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Characteristics of Refractories Applied in Glass Tanks

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Abstract

The performance of refractories influences significantly the lifetime of a glass tank and the quality of glass. The main general requirements addressed to the refractory material are: a feasible low level of glass defects and a feasible long service, which are in some cases contrary to each other. Thus, it is necessary to prove several characteristics essential for the behaviour of refractory material in a glass tank prior to its application, especially in the case of melting glasses where the products are subjected to strict specification conditions. The application examples of some testing methods used to characterize refractories, especially the fusion cast, intended to be used in contact with special glass melts and to qualify them for this application are shortly presented; e.g., examination of microstructure, analysis of thermal expansion behaviour, volume changes due to thermal cycling, static plate and dynamic corrosion tests as well as the blistering test with a continuous glass change. Taking into account the relations between parameters of the manufacturing process, the material microstructure and material properties, it is shown that an appropriately designed lab test and correct interpretations validated by the experience gathered during service in similar systems allow the proper choice and the right evaluation of refractories to be executed.
Keywords: Characterization, Fusion cast refractories, Glass tanks

CHARAKTERYSTYKA MATERIAŁÓW OGNIOTRWAŁYCH STOSOWANYCH W PIECACH SZKLARSKICH

Zachowanie sie materiałów ogniotrwałych w warunkach pracy pieców szklarskich w decydujący sposób wpływa na ich efektywny czas eksploatacji i jakość wytapianego szkła. Głównym wymaganiem stawianym materiałom ogniotrwałym w tym przypadku jest możliwie długi czas pracy przy jednocześnie niskim poziomie, pochodzących od materiałów ogniotrwałych, wad w szkle, co niejednokrotnie jest wewnętrznie sprzeczne. Przed zastosowaniem konkretnego materiału w piecu szklarskim niezbędne jest zatem sprawdzenie szeregu jego specyficznych technologicznie właściwości. W szczególności dotyczy to materiałów przeznaczonych do urządzeń produkujących szkło na produkty, których specyfikacja stawia szczególnie ostre wymaganie odnośnie jakości/wad szkła. Przedstawiono przykłady zastosowania niektórych metod badania własności materiałów ogniotrwałych, szczególnie tzw. topiono-odlewanych, służących ocenie ich jakości przed zastosowaniem w urządzeniach do produkcji szkła, zwłaszcza szkieł specjalnych, takich jak badania mikrostruktury, zmian objętości podczas obróbki cieplnej, odporności korozyjnej w warunkach testu statycznego i dynamicznego oraz określenie potencjału tworzenia pęcherzy w warunkach ciągłego testu dynamicznego. Wskazano, że dokonanie właściwego doboru materiału ogniotrwałego do konkretnych warunków jego zastosowania uzależnione jest od odpowiednio zaprojektowanych badan laboratoryjnych, właściwej interpretacji ich wyników wspomaganej przez ich ocenę w oparciu o wcześniejsze doświadczenia z podobnych wcześniejszych zastosowań w praktyce oraz po uwzględnieniu zależności istniejących pomiędzy parametrami produkcji materiałów ogniotrwałych, ich mikrostrukturą i właściwościami.
Słowa kluczowe: badania właściwości, topiono-odlewane materiały ogniotrwale, piece szklarskie

1. Introduction

Profound knowledge concerning physical and technological properties of refractories as well as that of interrelations between these properties and application properties, i.e., refractories behaviour during service are the crucial issues enabling the proper choice of refractories for a predefined purpose.

The main features defining the meaning of a “proper choice” in this context are constituted by factors like really accomplished life time and the output of the glass tank in comparison to their values assumed at the beginning of the project.

This outline explains how the efficiency of each glass tank project, being decisively influenced by investment costs of refractory lining and its performance during service, depends on the availability of extended and reliable characteristics of refractories.

There are at least two following specific situations creating the demand for reliable testing results which additionally stress the importance of the above mentioned relations:

(i) applications in the tanks intended to melt special glasses at very high temperatures (*i.e.*, 1650°C or above) for products subjected to extremely high quality requirements,

(ii) necessity to evaluate materials offered on the market by new or not approved manufacturers.

