Journal of Ceramic Processing Research. Vol. 9, No. 4, pp. 338~342 (2008)

J O U R N A L O F
Ceramic Processing Research

Evaluation of glass composites for sealing solid oxide fuel cells

Chun Lin Chu[a,*], Jye Lee[b] and Shyong Lee[a]
[a]*Department of Mechanical Engineering, National Central University, Chung-li, Taiwan*
[b]*Department of Electrical Engineering, Chang Gung University, Tao-Yuan, Taiwan*

Six metallic alloys, namely, Crofer22, ZMG232, an equivalent ZMG232, stainless steels SS430, SS304 and Inconel718 were investigated. A commercial Asahi Bulk Glass is sealed on these materials and evaluated for oxidation behavior under a hot air environment for various period of time and for thermal expansion. Then the resultant oxide scale was studied; with the microstructure and chemical composition of the crystalline phases investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopic (EDS) analysis. The results show the Asahi bulk glass on ZMG232 was good for compaction and adhesion; no vacancies in the glass. ZMG232 seems to be more suitable for Asahi bulk glass than the other alloys. The glass does not fully crystallize even after long-term heat treatments at 500-600 °C. Sealing glass over a long period of time during operation of a solid oxide fuel cell (SOFC) would generate thermal stresses in the seal and may have adverse effects on its mechanical performance. This may lead to cracking of the seal, resulting in mixing of the fuel and the oxidant gases.

Key words: Solid oxide fuel cell (SOFC), Interconnect, Glass.

Introduction

Considerable effort has been and continues to be exerted in the research of fuel cells as an alternative to fossil fuel in the hopes of providing more environmentally friendly and clean energy sources. Among the various fuel cells, a solid oxide fuel cell (SOFC) is the most efficient yet challenging one. An interconnect is a critical component in a SOFC as it functions to bridge structurally and electrically a number of sequentially stacked unit cells. Each of them contains an electrolyte, an anode and a cathode. Since the SOFC system operates at high temperature and oxygen is supplied for a chemical reaction with the fuel (mainly hydrogen or hydro-carbon compounds) in order to output electricity, oxidation of the interconnect is anticipated. The requirements for SOFC sealing materials are severe since the cells will operate at 800 °C for thousands of hours, with sealing materials exposed to both oxidizing and reducing conditions. The seals must be chemically and mechanically compatible with different oxide and metallic cell components and should be electrically insulating. Various glass and glass-ceramics based on borates, phosphates and silicates are being examined for SOFC seals [1, 2]. Previous relevant research was examined, which mainly involved sealing a glass compound on alloys and placing it at high temperature. It is noted that there exists a newly-developed and commercially-available alloy and glass for SOFC interconnect applications. This belongs to a ferritic stainless steel designated as Crofer22 APU which is offered by ThyssenKrupp of Germany [3]. Another material, ZMG232, provided by Hitachi Metals of Japan has also been seriously studied [4-6]. Another glass seal material, supplied by Asahi glass of Japan has also been investigated. It is difficult for the crystalline network to relax through creep all the thermal stresses caused by the remarkable difference of coefficients of thermal expansion (CTE) between glass and the interconnect. It was always the case that the interconnect cracked at the area in contact with the sealants, or the sealant broke near the interface between the sealants and interconnects in a thermal cycle. In fact, through modifying the interconnect structure [7] and inserting support materials, such as ceramic fibers [8], the sealant has not to endure a press stress. So we expect to develop a compaction sealing ceramic glass which has an excellent adhesion property through viscous flow under in a hot air environment for various periods of time. In this paper, we report sealing glass on metallic alloys into a furnace

*Corresponding author:
Tel : +886-3-4267-377
Fax: +886-3-4254-501
E-mail: jenlen.boy@msa.hinet.net

Table 1. Chemical composition of glass (wt%)

Glass composition	Asahi	GC1
Fe_2O_3	0.09	-
CaO	2.11	-
Al_2O_3	3.03	9.1
SiO_2	79.7	17.9
Na_2O	6.74	-
MgO	0.54	-
K_2O	8.24	-
B_2O	-	10.4
LaO_3	-	14.6
BaO	0.18	48.1

