ORIGIN OF DEFECTS RELATED TO THE CORROSION OF THE REFRACTORIES IN LEAD CRYSTAL GLASS

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This paper reports mechanisms of corrosion of the refractories used in industrial melting of lead crystal glass hollowware, and some chosen examples of defects linked to this corrosion. Sections prepared in worn refractories from dismantled furnaces and in different defects were characterised by SEM (scanning electron microscope) microanalysis.

INTRODUCTION

The identification of the source of the stones and cords arising in glass is a work of major importance [1, 2]. The actual glass quality requirements for hollow lead crystal glass ware and trinketry need a tight control of the production parameters in order to minimise these defects in the sold glassware. The defects related to their source are usually monitored by the production or control staff in the factories, with a polarised light microscope (PLM). A much more reliable identification can be obtained by the SEM (scanning electron microscope) microanalysis on selected samples after PLM examination. The chemical composition of the phases can then be determined. The three major sources of stones and cords are (1) contamination of raw materials (as received or in the factory), (2) corrosion of the refractories, or (3) devitrification. This paper deals with defects related with the corrosion of the refractories, for lead crystal glass melted in pots and in electric tank furnaces. The mechanism of corrosion for pot clays and for AZS fused cast refractories is reported too.

EXPERIMENTAL PROCEDURE

Many samples from different furnaces in different lead crystal glass factories were studied: (1) several hundreds of stones and cords, (2) worn pots, and (3) AZS linings from dismantled electric tank furnaces.

The samples were examined by PLM, and selected samples were cut and polished for SEM microanalysis. SEM images were obtained mainly from backscattered electrons. The chemical compositions were obtained by fully quantitative computation of the EDS (energy dispersive spectrometer) spectra with ZAF correction.

STONES AND CORDS ARISING IN GLASS MELTED IN POTS

Many factories still use pot furnaces for the melting of clear or coloured lead crystal glass. The pot clays contain approx. 20 to 40 wt.% Al_2O_3, depending on the melting process and the factory uses.

The fired sound pot clay in contact with glass is readily converted to a layer of composition close to leucite or orthose, in which the main crystallised compound is leucite ($KAlSi_2O_6$). Potash feldspar ($KAlSi_3O_9$) sometimes precipitates in this layer. A layer of glass continuously enriched in alumina and potassium oxide provided by the leucite layer, and depleted in lead, appears on the interface of leucite layer and glass.

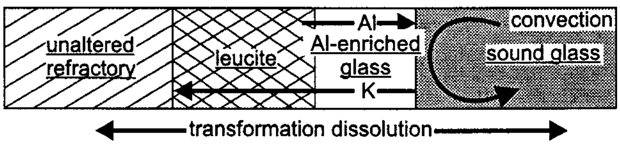

Figure 1. Wear of a refractory pot (section).

The evolution of the composition of the unaltered pot to the leucite layer and of the glass to the Al-enriched glass are shown in the ternary diagram K_2O - Al_2O_3 - SiO_2 below.

Under normal operating conditions, the layer of Al-enriched glass is continuously dissolved by the sound glass as long as the convection currents are well established. The percentage of alumina in the Al--enriched glass is too low to allow leucite precipitation. The interface of leucite layer and unaltered refractory moves towards the inner part of the refractory [3].

Local cracks may occur if the pot has been subjected to a thermal shock during the warming-up. The corrosion in these cracks or in superstructure is quite different: the Al-enriched glass is not dissolved by the sound glass.

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The local increase of the concentration in alumina allows the precipitation of dendritic leucite found in vitreous knots associated with aluminous cords.

