



HAL
open science

Critical review on blistering models of molten glass in contact with ZrSiO₄

J. Hell, J. Fouletier, M.C. Steil

► **To cite this version:**

J. Hell, J. Fouletier, M.C. Steil. Critical review on blistering models of molten glass in contact with ZrSiO₄. *Journal of Non-Crystalline Solids*, 2023, 604, pp.122133. 10.1016/j.jnoncrysol.2023.122133 . hal-04755056

HAL Id: hal-04755056

<https://hal.science/hal-04755056v1>

Submitted on 26 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Critical review on blistering models of molten glass in contact with ZrSiO₄

J. Hell, J. Fouletier, M. C. Steil*

Univ. Grenoble Alpes, Univ. Savoie Mt Blanc, LEPMI, Grenoble INP, CNRS, F-38000 Grenoble, France

Keywords: blistering phenomenon, molten glass, zircon, ZrSiO₄, mechanism

ABSTRACT: During the glass fabrication process, the contact between refractories and molten glass is sometimes subject to blistering phenomena. Various electrochemical reactions producing bubbles of gas within the molten glass or at the glass/refractory interface can be considered. The only consistent model accounting for the blistering phenomenon on zircon refractories has been proposed by F.G.K. Baucke, in 1988: the blistering phenomenon would result from oxidation of oxide ions by impurities present in the refractory. However, based on thermodynamic and kinetic considerations published in the literature, the assumptions underlying the model appear questionable.

1. Introduction

The major scientific and technological challenges in the manufacturing of soda-lime-silica based glasses are the improvement of glass quality, in particular special glasses for new applications which require a high final quality, i.e., solar cells, television, smartphone screens, etc. [1, 2]. During the glass fabrication process, large quantity of gases, such as CO₂ or H₂O, are released. Most of the gas bubbles are eliminated during the fining process: a small amount of fining agent is added to the glass forming batch, releasing fining gases and expanding the bubbles which rise more easily within the molten glass and burst at the surface [3, 4]. The

* Corresponding author.

E-mail address: marlu-cesar.steil@lepmi.grenoble-inp.fr (M.C. Steil).

contact between refractories and molten glass is subject to various blistering phenomena: release of gases trapped in the closed porosity of the refractory, reduction of oxides dissolved in the glass by impurities of the refractory, formation of gas bubbles at the glass/refractory interface on sites favorable to the nucleation of gas bubbles exceeding their solubility limit in the molten glass, etc. [5]. Redox mechanisms at the interface between glass and refractory can result in the production of gas, referred to as “redox shock” [6]. Various factors inducing blistering process have been identified: the nature of the glass/refractory couple, and the external conditions, i.e., temperature, atmosphere, fining level, redox state of the refractories, large temperature gradients, etc. In order to avoid the blistering phenomenon and, consequently, defects in final products, it is crucial to understand the different parameters playing a role in the phenomenon. In glass industry, three classes of refractories are used: (i) fused cast AZS ($\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{SiO}_2$), including ca. 20 % of a glassy phase [7], (ii) High Zirconia Fused-Cast refractories (HZFC) which consist of monoclinic zirconia (ca. 90 vol.%) embedded in a three-dimensional interconnected aluminosilicate glass (ca. 10 vol.%), (iii) dense zircon (ZrSiO_4 , ZS).

The first detailed mechanism accounting for the blistering phenomenon has been proposed by F.G.K. Baucke et al. [2, 8, 9] in the eighties, on zircon refractories. Later-on the same model has been taken up in van Dijk’s thesis to explain the blistering at the glass/fused-cast AZS interface [10]. We have, recently, proposed a mechanism for the blistering process with oxidized high-zirconia fused-cast refractories (HZFC) in contact with a soda-lime silicate glass: we have demonstrated that the blistering phenomenon is ascribed to oxygen semipermeation through the zirconia phase [6, 11].

Zircon is an attractive material for construction of gas tanks due to its excellent thermo-physical properties such as low thermal expansion, low thermal conductivity, good corrosion resistance against glass melts, no major structural changes, and a moderate resistance to thermal shock.

Consequently, a detailed mechanism of the formation of oxygen bubbles at the zircon/molten glass interface is of significant scientific, technical and economic interest. The objective of this work is to analyze the hypotheses on which Baucke's model is based concerning the phenomenon of blistering at the soda-lime silicate glass/zircon interface, at 1230 °C.

2. Baucke's main hypotheses and proposed mechanism

The model proposed by Baucke is based on experiments which are summarized hereafter. The studied refractory was zircon (ZS) of high density (less than 3 % apparent porosity), with impurities such as Fe_2O_3 (between 0.08 and 0.12 wt. %), TiO_2 and Na_2O . The glass melts were alkali calcium silicates with 15.5 mol% alkali oxide, 10.8 mol% CaO , and 73.7 mol% SiO_2 , and containing 0.2 wt.% Sb_2O_3 as a fining agent.

