Interface reactions between barium base sealant glasses and high chrom steel for SOFCs application

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Barium silicate based glass sealants for a solid oxide fuel cell (SOFC) design were developed. The sealants were applied as glass slurries to form partially crystallized seals. Several promising compositions were identified which met the requirements of a high thermal expansion coefficient α ($11\text{-}12\cdot10^{-6}K^{-1}$, similar to the steel), high electrical resistance, good chemical compatibility with the adjacent fuel cell materials, and evaporation stability against the fuel and flue gas atmospheres at operation temperatures of 800 to 900 °C. The long-term evaporation stability, time constancy of the thermal expansion coefficient α, and of the mineral phase content were investigated. Special attention was paid to the interaction between sealants and steel surface. The best candidate materials allowed to produce sandwich cells which remained gas tight (He leak test) under multiple thermal cycling between room and operation temperature. The mechanical strength of the seals exceeded 20 MPa with a Weibull exponent > 10.

1. Introduction

Adherence of enamel to conventional steel and alloys has been intensively studied during the period 1950-1970 by many researchers[1,2,3]. Good wetting, saturation of the oxide from steel at the interface (FeO for Fe steel), chemical equilibrium of the interfacial layer, and mechanical bond from some adherence promoters (CoO or NiO for enameling of iron steel) have been used as basic requirements of a good adhesion. Most enamel compositions contain alkali borosilicate or alkali phosphosilicate, which are quite different from the sealant developed for the SOFC. For the SOFC, such compositions cannot be used because of the requirements of chemical stability at operation temperatures of 800-900 °C in H_2 and H_2O atmospheres for more than 40,000 h. Instead, barium silicate based glasses have been developed. The best candidate sealants were modified by small additions of NiO, CoO, CuO, and V_2O_5. Special attention was paid to the interface reaction between sealants and steel surface.

2. Experiment

Additions of 2, 4, and 8 wt. % of NiO, CoO, and CuO (3, 10, and 20 wt. % for V_2O_5) to the base glass S25 were tested (see table 1). The amounts were chosen in such a way that the occurrence of high thermal expansion phases BS_2, B_2S_3 and C_2BS_3 during crystallization was maintained[4]. Glass batches were melted in an induction furnace at 1480 °C for 2 h. The glass was stirred for homogeneity during soaking and cooled in ice water. Dry samples were ground to a particle size < 63 µm. Pastes of glass powder with organic binders were used for joining tests. Some glass powders were inspected by heating microscope. Both glass samples and crystallized pressed powder samples were used for dilatometric and viscosimetry measurement.

The properties: thermal expansion coefficients α of glasses and partially crystallized glasses, viscosity, melting behavior and wetting properties, the crystallization behavior, and phase contents were investigated by: dilatometer, beam bending viscosimeter, heating microscope, DTA, and XRD, respectively. The microstructure of interfaces between seal and steel was studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

Table 1. Chemical compositions of different glasses in wt. %

oxides	glass codes											
	S25	A	B	C	D	E	F	G	H	I	J	K
SiO_2	28	26	24	19	28	27	25	26	19	27	22	15
BaO	49	52	53	55	49	48	47	51	55	50	50	50
CaO	6	5	5	4	6	6	5	5	4	5	4	2
Al_2O_3	3	3	3	2	3	3	3	3	2	3	3	3
B_2O_3	8	8	8	8	8	8	8	8	8	8	8	8
NiO	-	2	4	8	-	-	-	-	-	-	-	-
CoO	-	-	-	-	2	4	8	-	-	-	-	-
CuO	-	-	-	-	-	-	-	2	8	-	-	-
V_2O_5	-	-	-	-	-	-	-	-	-	3	10	20
additives*	6	4	3	4	4	4	4	5	4	4	3	2

* = further transition metal oxides

3. Results and discussion

Partially crystallized samples produced by sintering of pressed powder samples at 850 °C for 10 h were used for thermal expansion analysis. Additions of 20 wt. % V_2O_5 were found to increase the thermal expansion coefficient (α) more effectively than NiO, CoO, and CuO. This effect agrees well with data reported by Donald[5]. At lower amounts of 3-10 wt. % V_2O_5, a decrease of α is observed because of an increased crystallization rate. The results for S25, A, E, and I samples are presented in figure 1a, showing the unfavorable effect of low V_2O_5 content.

