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Glass-ceramic sealant for solid oxide fuel cells application: Characterization and performance in dual atmosphere

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HIGHLIGHTS

- A novel glass-ceramic seal for planar SOFC is designed and tested.
- The glass-ceramic shows good densification after the sintering process at 850 °C.
- Gas tightness test at 800 °C for 1100 h in dual atmosphere.
- Morphological and crystalline phase analyses conducted before and after tests.
- Assessed thermo-chemical compatibility with a preoxidised 441 steel.

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ABSTRACT

A glass-ceramic composition was designed and tested for use as a sealant in solid oxide fuel cell (SOFC) planar stack design. The crystallization behaviour was investigated by calculating the Avrami parameter (n) and the activation energy for crystallization (E_c) was obtained. The calculated values for n and E_c were 3 and 413.5 kJ/mol respectively. The results of thermal analyses indicate that this composition shows no overlap between the sintering and crystallization stages and thus an almost pore-free sealant can be deposited and sintered at 850 °C in air for 30 min. A gas tightness test has been carried out at 800 °C for 1100 h in dual atmosphere (Ar-H_2 and air) without recording any leakage. Morphological and crystalline phase analyses were conducted prior and following tests in dual atmospheres in order to assess the compatibility of the proposed sealant with the metallic interconnect.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising devices for future clean energy production. These systems convert chemical energy into electrical energy by red-ox reactions between a fuel and an oxidant with very high efficiency. In order to reach a useful power output, it is necessary to connect in series several cells [1,2]. The planar stack design (where single cells are stacked one on top of each other and separated by a metallic interconnect) is easier to manufacture and leads to higher power density production in comparison to the tubular one [1,3,4]. One of the most important components in a planar stack is the sealant whose function is to prevent mixing of the reducing and oxidising gasses. The SOFC sealant is exposed to demanding conditions of high temperature 750–800 °C and both oxidizing and reducing atmospheres. A good sealant must be chemically and physically stable and be able to maintain a hermetic seal at the operating conditions for thousands of hours. Furthermore it must have good thermo-mechanical and thermo-chemical compatibility with materials to which it is in contact. In particular, maintaining a stable interfacial bond between the sealant and both the metallic interconnect (typically ferritic

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stainless steel) and the electrolyte (typically yttria stabilized zirconia) is critical [3,5,6]. The use of metallic brazes could provide a possible bonding solution, however, these can be expensive and have been reported to be unable to survive in the dual atmosphere present of the device [5,7]. Among the candidate sealants, glasses and glass-ceramics are likely to be the materials of preference as they exhibit better resistance to the severe service environment (oxidizing and reducing) than brazing alloys [8–14]. On the other hand compressive seals like mica-based seals can result in high leakage levels and it may be necessary to use them in combination with brazes or glass (for example infiltrating the glass into mica papers) [3,15]. Glass-ceramics offer the opportunity to tailor their properties by varying the composition and may also provide the potential of self-healing due to the presence of a remaining glassy phase. In order to maintain a hermetic seal, the glass-ceramic must be strongly bonded with the electrolyte and with the interconnect; it must also maintain a value of the coefficient of thermal expansion (CTE) similar to those of the materials with which it is in contact. Such an approach will avoid crack formation and residual stresses during thermal cycling. Most of the research on glass-ceramic sealants has focused on BaO-containing glass-systems. The use of BaO tends to reduce the values of the glass transition temperature, T_g, and the glass softening temperature, T_s, while at the same time it increases the CTE value of the glass-ceramic. Depending on the glass composition, the formation of the monocelsian phase ($BaAl_2Si_2O_8$) which has a low value of thermal expansion (2–3 x 10^{-6} K^{-1}) is possible; however, the reaction of BaO at the interface with the steel along with the consequent formation of $BaCrO_4$ (with high CTE, around 20 × 10^{-6} K^{-1}) could lead to the detachment and spallation of the sealant [6,9].

Bonding and sealing processes involving the use of glasses are usually carried out above the glass softening point, in order to achieve good densification as well as good wetting thanks to viscous flow; furthermore controlled devitrification can lead to the formation of crystalline phases that improve the thermomechanical properties of the glass-ceramic.

