

SiO₂–CaO–B₂O₃–Al₂O₃ ceramic glaze as sealant for planar ITSOFC

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Abstract

A series of ceramic glazes based on the SiO₂–CaO–B₂O₃–Al₂O₃ system as sealant for intermediate temperature solid oxide fuel cell (ITSOFC) were investigated. Different ratios of B₂O₃/SiO₂ and Al₂O₃/CaO were investigated to control softening process, phase separation, and crystallization. When B₂O₃/SiO₂ ratio was in the range of 0.14–0.27, the glazes showed good wetting and bonding behavior with both 8 mol% yttria-stabilized zirconia (8YSZ) electrolyte and stainless steel interconnect which could satisfy the sealing demand at 850 °C. And the dimension stability can be kept for over 100 h by introducing ceramic felt and controlling the glazes viscosity in the range of 10⁴ to 10⁶ Pa s. By means of controlling Al₂O₃/CaO ratio in the range of 0.4–0.68, phase separation and crystallization were restrained effectively. After holding at 850 °C for 100 h, non-crystalline network in the glazes could be found, and a suitable viscous flow could well relax thermal stress. The sealing was effective even after 10 thermal cycles. Element analysis showed a good chemical stability at the ceramic glazes/stainless steel interconnect and ceramic glazes/8YSZ electrolyte interfaces.

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1. Introduction

Solid oxide fuel cell (SOFC) has been attracting a great attention as an important electric power source in the near future because of its high efficiency, environmental friendliness, and multifuel applicability. Planar-type SOFC are superior to tubular-type for their simple manufacturing process and the promise of a higher power density. At present, in order to reduce costs and improve long-term stability, planar ITSOFC operated at about 850 °C, is a common object of SOFC research and development throughout the world. For most planar SOFC designs, except single chamber SOFC [1] and Sulzer type SOFC [2], the gas-tight sealing is critical for a good performance.

An effective sealant should seal the different components of planar ITSOFC to prevent gas leakage. In order to maintain the gas-tight sealing during the whole operating process, the sealant should show chemical stability to the component materials with which it contacts in oxidizing and reducing atmospheres. Further requirements are the good wetting behavior and relaxation of thermal stress through either creep or viscous flow at operating temperatures. In general, glass ceramic sealants composed of crystalline network within a

glassy phase can in principle meet most of these requirements.

At present, there is a common idea: in order to keep the solid-like state and endure some press stress, the glass ceramics' viscosity should be greater than 10⁹ Pa s at 850 °C [3–5]. These “hard” sealants can modify their thermal expansion coefficients (TECs) close to that of the brittle 8YSZ to avoid thermal stress between them. On the other side, the TECs mismatch between sealant and interconnect has to be relaxed through high temperature creep. However, this “hard” sealing exhibited inferior thermal stress relaxation characteristics in a thermal cycle. It is difficult for the crystalline network to relax through creep all the thermal stress caused by the remarkable difference of TEC between 8YSZ and interconnect. It was always the case that the 8YSZ electrolyte cracked at the area in contact with the sealants, or the sealant broke near the interface between sealants and interconnects in a thermal cycle. In fact, through modifying interconnect structure [6] and inserting support materials, such as ceramic fiber [7], the sealant has not to endure press stress. So we expect to develop a “soft” sealing ceramic glaze which has excellent stress relaxation property through viscous flow in thermal cycling between temperatures at which the material can keep a solid-like state under self-weight press stress.

In this paper, the phase separation and the crystallization of glazes based on the SiO₂–CaO–B₂O₃–Al₂O₃ system were studied. The objective is looking for a suitable “soft” sealing

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Table 1
Glaze compositions in this work

Label	Glaze composition (mol%)						
	SiO ₂	CaO	B ₂ O ₃	Al ₂ O ₃	BZS ^a	B ₂ O ₃ /SiO ₂	Al ₂ O ₃ /CaO
A1	65	17.5	2.5	3.5	11.5	0.04	0.2
A2	59	17.5	8.5	3.5	11.5	0.14	0.2
A3	53	17.5	14.5	3.5	11.5	0.27	0.2
A4	47	17.5	20.5	3.5	11.5	0.44	0.2
B1	59	17.5	8.5	3.5	11.5	0.14	0.2
B2	59	15	8.5	6	11.5	0.14	0.4
B3	59	12.5	8.5	8.5	11.5	0.14	0.68
C1	53	15	14.5	6	11.5	0.27	0.4

^a Made in SICCAS (a kind of glaze stuffing, containing ZnO, BaO, K₂O, Na₂O, etc.).

glaze as sealant for the planar ITSOFC operated around 850 °C.