The viscosity measurement of glasses with 2 wt. % of CuO, NiO, V_2O_5, and CoO show a shift of the viscosity curves towards lower temperatures by 80, 40, 40, and 35 K, respectively (figure 1b).

XRD results of partially crystallized glasses show barium silicates (B_2S_3 and BS_2) and celsian phases (BAS_2; B = BaO, A = Al_2O_3, and S = SiO_2) in glass S25 (see figure 2a). Dibariumzincsilicate (B_2ZS; Z = ZnO) was found in all glasses containing NiO, CoO, and CuO, except for glasses with additions of V_2O_5. This phase was also found with glass S25 sintered at 800 °C however, after soaking for more than one week only. This means that NiO, CoO and CuO act as a nucleating agent for the formation of B_2ZS. By bond strength considerations, B_2ZS is expected to lower the overall thermal expansion coefficient.

The melting behavior and wetting properties detected by heating microscope show that glasses A, D, and I reach the point of spherical shape at temperatures similar to S25 (see

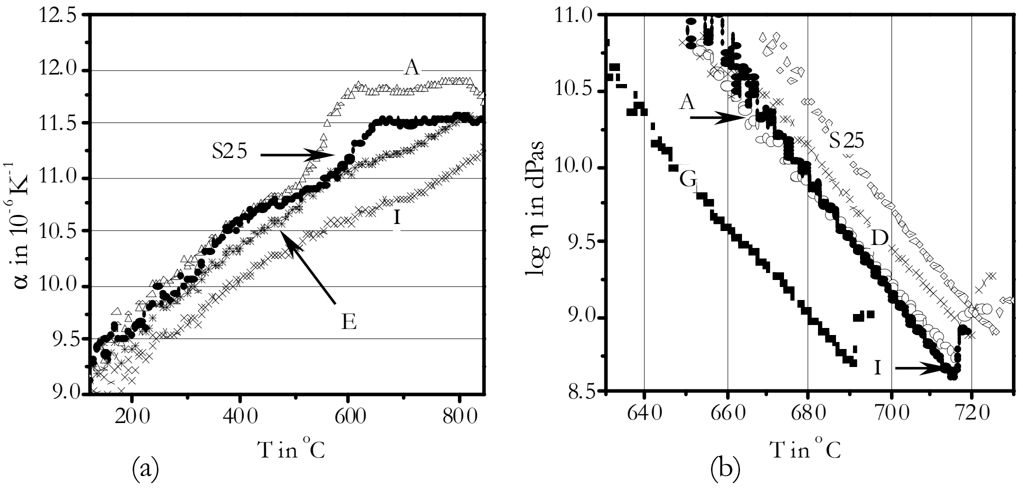


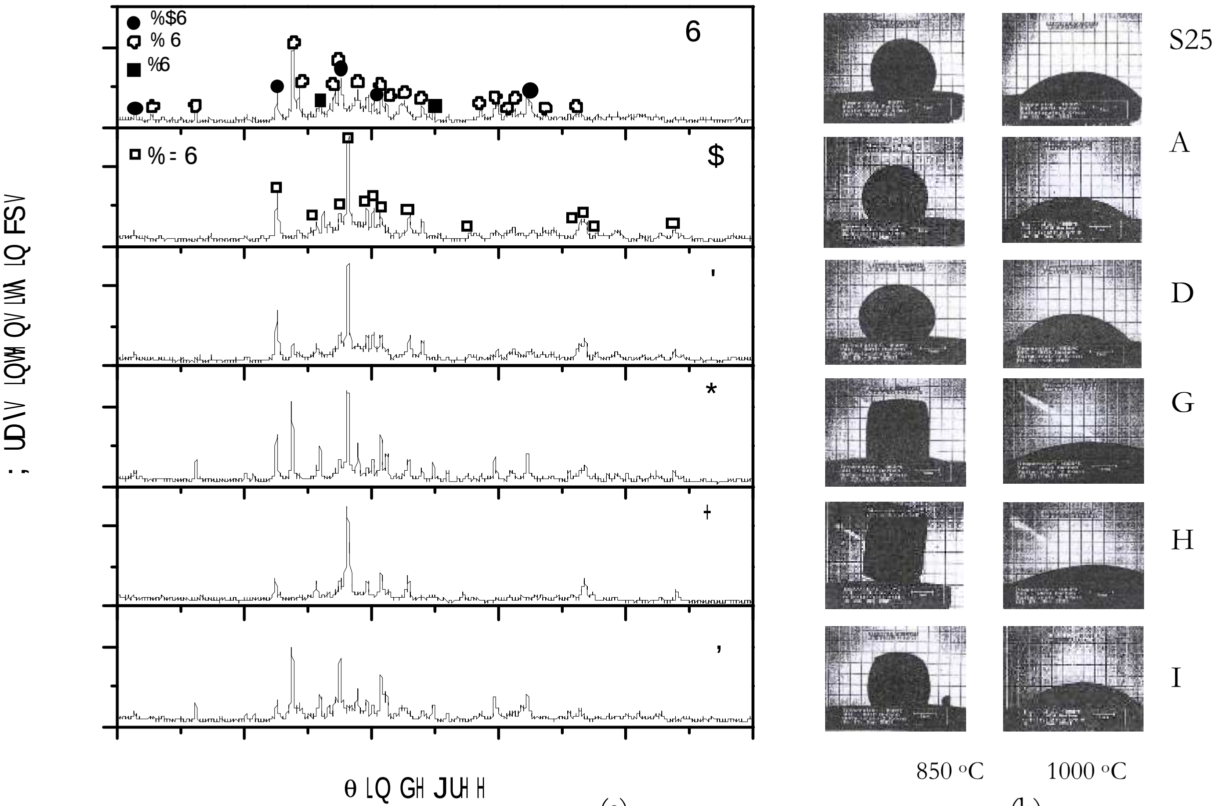
Fig. 1. Dilatometric measurement (a) of crystallized glasses after sintering at 800 °C for 7 d, and viscosity temperature function (b) for samples with additional oxides

figure 2b). At higher amounts of additional oxides, the point of spherical shape was shifted to higher temperatures due to faster crystallization. In this respect, copper oxide has a very strong effect: additions of only 2 wt. % lead to a fast transition from the rectangular shape to complete melting; the spherical shape is not observed at all.