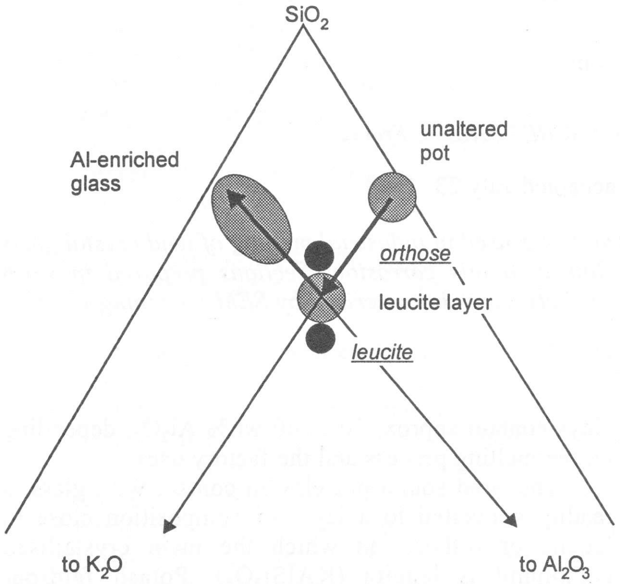


Figure 2. Pot corrosion : evolution of the ternary compositions (example with a 20% Al_2O_3 pot clay).

Grog particles

The pot clay is a mixture of refractory clays and grog particles. The alumina percentage in the grog particles is sometimes much higher than in clay. The corrosion speed will then be much lower for the grog particles than for the clay. The grog particles will be freed from their matrix of clay, and will be found as aluminous stones in glass (figure 3).

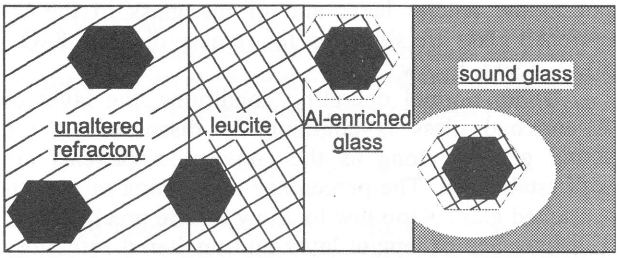


Figure 3. Mechanism of formation of grog particles stones (grog particles painted black).

Grog particles are easily identified by SEM microanalysis. The percentage of alumina in the fireclay grog found in stones is usually about 35 to 40 wt.% Al_2O_3 .

Leucite from the pot mouth

Leucite stones are easily identified by the PLM examination. The leucite stones from the cold parts of the pots in superstructure are associated with small micron-size droplets rich in lead and arsenic for a glass fined with arsenic as shown by the SEM microanalysis.

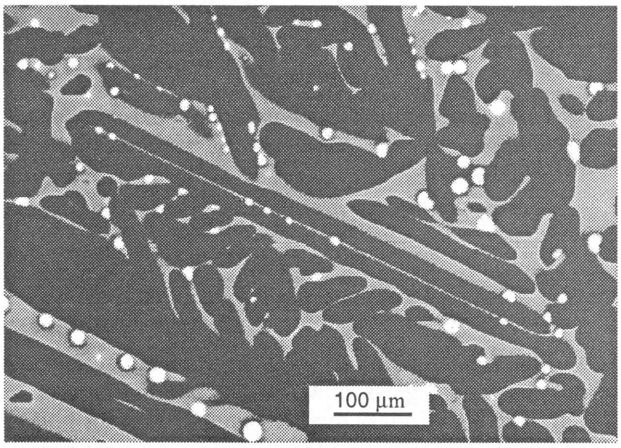


Figure 4. Dendrites of leucite (black) and droplets of the phase rich in Pb, As (white), SEM, polished section, backscattered electron image.

Miscellaneous: eskolaite crystallisation in a green glass

Stones containing eskolaite (Cr_2O_3) hexagonal platelets may arise in green lead crystal glass. On first sight one could think this defect is due to a devitrification of the glass. The SEM microanalysis allows to detect alumina in the solution sac (figure 5), when eskolaite is precipitated into a glass enriched in Al by the corrosion of the refractory. These defects may also arise from dropping of stalactites from the top of the pot.