The main experimental results reported by Baucke are schematized in Figure 1. When a cube of ZS with two layers, i.e., an oxidized flesh-colored material and a less oxidized light-grey material (Figure 1 a), was immersed in a molten glass, at 1230°C, oxygen evolved only on the oxidized surface. After a few days, bubbles formation stopped and, as illustrated Figure 1 b, a grey layer was formed on the cube. After cutting off the grey layer (Figure 1 c) oxygen evolved again on the oxidized surface.

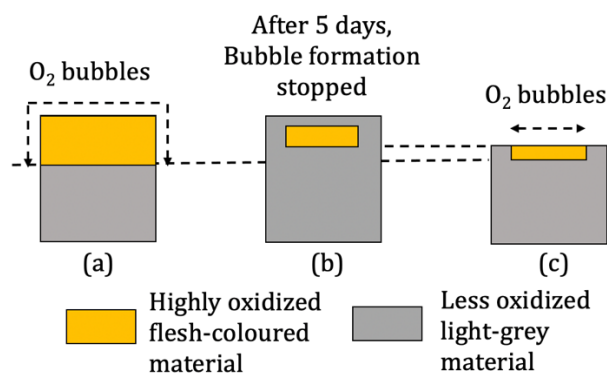


Fig. 1: Illustration of the blistering phenomenon on ZS refractories, after Baucke [8].

Baucke's mechanism is based on an electrochemical process at the interface between ZS and the glass melt, as schematized on Figure 2. The formation of oxygen bubbles would result from an oxidation of oxide ions, *i.e.*, non-bridging oxide ions, of the glass melt by impurities dissolved within zirconium silicate refractories, such as Fe^{3+} . Baucke considers that the blistering phenomenon can be explained according to an electrochromic-like mechanism [12], *i.e.*, the oxidation and reduction reactions do not take place at the same interface. It is assumed that the oxidation takes place at the ZS/glass interface and the reduction of Fe^{3+} at the interface between a reduced zone and the oxidized ZS. Consequently, a reduced layer is growing within the bulk ZS. The reaction rate is controlled by solid state diffusion of charge-balancing alkali ions.

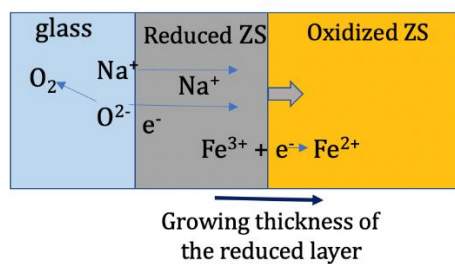


Fig. 2: Scheme of the blistering phenomenon at the interface between zircon refractory and a molten glass, from Baucke et al. [8].

The main hypotheses related to Baucke's model are the following:

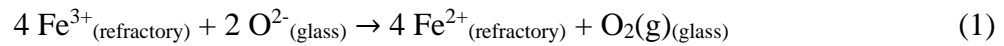
- (i) the blistering results from oxidation of oxygen ions, O^{2-} , by impurities present in the ZS refractory, such as iron oxide or titanium oxide,
- (ii) the blistering is only observed when oxidized zircon is in contact with the glass,
- (iii) Fe^{3+} ions are responsible for the formation of oxygen bubbles; no blistering was observed with reduced zircon, *i.e.*, iron impurities are in the reduced state (Fe^{2+}),
- (iv) zircon decomposition is excluded,
- (v) the refractory has to be conducting by sodium ions and electrons in the reduced zone in contact with the molten glass, to ensure charge balancing,

(vi) the blistering phenomenon is only observed with alkali glasses.

3. Examining the key assumptions in Baucke's model

3.1. Assumption 1: Fe^{3+} dissolved in zircon is more oxidizing than O_2

To address the problem of blistering, Baucke has considered the following global electrochemical reaction as being at the origin of the blistering process:



This reaction requires that Fe^{3+} ions are more oxidizing than oxygen O_2 . Various published works are in contradiction with this assumption.

In the early sixties, Baak and Hornyak [13], and Johnston [14] have carried out thermodynamic calculations and experimental works on the reaction $2 FeO + \frac{1}{2} O_2 = Fe_2O_3$ in sodium disilicate glasses. These authors, have shown that Fe^{3+} is formed spontaneously from Fe^{2+} at high oxygen pressures.

Reaction (1) would be spontaneous provided the difference of potential between the two redox couples is positive, with:

$$E = E(Fe^{3+}/Fe^{2+}) - E(O_2/O^{2-}) = E^\circ(Fe^{3+}/Fe^{2+}) - E^\circ(O_2/O^{2-}) + \frac{RT}{F} \ln \left(\frac{[Fe^{3+}][O^{2-}]^{1/2}}{[Fe^{2+}]p_{O_2}^{1/4}} \right) \quad (2)$$

For simplification, the concentrations of dissolved species have been used instead of activities. Moreover, the activity of O^{2-} ions can be considered as constant. This equation can be simplified, considering that the standard potential of the Fe^{3+}/Fe^{2+} couple is referred to the O_2 ($PO_2 = 0.2$ bar)/ O^{2-} couple, which will be written “ $E^\circ(Fe^{3+}/Fe^{2+})_{(V \text{ vs. Air})}$ ”, later on:

$$E = E^\circ(Fe^{3+}/Fe^{2+})_{(V \text{ vs. Air})} + \frac{RT}{F} \ln \left(\frac{[Fe^{3+}]}{[Fe^{2+}]} \right) \quad (3)$$

Experimental works have been published, reporting the determination of $E^\circ(Fe^{3+}/Fe^{2+})$ and of the $[Fe^{3+}]/[Fe^{2+}]$ ratio, in silicate glasses. C. Rüssel [15] has determined the variation of the

standard emf (electromotive force) of various polyvalent pairs in soda-lime-silicate glasses as a function of temperature (see Figure 3).