For the joining test of the samples in table 1, glasses S25, G, and H show the best thermal cycling ability over 15 cycles between room temperature and 800 °C. This was confirmed by a helium leak test. By contrast, glasses A, B, C, D, E, and F reach less than 4 cycles, and no gas tightness was found for glasses I, J, and K. The base glass S25 was selected for measuring the joining strength. Joining partners were heated to 850 °C for 10 h and cooled to room temperature before testing. The mechanical strength of the steel/sealant/steel sandwiches exceeded 20 MPa with a Weibull exponent > 10.

Figures 3a-d show the results of interface reactions between glasses and the high chromium steel substrate (sand brushed surface). Small white particles near the interface in samples A and G were identified by EDX as Ni and Cu, respectively. It should be mentioned that glass G tends to form bigger particles due to its high Gibbs energy of reaction. At high temperature, oxides in the glass (NiO, CuO, and PbO) are reduced to metal particles (Ni, Cu, and Pb) by metallic Fe, Cr or Mn, and metal ions bond with oxygen to form metal oxides (FeO, CrO or Cr_2O_3, and MnO). The following reactions calculated at 800 °C give an overview of these reduction-oxidation reactions:

$2Mn + O_2 = MnO$ $\Delta G = -612.8$ kJ/mol O_2 ,
$4/3Cr + O_2 = 2/3Cr_2O_3$ $\Delta G = -571.6$ kJ/mol O_2 ,
$2Zn + O_2 = 2ZnO$ $\Delta G = -480.3$ kJ/mol O_2 ,
$4/3Fe + O_2 = 2/3Fe_2O_3$ $\Delta G = -388.3$ kJ/mol O_2 ,
$2Co + O_2 = 2CoO$ $\Delta G = -316.8$ kJ/mol O_2 ,
$2Ni + O_2 = 2NiO$ $\Delta G = -285.8$ kJ/mol O_2 ,
$2Pb + O_2 = 2PbO$ $\Delta G = -223.9$ kJ/mol O_2 ,



(a) (b)

Fig. 2. X-rays patterns (a) of samples sintered at 850 °C for 10 h, and sintering behavior (b) of different glasses tested by heating microscope at a heating rate of 2 K/min to 1100 °C