2. Experimental

2.1. Preparation of original glass

The compositions of investigated glazes were listed in Table 1. The glazes based on the SiO₂–CaO–B₂O₃–Al₂O₃ system were made by a conventional glass-making technique. All the original reagents, SiO₂, CaCO₃, B₂O₃, Al₂O₃, and BZS, were of chemical grade. They were mixed in a ball mill, melted, and held at 1400 °C for 2 h, then poured onto steel molds, and finally annealed near the glass transition temperature (T_g) for 1 h.

2.2. Measurements of ceramic glaze properties

The transition and softening temperature of the ceramic glazes were tested by differential scanning calorimetry, DSC

(Netzsch STA449C) in air with a heating rate of 10 °C/min. The high-temperature viscosities of ceramic glazes were tested by a rotating viscometer (Theta Industries, Dilatronic II-HB), decreasing the temperature from 1200 °C down to the temperature corresponding to 10⁵ Pa s viscosity with a rate of 10 °C/min. As-prepared bulk glasses were held at 850 °C for 100 h, and then the phase were determined by X-ray diffraction, (XRD) (D/\max 2550 V).

To observe the high-temperature softening, wetting, and bonding behavior, experiments were carried out by following the report by Song and co-workers [8]. A cubic specimen of original glass with size of 3 mm × 3 mm × 3 mm were placed on 8YSZ flakes and was observed by thermal-microscope (MHO-2, Germany) from room temperature to hemisphere temperature at a heating rate of 10 °C/min. Because the target cell operating temperature is 850 °C, same glass specimens on 8YSZ flakes were heated up to 950 °C and held for 30 min, then slowly cooled down to 850 °C and held for 100 h to observe the dimension change. The TEC of A3 sample in Table 1, after heat treatment, was measured by thermal analyzer (Netzsch DIL402C).

To investigate the phase separation and crystallization, the powder of series B after heat treatment were observed by transmission electron microscopy (TEM) (JEOL JEM-2010) and energy dispersive X-ray analysis, EDX, (Link ISIS).

2.3. Investigation of thermal cycle characteristics

A schematic diagram of sealing test set-up for thermal cycle is illustrated in Fig. 1. The glazes were shaped into Ø 20 mm × 3 mm × 3 mm rings, and were placed between a stainless steel bipolar (1Cr18Ni9Ti, Cr 18 wt.% + Ni 9 wt.% + Ti 5 wt.% + Fe 78 wt.%) and a 8YSZ electrolyte plate, which was coated with platinum electrode on both sides to constitute a cell. A commercially available ceramic felt (SiO₂ 57 wt.% + Al₂O₃ 43 wt.%) was laid inside and

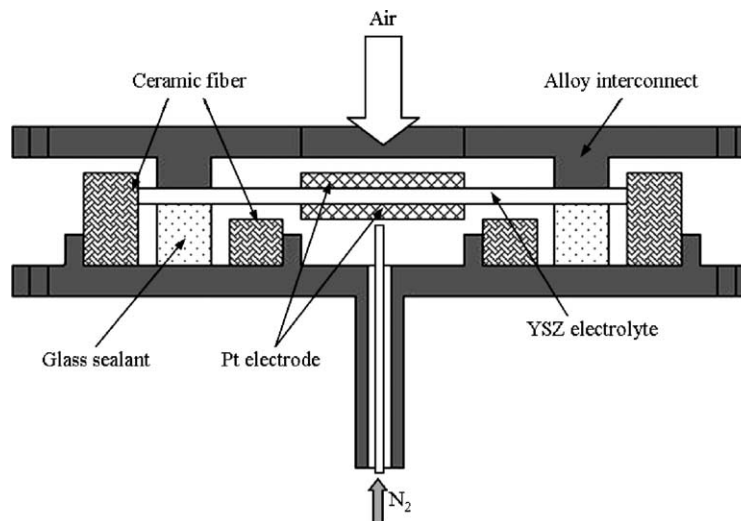


Fig. 1. A schematic diagram of sealing test set-up for thermal cycle.

outside of the glaze ring to support the interconnect. Some space was left between the glaze ring and ceramic felt for the deformation of glaze ring. The sealant was heated to 950 °C at 5 °C/min and held for 30 min, and then cooled to 850 °C at 5 °C/min and held. The voltage across the 8YSZ electrolyte was measured to check the leakage after N₂ (99.99%) was inducted into the sealed cavity to remove the air for 30 min. For thermal recycle, the system was cooled down to 450 °C at the rate of 5 °C/min and then heated up to 850 °C at the same rate. The steps were repeated for 10 recycles and the electromotive force was monitored. Finally the interface between sealing glaze and 8YSZ electrolyte was polished and analyzed by an electron probe X-ray microanalysis (EPMA-8705QH₂).