The costs of testing and those of quality approval are also a part of the project effectiveness balance. Thus, the scope of testing as well as the testing method applied have to be selected properly to achieve the most reliable evaluation at possibly low expenditures.

The optimum performance to be reached is the possibly long lifetime of the glass tank combined with the highest possible output. When related to properties of refractories it means possibly high corrosion resistance and a possibly low potential of a glass defect formation.

High corrosion resistance, in turn, requires a possibly low solubility of the refractory material in glass melt which sometimes can result in a higher level of glass defects if particles of such a material appear there, e.g., due to, erosive wear. This relation is the only example for situations where a compromise is the only possible solution in an attempt to optimize two or more properties contrary to each other.

Due to the specific composition and requirements related to the application site, each group of refractories applied for glass contact or superstructure needs a somewhat different spectrum of characterization.

To describe some typical procedures of characterization, some examples related to fusion cast (FC) refractories, especially high zirconia (HZFC) or FC AZS (alumina-zirconia-silica) are chosen to be discussed in the present paper.

2. Evaluated properties and their inter-relations with performance of refractories

The following properties are considered to have the main influence on the service performance of refractories and thus to be carefully examined and evaluated: composition and microstructure, thermal expansion behaviour and, among application properties, corrosion resistance and blistering potential.

2.1. Composition and microstructure

Inhomogeneities in both chemical and phase compositions are the well known features of fusion cast refractories. They are mainly the result of a zonal crystallization taking place in the gravity field and temperature gradient in the mould during cooling down after the pouring process, thus being influenced by these two factors.

Although it is not possible to eliminate completely these inhomogeneities, a good quality of refractory means in this relation optimizing the cooling and crystallization process to achieve a possibly homogeneous phase distribution.

The amount and distribution of the main phase components are crucial for the refractory behaviour, regarding the most important technological or application properties, i.e., corrosion resistance and blistering behaviour.

Assemblages of glassy phases or larger pores are not only the weak points within the microstructure, which will be preferably attacked by glass melt. A glassy phase is also collecting the main amounts of impurities, which, especially in the case of polyvalent ions, are the source of higher blistering potential. The latter in turn influence not only the glass defect and thus output level but also can significantly intensify the corrosion via the so called bubble drilling mechanism, especially at such critical sites as, *e.g.*, the throat cover block.

Some examples of macroscopically observed inhomogeneities correlated with microstructure pictures of these areas are shown in Figs. 1 and 2.

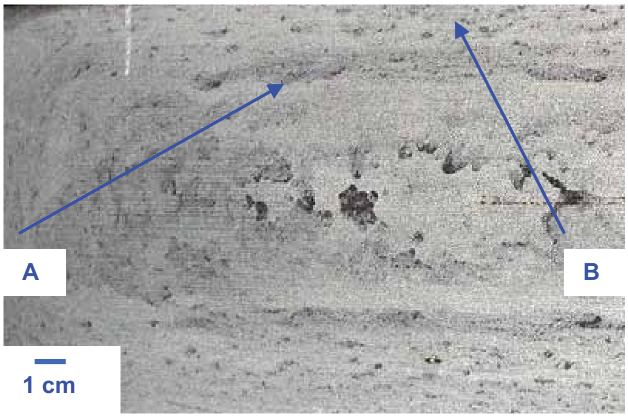


Fig. 1. Cut surface of the as-delivered HZFC block.

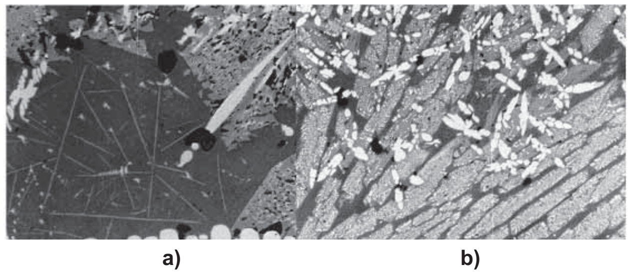


Fig. 2. Microstructure of the HZFC block shown in Fig. 1: a) the A area and b) the B area.

