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PROPERTIES OF PARTICLE–FILLED GLASS COMPOSITES USED FOR SEALING SOLID OXIDE FUEL CELLS*

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ABSTRACT

Sealant materials for solid oxide fuel cells (SOFCs) must meet a demanding set of performance criteria for operating lifetimes of up to 40,000 hr. The resulting seals must be gas tight at temperatures up to 1000 °C, resist stresses from thermal gradients and expansion mismatch of different stack materials, and perform reliably over long times at high temperatures in both oxidizing and reducing atmospheres. Ceramic and metal filled glass composite sealants provide for greater design flexibility than other approaches. The seal properties can be tailored by varying the composition, amount, and microstructure of the particulate phase. Composite properties such as glass transition temperature, viscosity, and thermal expansion coefficient can be altered by rational control of the glass chemistry and composite microstructure. Several specific materials combinations have been engineered to meet the demanding set of criteria for sealing materials in SOFCs and characterized by means of viscosity measurements at the proposed operating temperature of 750 °C. The influence of the matrix/particle interactions has been separated from the mechanical effects of the added phase in studies that systematically vary the chemical composition of the particles. Models for composite suspension viscosity were also used to interpret the observed variation in viscosity with composition and volume fraction of the filler.

INTRODUCTION

Seals for solid oxide fuel cell (SOFC) stacks are subject to some of the most challenging performance criteria in the field of ceramic joining[1]. The sealing material must adhere to fuel cell components and provide a leak-tight seal from room temperature to 1000 °C or more. The seal must remain hermetic while accommodating strains from SOFC components with different coefficients of thermal expansion (CTEs). It must be tolerant to thermal shock from temperature excursions. The seal material must not react adversely with the other cell components and it must be stable in oxidizing and reducing environments that may exceed 1000 °C[2, 3]. The seal also must be electrically insulating for some SOFC designs[4].

We are developing methods for sealing SOFCs that can be tailored to specific fuel cell designs. As mentioned above, SOFC stack materials having different coefficients of thermal expansion, in conjunction with the thermal transients and gradients experienced in normal operation, will produce potentially detrimental stresses in the cells and seals. These stresses may result in mechanical degradation and eventual failure of the cells and increasing reactant leakage rates, adversely affecting electrical performance. In our judgment the best way to mitigate those stresses is to incorporate either a ductile metal or a high viscosity glass into the seal that can relieve stresses through viscous creep. Other design and operational constraints on SOFCs frequently are in opposition, and they severely restrict the options for seal materials. Based on our prior experience in ceramic joining and on results obtained so far in this research, we believe we have greatest design flexibility with seals based on ceramic-filled glasses and metal-filled glass composites.

The key to a successful seal in this approach is to tailor the viscosity and other properties of the filled glass composite seal material. In this paper, we present data on the viscosity of glass composite seal materials as a function of temperature, powder composition, particle size, and filler volume fraction. We show that varying the compositions, amounts, and microstructures of the different phases can control properties such as glass transition temperature and thermal expansion coefficient. Thermochemical and composite microstructural models that allow us to target specific seal properties for a given design guide the choices.

EXPERIMENTAL

The glasses used in this study were multicomponent compositions in the alkaline earth borate and alkaline earth borosilicate families that were formulated in our laboratory[5]. Appropriate oxides and carbonates were mixed and melted in Pt crucibles in an electrical resistance furnace at 1600 °C and then cast as small patties on a steel plate. Glass transition temperatures varied from 550 °C to about 600 °C depending on composition. Some melts were fritted by pouring them into water. The glass was milled to a powder with alumina balls in alumina jars and the -200 mesh fraction was screened and then blended with the appropriate powder filler. The characteristics of the Ag and YSZ filler powders, which were from commercial sources, are given in Table I.

Table I. Powder particle properties used to fill glass composites.

Powder	Supplier	Purity	Particle Size
ZrO_2	Johnson Matthey Electronics	99+%	+325 mesh
Ag	Cerac Specialty Inorganics	99.99 %	-200, + 325

Composite viscosities were measured according to the ASTM C1351M-96[6] standard in a high temperature, multi-property characterization facility (Thermo-optical mechanical measuring instrument, TOMMI, Fraunhofer Institute fur Silicatforschung, Wurzburg, Germany.) The glass-powder mixtures were pressed into 1/4” diameter x 3/8” thick cylinders in a hydraulic press, placed in the TOMMI measuring chamber, a load of 1.0-3.0 N was applied, and the chamber was heated at 10 °Cmin^{-1} while digital images of the sample cross sections were acquired at over 5 second intervals. Shear viscosities were calculated from the change in specimen height with time for a given load.