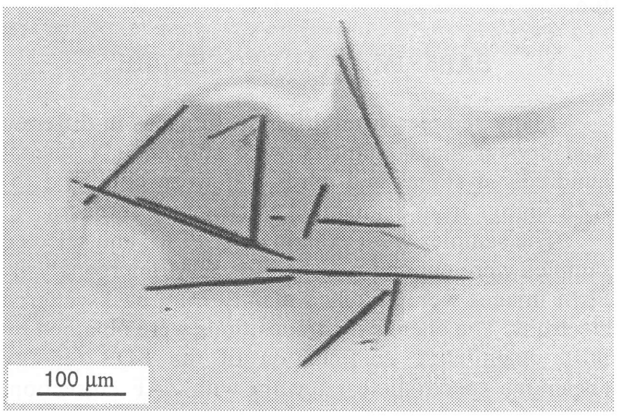


Figure 5. Hexagonal eskolaite platelets (black) in an aluminous solution sac (dark grey) - SEM, polished section, backscattered electron image.

STONES AND CORDS ARISING IN GLASS MELTED IN ELECTRIC TANK FURNACES

The analysed samples were collected from KTG type furnaces. The refractories in contact with glass are AZS fused cast, ER 1711 and ER 1681 grades. The electrodes are made of tin dioxide (cassiterite). The stones and cords produced by the corrosion of these materials are the alumina, zirconia, and/or tin enriched glasses or fragments of the worn refractory [4]. The phases present in the sound refractory are baddeleyite, corundum, and the siliceous vitreous phase.

Corrosion of the AZS fused cast refractories in the melting area

The phases present in a worn ER 1711 electrode block in contact with glass are listed below (figure 6):

- kaliophilite (K, Na)$_2$O.Al$_2$O$_3$.2SiO$_2$ (replacing the vitreous phase),
- beta-alumina (replacing corundum), only when the convection currents are low (drilling corrosion on electrode shelves). Beta-alumina is not observed in vertical portions of the walls in the melting area,
- primary corundum,
- primary baddeleyite (ZrO$_2$), being slowly dissolved by the glass.

The glass in contact with the worn AZS is enriched in alumina and zirconia, and depleted in lead (table 1).

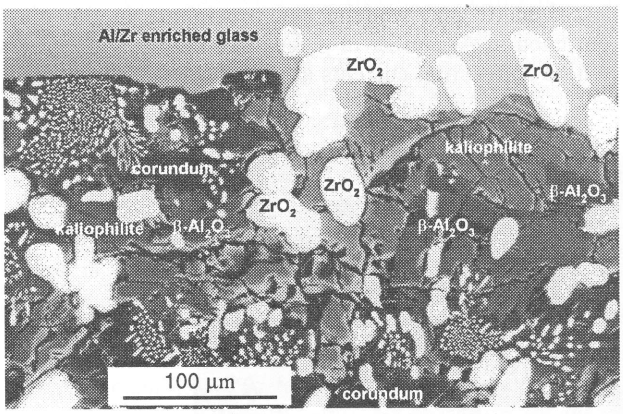


Figure 6. Section through a worn ER 1711 electrode block in the drilling corrosion area - SEM, polished section, backscattered electron image.

Corrosion of the AZS fused cast refractories in the feeder

The phases present in a worn ER 1681 stirrer in contact with glass are:

- leucite replacing the vitreous phase and a fringe of the corundum grains,
- primary corundum,
- primary baddeleyite,
- locally secondary vitreous phase enriched in potassium and lead.

The glass in contact with the worn AZS is enriched in alumina and zirconia, and depleted in lead.

Formation of wadeite (K$_2$O.ZrO$_2$.3SiO$_2$)

Wadeite found in lead crystal glass is reported in [6, 7]. Its formation in Ba-Sr alkali silicate glass in contact with zirconia refractories is reported in [5].

Cords associated with vitreous knots containing well-shaped wadeite crystals in hexagonal platelets can be found in the poured lead crystal glass .