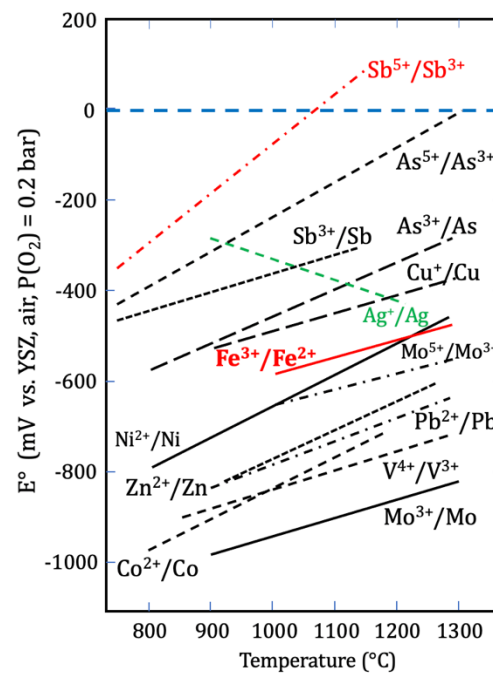


Figure 3: Variation of the standard potential E° (mV vs. Air) of various couples of polyvalent ions as a function of temperature in glass melts ($74 \text{ SiO}_2 - 16 \text{ Na}_2\text{O} - 10 \text{ CaO}$), E° in mV vs. YSZ/Pt, O_2 ($p_{\text{O}_2} = 0.2 \text{ bar}$), from Rüssel [15].

This result shows that, at temperatures higher than 1400°C , only $\text{Sb}^{5+}/\text{Sb}^{3+}$ and $\text{As}^{5+}/\text{As}^{3+}$ exhibit a positive standard potential vs. O_2 ($p_{\text{O}_2} = 0.2 \text{ bar}$)/ O^{2-} pair and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ standard potential is ca. -0.43 V vs. O_2 ($p_{\text{O}_2} = 0.2 \text{ bar}$)/ O^{2-} pair. Consequently, under standard conditions, Sb^{5+} and As^{5+} can oxidize O^{2-} in molecular oxygen. Thus, in the same conditions, Fe^{3+} cannot oxidized O^{2-} . Rüssel's results have been confirmed, later on, by de Best [16] who carried out voltammetry experiments in glass ($75 \text{ SiO}_2 - 15 \text{ Na}_2\text{O} - 10 \text{ CaO}$) containing 0.4 wt.% Fe_2O_3 (see Figure 4). There is a pretty good agreement between the standard potentials of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple obtained independently by these authors. Moreover, in Figure 4 is plotted the variation vs temperature of the standard potential of $\text{Fe}_2\text{O}_3/\text{FeO}$ in their solid form. For temperatures higher than 1000°C , a good agreement is observed. According to Rüssel et al. [17]

this agreement could be ascribed to clustering of iron in the molten glass. These clusters would have similar properties to those of crystalline species, *i.e.*, Fe₂O₃ and FeO.

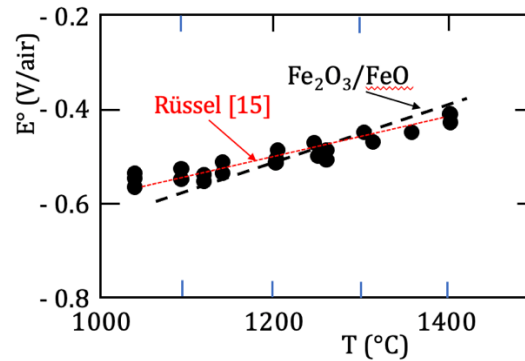


Figure 4: Variation of the standard potential of the Fe³⁺/Fe²⁺ couple in glass containing 0.4 wt.% Fe₂O₃ as a function of temperature. The calculated standard potential of the Fe₂O₃/FeO system in solid form, and the results obtained by Rüssel (see Figure 3) are plotted for comparison, from de Best [16].