Figure 1 shows a photograph of the experimental set up inside the TOMMI furnace. The specimen is shown under the alumina punch that applies the constant load as for a given heating schedule. The specimen is backlit illuminated inside the furnace and projects a silhouette that is captured by a CCD camera and recorded by the computer for image analysis.

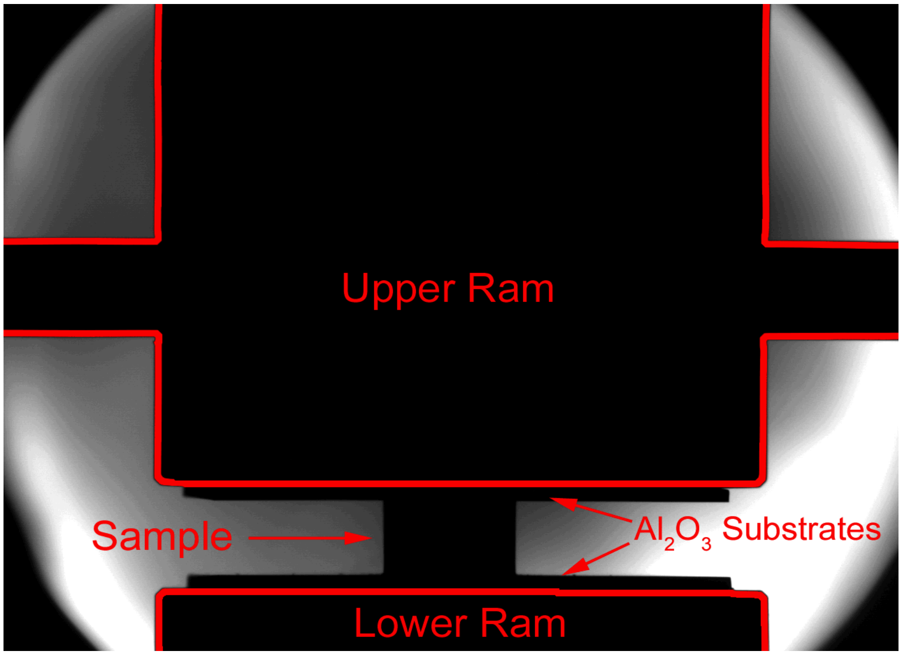

Figure 1. A photograph of the TOMMI furnace as it is set up for an experiment to measuring the viscosity of a glass-composite specimen. The change in specimen and height and width are monitored continuously using the TOMMI computer software and is then used to calculate viscosity as function of time at a given temperature.

The equation used to calculate the viscosity from the deformation data recorded using the TOMMI facility is shown in Equation 1[6]. The viscosity is calculated from the change in sample height with time, dh/dt. Other variables in the calculation are the sample volume, V, the applied load, M, the temperature, T, and the expansion coefficient, α.

$$\eta = 2\pi \frac{Mgh^5}{30V(dh/dt)(2\pi h^3 + V)(1+\alpha T)} \qquad \text{Equation (1)}$$

RESULTS AND DISCUSSION

Figure 2 presents the viscosities of a series of glass-YSZ composites measured as a function of temperature and volume fraction of YSZ. Glass 14A has a glass transition temperature, T_g=575 °C. The viscosities increase systematically with the amount of added YSZ, rising from about 8 MPa s for the pure glass to almost 110 MPa s for 5 vol% glass – 40 vol% YSZ. The effect on viscosity is greater for the 40 vol% YSZ composition because the effects of mechanical interference and impingement between the particles accelerate. The rise in viscosity in the 40 vol% YSZ composition is due to partial crystallization of the base glass, possibly nucleated by the added YSZ. Partial crystallization effectively increases the volume fraction of particles in the composite, which increases the viscosity. Figure 3 is a plot of viscosity at 700 °C as a function of YSZ volume fraction. The effect of increasing volume percent can also be se seen in the apparent shape of the pellet while at temperature under the same given load.

