Journal of the European Ceramic Society 19 (1999) 1101–1104

PII: S0955-2219(98)00382-3
0955-2219/99/$ - see front matter

BAS ($BaO{\cdot}Al_2O_3{\cdot}SiO_2$)-glasses for High Temperature Applications

K. Eichler,* G. Solow, P. Otschik and W. Schaffrath

The Fraunhofer-Institute for Ceramic Technologies and Sintering Materials, IKTS, Winterbergstr. 28, D-01277 Dresden, Germany

Abstract

The paper concerns the commercial BAS ($BaO{\cdot}Al_2O_3{\cdot}SiO_2$)-glass AF45 from the Fa. DESAG, Germany, and reports an investigation to test the suitability as sealing glass for the SOFC. Importantly the crystallization behaviour is characterized. A crystallization of the sealing glasses is necessary to fulfil the high requirements for joining. Samples are screen printed films with addition of MgO. The glass AF45 is a slowly crystallizing glass. In general the crystallization rate can be regulated within wide limits by means of MgO addition. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, joining, X-ray methods, glass ceramics, fuel cells.

1 Introduction

The long term stability of the solid oxide fuel cell (SOFC) implies a great challenge with respect to material research. In particular this concerns also materials for the necessary solder joints. In the Siemens planar concept of the SOFC the single ceramic and metallic parts of the stack must be joined together. These solder joints separate both the gas chambers at anode and cathode and insulate the stack to the atmosphere. Additionally the mechanical strength of the stack has to be guaranteed. A sealing glass has to fulfil high requirements, because the operation temperature of the SOFC is about 850°C and the operation period must be $\geq$5 years. Other requirements are:[1]

- no chemical reactions with the joining components and solder stability in oxidizing and wet reducing atmospheres;
- viscosity: 10^5 Pas at joining temperature (1000°C), $>10^9$ Pas at operation temperature (850°C);
- only a small thermal expansion mismatch with respect to SOFC components (TEC = 11×10^{-6} K^{-1});
- wetting angle on the joining components > 90°;
- leakage rate of the joining $<10^{-7}$mbar 1 s^{-1} per cm joined length;
- resisitivity > 2 kOhm cm^2.

These requirements can only be fulfilled by at least partially crystallized glasses. Additionally in the Siemens-SOFC stack a special viscosity–time behaviour of the sealing glass during manufacturing procedure is necessary. That means that after joining at 1000°C the solder glass has to be plastic at 950°C in 2 ... 3 h in order to allow small displacements of the single stack elements (put-down process). This can be achieved using only a slowly crystallizing glass. The investigation concerns a commercially BAS ($BaO{\cdot}Al_2O_3{\cdot}SiO_2$)-glass in supplied and modified form in order to test their suitability as sealing glass for the SOFC. The purpose of this paper was to characterize the crystallization properties.

2 Experimental

The composition of used glass materials is listed in Table 1. The glass powder was milled in a planetary ball mill for 24 h in water ($d_{50} = 3{\cdot}5\,\mu$m). The milled powder was mixed with fine-grained MgO powder. The mixed powders were characterized by heating microscopy. Screen printing pastes were made from the powders with an ethylcellulose binder. For screen printing Al_2O_3 and $CrFe5Y_2O_31$ (interconnector composition) were used as substrate materials. The thickness of the printed layers was about 200 μm. Free glass layers as well as glass layers between joined parts were investigated.

*To whom correspondence should be addressed. Fax: +49-0351-2553-605; e-mail: eichler@ikts.fhg.de

Table 1. Composition of the joining glasses (wt%)

Glass	Al_2O_3	*BaO*	SiO_2	B_2O_3	AS_2O_3	*MgO*
AF45[a/b]	11·0	24·0	50·0	14·0	0·5	0
AF45 (As free)[c]	11·1	24·1	50·2	14·1	0	0
AF45 + 5 MgO[d]	10·4	22·8	47·5	13·3	0·5	5·0
AF45 + 10 MgO[d]	9·8	21·6	45·0	12·6	0·5	10·0

[a]0·5% other components
[b]Fa. DESAG, Grünenplan, Germany (TEC (20 ...300°C $= 4{\cdot}5\times10^{-6}$ K^{-1}).
[c]Fa. Schott, Mainz, Germany.
[d]Fa. Siemens, Erlangen, Germany (d_{50} (MgO) = 1·5 μm).