Obviously, the potential of the Fe³⁺/Fe²⁺ couple is a function of the [Fe³⁺]/[Fe²⁺] ratio. This ratio varies with the “redox state” in the glass melt which depends on the preparation procedure [18], on dissolved impurities, on substances intentionally added, on the atmosphere [19, 20], on ionization radiations [21], etc. As an example, this phenomenon can be illustrated by the control of the glass coloration by changing the oxygen partial pressure. At high oxygen partial pressure, oxygen oxidizes Fe²⁺ ions dissolved in the glass, forming Fe³⁺ ions, that induces a yellow color. At low oxygen partial pressures, the glass becomes blue, due to Fe²⁺ ions. The low oxygen partial pressure is obtained with, for example, a CO/CO₂ gas mixture. Consequently, from a thermodynamic point of view, Fe³⁺ ions in excess are reduced by CO, and not by O²⁻ ions. The redox potential is a “mixed potential” which depends on the kinetics parameters of redox pairs involved, *i.e.*, Fe³⁺/Fe²⁺ and CO/CO₂ in this example.

Moreover, considering a redox pair, such as Fe³⁺/Fe²⁺, it is well known that increasing the basicity of the melt enhances the stability of the upper oxidation state at the expense of the

lower. Baucke and Duffy [22] determined the variation of the redox ratio (R) of lower to upper states of polyvalent ions vs. optical basicity [23], at 1400°C under air atmosphere, for various redox couples. Figure 5 shows the plot for the $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ redox system. A linear relationship was obtained, *i.e.*, $\log R = \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 3.2 - 6.5 \Lambda$. For an optical basicity of 0.57, at 1400°C, under air, the redox ratio is ca. 0.31.

According to the value of the standard potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple (see Figures 3 and 4), *i.e.*, ca. - 0.43 V vs. air at 1400°C, with a $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ ratio equal to 0.3, the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is equal to - 0.26 V vs. Air. To obtain a positive potential for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple vs. Air, the $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ ratio has to be lower than 0.05. Consequently, from a thermodynamic point of view, Fe^{3+} cannot oxidize O^{2-} ions, according to equation (1), for $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} > 0.05$.

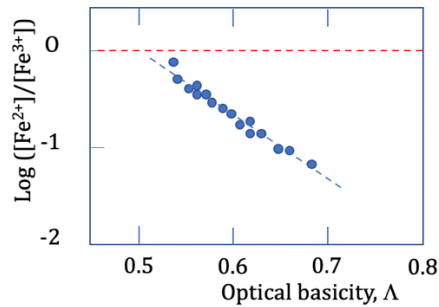


Figure 5: Relationship between $\log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ ratio and optical basicity in silicate melts, at 1400°C and air atmosphere, from Baucke and Duffy [22].

Following another approach, Pinet and Di Nardo [24–26] obtained similar results. These authors proposed a classification of the redox couples, based on a characteristic oxygen pressure ($p(\text{O}_2)_{\text{Charac}}$) which corresponds to the oxygen partial pressure for which the concentrations of reduced and oxidized forms of the couple are equal. The quantity $p(\text{O}_2)_{\text{Charac}}$ depends mainly on the redox couple considered, on the basicity and on the temperature of the glass melt. It may be defined as follows:

$$\log \frac{[Red]}{[Ox]} = \frac{n}{4} [\log p(O_2)_{Charac} - \log p(O_2)] \quad (4)$$

where n is the number of electrons involved in the redox equilibrium.

When $\log p(O_2)$ is higher than $\log p(O_2)_{Charac}$, $\frac{[Red]}{[Ox]}$ is lower than 1. In Figure 6 is plotted the variation of the characteristic oxygen pressure vs temperature in glasses with the same level of basicity. At 1400°C, the characteristic oxygen pressure for the Fe^{3+}/Fe^{2+} couple is ca. 10^{-3} bar. Consequently, under air, the redox ratio is noticeably lower than 1: under equilibrium, at 1400°C, $\frac{[Fe^{2+}]}{[Fe^{3+}]}$ is less than 0.27, which is very close to the value estimated by Baucke et al, *i.e.* 0.31.

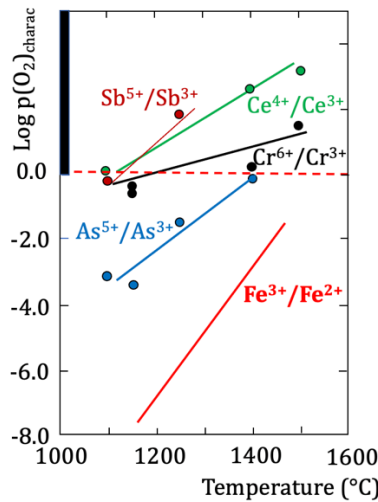


Figure 6: Variation of the characteristic oxygen pressure vs temperature in glasses with the same level of basicity (optical basicity: 0.57 ± 0.02), from Pinet and Di Nardo [24, 25].

It could be noted that the same type of results has been also observed on borosilicate glasses [27].

$Fe(III)$ ions cannot oxidize O^{2-} because $E([Fe^{3+}]/[Fe^{2+}])$ is lower than $E([O_2]/[O^{2-}])$, and, consequently, $Fe(II)$ ions oxidize spontaneously oxygen. This is in agreement with results of Pigeonneau *et al.* who have shown that the shrinkage of oxygen bubbles is observed in ferrous ions rich glasses and that the shrinkage rate increases with the ferrous ion concentration [28].