3. Results and discussion

3.1. Influence of B₂O₃/SiO₂ ratio on wetting, bonding, and dimension stability

Fig. 2 shows the high-temperature softening behavior of glaze series A. It was found that the softening process is similar and can be divided into three stages: the rounding of the corner of glass cubic (stage 1); the swelling to sphere in the lateral direction and maintaining the longitudinal height (stage 2); the shrinking of the sphere in longitudinal direction and nearly forming a hemisphere (stage 3). With the

increase in B₂O₃/SiO₂ ratios, the rounding starting temperature (T_1), the starting and ending temperature of stage 2 (T_2 and T_3) and hemisphere temperature (T_4) decreased evidently. This was caused by the property of B₂O₃ to form boron–oxygen triangle, which loosened the Si–O network, decreased the glazes viscosity and made the sealant wet more easily. During stage 2, it was observed that the contacting area between glaze cubic and 8YSZ flake was sustained basically, and the longitudinal height of glaze cubic kept constantly with good adhesion to the 8YSZ surface. It seemed that the stage 2 could be used for sealing.

Fig. 3 showed the dimension change of glaze series A after heat treatment described in the experiment section. A1 had no change basically, A2 and A3 kept the longitudinal height and expanded in the lateral direction, and however A4 shrank in the longitudinal height obviously. We observed the bonding state of series A: A1 could not bond with 8YSZ flake basically. The good adherences for A2, A3, and A4 (Fig. 4) might be explained as that the suitable softening behavior leads to a good wetting and bonding at 950 °C.

Depending on the dimension change and bonding experiments, it could be concluded that stage 2 was a suitable sealing stage, in which not only dimension stability could be kept, but also good adherence to 8YSZ flake was obtained. Compared with sealing temperature (850 °C), the T_2 of A1 was too high and T_3 of A4 was too low, suitable B₂O₃/SiO₂ ratio was in the range of 0.144–0.274.

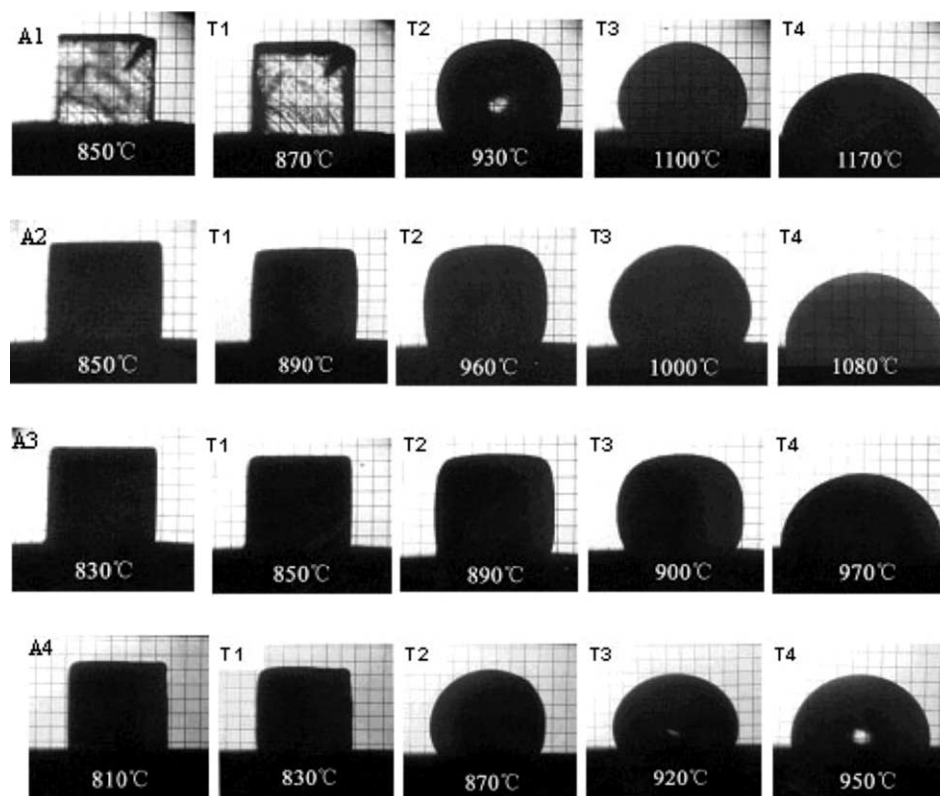


Fig. 2. High-temperature softening behavior of the cubic of glazes series A (heating rate of 10 °C/min).