Table 2. Chemical compositions of the alloys (wt%)

Alloys	Fe	Ni	Cr	Mn	Si	Al	V	Mo	Ti	Nb	C	Re
1. Crofer22	Bal.	0.02	22.57	0.47	0.03	-	0.02	0.01	0.06	0.01	0.01	0.06La
2. ZMG232	Bal.	0.01	22.3	0.5	0.4	0.21	-	-	-	-	-	0.04La + 0.02Zr
3. Equivalent ZMG232	Bal.	0.3	23.57	0.56	0.16	-	0.07	0.01	-	0.01	0.03	0.01La + 0.01Zr
4. SS430	Bal.	0.16	17.13	0.8	0.42	-	-	-	-	-	-	-
5. SS304	Bal.	8.22	19.05	1.64	0.44	0.01	-	-	-	-	-	-
6. Inconel718	18.8	Bal.	19.13	0.28	0.08	0.5	3.1	-	-	-	-	-

maintained at 800 °C. It should be interesting and demanding to know the oxidation behavior of the alloys containing the pressurization. The effects of the amounts of vacancies and possible seals on chemical properties are examined. Post-test analyses were also performed to characterize the compaction and adhesion of the glass.

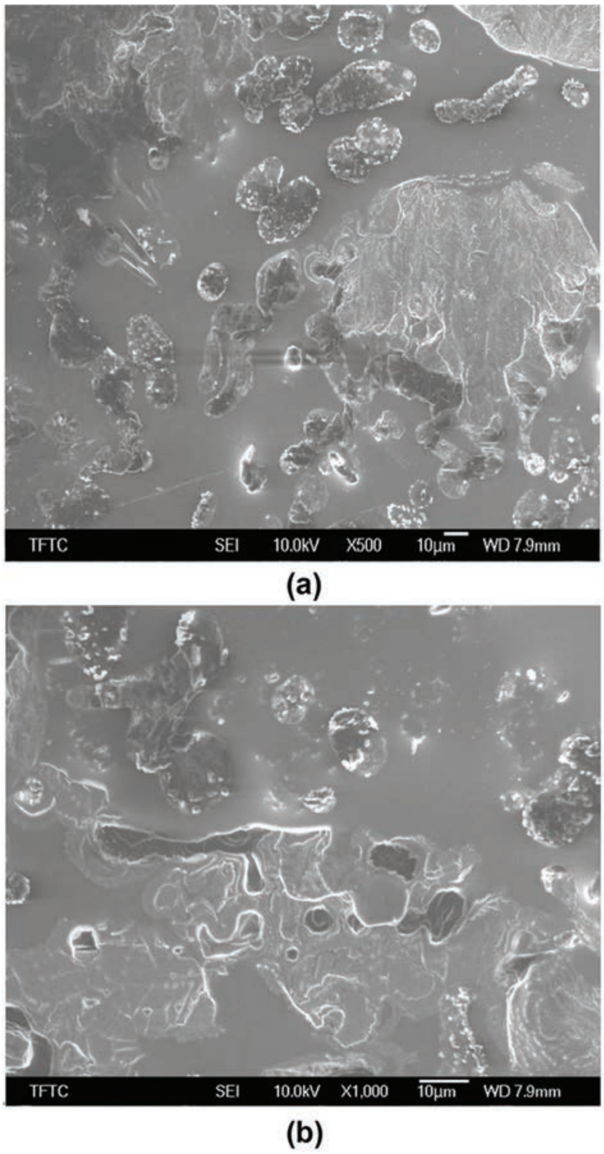

Fig. 1. Micrographs of the sealed glass (in 800 °C hot air) surfaces of Crofee22 displaying two morphologies: (a) and (b) enlarged micrograph.