F. G. K. Baucke has proposed a mechanism of blistering based on electrochemical reactions between glass melts and zircon, involving Fe^{3+} dissolved in the refractory. No measurement of the $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ ratio within the refractories was given. However, we have shown, using XANES experiments, that after high temperature heat treatment, under air, of zirconia-based refractory, FeO and Fe_2O_3 , represent, 22 wt.% and 78 wt.%, respectively [11], corresponding to a $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ ratio of ca. 0.6, far from the value required for the difference of potential between the two redox couples involved in reaction (1) be positive.

All these results, which are consistent despite different and sometimes empirical methodologies, disagree with the hypothesis of Baucke, *i.e.*, Fe^{3+} , in silicate glasses, under air, cannot oxidize O^{2-} to form molecular oxygen, thermodynamically.

3.2. Assumption 2: Dissociation of zircon does not occur

Another hypothesis underlying Baucke's model is that the dissociation of zircon, at the ZS/glass melt interface, to form ZrO_2 and SiO_2 is restricted to high-temperature high-alkaline environments, and was excluded in the proposed model. The reaction layer below the ZS/glass melt interface has been observed mainly visually: from a "flesh-colored" to "light-grey", with a sharp boundary. No investigation indicating the possible formation of new phases has been carried out. The reaction layer (200 μm thick, in 24 hours) was only analyzed by electron microprobe, indicating an increase of the sodium ion concentration.

Many works have been devoted to the determination of the temperature of the solid-state dissociation of zircon ($\text{ZrSiO}_4 \rightarrow \text{ZrO}_2 + \text{SiO}_2$). However, the published data differ considerably, with a decomposition temperature ranging between 1258°C [29] and 1700°C [30, 31]. The discrepancies can be explained by: (i) the structure of the products which depends on

temperature, i.e., monoclinic or tetragonal zirconia and SiO₂ as a glassy phase, quartz or cristobalite, (ii), the role of impurities, (iii), the difficulty of thermodynamic measurements at high temperature. The thermodynamic functions have been determined by solid-electrolyte potentiometric method [32], calorimetry [33, 34], solubility measurements [35], or equilibrium under CO/CO₂ gas mixtures followed by quenching [36]. In Figure 7 is plotted the variation of the Gibbs Free Energy of zircon dissociation as a function of temperature from various authors [32, 36–39].

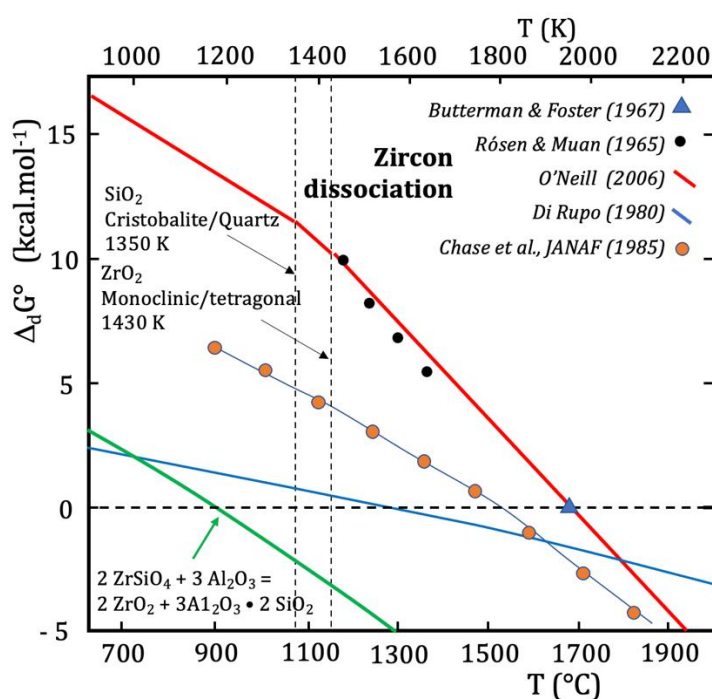
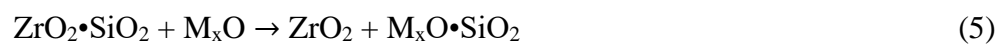


Figure 7: Gibbs Free Energy of dissociation of zircon, ZrSiO₄.

At the present time, it seems well established that the mineral zircon, as a chemically pure substance, decomposes in solid state at a temperature of $1676 \pm 7^\circ\text{C}$ giving a mixture of tetragonal zirconia and β -cristobalite. The milling pretreatment and grain size of zircon affect the dissociation temperature [29, 40]. However, the stability of zircon depends mainly on the type and concentration of impurities in the zircon raw materials [31, 41, 42]. As an example, as shown in Figure 7, the formation of mullite by reaction of zircon with alumina is thermodynamically possible at ca. 900°C [38]. The impurities are either present in natural

zircon or added intentionally to increase the final density and reduce porosity after high temperature sintering [43]. Moreover, it has been shown that impurities forming a silica-rich liquid phase around the zircon grain increase the decomposition rate [44]. The zircon stability in contact with molten glass has also been studied [2, 8, 9, 45]. Corrosion of zircon is greatly affected by the composition of the glass. The impurities showing a high reactivity towards silica have a strong effect on the dissociation phenomena. If MO_x is a component of the glass, the reaction of each component with zircon can be expressed by the equation:



Empirical laws have been proposed to evaluate the role of silicate melts constituents on the zircon dissolution rate [45]. Zircon is an acid material, and consequently alkali components in the glasses are the most corrosive [46].