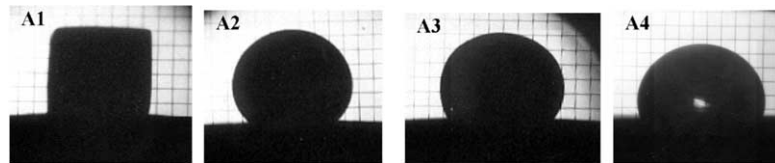


Fig. 3. Dimension changes of the cubic glazes of series A at 950 °C for 30 min followed a hold at 850 °C for 100 h.

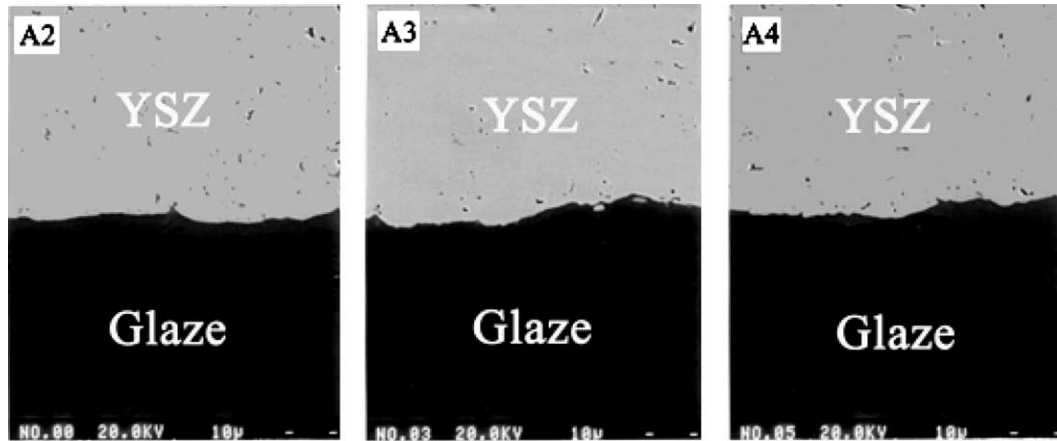


Fig. 4. SEM cross-sectional views of the series A glazes/8YSZ interface held at 950 °C for 30 min followed that at 850 °C for 100 h.

3.2. Influence of B_2O_3/SiO_2 ratio on high-temperature viscosity

In order to quantitatively characterize the high-temperature softening behavior of the glazes, the viscosity changes of series A against temperature were measured. It is apparent from Fig. 5 that the viscosity increases from 10^1 to 10^6 Pa s with decreasing temperature in the range 1100–850 °C. Because the anionic association of glaze, which is the main factor to influence high-temperature viscosity (η), was not apparent and the active energy of viscosity was approximately a constant, $\log \eta$ was linearly dependent on $1/T$, and by the Vogel–Tammann–Fulcher formula [9] it can be

expressed as

$$\log \eta = \alpha + \frac{B}{T} \quad (1)$$

where $B = \Delta u \log_e / K$ and $\alpha = \log A$. Δu is the viscous activation energy, K the Boltzmann constant, and A a constant depending on composition. At the same temperature, the viscosities of series A decreased with increasing B_2O_3/SiO_2 ratio, and the relationship between them was almost the same at different temperatures (Fig. 6). When viscosity was greater than $10^{4.5}$ Pa s, for the limited torsional moment range of viscosimeter, viscosities of A1, A2, and A3 could not be measured accurately at 850 °C. If neglecting the

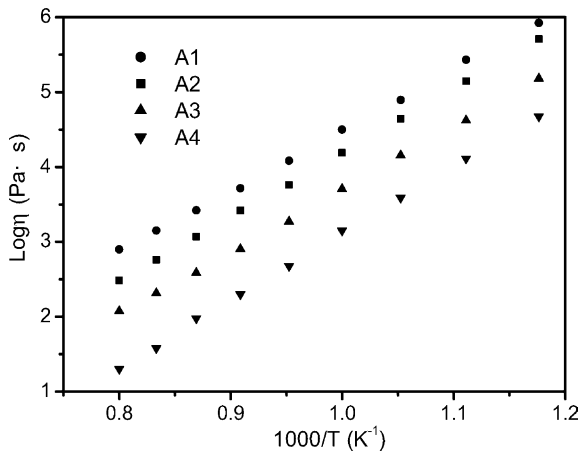


Fig. 5. Temperature dependence of viscosity η . The open plots were the calculated value.