Experimental

Sealing glass on six metallic alloys samples were subjected to oxidation treatments in a hot air environment. The listed compositions were determined by Induction Coupled Plasma (ICP)-AES and Spark-OES instruments; the results are shown in Table 1 and Table 2. The surface of the samples was polished with SiC abrasive paper up to 1200-grit, and washed in an ultrasonic cleaner in distilled

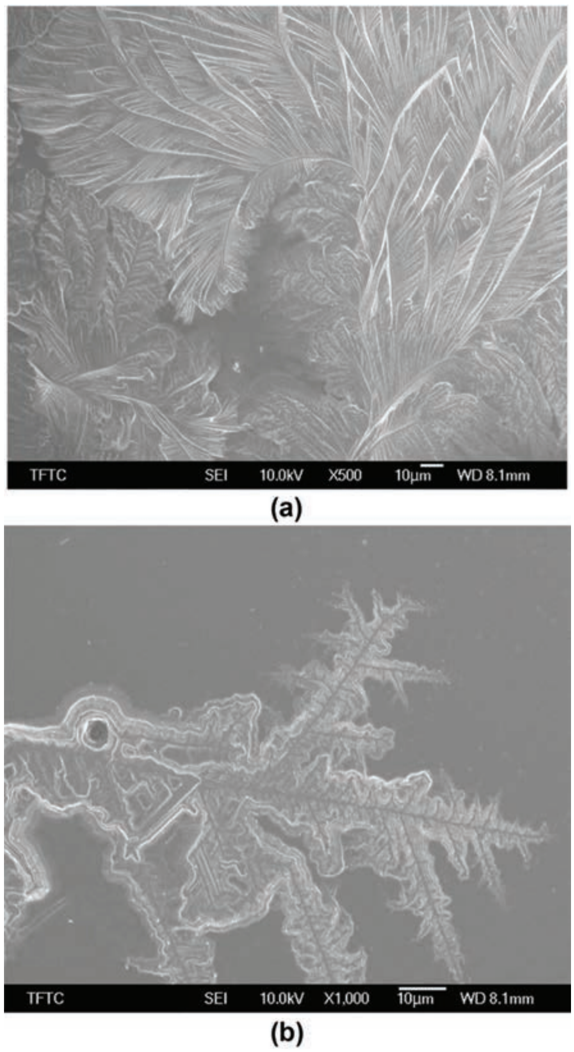

Fig. 2. Micrographs of the sealed glass (in 800 °C hot air) surfaces of ZMG232 displaying two morphologies: (a) and (b) enlarged micrograph.

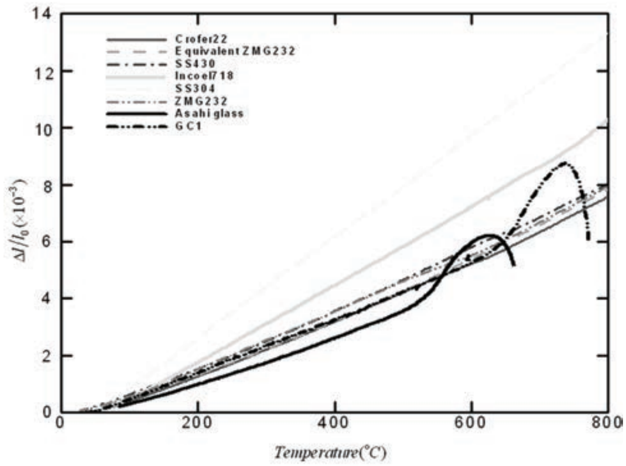

Fig. 3. Thermal expansion of metallic alloys and glass.

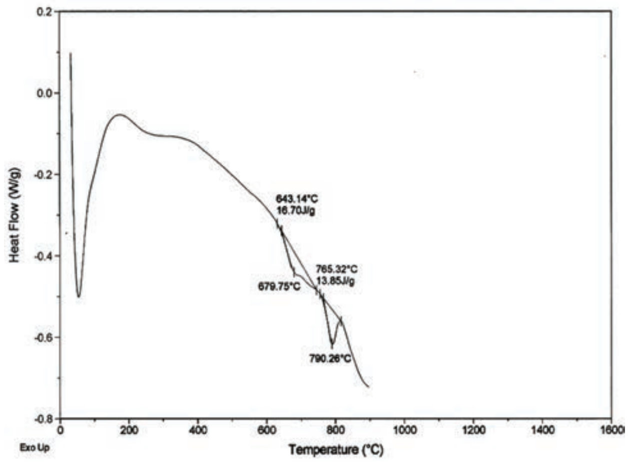

Fig. 4. DSC measurement on the glass ceramic 1 showing several characteristic temperatures.

glass, heated in a furnace to 800 °C in hot air and held for various times (100 and 200 hours). The microstructures of the polished cross-sections of heat treated bulk glass specimens were observed using SEM associated with EDS. Prior to analysis, a thin layer of Pt or carbon was evaporated onto the SEM specimens for electrical conductivity. The CTE of the selected alloys and Asahi glass was determined with a Linseis L75 dual push-rod dilatometer.

