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## **Study of a glass-ceramic sealant over the stack lifetime**

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### **Abstract**

The gas-tightness of the stack is a major issue in high temperature electrolyzers used for hydrogen production. The seals between interconnects and interfaces must comply with very demanding specifications. In addition to sealing constraints, specific mechanical, thermomechanical and chemical properties are required for the material as well as sufficient electrical resistivity. The complex geometries of seals favor the use of paste made of glass powder suspended in organic solvents. This way, the seal can be easily and precisely deposited on the interfaces to be sealed. A heat treatment is then applied to shape the material and ensure the formation of gas-tight interfaces. During this thermal process, the material crystallizes, resulting in a glass-ceramic. In order to control and maintain a proper seal, it is important to master the glass-ceramic microstructure as a function of time and temperature over the stack lifetime.

This paper presents the study and modeling of the material crystallization. Phases are first identified (SEM, XRD) and their evolution as a function of temperature is characterized. Crystal surface fraction is quantified as a function of time and temperature by image analysis. Glass-ceramic crystallization kinetics are then modeled using the Johnson-Mehl-Avrami-Kolmogorov model. Finally, results are compared with data obtained from a seal having operated for several months. This allow us to obtain a better description of the seal microstructure evolution during the stack operation.

## Introduction

The SOC (Solid Oxide Cell) high temperature electrolysis technology, used for hydrogen production, is based on a successive stack of single electrolysis cells and metallic interconnects ensuring both the collection of oxygen and hydrogen, and the electronic conduction between the different Single Repeat Units. In such complex systems, ensuring the sealing of this ceramic/metallic multilayer assembly is technically very challenging. The seal material must comply with very demanding specifications. In addition to sealing constraints, specific mechanical, thermomechanical and chemical properties are required for the material as well as sufficient electrical resistivity [1]. It must also be compatible with both high temperatures and various atmospheres ( $H_2$ ,  $O_2$ ,  $H_2O$ ). Very few materials are suitable and oxide materials, such as glass-ceramics, are the reference materials for such seals [2].

The complex geometries of seals favor the use of paste made of glass powder suspended in organic solvents. This way, the seal can be easily and precisely deposited on the interfaces to be sealed. A heat treatment is then applied to shape the material and ensure the formation of gas-tight interfaces. During this thermal process, the material crystallizes resulting in a glass-ceramic. In order to control and maintain a proper seal, it is important to master the glass-ceramic microstructure as a function of time and temperature over the stack lifetime. Indeed, a detailed knowledge of the material microstructure is necessary to control its mechanical properties.

The aim of this work is to study the crystallization of a glass from the  $MgO-Al_2O_3-BaO-SiO_2-B_2O_3$  system. Such systems have been studied as sealants and have shown a good compliance with the seal specifications [2-4]. We work here with a simplified system, where interactions with gas (steam,  $O_2$ ,  $H_2$ ) and interconnects are not considered yet. The first part of this paper describes the glass-ceramic microstructure. The crystalline fraction of the majority phase is then determined as a function of time and temperature. In the second part, glass-ceramic crystallization kinetics are then modeled using the Johnson-Mehl-Avrami-Kolmogorov model. Results are compared with data obtained from a seal having operated for several months.

## 2. Experimental and modeling

### 2.1 Experimental

The studied material is from the  $MgO-Al_2O_3-BaO-SiO_2-B_2O_3$  system.  $BaO$  and  $B_2O_3$  contents are respectively below 35 and 15 mol.%.  $MgO$  and  $Al_2O_3$  contents are below 10 mol.%. Such a glass is obtained by double melting of raw materials with intermediate grinding, in Pt/Rh crucible at  $1300^\circ C$ , followed by quenching. Thermal treatments of 1g glassy powder ( $d_{50} = 16 \pm 4 \mu m$ ) are performed in a Pt/Au crucible in the range of  $700^\circ C$  to  $850^\circ C$  with a  $50^\circ C$  step and for different durations (from 2 minutes to 48 hours). The crucible is introduced into a tube furnace preheated to heat treatment temperature. At the end of the treatment, the sample is air-cooled to avoid any further crystallization. Samples treated for 24 and 48h duration are heated at  $5^\circ C \cdot min^{-1}$  to reach target temperature and air-cooled at the end of the treatment [9]. It is assumed that crystallization occurring during the temperature range does not significantly change the result for such durations.