Before joining, the screen printed layers were presintered at 800°C/0·2 h. The parts were joined at load of 400 p cm^{-2}. The joining temperature–time profile corresponds to the manufacturing and operation conditions of the SOFC.

$$20°C \xrightarrow{2\,K\,min^{-1}} 1000°C/0{\cdot}5\ h \xrightarrow{2\,K\,min^{-1}}$$
$$950°C/3\ h \xrightarrow{2\,K\,min^{-1}} 850°C/t \xrightarrow{10\,K\,min^{-1}} 20°C$$

Crystalline phases formed during the heat treatment of the glass were identified using XRD patterns recorded at room temperature on the glass surface, in the bulk of the joining glass layer and on the interface glass/substrate.

3 Results and Discussion

Using the above-mentioned temperature–time profile, the following crystal phases could be observed:

- $BaAl_2Si_2O_8$ in the polymorphs
  - Hexacelsian TEC (20...1000°C) $= 7{\cdot}1\times10^{-6}$ K^{-1} (Ref. 2)
  - Celsian TEC (20... 300°C) $= 2{\cdot}29\times10^{-6}$ K^{-1} (Ref. 2)
- SiO_2 in the polymorphs
  - Cristobalite TEC (20... 300°C) $= 50\times10^{-6}$ K^{-1} (Ref. 3)
  - Quartz TEC (20... 600°C) $= 23\times10^{-6}$ K^{-1} (Ref. 3)
- $MgSiO_3$ (only at $T \geq 1000$°C) in the polymorph
  - Protoenstatite TEC (20 ... 800°C) $= 11\times10^{-6}$ K^{-1} (Ref. 4)

The crystallization in the glass AF45 is surface driven. Therefore a crystallization in the bulk can be obtained by use of glass powders. The free surfaces on glass powders used in screen printing pastes promote crystallization in the glass volume in any way. The addition of fine-grained MgO to the glass AF45 (see Table 1) causes an increase of crystallization rate, nevertheless no additional Mg-containing crystalline compounds could be observed (at least in the range below 1000°C). Thus the formation of nuclei for enhanced crystal growth can be favoured by addition of fine-grained MgO.

Figure 1 depicts the deformation of pressed cylindrical shaped specimens with increasing temperature and different quantities of MgO. A marked change of viscosity with increasing MgO content is obvious. In a mixture of AF45 + 10 MgO the cylindric shape is stabilized by crystallization processes, which influences the viscosity. When the specimen approaches the spherical shape, the viscosity is close to 10^5 Pas and enables joining.

Figure 2 shows crystallization results in free screen printed glass layers. These results, obtained both from the interface and the volume of the screen printing layers, are also relevant to soldered joints. Again a significant increase of crystallization rate could be proved by addition of MgO. Both at 800 and 1000°C nearly no crystallization could be recognized; thus a stable glassy state can be maintained during the technological steps of the stack joining and the put-down process. At the operating temperature the crystallization occurs strongly and solidifies the joining due to the increasing viscosity. Furthermore the dissolution of the formerly grown crystals at temperatures of about 1000°C is demonstrated in Fig. 2. This could be proved directly too. At high operation temperatures the glass ceramic approaches the ther-

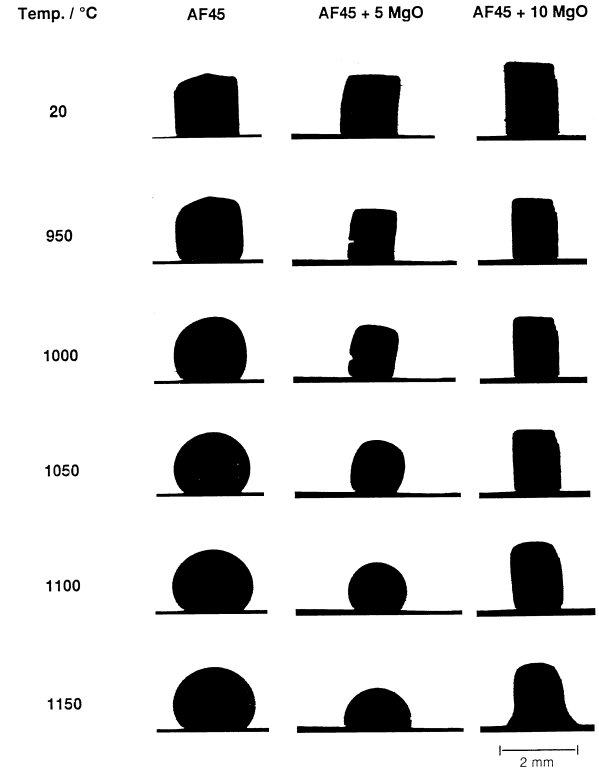

Fig. 1. Shape change of glass powder samples of AF45 as a function of temperature and MgO content.