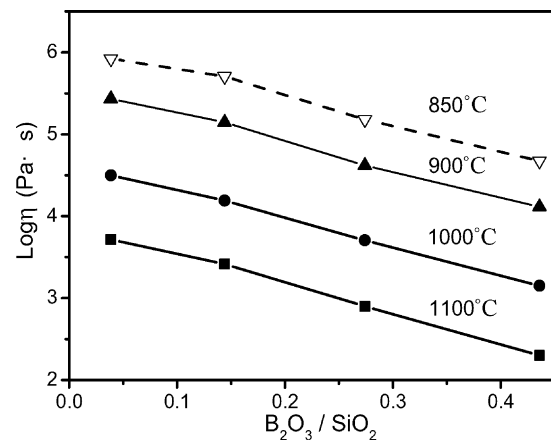


Fig. 6. Relationship between viscosity η and B_2O_3/SiO_2 ratios at different temperatures.

anionic association, according to the linear relation between $\log \eta$ and $1/T$, the viscosities could be estimated. Combining Figs. 4 and 5, it can be concluded that during the softening process of glaze series A, the viscosity ranges of stage 3 and stage 2 were $10^{3.5}$ to 10^4 Pa s and 10^4 to 10^6 Pa s, respectively, and viscosity of stage 1 was greater than 10^6 Pa s.

The softening behavior and viscosity experiments showed that the glazes series A can keep the dimensional stability under itself weight when its viscosity were higher than 10^4 Pa s, and when its viscosity were in the range of 10^4 – 10^6 Pa s, it also showed good wetting and bonding behavior with 8YSZ that can satisfy the sealing demand.

3.3. Influence of B_2O_3/SiO_2 ratio on phase separation and crystallization

In order to keep a good ability of stress relaxation during thermal cycle of SOFC, after joining at 950°C the glaze has to keep the viscous flow state during the whole ITSOFC operating process. It means that the crystalline network of glaze must be avoided. This can be achieved by suppressing the crystallizing of glaze.

Fig. 7 shows the DSC of glaze series A, there are endothermic valleys which correspond to transition temperatures of original glasses in the range of 640 – 670°C . With the increasing B_2O_3/SiO_2 ratio, the valley shifts to lower temperature. But no evident exothermic peak was observed from DSC figure. Moreover, the DSC curve became flatter, which indicates that there is no strong exothermic effect of crystallization.

The glaze series A were heated up to 950°C and held for 30 min, then cooled down to 850°C and held for 1 h. The as-prepared glazes were examined by XRD. All the glazes of series A have been found to be X-ray amorphous from a broad halo appearance in the XRD pattern. But the original glasses changed from transparency to ivory white. It was caused by phase separation. The transition temperature of A1 was 870°C , but A2 and A3, which have higher B_2O_3/SiO_2 ratios, had already transitioned below 850°C (Fig. 2). Lower

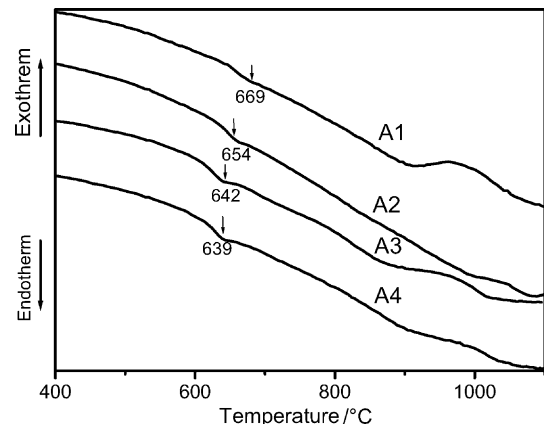


Fig. 7. DSC thermograms of series A at a heating rate of $10^\circ\text{C}/\text{min}$.

B_2O_3/SiO_2 ratios caused higher viscosities that resulted in deficient phase separation.