Results and Discussion

Surface microstructure and formed phases

The joining experiments were carried out on the metallic specimens of the glass itself. In order to investigate the joining behavior of the metallic specimens to the Asahi glass in detail, the samples were heated in a hot air environment for 100 or 200 hours. The samples were

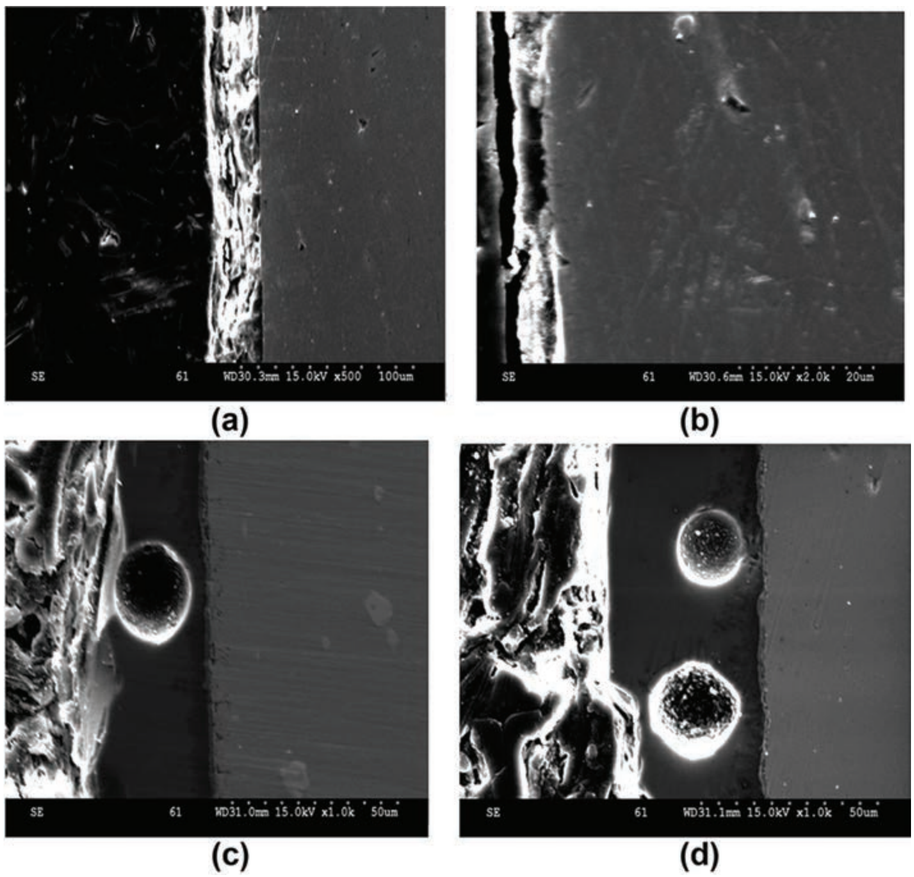

Fig. 5. Micrographs of polished cross-sections Interface of (a) SS430, (b) Inconel718, (c) Crofer22 APU and (d) Equivalent ZMG232 at 800 °C for 100 hours.

metallographically prepared and analyzed by SEM. Figure 1 and 2 show SEM micrographs at various magnifications taken from Crofer22 and ZMG232 on glass specimens