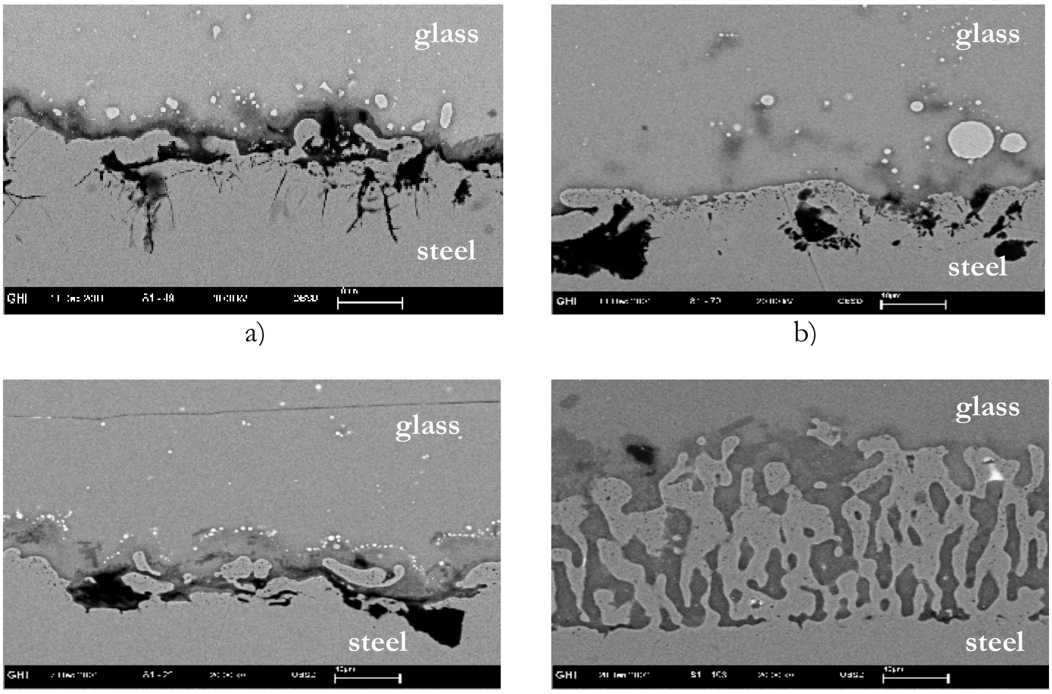
$4Cu + O_2 = 2Cu2O \qquad \Delta G = -180.2\ kJ/mol\ O_2$,

$2Cu + O_2 = 2CuO \qquad \Delta G = -120.2\ kJ/mol\ O_2$.

From the above reactions, CuO has the highest potential to oxidized Cr or Fe metal to Cr_2O_3 and FeO. Very small particles of PbO were found in glass S25. These particles were located at the interfacial reaction layer (thickness ~ 10 μm). EDX analysis showed a high content of Cr and Fe in the layer. Samples A and G did not have any reaction layer and therefore metal particles could diffuse closer to the metal surface. Cr and Fe (dark color in figure 3b) were found to have penetrated deeply into the glass matrix. So CuO supports the transport of Cr thus avoiding the formation of chromate phase in the interface which otherwise strongly impair sticking. Perhaps, the low viscosity of this glass also supports this mechanism. Figure 3d shows a very strong corrosion of the metal surface. The sample was prepared under strongly reducing condition. This result may be caused by the formation of metal nitrides, reaching 200 μm into the glass.

4. Conclusion

Additional oxides, atmospheres, and steel surface conditions influence the wetting properties and adhesion of the joint. Additions of NiO , CoO, and V_2O_5 increase the crystallization velocity which results in a poor gas tightness. CuO oxide supports the transport of Cr from steel surface into the glass matrix and enhances sticking by suppressing the formation of detrimental chromate phases at the interface. The interfacial reaction mechanisms between glass and steel can be explained by thermodynamic reactions. Calculated results of ΔG show that CuO and PbO are easily reduced to Cu and Pb metal particles by metallic Cr, Fe and Mn. From the thermal cycling test, glasses S25, G, and H are the most promising candidate sealants for the planar SOFC.



a) b)

c) d)

Fig. 3. SEM images of glasses; a) A in air, b) G in air, c) S25 in air, and d) S25 in N_2, 60 l/h; all samples were prepared in the heating microscope at 2 K/min to 1100 °C; the size bar equals 10 μm.

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