The XRD patterns of the glaze series A held for 100 h was shown in Fig. 8. It is apparent that series A has crystallized partly. The major crystalline phase was $\beta\text{-CaSiO}_3$ in A1, A2, and A3, but only little cristobalite phase was observed in A4. Although the intensity of crystalline phase in A3 was the highest in series A, TEC value of A3 did not show the characteristic increasing phenomenon as for normal ceramic glass, which results from bulk crystallization. Below 670°C , the average TEC value of A3 was $9.9 \times 10^{-6} \text{K}^{-1}$. However, the TEC decreased down to 0 with increasing temperature. Therefore, it could be concluded that the crystalline phase in series A was insufficient to form a crystalline network and the glaze still kept a softening state. Crystallization in series A would not influence the ability of stress relaxation too much. But from SEM of cross-section of the glaze A3 (Fig. 9), the dendrite of $\beta\text{-CaSiO}_3$ were observed, which appeared heterogeneous without orientation. Beside of them, holes and component heave were found. This is harmful for sealing. Therefore, the crystallization must be restrained.

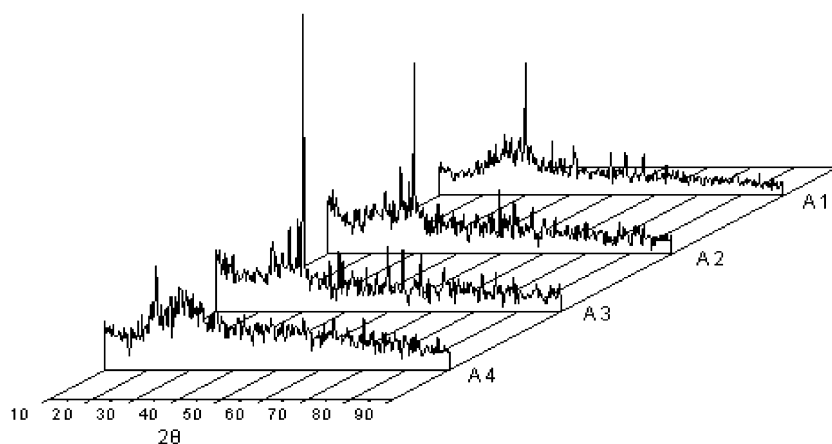


Fig. 8. XRD patterns of the glazes of series A after heat treatment at 950°C for 30 min followed by hold at 850°C for 100 h.

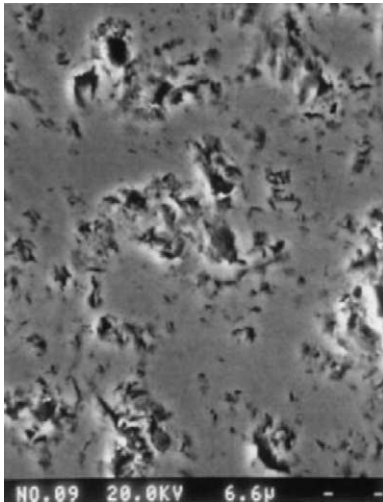


Fig. 9. SEM cross-sectional views of A3 glazes/8YSZ interface held at 950 °C for 30 min followed that at 850 °C for 100 h.

3.4. Influence of Al_2O_3/CaO ratio on phase separation and crystallization

It was reported that the crystallization could be suppressed by controlling the scale of phase separation [10–13]. Because obvious phase separation was observed for B_2O_3/SiO_2 ratio between that of A2 and A3, we studied the influence of Al_2O_3/CaO ratio on the scales of phase separation in glaze series B.

Fig. 10 was the TEM micrograph of series B after heat treatment at 950 °C for 30 min followed by hold at 850 °C for 100 h. It showed that bright isolated phase had been formed among the continuous dark phase. With increasing Al_2O_3/CaO ratio, the size of the isolated phase decreased obviously. It was 150–170 nm in B1, 70–100 nm in B2 and below 5 nm in B3. Because the system had enough

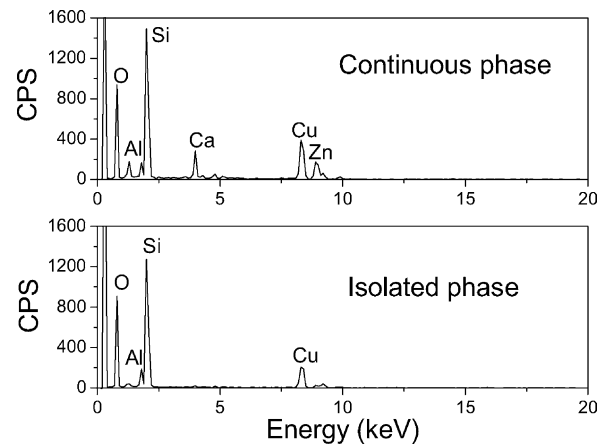


Fig. 11. EDX analysis of isolated and continuous phase in series B.

non-bridging oxygen, minor constituent Al^{3+} would form $[AlO_4]^-$ tetrahedron. In the similar system, from Raman spectroscopy analysis, Yang et al. reported that $[AlO_4]^-$ tetrahedron mainly entered into laminated and network structure. It caused homogenization of non-bridging oxygen and increase in network linking degree [10]. Since the homogeneous non-bridging oxygen brought about the uniform distribution of Ca^{2+} , phase separation was restrained.