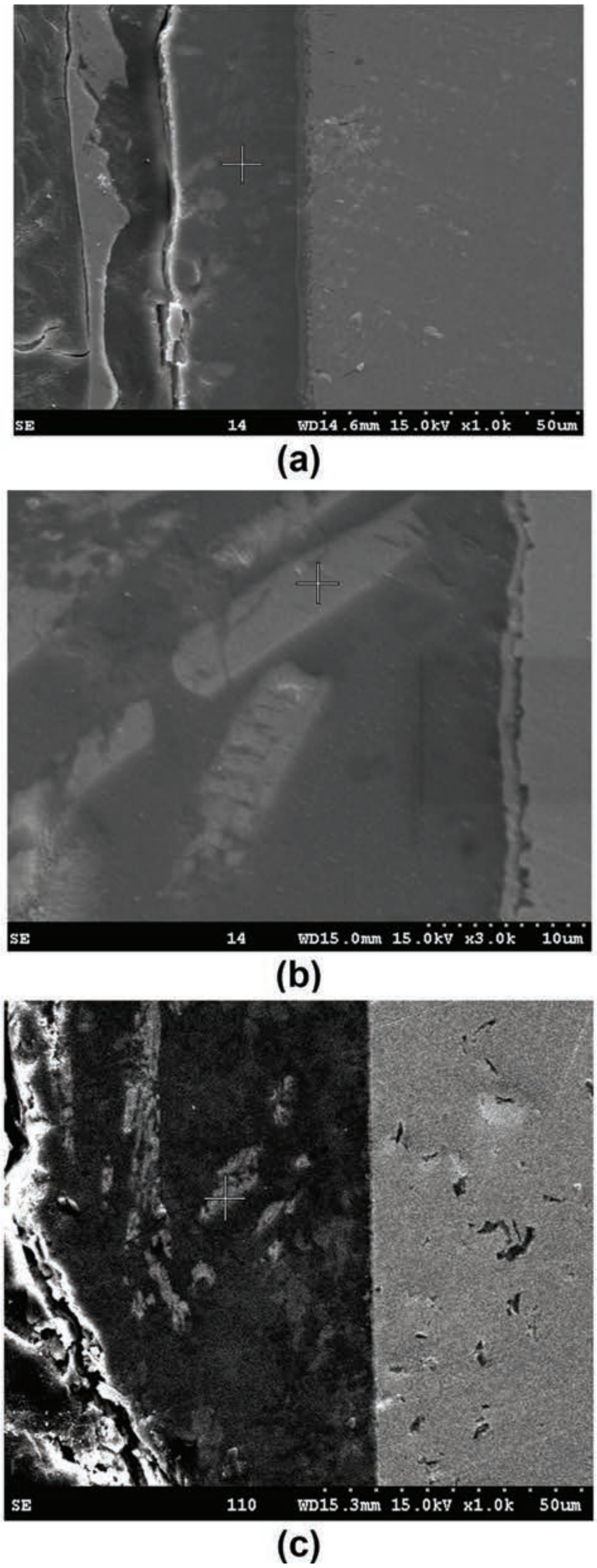

Fig. 6. Micrographs of polished cross-sections (in 800 °C hot air for 200 hours) interface of (a) ZMG232, (b) SS304, and (c) SS430 with EDS analysis at 800 °C.

heat treated for 100 h at 800 °C. The Crofer22 sample possesses a similar morphology which was also observed by Norbert H. [9]. The micrograph shows a fractal structure and each grain-boundary should be an oxide compound as the SEM/EDS analysis displays a significant oxygen content. Seen from the micrograph, it is an open structure with dendritic arms, showing a typical fractal character.

Thermal expansion

The high operating temperature of a SOFC requires that the CTE of the components be matched with glass to avoid thermal stresses [10, 11]. Figure 3 shows the thermal expansion behavior of the selected metallic alloys and Asahi glass as a function of temperature. The CTE of austenitic stainless steels (e.g. SS304) and nickel-based alloys (e.g. Inconel718) are much higher than other metallic alloys. As expected, the FCC matrix the selected nickel-based alloys demonstrate a higher CTE than the BCC ferritic stainless steels, which typically have a CTE of $11.0\text{-}13.0 \times 10^{-6}K^{-1}$. The Asahi glass has the lowest CTE at $8.0 \times 10^{-6}K^{-1}$ from room temperature to 600 °C. The CTE of Asahi glass is not in the same range as the CTE of other SOFC components: the cathode, anode, electrolyte and interconnect.