Obviously, the actual mechanism of the blistering process on zircon is not clearly understood and new experiments are required. However, the glass/zircon reactivity seems to be a key parameter. One of the main observations in Baucke's experiments is that the blistering process occurs when zircon is oxidized and does not occur when zircon is reduced. It has been shown [47] that the presence of Fe^{3+} ions increases the acidity of zircon and, consequently, its reactivity with soda-lime-silica glasses. This interpretation could be corroborated by the works of Mel'nikova [48] which indicated that for reducing the formation of bubbles in alkali glasses, either a vitreous phase containing a few percent of alkali could be added to the zircon composition, or a surface treatment of zircon with alkali solutions could be made.

Following the literature, for the interpretation of the blistering process, in contradiction with Baucke's hypothesis, the corrosion of zircon in contact with a molten glass containing ca. 15 mol% Na_2O and 10 mol% CaO has to be considered. Obviously, the precise role of corrosion products on the blistering process has to be clarified, as an example, by *in operando* experiments [11].

4. Conclusion

Results published in the literature confirm that the blistering phenomenon of an alkali glass in contact with zircon cannot be explained by Baucke's model. It should be pointed out that *in situ* measurements of the composition of the bubbles and precise analyzes of the glass / zircon interface are necessary to propose a mechanism which agrees with thermodynamic considerations and based on experimental evidence.

CrediT authorship contribution statement

J. Hell: Writing, **J. Fouletier:** Formal analysis, Writing – review & editing, **M. C. Steil:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] H. A. Schaeffer, Scientific and technological challenges of industrial glass melting, *Solid State Ionics* 105 [1-4] (1998) 265–270, [https://doi.org/10.1016/S0167-2738\(97\)00478-5](https://doi.org/10.1016/S0167-2738(97)00478-5).
- [2] *Electrochemistry of Glasses and Glass Melts, Including Glass Electrodes*, Edited by H. Bach, F.G.K. Baucke and D. Krause, Springer Verlag, Berlin, 2001, <https://doi.org/10.1007/978-3-662-04486-5>.
- [3] M. Hujova, M. Vernerova, Influence of fining agents on glass melting: A review, Part 1, *Ceramics-Silikaty*, 61 [2] (2017) 119–126, <https://doi.org/10.13168/cs.2017.0006>.
- [4] M. Hujova, M. Vernerova, Influence of fining agents on glass melting: A review, Part 2, *Ceramics-Silikaty*, 61 [3] (2017) 202–208, <https://doi.org/10.13168/cs.2017.0017>.
- [5] J. Ullrich, E. Muijsenberg, Studying Bubble Glass Defects that are caused by Refractory Materials, 71st Conf. on Glass Problems, 19-20 Oct. 2010, *Ceram. Eng. Sci. Proceedings*, Vol. 32, Issue 1, Edited by C. H. Drummond, III, Wiley, 2011, pp. 67-79, <https://doi.org/10.1002/9781118095348.ch7>.
- [6] J. Hell, P. Vespa, I. Cabodi, O. Citti, F. Fournet-Fayard, J. Fouletier, M. C. Steil, Role of zirconia phase transformation, interface processes, and Ta₂O₅ doping on the blistering phenomenon of molten glass in contact