Polished sections of the resulting glass-ceramic samples are analyzed using Scanning Electron Microscopy (SEM SUPRA 55 ZEISS, BRUKER EDS detector) for microstructure and crystalline surface fraction determination. The surface crystallization percentage is determined by processing 6 BSE-SEM images with ImageJ software. Images are acquired with a magnification of 1500 and a resolution of 4096 pixels and 16 $\mu$ s/point.

## 2.2 Johnson-Mehl-Avrami-Kolmogorov model (JMAK) [5-7]

The phenomenological JMAK model describes the kinetics of isothermal phase transformation. It provides the equation for crystallization as a function of time at a given temperature. Initially developed for metals, this model is also used for glass-ceramics [6]. The kinetic problem can be outlined according to the following assumptions [7]:

- The phase transformation occurs by nucleation and growth processes,
- Germs are randomly distributed throughout the volume,
- Crystalline growth has no preferred direction and stops when crystals overlap; crystals are therefore spherical,
- Only one type of crystal is present in the glass-ceramic [8].

According to the JMAK equation, the volume fraction  $x$ , crystallized after an isothermal transformation at a temperature  $T$  and for a duration  $t$ , is given by [6]:

$$x = 1 - \exp[-(kt)^n] \quad (\text{Eq.1})$$

where  $k$  is the reaction-rate constant ( $\text{s}^{-1}$ ) and  $n$  is known as the Avrami parameter which reflects the dimensionality of the crystal growth. The temperature dependence of  $k$  is expressed by the Arrhenius equation as:

$$k = k_0 \exp\left[-\frac{E_a}{RT}\right] \quad (\text{Eq.2})$$

Where  $k_0$  is a frequency factor ( $\text{s}^{-1}$ ),  $E_a$  is the activation energy for the overall crystallization transformation ( $\text{J}\cdot\text{mol}^{-1}$ ), and  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). From Eq.1, we obtain:

$$\ln[-\ln(1-x)] = n \ln t + n \ln k \quad (\text{Eq.3})$$

According to this model, for experimental data of crystallized volume fraction  $x$  at a temperature  $T$ , the plot of  $\ln[-\ln(1-x)]$  vs.  $(\ln t)$  gives a straight line whose slope is  $n$ . From Eq.2, the values of  $(\ln k)$  determined this way at different temperatures, when plotted as a function of reciprocal temperature, yield the value for the  $E_a$  activation energy for crystallization.

This simple model is rigorously adapted for spherical crystals only. In the case of crystallization with a preferred growth direction, equations can be adapted [5].

Considering the equilibrium crystalline fraction  $C_{eq}$  at a temperature  $T$ , the crystalline fraction  $C(t)$  as a function of time, can be calculated with the following equation:

$$C(t) = C_{eq} \cdot \{1 - \exp[-(kt)^n]\} \quad (\text{Eq.4})$$

### 3. Results and discussions

#### 3.1 Glass-ceramic microstructure

The glass-ceramic microstructure has been previously characterized using Scanning Electron Microscopy and X-Rays Diffraction [9]. Figure 1 displays a BSE-SEM image of a sample heated at 750°C for 48 hours. It is characteristic of the obtained glass-ceramic microstructure. In addition to the residual glass phase, three different crystalline phases are observed: a  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  phase (light grey and polyhedral crystals) which is the first to appear with temperature, a  $\text{BaMg}_2\text{Si}_2\text{O}_7$  phase (dark slats) and an Al-rich phase (very small needle-like dark crystals,  $< 5\mu\text{m}$ ) [9]. The latter one is the last phase to appear with time and its existence domain is in the  $\sim 750\text{-}800^\circ\text{C}$  range. Despite its small quantity, it is believed to be  $\text{BaAl}_2\text{Si}_2\text{O}_8$  crystals. In most of the considered samples ( $t < 24\text{h}$ ), such crystals are not yet present.

