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Mechanical and thermal characterization of a ceramic/glass composite seal for solid oxide fuel cells

Bodhayan Dev [a], Mark E. Walter [a,*], Gene B. Arkenberg [b], Scott L. Swartz [b]

[a] Department of Mechanical and Aerospace Engineering, The Ohio State University, 201 West 19th Avenue, Scott Laboratory, OH 43210, USA
[b] NexTech Materials Ltd., 404 Enterprise Drive, Lewis Center, OH 43035, USA

HIGHLIGHTS

- Investigation of ceramic/glass composite for high temperature sealing.
- Micro-voids evolve with increased heating and cooling rates.
- An appropriate heating and cooling rate for curing the seals was determined.
- Thermally induced dimensional responses of cycled seals were determined.
- Microstructure and mechanical properties of cycled seals were studied.

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ABSTRACT

Solid oxide fuel cells (SOFCs) require seals that can function in harsh, elevated temperature environments. Comprehensive characterization and understanding of seals is needed for commercially viable SOFCs. The present research focuses on a novel ceramic/glass composite seal that is produced by roller compaction or tape casting of glass and ceramic powders and an organic binder. Upon heat treatment, micro-voids and surface anomalies are formed. Increased heating and cooling rates during the heat treatment resulted in more and larger voids. The first goal of the current research is to suggest an appropriate heating and cooling rate to minimize the formation of microstructural defects. After identifying an appropriate cure cycle, seals were thermally cycled and then characterized with laser dilatometry, X-ray diffraction, and sonic resonance. From these experiments the crystalline phases, thermal expansion, and elastic properties were determined. Subsequently compression testing with an acoustic emission (AE) sensor and post-test microstructural analysis were used to identify the formation of damage. By fully understanding the characteristics of this ceramic/glass composite seal, next generation seals can be fabricated for improved performance.

1. Introduction

With high efficiencies and low emissions, SOFCs have the potential to change the production and distribution of electrical energy. High temperature operation in the 700–850 °C range is necessary for performance and fuel utilization. The selection of materials for SOFCs has always been a challenge due to this high operating temperature regime; in particular, appropriate materials are expensive and long term stability is a significant concern.

Planar SOFC designs require hermetic sealing between each individual cell to avoid intermixing of air–fuel and to avoid any short circuit in the cell [1–3]. Seals need to have long-term stability and not cause degradation of adjacent materials at the elevated temperatures and in the harsh environments typical to SOFC operation. The performance and life time of a seal depend on the degree to which gas flow within the material and at the interface is inhibited. Therefore, failure of seals is the result of cracking/damage within the bulk and gaps or separation of the interface.

The two mainstream methods for sealing in SOFCs are compressive sealing and chemical bonding sealing [4,5]. In compressive sealing a compliant material is sandwiched between two sealing surfaces and is compressed by an externally applied load. The primary advantage of compressive sealing is tolerance to coefficient of thermal expansion (CTE) mismatches. The disadvantages of the compressive sealing method are the lack of materials that are compliant at high temperature, the chemical reactions occurring in the aggressive SOFC environment, and the need for complicated

* Corresponding author. Tel.: +1 614 292 6081; fax: +1 614 292 3163.
E-mail address: walter.80@osu.edu (M.E. Walter).

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apparatus that provides mechanical loading [6,8]. The bonding seals approach relies on chemical bonding to provide hermetic sealing. The primary advantages of bonding seals are superior chemical stability under reactive atmospheres and not needing an external load frame for effective sealing [7]. The main disadvantages of bonding seals are brittleness at low temperatures which results in susceptibility to CTE mismatch [8] and poor long term durability resulting from softening and crystallization of the glass phases [7,8]. True hermetic sealing is difficult, if not impossible, to achieve in an environment where temperatures can change. For this reason, the proposed approach is focused on a ceramic/glass composites approach with imperfect, but still acceptable, sealing under compressive loading.

Over the past few decades, extensive research has been carried out in selecting an appropriate composition for glass seals for SOFC applications. It is generally accepted that barium or boron-based systems are required in order to mitigate crystallization at these temperatures [8]. Within these types of systems, authors have studied crystallization kinetics [8,10–12,14,15], CTE development [9,16], particle and powder sizes [21,22], and flow and sintering behavior [7,18,19]. The G-18 glass system developed at Pacific Northwest National Laboratory (PNNL) was developed specifically for SOFCs. As such, this system has been uniquely characterized with measurements of thermal expansion [8,17,20,22], crystallization [22], wetting angle [22], microstructural evolution [23], interaction with interconnect and electrolyte materials [22], mechanical properties [20], and bond strength [17]. The G-18 system has also been modified with different compounds to improve contact angle and thermal expansion characteristics [22]. However G-18 was designed for temperatures up to 700 °C, and when above 700 °C, crystalline phases become unstable and the CTE varies with thermal cycling [22,23]. G-18 also reacts with other SOFC components to form porous interfaces that are susceptible to fracture [24].