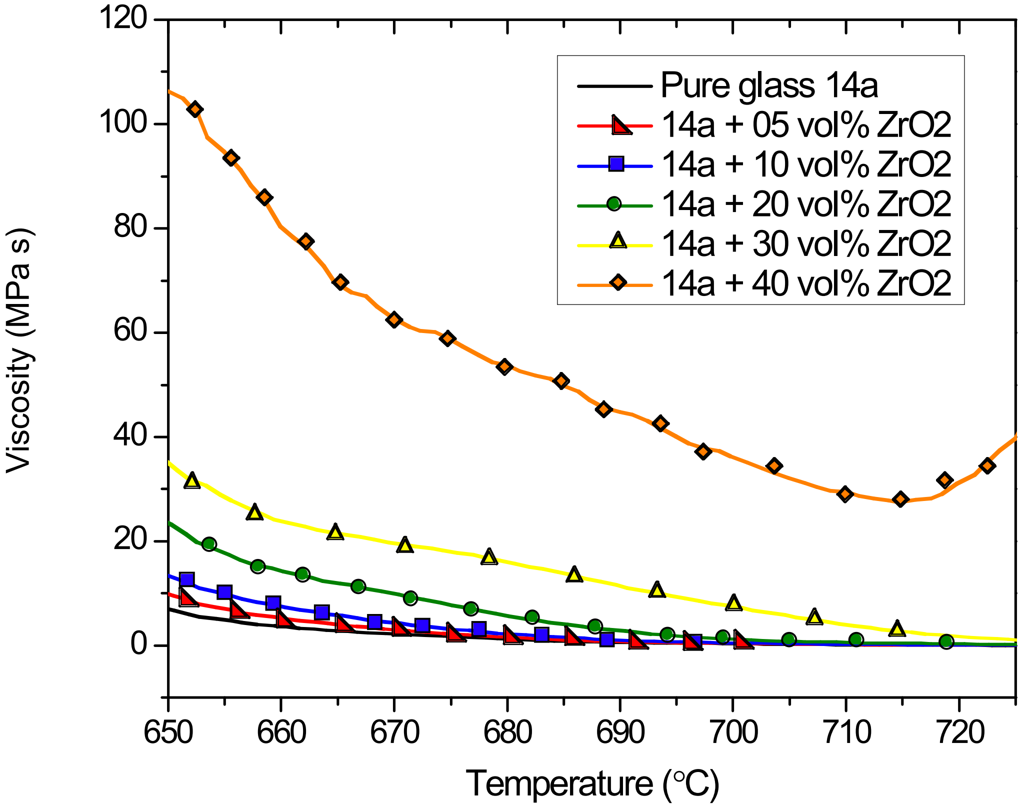

Figure 2. Viscosity flow profiles for glass 14 filled with increasing volume fraction ZrO_2 power particles.

Figure 4 is a set of viscosity curves similar to those in Figure 2, except the filler powder is Ag and the matrix glass is a different alkaline earth borate, this one with a T_g of 569 °C. The behavior of the Ag-filled glass composite is like that of the glass-YSZ composites, except that there is no increase in viscosity for the highest filler fraction above 700 °C. Figure 5 is a comparison of composite viscosities for the same glass 14A with similar amounts of Ag or YSZ powder. The data show that the effect on viscosities is similar for the two powders. One can conclude from this result that the increase in viscosity is a mechanical effect rather than one controlled by chemical interaction between the glass and the particles.

The viscosities of liquid-particle suspensions have been discussed in the colloid literature[7-9] and those results are applicable to our research. A number of models are available [10]and of those, the one due to Eilers[11] equation 2, provides the best fit.

$$\eta_r = \left(1 + \frac{k\phi}{(1-\phi/\phi_c)}\right)^2 \qquad \text{Equation (2)}$$