From the EDX analysis (Fig. 11), the Ca^{2+} content of isolated phase was much lower than that of continuous phase. The formation of such isolated phase would increase the Ca^{2+} concentration in the continuous phase. When Ca^{2+} accumulated to a certain content, it might trigger the formation of crystalline phase. This would be the reason why crystallization was promoted by phase separation. However, if the dimension of isolated phase was small enough and it distributed uniformly, the composition of continuous phase could not meet the fluctuation that crystallization needed, as a result, the crystallization would be suppressed. The

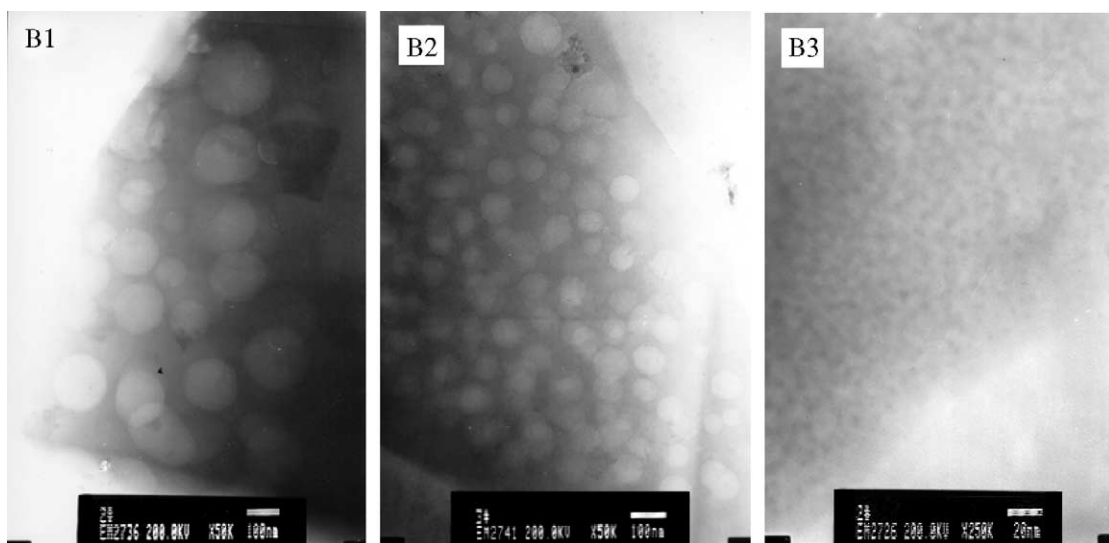


Fig. 10. TEM micrograph of the glazes powder of series B after heat treatment at 950 °C for 30 min followed by hold at 850 °C for 100 h.

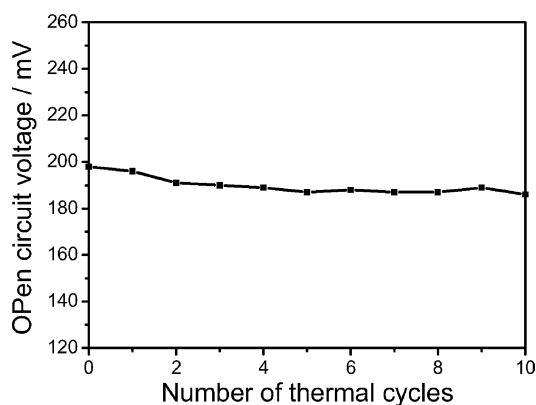


Fig. 12. Change in cell open voltage for C1 by thermal cycles: (a) stainless steel interconnect/ceramic glaze interface; (b) 8YSZ electrolyte/ceramic glaze interface.

experiment in B3 well confirmed this view point. Because the size of separated phase was lower than the wavelength of visible light and the crystallization was suppressed, the glaze still kept transparent even after being treated at 850 °C for 100 h. Clearly, it can be concluded that the decreased size of isolated phase, which is promoted by increasing $\text{Al}_2\text{O}_3/\text{CaO}$