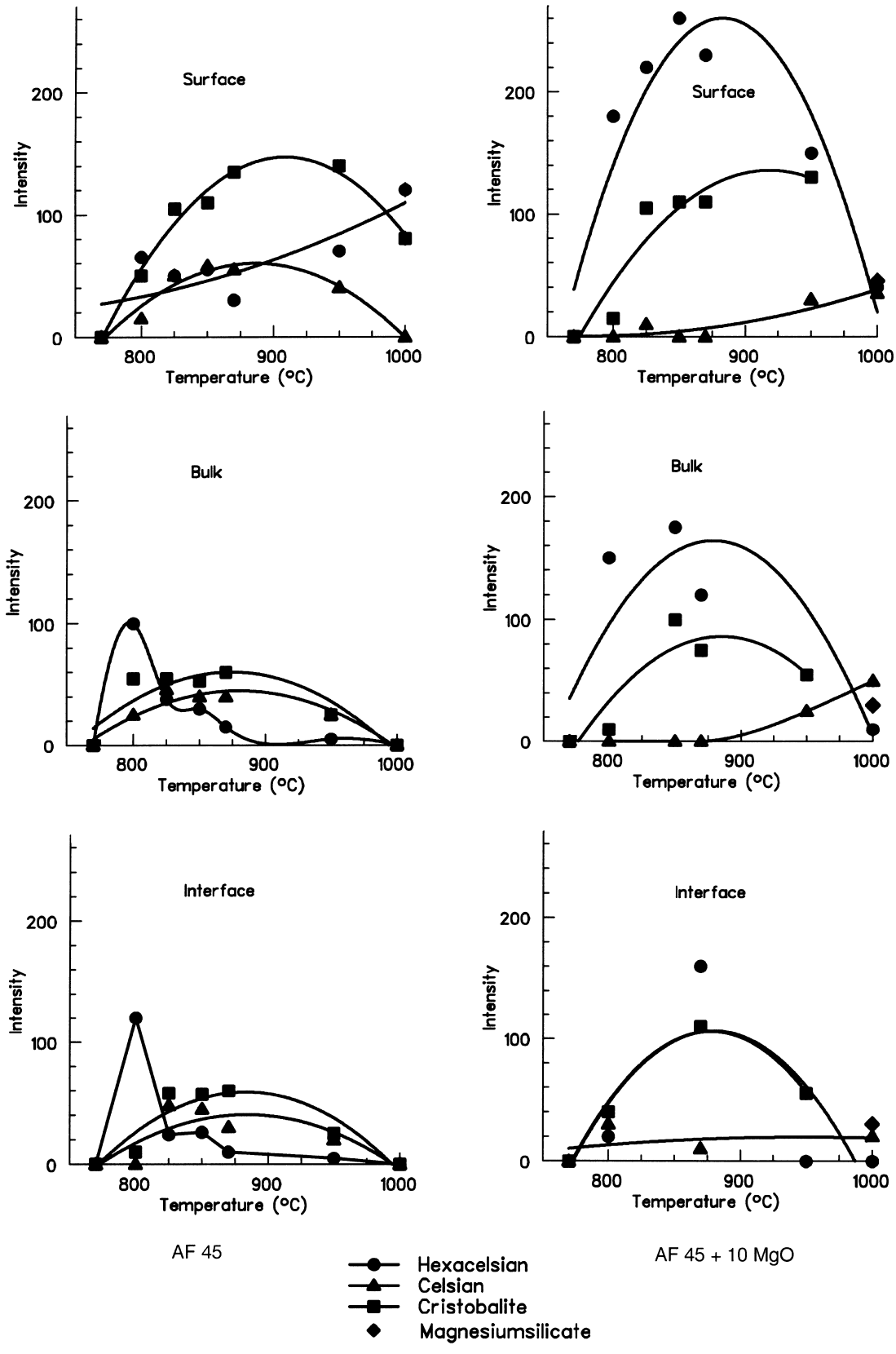

Fig. 2. The crystallization behaviour of the glasses AF45 (left side) and AF45 + 10 MgO (right side) as screen printed films after heat treatment 20°C $\xrightarrow{2\ \mathrm{K\ min^{-1}}}$ T/60 h $\xrightarrow{10\ \mathrm{K\ min^{-1}}}$ 20°C (comparison of the relative intensities of the largest peaks in the XRD patterns).

modynamic equilibrium. This should be considered with regard to temperature changes because according to the TTT (time–temperature-transformation)-diagram crystal type and quantity depend on the temperature.

