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Fracture toughness of glass sealants for solid oxide fuel cell application

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ABSTRACT

Glass and glass-ceramics are versatile materials and have been widely used for sealing in the ongoing development of intermediate temperature solid oxide fuel cell (SOFC) technology where its integrity is crucial for reliable operation of the stack. The fracture toughness is a key parameter required for the prediction of the mechanical performance of a seal glass. A comparative indentation study on two RE-glasses (RE=La and Y) was performed to evaluate their fracture toughness. Indentation toughness was calculated both through measurements of the indentation crack lengths and of crack-opening displacements in the near regions of a crack tip. Both approaches exhibited good agreement. La-containing glass showed higher stiffness, hardness and fracture toughness, which has been related to the in-situ toughening mechanism caused by devitrification and formation of crystalline phases.

1. Introduction

Due to the brittle nature of glass and glass ceramic seals for solid oxide fuel cell (SOFC) applications, these materials are susceptible to localized surface damage in the form of cracking when subjected to indents by sharp objects or high stress levels such as formed during thermal cycling [1,2]. To ensure robust seal designs, it is necessary to evaluate chemical, physical and mechanical properties of the sealing and the interfaces towards neighbor components. The fracture toughness or critical stress intensity factor K_{IC} is a crucial parameter required for the prediction of the mechanical performance of glass seal materials, i.e. tagging critical failure sizes and dimensioning products for designated stress regimes. Vickers indentation are widely used to evaluate the toughness properties of brittle materials because this method is relatively simpler, quicker hence also cheaper than other alternative techniques [3,4]. For a sample of median–radial crack, toughness is easily estimated by indentation crack length (ICL) method as follows:

$$K_{IC} = \gamma\left(\frac{E}{H}\right)^{1/2}\frac{P}{c^{3/2}} \quad (1)$$

where c is the length of surface radial cracks, P the applied load, E Young's modulus, H the material hardness and γ is constant [5]. A rather more complex way for evaluating toughness is to measure crack-opening displacements (COD) close to the crack tips [6], which yields more reliable values for the intrinsic toughness as previously demonstrated by Burghard et al. [7] through deconvolution of residual contact stress for normal and anomalous glasses. In this paper we compared ICL and indentation COD (ICOD) toughness evaluation methods for two glasses fabricated for sealing applications. Finally, the mechanical characteristics of the glass sealings are discussed on the basis of their chemical composition and devitrification behavior.

2. Materials and methods

To fabricate the nominal composition of 30–35 mol% SiO_2, 3–8 mol% B_2O_3, 3–8 mol% Al_2O_3, 30–35 mol% SrO, 15–20 mol% CaO, and 3 mol% La_2O_3 or 3 mol% Y_2O_3, two glasses were synthesized and designated as GL (La-containing) and GY (Y-containing). All the chemicals were analytical reagents in the form of oxides and carbonates (purity ≥ 99.9%). Raw materials were melted in a Pt crucible at 1450 °C in air in an electric kiln for 60 min. To get better homogenization, glasses were quenched, crushed and re-melted at least twice. Glass frits were prepared by quenching of glass melts in cold distilled water and milling the prepared cullets in a planetary ball-mill to the final median size of 3–4 μm. The glass powders were pressed into pellets, which were subsequently sintered at 850 °C with a dwelling time of 30 min in an attempt to mimic conditions when the glasses are used for sealing applications. The precipitated crystalline phases after heat treatment were identified by means of XRD analysis using the Bruker D8 Advance spectrometer working with a CuKα radiation beam at 40 kV.

Indentation experiments were conducted using a Vickers diamond pyramid (Duramin A300 Struers, Germany) at ambient temperature (25 °C) and relative humidity (98%). A load of 49 N and a dwell time of 10 s were used to make indents on the

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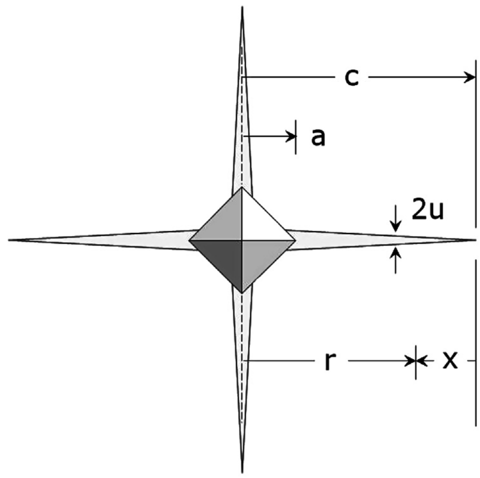

Fig. 1. Schematic representation of a radial crack induced by Vickers indentation.

polished surface of samples. After allowing the indents to sit in normal atmosphere for 24 h during subcritical growth, scanning electron microscope was used to determine the geometry parameters according to Fig. 1. Three radial cracks were selected to determine the opening profiles $u(x)$. Displacements at positions $x=c-r$ were measured to distance of ~50 μm from the crack tip resulted in 20–30 data points per crack. Hardness values were measured directly as $H=P/2a^2$ and elastic moduli were evaluated at ambient temperature by impulse excitation method according to ASTM C 1259 [8].

