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Development and characterization of glass-ceramic sealants in the ($CaO-Al_2O_3-SiO_2-B_2O_3$) system for Solid Oxide Electrolyzer Cells

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HIGHLIGHTS

► New glass-ceramic formulation for sealing applications.
► Influence of heat treatment on the seal behavior and crystallization process.
► Glass-ceramic/Metal and glass-ceramic/ceramic interfaces and interactions.
► Effect of V_2O_5, K_2O and TiO_2 on thermal properties.
► Determination of crystallization kinetic parameters of the selected composition.

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ABSTRACT

The efficiency of glass-ceramic sealants plays a crucial role in Solid Oxide Electrolyzer Cell performance and durability. In order to develop suitable sealants, operating around 800 °C, two parent glass compositions, CAS1B and CAS2B, from the $CaO-Al_2O_3-SiO_2-B_2O_3$ system were prepared and explored. The thermal and physicochemical properties of the glass ceramics and their crystallization behavior were investigated by HSM, DTA and XRD analyses. The microstructure and chemical compositions of the crystalline phases were investigated by microprobe analysis. Bonding characteristic as well as chemical interactions of the parent glass with yttria-stabilized zirconia (YSZ) electrolyte and ferritic steel-based interconnect (Crofer®) were also investigated. The preliminary results revealed the superiority of CAS2B glass for sealing application in SOECs. The effect of minor additions of V_2O_5, K_2O and TiO_2 on the thermal properties was also studied and again demonstrated the advantages of the CAS2B glass composition. Examining the influence of heat treatment on the seal behavior showed that the choice of the heating rate is a compromise between delaying the crystallization process and delaying the viscosity drop. The thermal Expansion Coefficients (TEC) obtained for the selected glass ceramic are within the desired range after the heat treatment of crystallization. The crystallization kinetic parameters of the selected glass composition were also determined under non-isothermal conditions by means of differential thermal analysis (DTA) and using the formal theory of transformations for heterogeneous nucleation.

1. Introduction

Continuous economic and demographic growth along with higher living standards leads to a rising demand for energy. On the other hand, the depletion of fossil fuel reserves and the emission of greenhouse gases constitute a menace to the present and the future generations in terms of energy availability, environmental pollution, global warming and health hazards. Hydrogen has been identified as a potential alternative fuel as well as an energy carrier for the future energy supply. Water electrolytic hydrogen is currently the most practical and promising technology and especially the most environmentally friendly manner for large-scale renewable hydrogen production.

Research into hydrogen production using high temperature electrolysis methods have increased significantly in the last few years [1]. High Temperature Electrolysis (HTE) using Solid Oxide Electrolyzer Cells (SOECs) is a promising method involving electrochemical reactions that convert electric power into chemical energy. Although the SOEC technology has indeed been developed,

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manufacturing of SOEC stacks requires the development of gas-tight seals, as rapid degradation of the cell performance is observed when small leaks are present [2]. Sealing is required along the edges of the electrodes, electrolyte and interconnect, as well as between individual cell stacks, to prevent mixing of gases in the anode and the cathode, and to provide electrical insulation to prevent shunting. The production of reliable joints is currently the main limitation in the production units and justifies the research effort in this field [3–5]. The requirements for the sealants are stringent as they need to withstand severe environmental conditions at high operating temperature (800 °C) in SOEC stacks. The sealants must simultaneously meet several requirements such as gas tightness, chemical inertness to the adjoining cell components, electrically insulation, and coefficient of thermal expansion (CTE) compatibility with other cell components, suitable viscosity, and good adherence with the adjoining components [3,4,6,7].

Sealing materials can be classified in two categories: (i) Compressive seals such as metallic or mica-based, and (ii) rigid seals such as glass, glass-ceramics, or brazes [4,8]. Many studies were dedicated to the formulation and characterization of these sealing matrix [4,7,9–12]. However, glass and glass-ceramics with carefully tailored chemical compositions are able to meet most of the requirements [13–15]. Glass and glass-ceramic sealants exhibit strong bonding to the interface; their adherence to the cell provides hermetic sealing. Although glass present the faculty of self-healing, which can be very beneficial in case of cracking [16–20], their excessive devitrification at operating temperatures leads to drastic changes in their physicochemical properties. This shortcoming can be avoided by employing glass-ceramics sealants whose crystallization can be controlled. However, for such materials the self-healing faculty is partially or even completely lost; therefore, glass-ceramic properties have to be completely determined, starting from their vitreous state, in order to be perfectly adapted to adjacent cell components. Their performance depends on their components, compositions and arrangement in the network structure which is very complex and not yet fully understood. The formulation process of a glass ceramic is highly complex especially due to the large number of elements that can be included.