Microstructure of the areas A and B is shown in Figs. 2a and b, respectively.

Inhomogeneities in FC AZS refractories are often macroscopically less conspicuous than in the case of HZFC due to the lack of colour contrast. The comparison of microstructure, however, as shown in Fig. 3, gives an idea about a possible variety.

One of the most important reasons for that is the difference in the total amount of glassy phase being in the case of FC AZS with ca. 20-30 vol.% about 2-3 times higher than in the case of HZFC with ca. 10 vol.%.

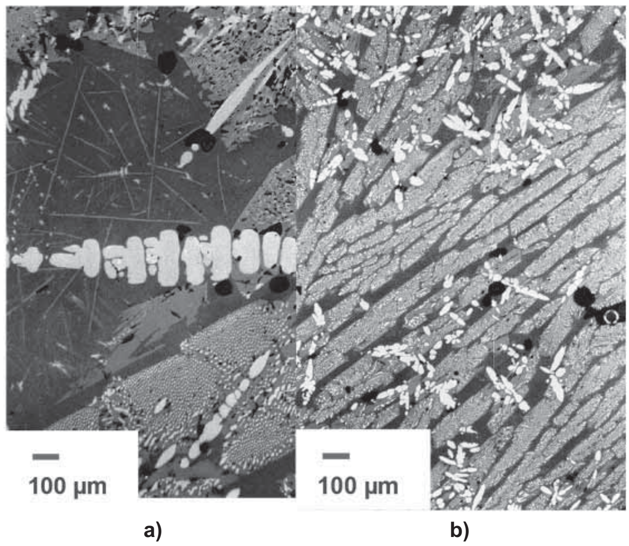


Fig. 3. Examples of different microstructures of FC AZS material.

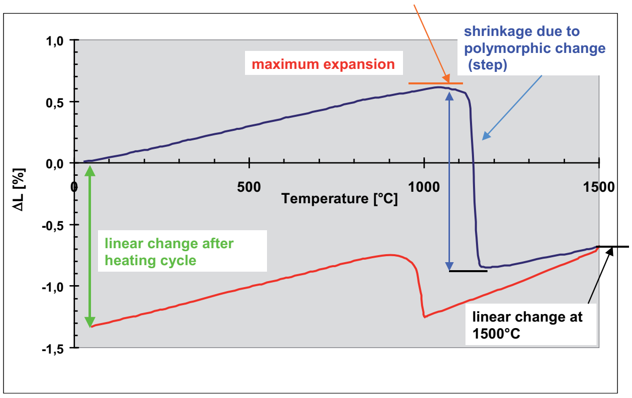


Fig. 4. Characteristics of the thermal expansion behaviour of ZrO_2-containing refractories.

2.2. Thermal expansion behaviour

Thermal expansion behaviour is, especially in the case of refractories containing zirconia as a main phase component, due to volume changes accompanying its polymorphic transformations, a very important feature influencing their performance and determining measures to be undertaken in the construction and technical process to optimize the glass tank service.

To characterize the material as delivered the classic dilatometry is applied to determine quantitatively the following characteristics marked in Fig. 4 on the typical diagram:

