sealing SOFCs [28,29]. As for the AMB joining, a high vacuum or inert gas atmosphere is required in order to avoid the oxidation of active elements (Ti, Zr or Cr) in the matrix braze. Besides, active elements will be oxidized during the operation of SOFCs, leading to a rapid deterioration in the joining strength and hermeticity [30,31]. Reactive air brazing (RAB) can be carried out in air, and the obtained joints have inherent high-temperature oxidation resistance [32–35]. Although the RAB joining has unique advantages in sealing SOFCs, it still has many drawbacks. The joining temperature is usually higher than 950 °C, which easily results in the excessive oxidation of the ferritic steel interconnect. At the same time, these oxide scales will react with the oxide component (typically CuO) from RAB braze, forming a relatively thick layer of Cu/Cr/Mn/Fe-oxides (>20 μm) [36–38]. This reaction layer has been proved to be the mechanically weak part in the joint. In addition, high-temperature joining also increases the costs of production and reduces the productivity, which are not conducive to the large-scale industrial production of the SOFCs. Such problems have seriously restricted the development of SOFCs.

Significant improvements can be achieved by sealing SOFCs at a low-temperature in a short time. Meanwhile, the joints should have the capability to be served at high-temperature (~800 °C for the SOFCs) [39]. At present, the nanotechnology can meet those requirements, which have been widely used in the field of electronic packaging [40–44]. The nanoparticle pastes, especially Ag nanoparticle paste, show prominent advantages in achieving high strength joints and serving at high-temperature [45–49]. Zhou et al. [50] reported that the sintering rate between the Ag nanoparticle and the flat substrate was relatively slower than that between Ag nanoparticles themselves. It was deduced that the interface between the Ag nanoparticle paste and the flat substrate would become the mechanical weak part in the joint and was easy to mechanical failure [51,52]. In order to improve this situation, Zhou et al. [50] modified the surface morphology of the flat copper substrate by fabricating a 3D nanohierarchical Ni/Au nanomace array on its surface. The 3D nanohierarchical Ni/Au nanomace film was effectively sintered with Ag nanoparticles, and the shear strength of 3D Ni/Au nanomace joints was 6 times than that of the flat Ni/Au joints. It was concluded that modifying the surface morphology was an effective way to increase the sintering efficiency and the shear strength for nanoparticle joining [53–55]. To the best knowledge of authors, the nanoparticle paste was hardly used for sealing SOFCs. The Crofer22APU interconnect and the NiO-YSZ anode support are key parts in the SOFCs that need to be sealed together for anode supported cell. There were no reports about modifying the surface morphology of the Crofer22APU interconnect and the NiO-YSZ anode support in order to improve the joint properties of the SOFCs sealed by nanoparticle paste.

In this study, a 3D Ni nanosheet array was fabricated on the "faying surface" of Crofer22APU interconnect by the electroplating method. The phrase of "faying surface" represents the surfaces of the Crofer22APU interconnect and the NiO-YSZ anode support where need to be sealed together. Then an Au film was prepared on the Ni nanosheet surface by ion sputtering, forming a 3D Ni/Au nanosheet structure. For the NiO-YSZ anode support, a flat Ni film was first fabricated on its faying surface by the electroless plating method. Then it was served as a substrate surface to prepare a 3D Ni/Au nanosheet structure using same methods as described above. After that, both of them were subjected to vacuum heat treatment, which improved the bonding strength between the Ni/Au film and the substrate. Finally, small-size Ag nanoparticles (~12 nm) were employed to seal the Crofer22APU interconnect and the NiO-YSZ anode support. The sintering process was systematically observed and analyzed. The effects of oxidizing atmosphere on the stability of as-sealed samples were carefully discussed.

Experimental procedures

The fabrication of 3D Ni nanosheet array and the sintering process with Ag nanoparticles are displayed in Fig. 1. The details were listed as follows. All reagents were of analytical pure grade and used as received condition without further purification.

Fabrication of Ni/Au nanosheet array on the Crofer22APU and NiO-YSZ

The Crofer22APU ferritic stainless steel mainly consisted of (in wt.%) 22.2 Cr, 0.46 Mn, 0.03 Si, 0.06 Ti, 0.02 Al, 0.02 Ni, 0.07 La and balance Fe, which was purchased from the Thyssenkrupp VDM Essen, Germany. The specimens with a size of 25 mm × 10 mm × 0.1 mm were cut from a piece of stainless steel sheet. Since the thermal stress was not considered in the present work, a thin Crofer22APU was used. Actually, the 0.1 mm thick Crofer22APU might not be enough to simulate the actual thermal stresses. The electroplating method [50,56,57] was employed to fabricate the Ni nanosheet on the Crofer22APU sheet. Ni sheet (99.9%) was chosen as the anodic electrode. The Ni sheet (99.9%) was connected to the positive pole, and the Crofer22APU sheet was connected to the