Rather than using a "pure" glass approach that starts with a single glass that partially crystallizes into a glass–ceramic, the proposed research deals with two-phase ceramic/glass composites. The ceramic/glass composite approach is an emerging method of high temperature sealing. The processing of the seal begins with a high percentage of Al_2O_3 ceramic powder, an organic binder, and glass powder. The powders are either role compacted or tape cast into flat sheets. Binder burn-out and consolidation of the glass powder occurs during a heat treatment at 800 °C for 4 h. The resulting microstructures consist of glass particles within a matrix of Al_2O_3 powder. The advantage to this approach is that the alumina provides rigidity that minimizes CTE mismatch issues and allows some degree of resistance against compressive loading. However, the methods and results for determining an appropriate curing cycle have not been studied. Most of the past research had chosen an arbitrary curing cycle without mentioning the actual reason behind selecting it [4,8,13,23].

The current research proposes a rigorous procedure to cure the green seals in an appropriate manner that expedites the initial binder burnout process without compromising the seal performance. The study and identification of an appropriate cure cycle is followed by study of the mechanical response of seals that have been cycled multiple times. Given the need to first establish an appropriately cured seal, this paper is organized into four main sections: material system, seal cure, cycled seal characterization, and cycled seal results and discussion.

2. Material system

NexTech Materials, Ltd. employs a novel sealing approach of combining mechanical loading with minimum surface bonding to attain the desired seal performance for SOFCs. The seal itself has a ceramic to glass ratio of 60:40, and is processed by either roll compaction or tape casting of nominally 14 μm glass and 0.5 μm ceramic (alumina) powders mixed with a proprietary binder system developed at Ragan Technologies Inc. (RTI). The glass powders used in the composite seal are a commercial product of Viox and have the trade name "V-1716". The glass composition is the G-18 system invented by Pacific Northwest National Laboratory. G-18 is a barium calcium aluminosilicate-based glass containing the following weight percent mixture of oxides: 35% BaO, 35% SiO_2, 5% Al_2O_3, 15% CaO, and 10% B_2O_3 [28]. The glass transition temperature and melting point of the aforementioned glass have been estimated to be around 620 and 940 °C respectively [7,22]. A typical seal thickness for actual stacks is ~0.25 mm. The glass and alumina phases are shown in the SEM backscatter image provided in Fig. 1.

Thermogravimetric analysis (TGA) was performed on the green seals heated at 2 and 15 °C per minute until 800 °C. TGA was performed to characterize binder burnout and study the effect of different heating rates on binder burnout. As observed in Fig. 2, the seals start to lose weight around 100 °C. The difference in the response curve for 2 and 15 °C heating rates is due to non-uniform temperature distribution within the seal heated at the faster rate. The sudden changes in the slope of the response curve can be attributed to the evaporation or volatilization of different organics in the binder [29,30]. The other phases of the ceramic/glass seal do not volatilize. The TGA curves level out at slightly different temperatures, indicating that the binder burnout is dependent on heating rate. However, since there is no longer measurable weight loss at temperatures above approximately 600 °C and heating of all samples went above 600 °C, it is assumed that binder burnout is complete for all heating rates.

3. Seal cure

The curing process in the present research includes a heating cycle, followed by a 4 h dwell period, and finally a cooling cycle back to room temperature. Smeacetto et al. [3] and Brochu et al. [27] postulated that micro-voids can originate during the curing process primarily due to entrapment of unwanted gases, binder burnout, and also due to differences in the CTE of glassy and ceramic phases. Void formation would be detrimental to the quality of the seal and negatively impact the mechanical response of the seal. The authors are unaware of studies which have investigated void formation as a function of heating or cooling rate.

To expedite the initial curing process in seals, a faster heating and cooling cycle is preferred. However, a faster curing process may

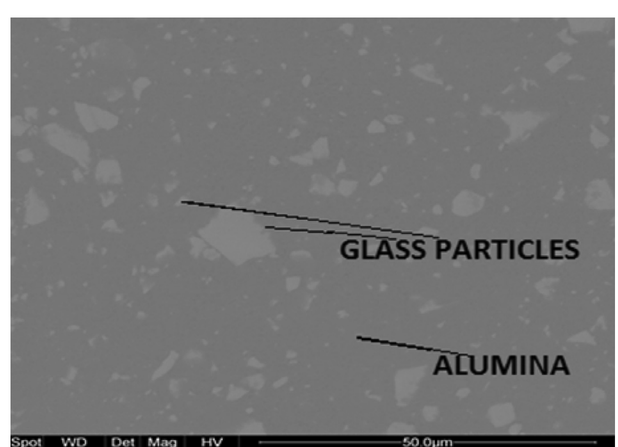

Fig. 1. A backscattered SEM image of a 0.25 mm thick green seal.