DSC measurements

A sample from glass ceramic 1 was measured and its glass transition temperature was determined to be between 643.14 °C and 679.75 °C. The average figure, 661.14 °C, is close to the glass transition temperature (650-680 °C) as shown in the barium-calcium aluminosilicate glass phase diagram [2]. The Fig. 4 endothermic peak at 643.14-679.75 °C is due to the glass transition and the broad exothermic peak is due to crystallization of the glass. The second endothermic peak at 765.32-790.26 °C is from the melting of crystalline phases and/or residual glass.

Microstructures of cross sections of the interface of alloys and asahi bulk glass

The metallic alloys were cross-sectioned of the surface morphology on glass flakes. SEM/EDS micrographs taken from polished cross-sections of glass specimens heat treated at 800 °C for different times are shown in Fig. 5 and 6. The glass/alloy interface for Crofer22 had two layers. The oxidized surface of Inconel718 is very different from the other alloys, exhibiting exfoliation form (Fig. 6(b)). EDS composition analysis shows a significant content of O, which are observed in the oxidized alloys as depicted in

Table 3. Chemical composition of the oxides formed after 200 h in hot air (SEM-EDS from Fig. 6) (at. %)

Element	O	Cr	Fe	K	Si	Ni	Na	Ca	Al
1. ZMG232	1.8	18.4	62	1.0	12.8	0.3	1.0	0.8	2.2
2. SS304	6.6	6.5	19.8	4.7	37.2	2.0	3.3	0.9	2.7
3. SS430	7.7	10.1	50.5	1.2	23.6	-	2.0	1.2	3.8

Table 3. A fight barrier layer is formed on the bulk original alloy, which is crystallization as the X-ray diffraction analyses forecast. The Asahi bulk glass on ZMG232 was good for compaction and adhesion; there was no vacancies and fissures in the glass. ZMG232 seems to be more suitable for Asahi bulk glass than the others.

Conclusions

The oxidation behaviors of six metallic alloys were examined and analyzed. Microstructures and physical properties have been studied. The properties of the Asahi glass and metallic alloys of this study are compatible with those of the solid oxide fuel cell components. On the other hand, the Asahi bulk glass on ZMG232 was good for compaction and adhesion. This glass does not fully crystallize even after long-term heat treatments at 500-600 °C, the operating temperature for SOFC. The CTE of Asahi glass cannot match other SOFC components (electrolyte, cathode, anode and interconnect) to minimize thermal stresses.

References

1. R. Zheng, S.R. Wang, H.W. Nie and T.-L. Wen, J. Power Sources 128 (2004) 165-172.
2. N.P. Bansal and E.A. Gamble, J. Power Sources 147 (2005) 107-115.
3. Z. Yang, G. Xia, P. Singh and J.W. Stevenson, Solid State Ionics 176 (2005) 1495-1503.
4. W.J. Quadakkers, J. Pirón-Abellán and V. Shemet, Mate. Res. 7[1] (2004) 203-208.
5. T. Horita, Y. Xiong, H. Kishimoto, K. Yamaji, N. Sakai and H. Yokokawa, J. Power Sources 131 (2004) 293-298.
6. T. Horita, Y. Xiong, K. Yamaji, N. Sakai and H. Yokokawa, J. Power Sources 118 (2003) 35-43.
7. S. Taniguchi, M. Kadowaki, T. Yasuo, Y. Akiyama, Y. Miyake and K. Nishio, J. Power Sour 90 (2000) 163-169.
8. S.P. Simner and J.W. Stevenson, J. Power Sour. 102 (2001) 310-316.
9. N.H. Menzler, D. Sebold, M. Zahid, S.M. Gross and T. Koppitz, J. Power Sources 152 (2005) 156-167.
10. J.W. Fergus, Mater. Sci. Eng. A 397 (2005) 271-283.
11. Z. Yang, G.G. Xia and J.W. Stevenson, J. Power Sources 160 (2006) 1104-1110.