Figure 3 shows the acceleration of crystallization in soldering joints by means of MgO addition. AF45 glass reached a final state of crystallization after 200 h, accompanied with the beginning of the cristobalite–quartz transformation. Quartz is

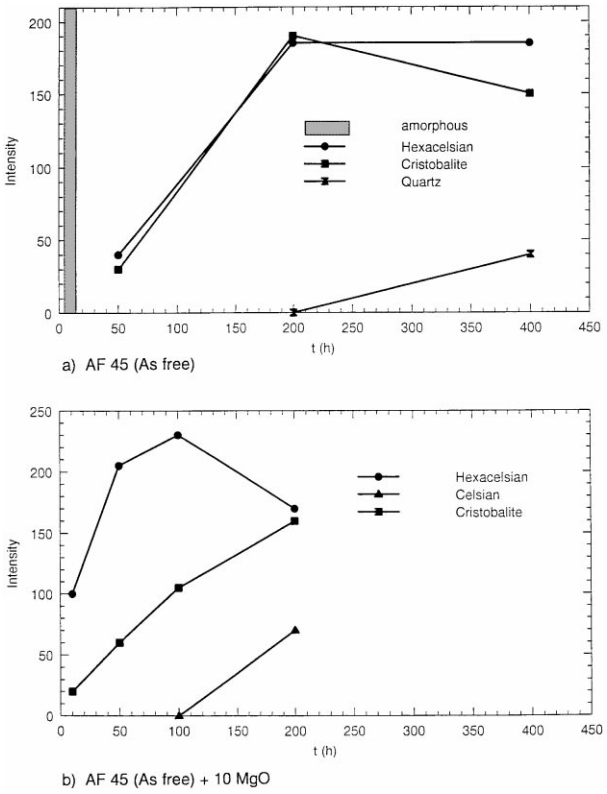

Fig. 3. Development of crystalline phases in the glasses (a) AF45 (as free) and (b) AF45 (as free) + 10 MgO in the bulk of the joining layer after heat treatment 20°C —$^{2\ K\ min^{-1}}$→ 1000°C/0·5 h—$^{2\ K\ min^{-1}}$→ 950°C/3 h—$^{2\ K\ min^{-1}}$→ 850°C/t —$^{10\ K\ min^{-1}}$→ 20°C.

thermodynamically stable at the operating temperature, whereas cristobalite acts detrimentally in the course of thermal cycling procedures with respect to a volume change of about 8%, caused by the change of the crystal structure of cristobalite at 200°C. Hexacelsian has proved to be stable and celsian was not indicated. AF45 + 10 MgO glass already showed crystallization during the put down process at 950°C and continued crystallization at 850°C, resulting in equal amounts of crystalline matter. In general the crystallization rate can be regulated within wide limits by means of MgO addition. Soldering joints exhibit moderate and tolerable compression stresses after cooling to room temperature.

4 Conclusions

The commercial BAS-glass AF 45 with MgO additions is suitable for joining SOFC components especially when a slowly crystallizing glass is necessary for the manufacture of the SOFC. A crystallization kinetics of the glass is important to fulfil the high requirements of small TEC mismatch and viscosity–time behaviour. Crystallization kinetics is adjustable through MgO concentration in the glass.

References

1. Jansing, T., Fleck, R., Kleinlein, W., Schichl, H. and Nürnberger, S., Fügetechnik von Einzelzellen zu SOFC-Einheiten mittels Glasloten. Lecture, IDGG-Glasforum, Würzburg, October 1997.
2. Bansal, N. P. and Hyatt, M. J., Crystallization and properties of Sr–Ba aluminiosilicate glass–ceramic matrices. *Ceram. Eng. Sci. Proc.*, 1991, **12**, 1222–1234.
3. *Engineered Materials Handbook, Vol. 4, Ceramics and Glasses*. ASM International, The Materials Information Society, USA, 1991, p. 499.
4. Petzold, A. and Hinz, W., *Silikatchemie*. VEB Deutscher Verlag für Grundstoffchemie, Leipzig, 1976, p. 163.