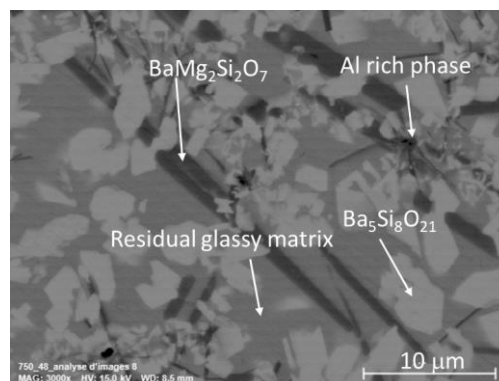


Figure 1. BSE-SEM image of the glass powder sample heated at 750°C for 48 hours

#### 3.2 Crystalline surface fraction as a function of time

Further quantitative analysis have been performed in order to determine  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystals surface fraction. They represent the majority of crystals and the methodology is first applied to them. BSE-SEM images show a good contrast between the  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystals and the rest of the sample. It has previously been shown that image analysis is suitable for quantification of these crystals surface [9]. The first step consists in binarizing the image, and then converting it to gray levels. A thresholding is then carried out according to the light intensity in order to distinguish the  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystals from the rest of the sample (Figure 2). The surface crystallization percentage is determined by processing 6 images with ImageJ software.

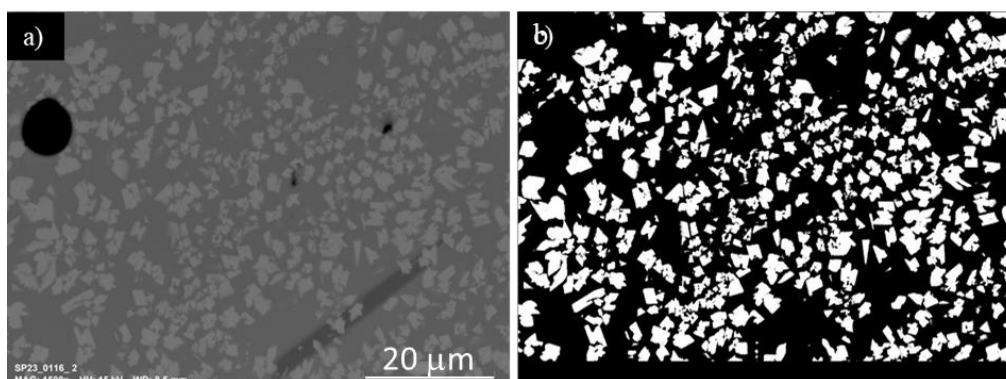


Figure 2. Illustration of the BSE-SEM image analysis for the  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystals

Figure 3 displays the  $Ba_5Si_8O_{21}$  crystalline surface fraction as a function of time for temperatures in the 700-850°C range. A change in kinetics with temperature is clearly to be seen. At 700°C, the equilibrium crystalline fraction is not reached after 24h, whereas it seems to be reached in less than a few hours from 750°C. At 850°C, the crystalline surface fraction seems to slightly decrease with longer durations and may be influenced by the others formed phases. Such data, after 24h thermal treatment, clearly show the decrease with temperature, in the amount of crystallized  $Ba_5Si_8O_{21}$ . This is in accordance with the crystallization theory [10] and a liquidus temperature around 975-1000°C, where  $Ba_5Si_8O_{21}$  crystals are not present any more.

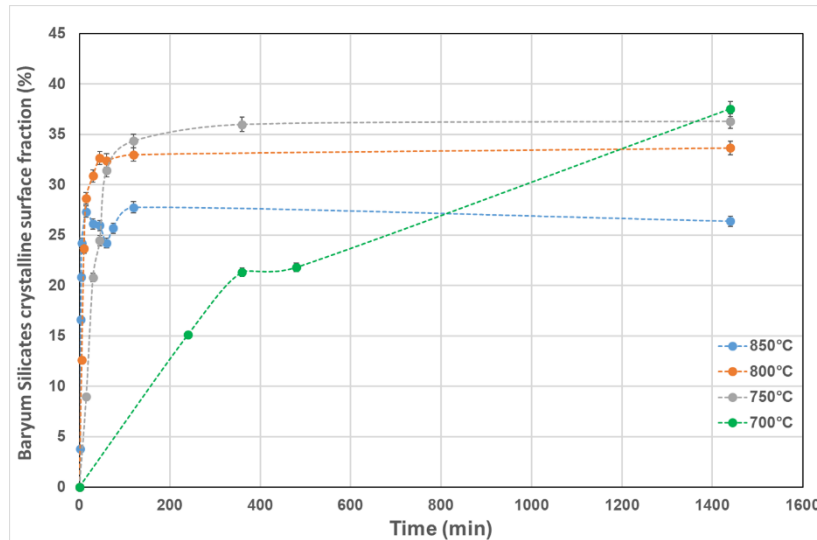


Figure 3. Evolution of the barium silicates crystalline surface fraction as a function of time, for different temperatures

### 3.2. JMAK modelling

Due to the  $Ba_5Si_8O_{21}$  crystals polyhedral shape, JMAK model is used, as first step. JMAK kinetics parameters are determined when crystallization is ongoing i.e. before equilibrium is reached (plateaus on Figure 3). Except for the crystallization at 700°C, durations shorter than one hour are considered. Figure 4 represents the graphic determination of the JMAK model parameters and Table 1 summarizes the determined values of the Avrami parameters and the reaction rate constants in the 700-850°C range.