Glass-ceramics from several systems have been investigated and their suitability for sealing applications within SOECs have been discussed in previous work [21,22]. It was concluded that glass-ceramics based on the $CaO-Al_2O_3-SiO_2$ (CAS) system meet most of the requirements for efficient sealing, especially in terms of chemical durability. The objective of this work is to determine the most suitable CAS-based glass-ceramic composition for sealing applications. Given the refractory character of the CAS-based glass and their high viscosity at the SOEC operating temperatures (<900 °C), two parent glass compositions (CAS1 & CAS2) were selected on the basis of their liquidus temperatures (T_L) which correspond to the lowest melting points in the CAS system, 1170 and 1265 °C respectively for CAS1 and CAS2 (Fig. 1 & Table 1). About 6 wt% of B_2O_3 was systematically added to the parent glass compositions as a flux. CAS1 and CAS2 glass compositions containing 6 wt% B_2O_3 are designated CAS1B and CAS2B.

A comparative study of both glass compositions, based on experimental data, was carried out and one of the compositions was selected. Optimized compositions have been defined with minor additions of V_2O_5, K_2O and TiO_2. The crystallization kinetics of the optimized glass composition were investigated by Differential Thermal Analysis (DTA).

2. Experimental procedure

2.1. Glass preparation

Batches were prepared from reagent grade SiO_2, Al_2O_3, $CaCO_3$, H_3BO_3, V_2O_5 and KNO_3. The thoroughly mixed batches were placed in a Pt/10% Rh crucible and heated to 900 °C in a muffle furnace for 1 h in order to eliminate carbonates and nitrates, after which the batches were melted at 1550 °C for 3 h. The melt was then poured

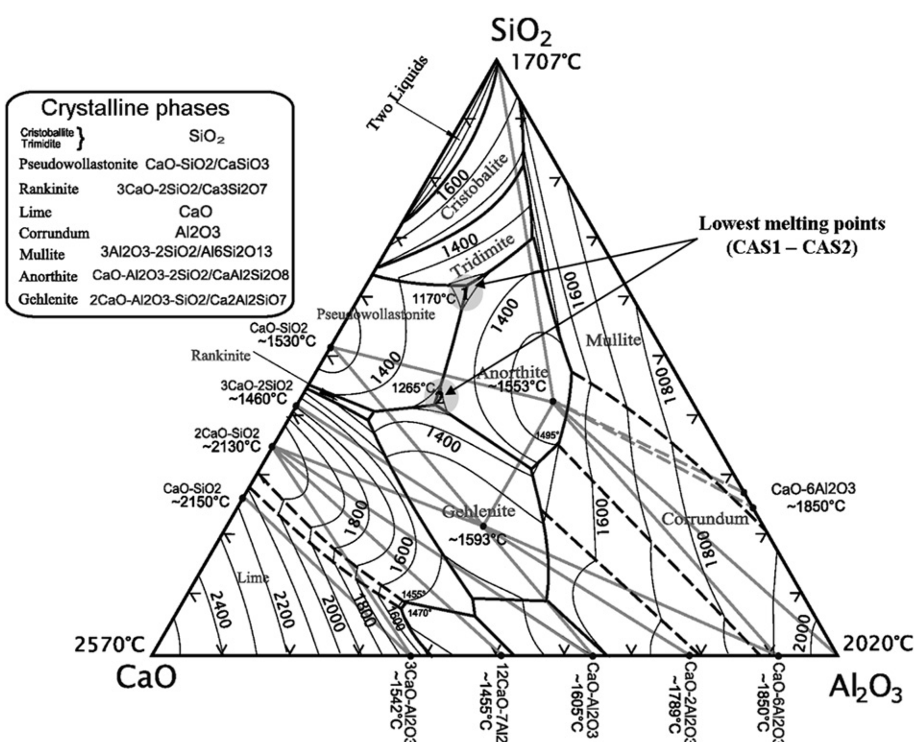

Fig. 1. CAS1 and CAS2 glass positions on the $CaO-Al_2O_3-SiO_2$ pseudo ternary phase diagram (wt%).