The aim of the work that is reported here is to develop a glass-ceramic system with excellent combination of properties including thermal stability and good sintering and densification behaviour that would effectively lead to a fully densified glass-ceramic at 850 °C. The sintering and crystallization behaviour as well as the thermal stability and compatibility between this sealant and a preoxidised steel have been examined. In addition, the ability of the glass-ceramic sealant to form and maintain gas tightness in dual atmosphere conditions for a period of up to 1100 h has been investigated. Some groups have worked extensively on the diopside ($CaMgSi_2O_6$) system. Much of this work has been driven by the research group of Ferreira [16] who have produced detailed studies on a number of diopside-based glass systems including rare-earth and strontium-containing aluminosilicate glass ceramic sealants. Reddy et al. [17] also studied the effect of strontium-to-calcium ratio on the structure, the crystallization behaviour and properties of diopside-based glasses. These investigations on diopside systems have yielded promising results for use as sealants in SOFC applications [18]. The work which is reported here has considered the addition of sodium oxide in diopside owing to its lower cost and its possible benefits with regard to ease of processing.

The possibility of adverse effects in the presence of alkaline-earth metal oxides in sealing glasses for SOFC applications is discussed in Chou et al. [19] who observed detachment of the sealant due to the formation of alkaline-earth chromates (i. e. BaCrO4 and SrCrO4). The same glass was used as a sealant for aluminized Crofer22APU and in this case the alumina layer on the steel dissolved, suggesting that the presence of alkalis in the sealing glass made the glass more corrosive than alkali-free glass. In another study [20], a glass containing about 17 mol% alkali metal oxides (K_2O and Na_2O) was used in contact with an aluminized SS441 substrate; isothermal ageing in dual environment exhibited good hermetic behaviour during a test that was conducted for 1000 h. The glass was found to be compatible with the alumina coating since no adverse reactions were detected.

In the present study, a glass-ceramic composition was therefore specially formulated expecting a reduction in the characteristic temperatures leading to processing benefits. The possibility of formation of sodium chromate is a concern and as result other groups have so far not considered the use of sodium in diopside systems. However, when working on alternative glass-ceramic systems, the present authors [11,14] previously showed that such problems may be overcome by tailor-making compositions where sodium was able to diffuse away from the sealant-interconnect interface and thus prevent any undesirable effects.

2. Experimental

2.1. Glass and glass-ceramic characterization

A glass with the composition reported in Table 1, has been designed using data from the SciGlass® database (Science Serve GmbH, SciGlass 6.6 software, Newton, MA, USA). The glass, labelled V9, was produced by melting in a furnace the raw materials (carbonates and oxides) at 1600 °C for 1 h in a Pt–Rh crucible.

The molten glass was quenched by casting onto a brass plate. The V9 glass was then ground using a zirconia ball mill and subsequently sieved. Differential thermal analyses (DTA) (Netzsch, Eos, Selb, Germany) were conducted on glass powders with three different particle sizes (<25 μm, 25–38 μm, and 38–63 μm) at a heating rate of 5 °C/min from room temperature to 1300 °C. Hot-stage microscopic analysis (HSM) (Expert System Solution, Modena, Italy) was recorded at 5 °C/min on compacted V9 glass powders of particle size <25 μm to determine the characteristic temperatures of the glass and its sintering behaviour. The DTA and HSM results were used to select the thermal treatment for the formation of the glass-ceramic and the sealing process as used in the investigation. The selected conditions were a thermal treatment at 850 °C for 30 min in air and heating rate of 5 °C/min. Additional DTA analyses at different heating rates (10/20/30/40 °C/min) were carried out in order to study the crystallization behaviour of the glass-ceramic system.

Dilatometry (DIL) (Netzsch, DIL 402 PC/4) was performed at a heating rate of 5 °C/min for the as-cast V9 glass, the V9 glass-ceramic in order to evaluate the coefficient of thermal expansion, CTE, and the dilatometric softening temperature (T_s) before and after the devitrification process (heat treatment at 850 °C, 30 min, air) and after the dual atm test at 800 °C for 1100 h. The dilatometric measurements were conducted using cylindrical samples of diameter 4 mm and height of around 5 mm (for as cast before and after the devitrification process samples) and on a small glass-ceramic bar (5 mm length) for the sample after 1100 h at 800 °C.

Three samples were used to determine the glass transition temperature; T_g was taken at the onset, obtained by the intersection of the two tangents at the start of the endotherm. Three samples were used for determination of the mean CTE value and the error was ±0.16 × 10^{-6} K^{-1}.

The glass-ceramic was subjected to chemical and morphological analyses using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (using Merlin microscope of ZEISS). The samples were prepared for these analyses by polishing using SiC paper. The crystalline phases were studied by means of X-ray diffraction on powdered samples (XRD; Bruker AXS D8 Advance, Bruker, Germany). A semi-automatic phase identification