3. Results

Fig. 2-a and b shows SEM images of the Vickers indents made at load $P=49$ N in glasses GL and GY. These images are considered as an overview of the materials response to the Vickers indentation. As it is seen, cracks are visible along the median line of the indent. Crack propagation in GY follows a more linear pattern; while some irregularity was characterized in GL. Y^{+3} retarded crystallization in GY sample, leading to higher glass contents. This is confirmed by XRD patterns of sintered samples (Fig. 2-c and d), where a broad hump and low intensity diffracted peaks signify the higher glassy nature in the GY sample.

Indentation crack length toughness (ICL) was evaluated from Eq. (1) in conjunction with a fixed coefficient $\gamma=0.016$ for 12 indents. The results are listed in Table 1. To determine the toughness of the glasses from the COD profiles, the displacement data, $u(x)$, were fitted as following [7,9]:

$$u(x)=\left(\frac{K_c}{E'}\right)\left(\frac{8x}{\pi}\right)^{1/2}+B_1x^{3/2}+B_2x^{5/2}+\dots \quad (2)$$

where $E'=E/(1-\nu^2)$ is plane strain Young's modulus, ν is Poissons's ratio, x is the distance from the crack tip, and B_1 and B_2 are the higher order stress intensity coefficients. The second and third terms on the right of Eq. (2) are included to consider deviations from ideal parabolic contours at large x, especially pronounced for the relatively small cracks. Near-tip measured COD data are plotted in Fig. 3 as a function of the crack tip coordinate x and the K_c values obtained by fitting are presented in Table 1.

4. Discussion

Mechanical characteristic of the examined materials are compared in Table 1. Despite the almost glassy nature, these materials demonstrate high hardness and elasticity modulus compared to typical glasses or glass-ceramics designed for SOFC applications. This might be a consequence of the rare-earth elements in the composition as generally rare-earth glasses are of high hardness and modulus of elasticity [12,13]. Comparative values taken from literature are presented in Table 1 for a barium–calcium–aluminosilicate glass-ceramic (G18) [10] and a barium–calcium–silicate glass-ceramic reinforced with YSZ particles (HYSZ) and YSZ fibers (HZYBF) [11].

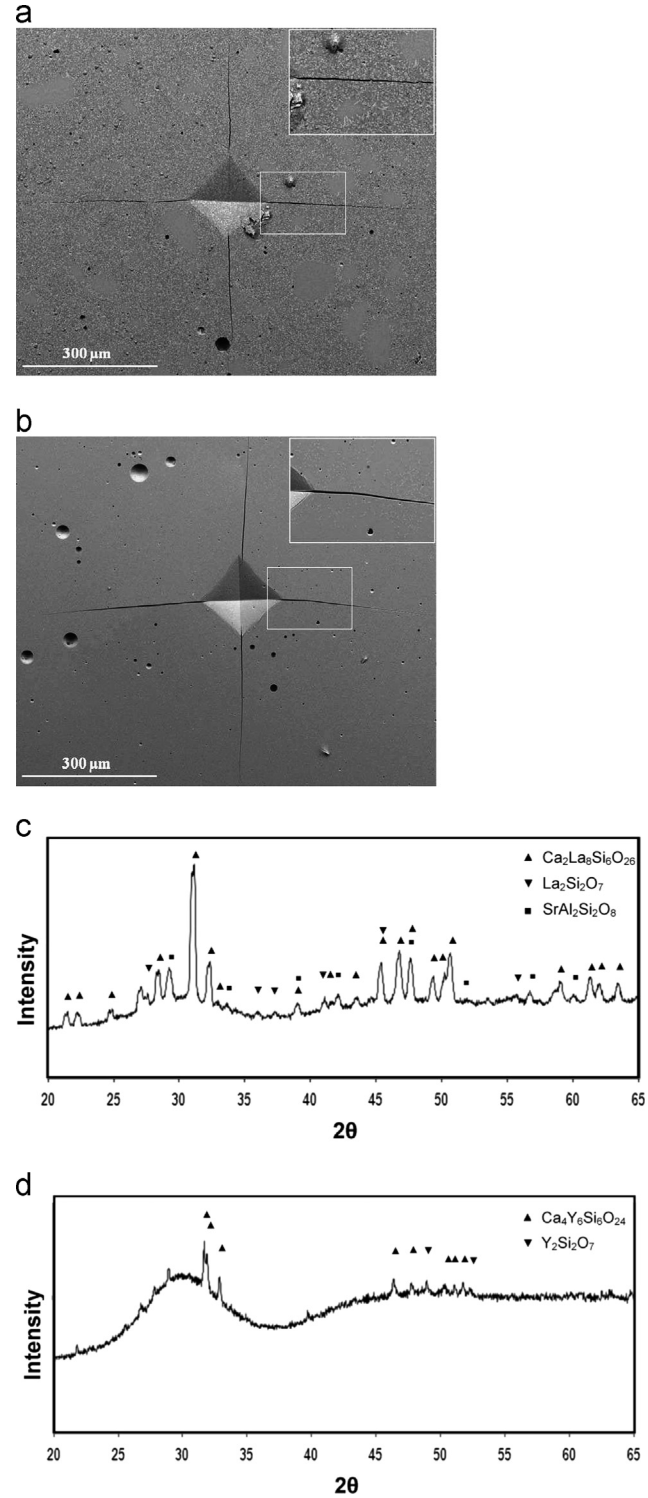

Fig. 2. SEM images of the radial cracks (emanated from the corners of a Vickers impression on the polished surface) and XRD patterns of glass powder bars (sintered at 850 °C-0.5 h) for (a and c) GL and (b and d) GY.