- with zirconia-based refractories, *J. Europ. Ceram. Soc.* 42 [1] (2022) 296–305, <https://doi.org/10.1016/j.jeurceramsoc.2021.09.058>.
- [7] F. W. Krämer, Analysis of Gases Evolved by AZS Refractories and by Refractory Glass Melt Reactions – Techniques and Results – Contribution to the Bubble-Forming Mechanism of AZS Material, *Glastechnische Ber.-Glass Sci. Technol.* 65 [4] (1992) 93–98.
- [8] F. G. K. Baucke, G. Röth, Electrochemical mechanism of the oxygen bubble formation at the interface between oxidic melts and zirconium silicate refractories, *Glastechnische Ber.* 61 [5] (1988) 109–118.
- [9] F. G. K. Baucke, Fundamental and applied electrochemistry at an industrial glass laboratory—an overview, *J. Solid State Electrochem.* 15 [1] (2011) 23–46, <https://doi.org/10.1007/s10008-010-1123-8>.
- [10] F. A. G. van Dijk, Glass defects originating from glass melt/fused cast AZS refractory interaction, PhD Thesis, Techn. Univ. Eindhoven, 1994, <https://doi.org/10.6100/IR417346>.
- [11] J. Hell, P. Vespa, I. Cabodi, O. Citti, F. Fournet-Fayard, J. Fouletier, M. C. Steil, Blistering phenomenon of molten glass in contact with zirconia-based refractories, *J. Europ. Ceram. Soc.* 41 [10] (2021) 5359–5366, <https://doi.org/10.1016/j.jeurceramsoc.2021.03.063>.
- [12] F. G. K. Baucke, Electrochromic Mirrors with Variable Reflectance, *Solar Energy Mat.* 16 [1-3] (1987) 67–77, [https://doi.org/10.1016/0165-1633\(87\)90009-8](https://doi.org/10.1016/0165-1633(87)90009-8).
- [13] T. Baak, E. J. Hornyak, Jr., The Iron-Oxygen Equilibrium in Glass: Effect of Platinum on $\text{Fe}^{2+}/\text{Fe}^{3+}$ Equilibrium, *J. Am. Ceram. Soc.* 44 [11] (1961) 541–44.
- [14] W. D. Johnston, Oxidation-Reduction Equilibria in Iron-Containing Glass, *J. Amer. Ceram. Soc.* 47 [4] (1964) 198–201.
- [15] C. Rüssel, Redox Behavior and Electrochemical Behavior of Glass Melts, in *Properties of Glass-Forming Melts*, Chap. 3, Edited by L. D. Pye, I. Joseph and A. Montenero, CRC Press, Taylor & Francis Group, London, 2005, <https://doi.org/10.1201/9781420027310>.
- [16] A. W. M. de Best, Redox behaviour and fining of molten glass, PhD Thesis, Techn. Univ. Eindhoven, 1994, <https://doi.org/10.6100/IR426291>.
- [17] C. Rüssel, R. Kohl, H. A. Schaeffer, Interaction between oxygen activity of Fe_2O_3 doped soda–lime–silica glass melts and physically dissolved oxygen, *Glastechnische Ber.* 61 [8] (1988) 209–213.
- [18] M. Yamashita, T. Akai, R. Sawa, J. Abe, M. Matsumura, Effect of preparation procedure on redox states of iron in soda-lime silicate glass, *J. Non-Cryst. Solids* 354 (2008) 4534–4538, <https://doi.org/10.1016/j.jnoncrysol.2008.07.002>.
- [19] T. T. Volotinen, J. M. Parker, P. A. Bingham, Concentrations and site partitioning of Fe^{2+} and Fe^{3+} ions in a soda–lime–silica glass obtained by optical absorbance spectroscopy, *Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B* 49 [5] (2008) 258–270.
- [20] M.M. Smedskjaer, Q. Zheng, J.C. Mauro, M. Potuzak, S. Mørup, Y. Yue, Sodium diffusion in boroaluminosilicate glasses, *J. Non-Cryst. Solids* 357 (2011) 3744–3750, <https://doi.org/10.1016/j.jnoncrysol.2011.07.008>.
- [21] M. Fialin, C. Wagner, Redox kinetics of iron in alkali silicate glasses exposed to ionizing beams: Examples with the electron microprobe, *Journal of Non-Crystalline Solids* 358 (2012) 1617–1623, <https://doi.org/10.1016/j.jnoncrysol.2012.04.026>.