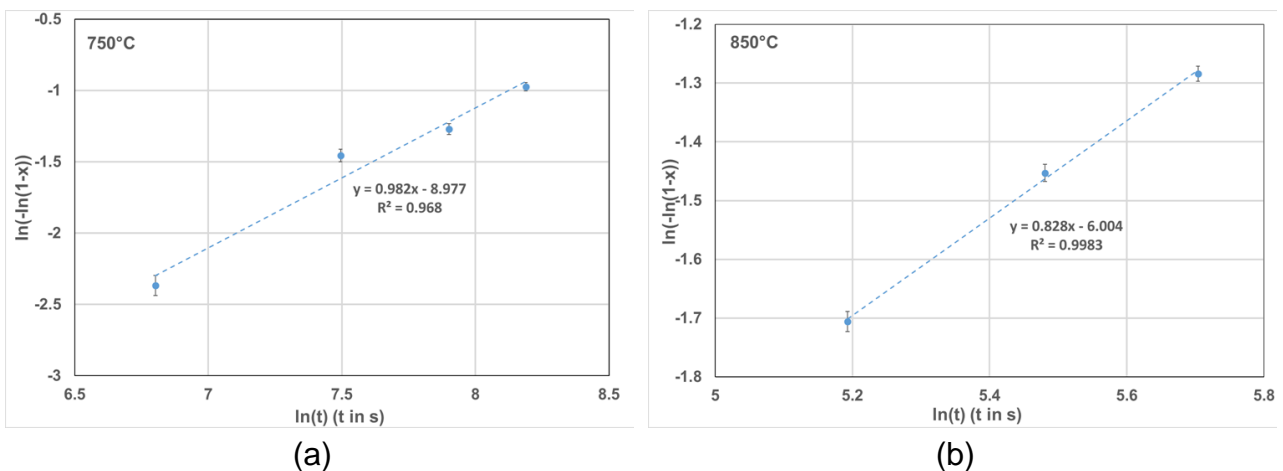


Figure 4. Graphic determination of  $n$  (Avrami coefficient) and  $k$  (reaction rate) JMAK parameters for  $Ba_5Si_8O_{21}$  crystallization: (a) at 750°C and (b) at 850°C

The average value of the Avrami parameter ( $0.89 \pm 0.09$ ) in between 750 and 850°C indicates that this glass crystallizes primarily by surface crystallization, which is consistent with the use of glass powder ( $d_{50} = 16 \pm 4 \mu\text{m}$ ). However, at 700°C, this parameter is lower and a change appears in between 700 and 750°C, which suggest a change in the crystallization mechanisms. It has previously been shown that  $\text{Ba}_x\text{Si}_y\text{O}_{x+2y}$  crystals are slightly changing stoichiometry with the temperature rising in the 680-750°C range; from  $\text{Ba}_2\text{Si}_3\text{O}_8$  to  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  [9]. This might have an influence on the Avrami parameter.

Parameter	700°C	750°C	800°C	850°C
n	0.62	0.98	0.86	0.83
k (s <sup>-1</sup> )	$4.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$	$7.1 \cdot 10^{-4}$

Table 1. JMAK model parameters value for the  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystallization from 700 to 850°C

Figure 5a compares the theoretical crystalline surface fraction curve as a function of time (given by Eq.4), with the experimental data at 750°C. Crystallization kinetics are not satisfying; JMAK model underestimates the initial crystallization speed. Therefore,  $k$  parameter has been adjusted in order to fit the experimental data [11]. Theoretical and experimental curves are very close (Figure 5b). The parameters allowing the plot of the crystalline surface fraction as a function of time are reported Table 2 (n, k,  $C_{\text{eq}}$ ). They give a description of the glass-ceramic microstructure evolution with time, considering only the  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  major phase. At 700°C, crystallization ‘equilibrium’ being not reached for the tested durations, no data are given yet. Thermal treatments for longer durations are to be performed. Besides, such a methodology will be applied to the two other crystalline phases present in the glass-ceramic. JMAK model has to be tested as it is initially developed for a sole crystalline phase.