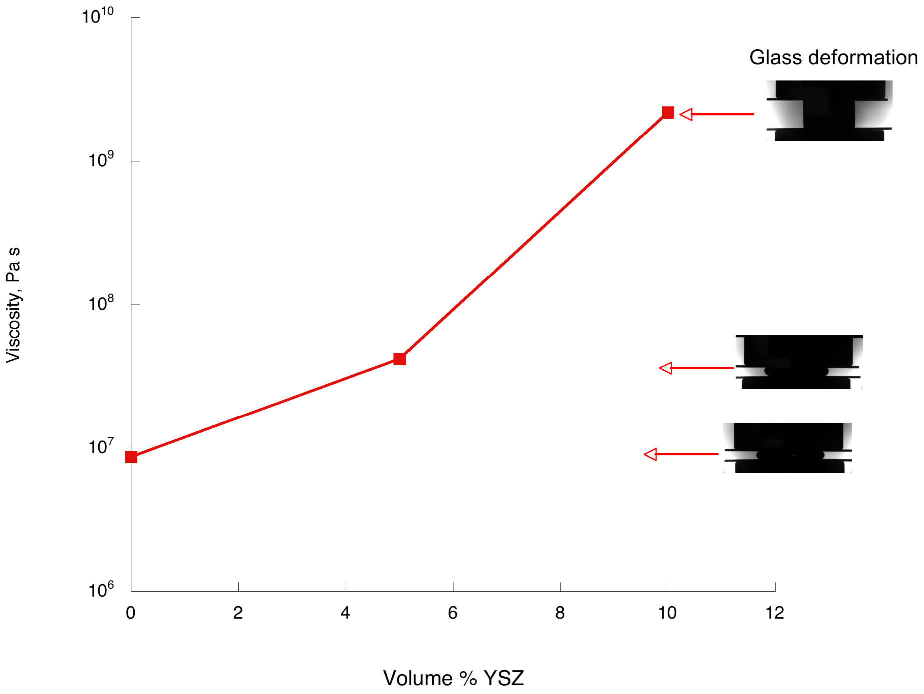

Figure 3. A plot of viscosity values measured at 700 °C for glass filled composites with increasing volume percent YSZ. The images shown next to each data point correspond to the specimen during testing in the TOMMI facility.

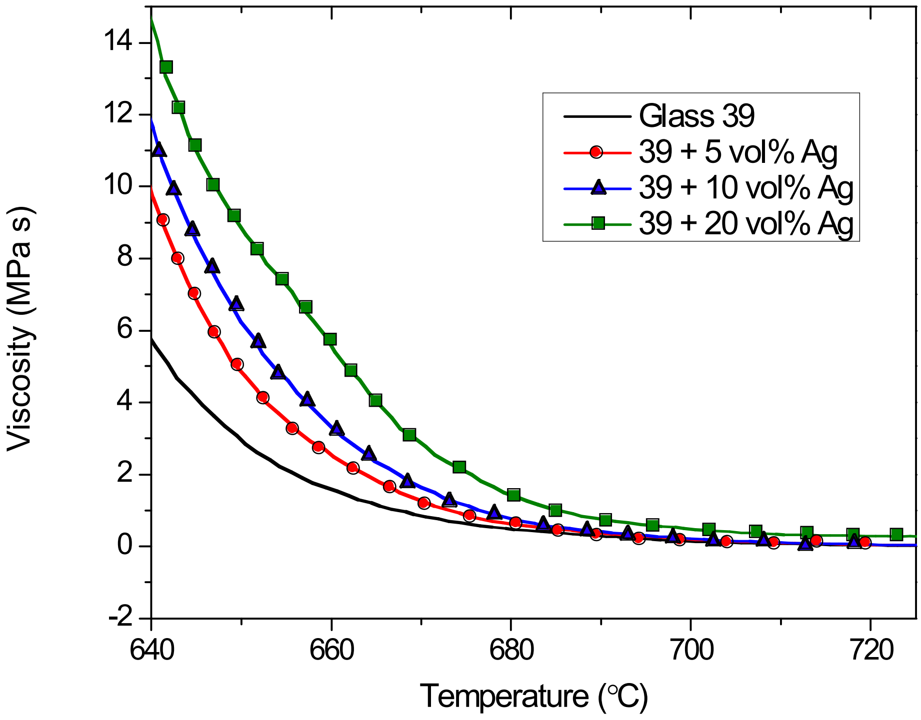

Figure 4. Viscosity of glass filled Ag particles composites as a function of volume fraction Ag and temperature. Adding Ag powder systematically increases glass composites viscosity.