- [22] F. G. K. Baucke, J. Duffy, Redox reactions between cations of different polyvalent elements in glass melts: an optical basicity study, *Phys. Chem. Glasses* 34 [4] (1993) 158–163.
- [23] J. A. Duffy, M. D. Ingram, An Interpretation of Glass Chemistry in Terms of the Optical Basicity concept, *J. Non-Cryst. Solids* 21 [3] (1976) 373–410, [https://doi.org/10.1016/0022-3093\(76\)90027-2](https://doi.org/10.1016/0022-3093(76)90027-2).
- [24] O. Pinet, C. Di Nardo, Les phénomènes d'oxydoréduction dans les verres, Note technique, CEA, NT/SCD/N°99–26, 1999, in French.
- [25] C. Di Nardo, Étude et contrôle des réactions d'oxydoréduction au cours de l'élaboration des matrices vitreuses de confinement des déchets nucléaires, PhD Thesis, Université de Montpellier-CEA VALRHO, 2002, in French.
- [26] O. Pinet, J. Phalippou, C. Di Nardo, Modeling the redox equilibrium of the Ce^{4+}/Ce^{3+} couple in silicate glass by voltammetry, *J. Non-Crystalline Solids* 352 [50-51] (2006) 5382–5390, <https://doi.org/10.1016/j.jnoncrysol.2006.08.034>.
- [27] D. S. Goldman, Oxidation Equilibrium of Iron in Borosilicate Glass, *J. Am. Ceram. Soc.* 66 [3] (1983) 205–209.
- [28] F. Pigeonneau, D. Martin, O. Mario, Shrinkage of an oxygen bubble rising in a molten glass, *Chem. Eng. Sci.* 65 [10] (2010) 3158–3168, <https://doi.org/10.1016/j.ces.2010.02.003>.
- [29] R. S. Pavlik, H. J. Holland, E. A. Payzant, Thermal decomposition of zircon refractories, *J. Am. Ceram. Soc.* 84 [12] (2001) 2930–2936, <https://doi.org/10.1111/j.1151-2916.2001.tb01117.x>.
- [30] A. Kaiser, M. Lobert, R. Telle, Thermal Stability of Zircon ($ZrSiO_4$), *J. Europ. Ceram. Soc.* 28 [11] (2008) 2199–2211, <https://doi.org/10.1016/j.jeurceramsoc.2007.12.040>.
- [31] P. Peña, S. de Aza, The zircon thermal behavior: effect of impurities. Part 1, *J. Mater. Sci.* 19 (1984) 135–142, <https://doi.org/10.1007/BF00553002>.
- [32] H. St. C. O'Neill, Free energy of formation of zircon and hafnon, *American Mineralogist* 91 (2006) 1134–1141, <https://doi.org/10.2138/am.2006.2071>.
- [33] A. J. G. Ellison, A. Navrotsky, Enthalpy of Formation of Zircon, *J. Am. Ceram. Soc.* 75 [6] (1992) 1430–1433, <https://doi.org/10.1111/j.1151-2916.1992.tb04205.x>.
- [34] M. Akaogi, S. Hashimoto, H. Kojitani, Thermodynamic properties of $ZrSiO_2$ zircon and reidite and of cotunnite-type ZrO_2 with application to high-pressure high-temperature phase relations in $ZrSiO_4$, *Phys. Earth Planetary Int.* 281 (2018) 1–7, <https://doi.org/10.1016/j.pepi.2018.05.001>.
- [35] R. C. Newton, C. E. Manning, J. M. Hanchar, C. V. Colasan, Free energy of formation of zircon based on solubility measurements at high temperature and pressure, *American Mineralogist* 95 (2010) 52–58, <https://doi.org/10.2138/am.2010.3213>.
- [36] E. Rosén, A. Muan, Stability of Zircon in the Temperature Range 1180°C to 1366°C, *J. Am. Ceram. Soc.* 48 [11] (1965) 603–604.
- [37] W. C. Butterman, W. R. Foster, Zircon stability and the ZrO_2 - SiO_2 phase diagram, *American Mineralogist* 52 (1967) 880–885.
- [38] E. I. Dirupo, M. R. Anseau, Solid State Reactions in the $ZrO_2 \cdot SiO_2$ - α Al_2O_3 System, *J. Mater. Sci.* 15 (1980) 114–118, <https://doi.org/10.1007/BF00552434>.
- [39] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, *Janaf Thermochemical Tables*, 3rd Edition, *J. Phys. Chem. Ref. Data*, 14, Suppl. 1, 1–1856 (1985).

- [40] M. R. Gauna, M. S. Conconi, G. Suarez, E. Aglietti, N. M. Rendtorff, Dense Zircon ($ZrSiO_4$) Ceramics by a Simple Milling-Sintering Route, *Sci. Sintering* 49 (2018) 15–28, <https://doi.org/10.2298/SOS1904445H>.
- [41] R. S. Pavlik Jr., D. R. Sempolinski, R. Froberg, Purification of Porous Zircon by Carbochlorination, *J. Am. Ceram. Soc.* 87 [9] (2004) 1653–1658, <https://doi.org/10.1111/j.1551-2916.2004.01653.x>.
- [42] C. Aksel, M. Dexet, N. Logen, F. Porte, F. L. Riley, F. Konieczny, The influence of zircon in a model aluminosilicate glass tank forehearth refractory, *J. Eur. Ceram. Soc.* 23 [12] (2003) 2083–2088, [https://doi.org/10.1016/S0955-2219\(03\)00025-6](https://doi.org/10.1016/S0955-2219(03)00025-6).
- [43] M. Awaad, S. H. Kenawy, Sintering of zircon: the role of additives, *Brit. Ceram. Trans.* 102 [2] (2003) 69–72, <https://doi.org/10.1179/096797803225001551>.
- [44] P. Tartaj, C. J. Serna, J. S. Moya, J. Requena, M. Ocana, S. De Aza, F. Guitian, The formation of zircon from amorphous ZrO_2 - SiO_2 powders, *J. Mater. Sci.* 31 (1996) 6089–6094, <https://doi.org/10.1007/BF01152164>.
- [45] A. Borisov, L. Aranovich, Zircon solubility in silicate melts: New experiments and probability of zircon crystallization in deeply evolved basic melts, *Chem. Geol.* 510 (2019) 103–112, <https://doi.org/10.1016/j.chemgeo.2019.02.019>.
- [46] K. Kato, N. Araki, The Corrosion of Zircon and Zirconia Refractories by Molten Glasses, *J. Non-Cryst. Solids* 80 [1–3] (1986) 681–687, [https://doi.org/10.1016/0022-3093\(86\)90462-X](https://doi.org/10.1016/0022-3093(86)90462-X).
- [47] A. Leboutellier, P. Courtine, Improvement of a bulk optical basicity table for oxidic systems, *J. Solid State Chem.* 137 [1] (1998) 94–103, <https://doi.org/10.1006/jssc.1997.7722>.
- [48] G. Mel'nikova, T. A. Nesterova, I. V. Razdol'skaya, Zircon refractory for Glass-Melting, *Glass Ceram.* 42 [7] (1985) 295–298, <https://doi.org/10.1007/BF00694599>.