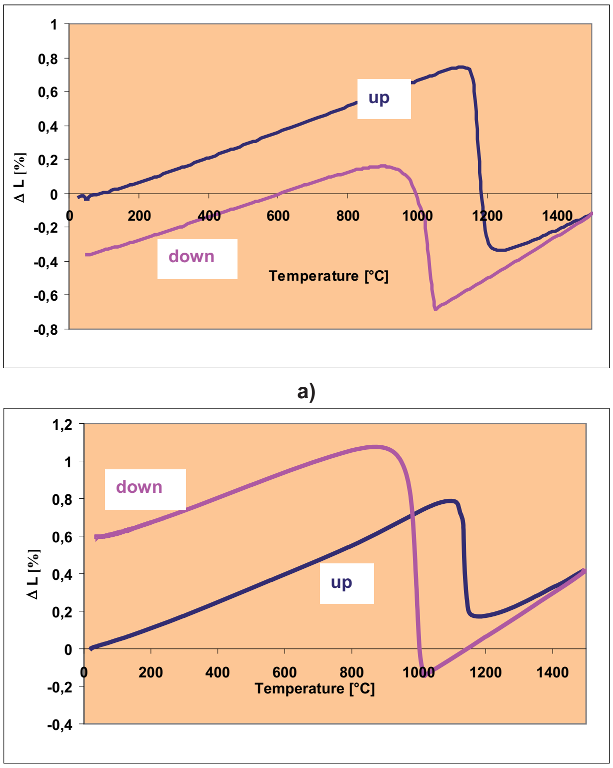
- temperature and value of the maximum expansion,
- shrinkage during polymorphic change,
- linear change at service temperature,
- linear change after heating/cooling cycle.

Some typical data of the discussed characteristics, determined for different brands of HZFC and AZS refractories, are presented in Table 1.

An example shown in Fig. 5 illustrates possible changes which can be observed in the original dilatometric characteristic of HZFC refractory (Fig. 5a) as a result of thermal treatment and/or interaction of the contact layer with glass melt during service.

Table 1. Characteristics of thermal expansion behaviour of ZrO_2-containing refractories.

Sample symbol	Maximum expansion at temperature		Shrinkage due to polymorphic change (step) at temperature		Expansion at 1500°C	Linear change after heating cycle
	[%]	[°C]	[%]	[°C]	[%]	[%]
(HZFC) A	0.6	1050	1.5	1120	-0.6	-1.3
(HZFC) B (along*)	0.8	1100	0.6	1120	0.4	0.6
(HZFC) B (cross)	0.8	1100	1	1110	0.0	0.0
(FC AZS 32) C (along)	0.8	1090	0.3	1150	0.9	0.2
(FC AZS 32) C (cross)	0.8	1090	0.3	1160	0.8	0.1



a)

b)

Fig 5. Examples of different types of thermal expansion behaviour observed on HZFC samples.

2.3. Volume change during thermal cycling

To understand and to evaluate the phenomena occurring during service, which can also be implicated by irreversible processes, further investigations have to be carried out to determine refractory behaviour during multiple temperature changes. Additionally to temperature cycling in the dilatometer (several measurements on the same sample) volume changes of larger cylindrical samples (diameter and height of 50 mm) after temperature cycling (20 or 40 cycles) within the range 800-1250°C are determined to compare the material stability.

Table 2. Characteristics of HZFC samples subjected to thermal cycling within 800-1250°C.

Sample	Number of cycles	Apparent density [g/cm³]	Open porosity [%]	Volume change [%]	Remarks
B(1)	0	5.40	0.2		
B(1)	20	5.30	1.7	1.8	no cracks
B(2)	0	5.42	0.3		
B(2)	40	5.26	2.9	3.0	no cracks
C(1)	0	5.29	1.2		
C(1)	20	4.62	13	12.5	cracks, powder
C(2)	0	5.28	1		
C(2)	40	4.12	22.3	22.1	vs cracks, powder

a) b)

Fig. 6. Samples of two different HZFC brands after 40 cycles within the temperature range of 800-1250°C.

Some examples of the data concerning changes in apparent density, open porosity and volume of HZFC samples after such a kind of heat treatment are presented in Table 2.

As it can be seen, different brands of HZFC refractories perform quite differently regarding the response to thermal cycling between 800 and 1250°C, which is additionally visualised in Fig. 6, showing the samples appearance after testing.

3. Application properties

3.1. Corrosion resistance

The corrosion resistance of the refractory material applied in the glass contact, especially at the critical positions, is the crucial property limiting the lifetime of the tank as a whole (see *e.g.* [1, 2]). Thus, there is a lot of interest to choose the appropriate material, possibly using laboratory tests, which allow the author to avoid large risks and high expenses.