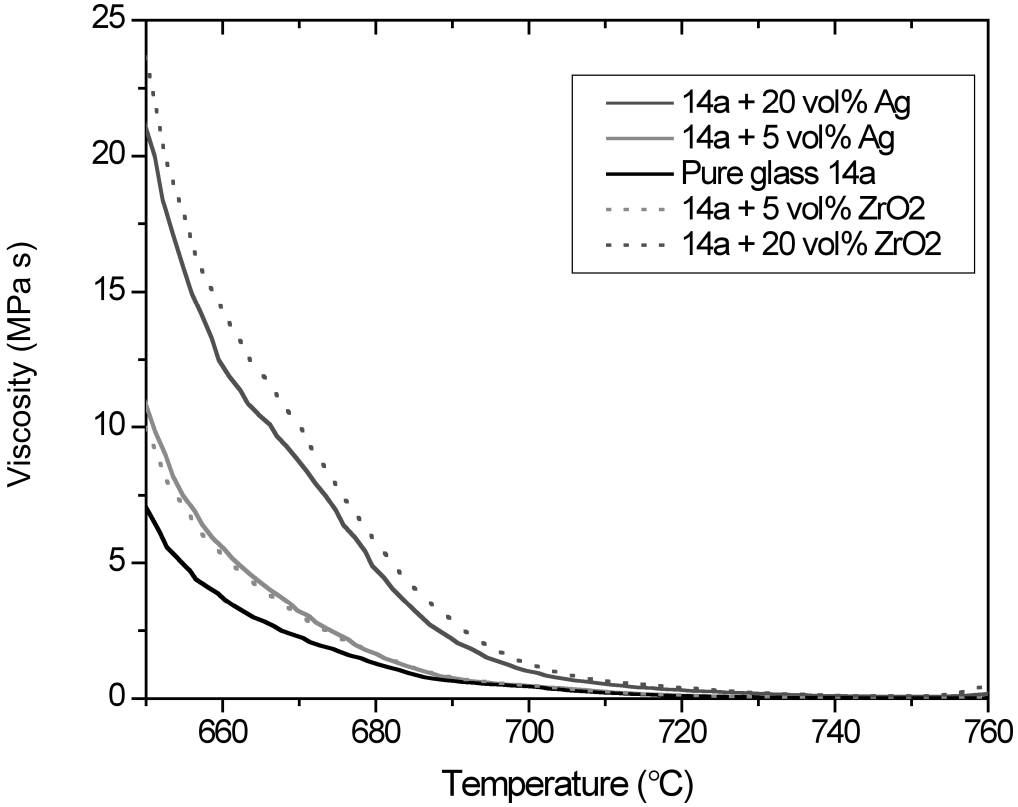

Figure 5. Comparison of glass-YSZ and glass-AG composites shows the effect of powder fillers on glass viscosity is independent of filler composition.

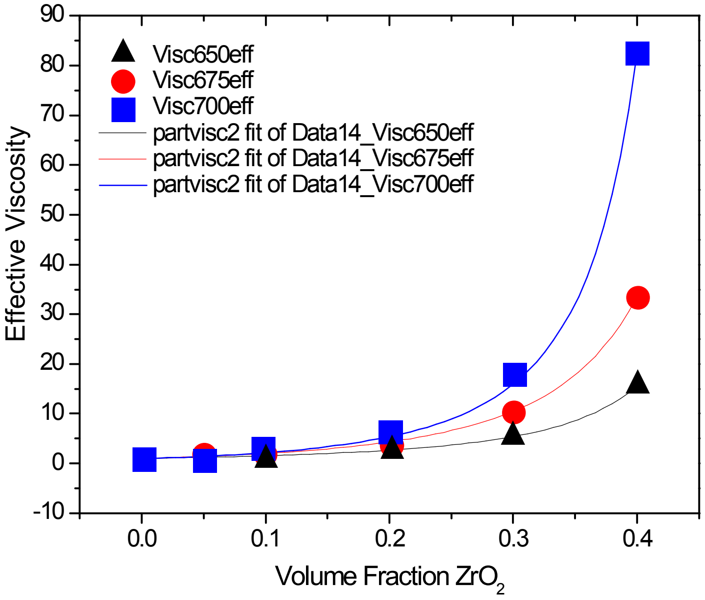

Figure 6. Viscosity data for YSZ filled glass composites can be modeled using Eilers formula.

Table II. Fitting parameters for Eilers model.

Model	Temp (°C)	R^2	K	Φ_c
Eilers	650	.9937	2.0147 ± .261	.5517 ± .029
	675	.9999	3.4889 ± .060	.5643 ± .004
	700	.9984	3.9882 ± .360	.4983 ± .012