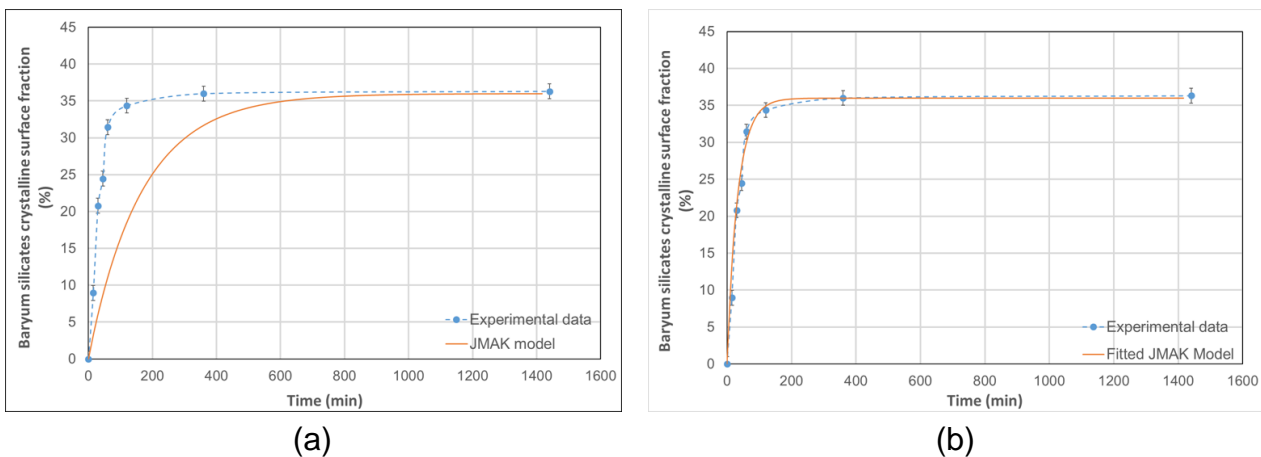


Figure 5. Comparison of the experimental  $\text{Ba}_5\text{Si}_8\text{O}_{21}$  crystalline surface fraction data with JMAK model calculated data at 750°C: (a) original model and (b) fitted model

Parameter	750°C	800°C	850°C
n	0.98	0.86	0.83
k (s <sup>-1</sup> )	$5.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-3}$	$7.3 \cdot 10^{-3}$
$C_{\text{eq}}$ (surf.%)	36	34	27

Table 2. JMAK model parameters values after adjustment for each temperature

A preliminary comparison has been performed between the glass-ceramic obtained previously by glass powder thermal treatment and the glass-ceramic seal recovered from a stack having operated for several months. From the stack temperature evolution, previous experimental data at 750°C have been used. These results indicate that the operated seal sample contains same crystalline phases as the initial glass-ceramic after 48h at 750°C. The Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub> crystalline surface fraction data are similar: respectively 34 ± 3% and 36 ± 1%.

#### 4. Conclusions and perspectives

A glass-ceramic obtained after thermal treatments of a MgO-Al<sub>2</sub>O<sub>3</sub>-BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass, designed as sealant in SOC stacks, has been characterized in the 700 to 850°C range. The glass-ceramic consists mainly of a barium silicate crystalline phase (polyhedral Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub> crystals), two minor phases and the residual amorphous glass phase.

Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub> crystal surface fraction as a function of time and temperature has been determined by BSE-SEM image analysis. The 'equilibrium' crystalline fraction is reached very quickly above 750°C (< 2h). A further Johnson-Mehl-Avrami-Kolmogorov (JMAK) modelling was applied to this system to determine the kinetics parameters and calculate the Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub> crystallized fraction after isothermally heating for a given duration. Calculated data are close to the experimental ones. Besides, the comparison of those results with data obtained from a seal having operated for several months are consistent.

This study will be continued to fully characterize the evolution, versus time and temperature, of the other crystalline phases as well as the composition of the residual glass. A detailed knowledge of the material microstructure is necessary in order to optimize the thermal treatment for the glass-ceramic formation and anticipate the possible microstructural evolution of the glass-ceramic seal operating in the stack.

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