The laboratory corrosion tests alone are generally not able to give a basis for a direct and accurate prediction of the tank lifetime. They can, however, supply a pretty good relative assessment of different refractories when compared under the corrosion attack of the same glass melt. Such results combined with the practical experience gathered by the application, *i.e.*, corrosion behaviour in the real tank, can significantly contribute to the lifetime prediction and optimization of the glass tank performance. The well known established laboratory testing methods of the corrosion resistance applied for refractories intended to be used in contact with glass melt are: (i) static plate corrosion test, as recommended by TC 11 of ICG [3] and (ii) dynamic corrosion test, the method of rotating cylinder with wear measurement on the bottom surface (see *e.g.* [4-6]).

As the result of evaluation of the static plate corrosion test two values determined on the samples cross sections are received: (i) wear at the glass line influenced mainly by the surface convection, and (ii) wear under the glass line influenced mainly by density convection, as an average of several measurements.

The dynamic corrosion test carried out with the method of a rotating cylinder is suitable to determine the temperature and/or time dependence of the corrosion rate on the glass stream velocity under the defined conditions of forced convection [7].

It is important that the discussed corrosion tests offer the possibility not only to determine the wear values but also, by examining the glass after testing, to assess the potential of glass defect formation.

3.2. Blistering behaviour

Another factor limiting the glass tank yield is the glass defects level while blisters are regarded as one kind of these defects.

To assess the blistering potential of refractory in contact with glass melt a dynamic continuous test can be used [8], setup of which is shown in Fig. 7.

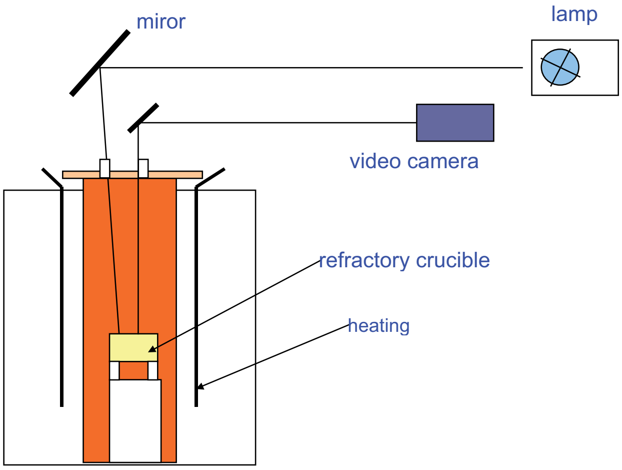


Fig. 7. Setup of the testing device for dynamics blister test.

The blisters formed on the contact surface of the crucible made of the refractory to be tested and glass melt can be observed and counted at the picture taken by a video camera which is then digitalized and which can be stored.

The evaluation of the blistering potential is usually (standard tests) carried out twice a day within about twenty days. To maintain the original glass melt composition a new glass portion is put every day into the crucible.

As a result, the dependence of the blistering rate and the blister number on test time can be determined, as it is shown as example in Fig. 8.

Applying this method of testing different kinds of refractories can be relatively compared, concerning their blistering potential in contact with definite glass melts.

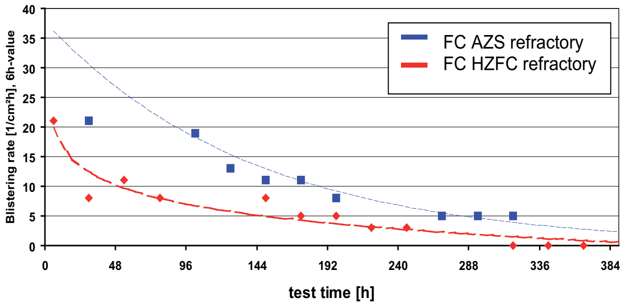


Fig. 8. Typical diagram of blistering rate vs. testing time.

3.3. Interrelation between properties and performance of refractories

Some examples of complex influence of the refractory properties, on the performance of refractories in contact with glass melts are chosen to present them below in order to show the importance of the laboratory testing in the sophisticated process of refractory evaluation and selection.