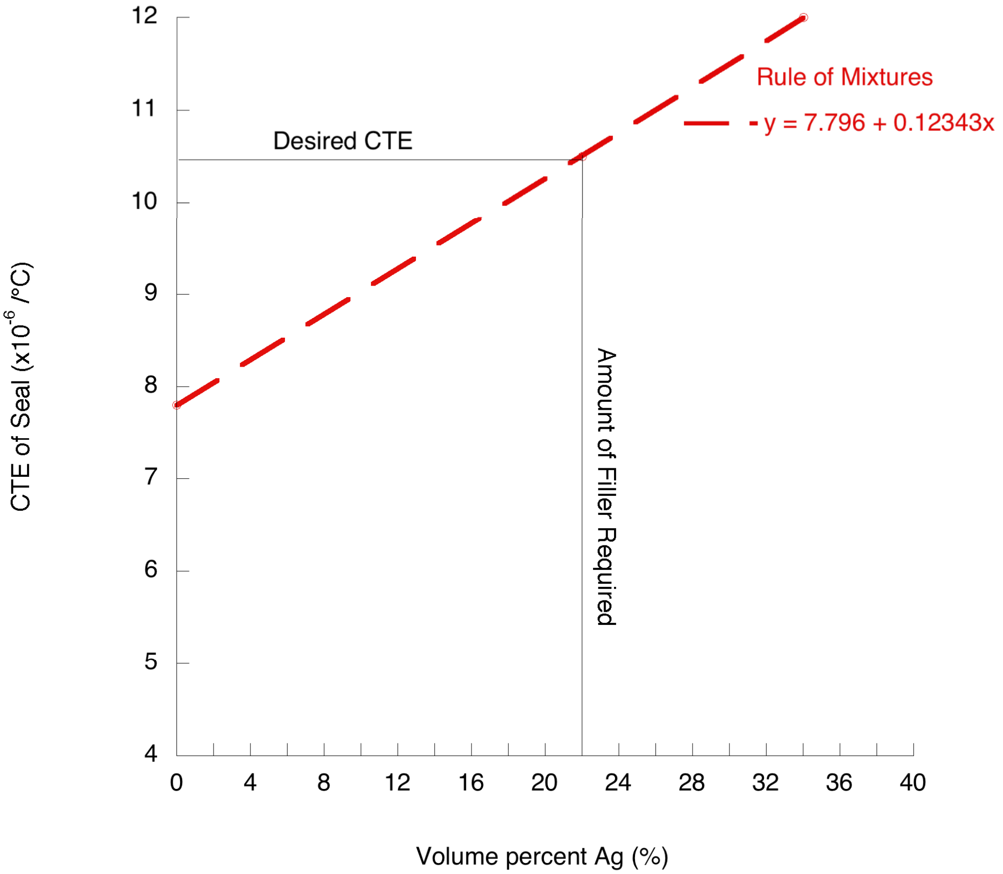

Figure 7. Expansion coefficients of glass-powder composites closely follow rule of mixtures behavior. In this example the desired CTE=10.5 x 10^{-6} °C^{-1} was required to match a particular stainless steel alloy with a Ag filled glass composite.

In the Eiler model k is inversely proportional to the powder particle size, ϕ is related to powder volume fraction, and ϕ_c is the critical volume fraction above which, the flow assumption no longer hold. Figure 6 presents the fit of some of our data on YSZ-glass 14A composites to the Eiler model showing excellent agreement. Table II gives the fitting parameters resulting from application of the model.

As mentioned above, properties of glass-powder composites other than viscosities can be tailored by varying composite compositions. One example is presented in Figure

7, where a simple rule-of-mixtures calculation was used to target a precise CTE. In this case the desired CTE was 10.5 x 10^{-6} °C^{-1} to match a particular stainless steel alloy. The calculation gives a composition of 22 vol% Ag-78 vol% glass 14A. Subsequent formulation of that composite composition gave a CTE of 10.5 x 10^{-6} °C^{-1}.

CONCLUSIONS

Adding particulates with increasing volume percent, of either metal or ceramic, to these glasses causes an increase in the viscosity regardless of the glass composition. Also, for a given glass composition the measured viscosity values for composites filled with the YSZ or Ag into the same regardless of filler composition. Classical suspension rheology models are applicable to this glass filled composites systems. The Eiler formula was used to show the dependence of volume fraction filler to measured increased viscosity values.
A wide range of viscosity and temperature profiles for seal materials can be engineered with this approach. By varying the volume fraction of the filler material the measured viscosity values at a given temperature can increase up to twenty times for a given glass composition. Glass composites allow a wide range of properties and seal designs. In addition to controlling the viscosity of the seal with the filler particles the compatibility of the seals can also be design to match the CTE of the sealing materials.

FOOTNOTES

*Part of this paper was taken from a thesis submitted by Bryan D. Gauntt in partial fulfillment of the requirements for the MS degree in Materials Engineering at New Mexico Tech, Socorro, NM.

ACKNOWLEDGMENTS

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