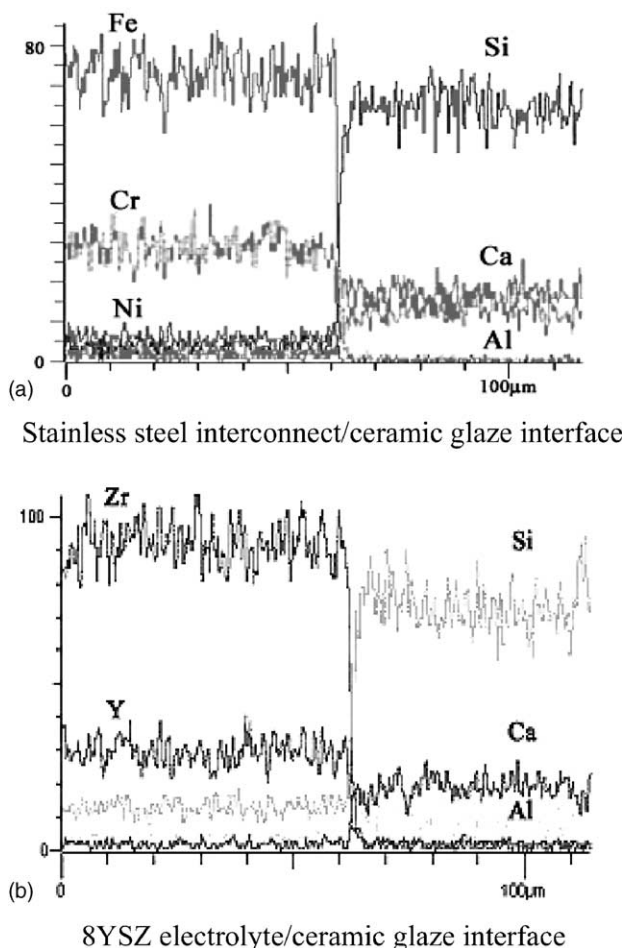


Fig. 13. Cross-section EPMA results for C1 treated at 850 °C for 100 h.

ratios, will suppress the crystallization that is harmful to “softening” sealing and compositional uniform.

3.5. Investigation of thermal cycling test

From the above results, combined $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio as in A3 with $\text{Al}_2\text{O}_3/\text{CaO}$ ratio as in B2, the composition of C1 was selected for thermal cycling test (according to Section 2.3). The test unit was arranged as an oxygen concentration cell, and the electromotive force (EMF), E_r , is given by the Nernst equation:

$$E_r = \frac{RT}{4F} \ln \frac{P_{\text{O}_2(\text{air})}}{P_{\text{O}_2(\text{N}_2)}}$$

Where R is the gas constant, T the temperature, F the Faraday constant, and P_{O_2} the partial pressure of oxygen at the electrodes. Fig. 12 showed the change of EMF with thermal cycles. The voltage at 850 °C nearly kept stable after 10 cycles, indicating that the sealing was effective even after 10 thermal cycles. After the test, no crack and hole were found at the ceramic glazes/stainless steel interconnect and ceramic glazes/8YSZ electrolyte interfaces. And the ceramic glaze was bonded closely with 8YSZ electrolyte and stainless steel interconnect. Fig. 13 exhibits EPMA results for a cross-section of C1 which was held at 850 °C for 100 h. No obvious diffusion of elements was found at the ceramic glazes/stainless steel interconnect and ceramic glazes/8YSZ electrolyte interfaces.

4. Conclusion

The glazes based on the $\text{SiO}_2\text{--CaO--B}_2\text{O}_3\text{--Al}_2\text{O}_3$ system is a suitable “soft” sealant for ITSOFC. The good wetting and bonding behavior with 8YSZ electrolyte and stainless steel bipolar can satisfy the sealing demand. Suitable viscous flow can well relax thermal stress resulted from the difference of TECs in thermal recycles of SOFC components. The dimension stability can be kept for 100 h through controlling the glaze viscosity in the range of 10^4 to 10^6 Pa s. The study of glaze series B shows that decrease in the particle size of isolated phase, promoted by increasing $\text{Al}_2\text{O}_3/\text{CaO}$ ratio, will suppress crystallization, which is harmful for “soft” sealing by keeping compositional uniform. Increasing the $\text{Al}_2\text{O}_3/\text{CaO}$ ratio can ensure that the sealant glazes could not form the crystalline network even at 850 °C for 100 h. The thermal recycling test indicated that the sealant glaze with the composition of C1 is the most suitable for recycle sealing of SOFC operated at 850 °C and shows a good chemical stability.

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