The importance of the thermal expansion behaviour and volume change during temperature changes (modelled in the lab test by thermal cycling) can be stressed by the analysis of the examples of different behaviour.

The thermal expansion behaviour determined on a sample as delivered and possibly also during further heating cycles as well as after service gives very important information for the tank construction and tank maintaining, especially for heating up and cool down procedures and helps find the right way to control stresses and static behaviour of the tank construction by an appropriate strain control. The examples of different thermal expansion behaviours have been shown in Fig. 5.

It is a matter of the appropriate composition and thus of the properties of the glassy phase combined with its amount and distribution, driven (among others) by the parameter of cooling process, to reach a possibly high volume stability of the material thermally treated in such a way. A glassy phase should allow the relaxation of the strains arising as the result of a multiple phase transformations of the crystalline phase (ZrO_2) connected with volume change to avoid the decay of material as shown in Fig. 6b.

The influence of the phase composition and especially glassy phase distribution within the HZFC refractory on the corrosion behaviour and thus on refractory performance and glass tank lifetime is illustrated in Fig. 9. The presence of larger inhomogeneities, so called "worm tracing", containing glassy phase ("glass worms") or pores ("pore worms"), *e.g.*, as shown in Figs. 2 and 10, leads in contact with the glass melt to the accelerated corrosion within these areas. It can also be observed on the samples examined in the laboratory static plate corrosion test and during the evaluation of the glass tank lining after the working campaign.

Another aspect of phase composition and phase distribution dealing simultaneously with corrosion and blistering behaviour and thus with glass defect potential of refractory is the fact that a glassy phase in the fusion cast refractories is known to concentrate the most impurities in it.

Some of these impurities, especially polyvalent cations, are according to some hypotheses (see e.g. [9-10]) to be blamed for blister forming. It occurs as a result of shifting of the chemical equilibrium involving oxygen or other gases. Thus, the gas product release is sensible of changes of the relevant partial pressures or/ and temperatures .

Thus, larger glassy phase areas are not only areas which are more vulnerable as far as the corrosion process is concerned but are also, as a rule, the areas of higher blistering activity.

Such behaviour was proved by means of the dynamic blistering test allowing continuous observations of the refractory/glass melt contact surface at high temperature to be performed and at the same time the possibility to distinguish between the phase components on the crucible bottom surface.

An interesting example showing the blister formation in situ within the area of glassy phase of HZFC refractory is presented in Fig. 10.

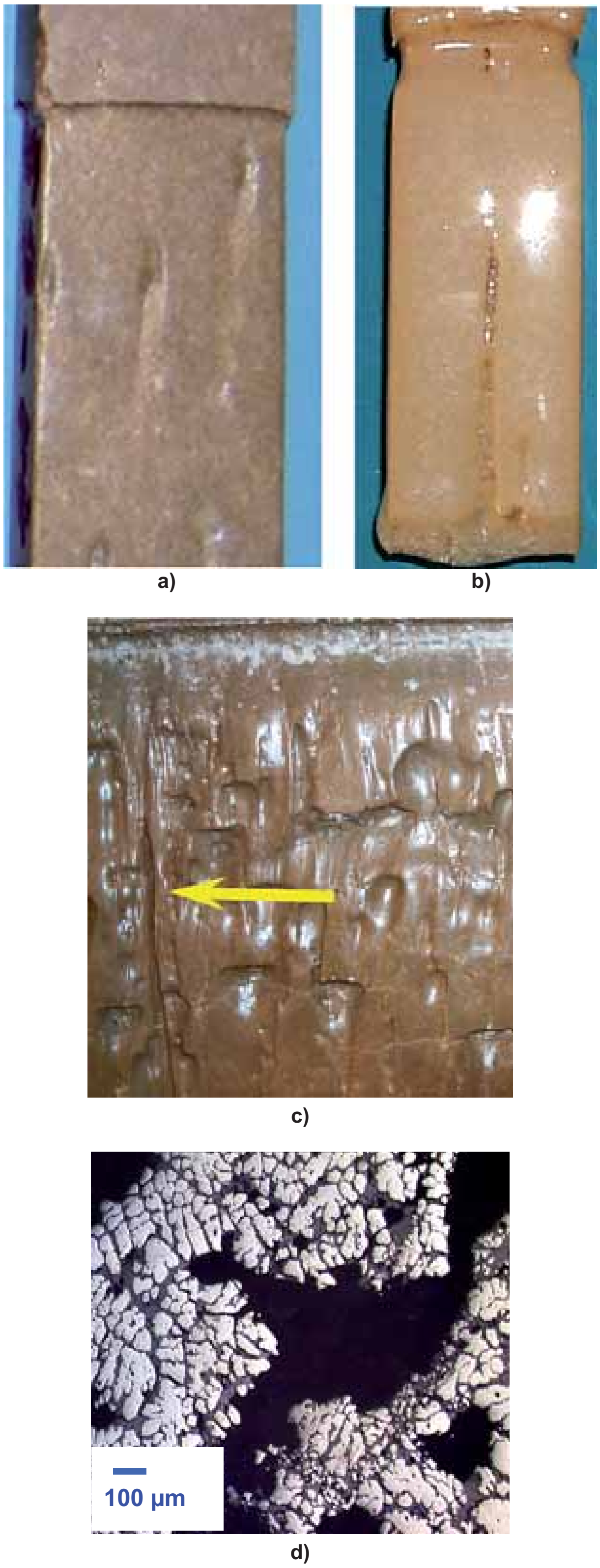
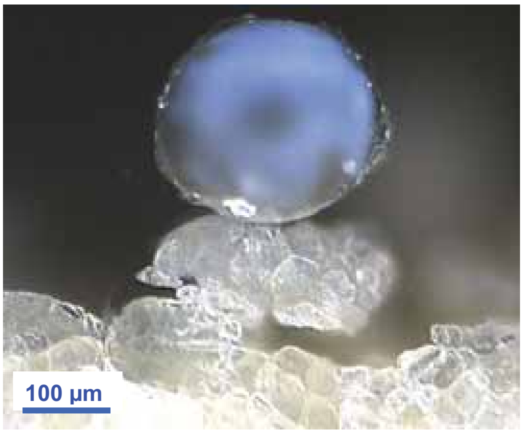
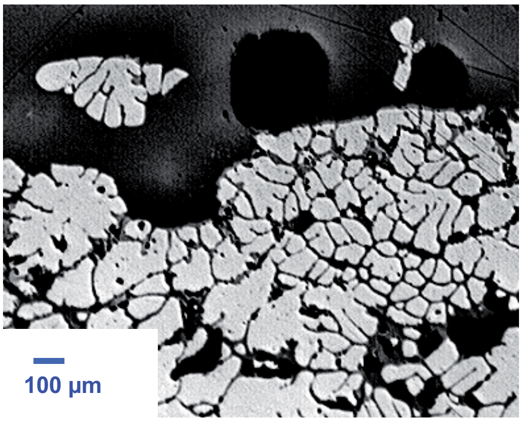


Fig. 9. The effect of inhomogeneities on corrosion behaviour of HZFC refractory: a) and b) local wash outs in the static plate corrosion samples, c) local wash out in one of the soldier block of a real glass tank, d) microstructure of the HZFC after service within the regions like these shown in a-c; to compare with Fig. 2 also.



a)



b)

Fig. 10. Blister formation in the glass melt on the contact surface of HZFC refractory.

It illustrates also one of the mechanisms of solid glass defects formation, showing pushing out of the zirconia primary crystals from the refractory into the glass melt by the blister formed as a result of reactions taking place within the refractory glassy phase/glass melt contact area.

4. Conclusions

It is shown that well prepared and appropriately designed laboratory investigations help to evaluate "unknown" refractory, regarding its applicability in contact with a definite glass melt to avoid too high risks.

Good understanding of the interrelations between the parameter of the manufacturing process, material microstructure and material properties is an essential requirement for the correct tests design and interpretation of their results. It is helpful if the results of laboratory test can be validated by the experience gathered during service in similar systems and in post mortem investigations.

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