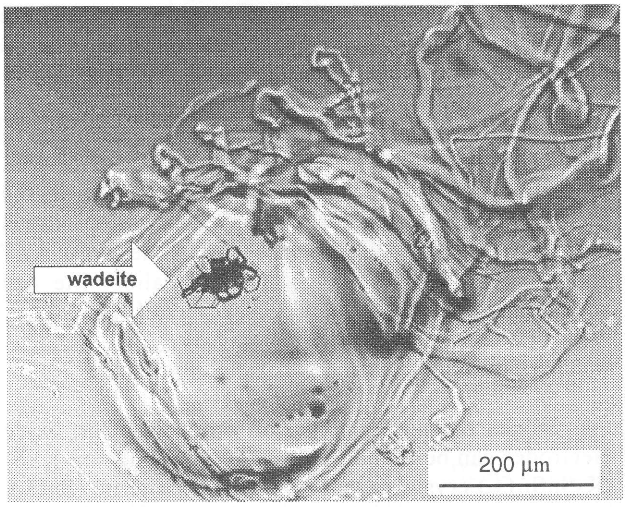


Figure 7. typical vitreous knot containing crystals of wadeite - PLM

In places where the convection currents are present, no well-shaped wadeite crystals were observed in the Al/Zr-enriched glass in contact with worn AZS. In the melting area, when convection currents are low,

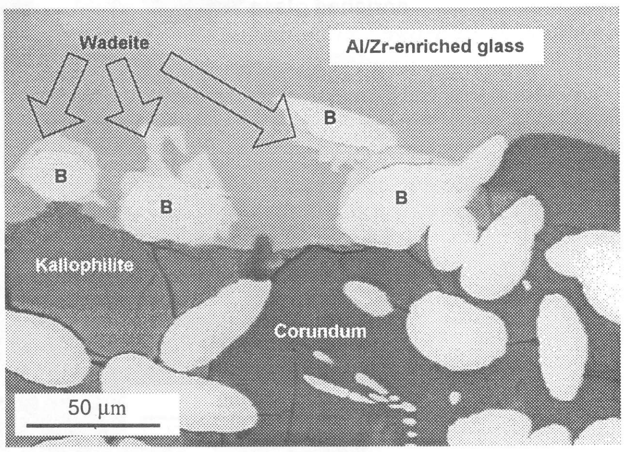


Figure 8. Section through an ER 1711 block in the melting area showing small crystals of wadeite - SEM, polished section, backscattered electron image.

Table 1. Composition of the phases for samples in the melting area.

(wt.%)	Glass in contact with worn AZS			worn AZS		
	Modified glass	glass in cracks	wadeite	leucite	kaliophilite	beta – alumina
Al_2O_3	7 to 10	6 to 8		24	34	92 to 95
SiO_2	60 to 67	45 to 60	47	56	39	0 to 1
Na_2O	2 to 3	3 to 4			1 to 5*	
K_2O	11 to 13	8 to 11	22	20	21* to 27	5 to 7
PbO	6 to 8	10 to 35				
ZrO_2	4 to 6	2 to 4	31			

* Na-enriched and zoned kaliophilite between glass and worn AZS in cracks

small wadeite crystals can locally be observed. These ten micrometer-sized crystals precipitate around baddeleyite grains being dissolved by the Al/Zr-enriched glass.

The Al/ Zr-enriched glass stays a long time in contact with the worn AZS in cracks. Wadeite well shaped crystals can be found there, as well as in the melting area and in the feeder. A layer of kaliophilite is observed in the melting area, between the worn AZS and the Al/ Zr-enriched glass. This kaliophilite can show zoning related to its sodium content [7].

Tin oxide electrodes corrosion products

Stones containing corrosion products of tin oxide electrodes can be found in glass. They usually are KSS_3 ($K_2SnSi_3O_9$) crystals associated with cassiterite (SnO_2). In some cases, zirconium may partially replace tin in the KSS_3 crystals.

Mechanism of corrosion of the AZS fused cast refractories

The corrosion process of the AZS fused cast refractories involving K_2O can be described as follows (table 2):

- potassium penetrates the vitreous phase which is readily changed into kaliophilite in the hot places of the furnace, or into leucite in other places,
- corundum is changed into potassic beta-alumina in the hot places of the furnace, or into leucite in the other places, if convection currents are low.
- the worn AZS is then dissolved by the glass which becomes richer in aluminium and zirconium.

Leucite and wadeite can precipitate in the glass enriched in Al and Zr in places like cracks and corners where convection currents are low.

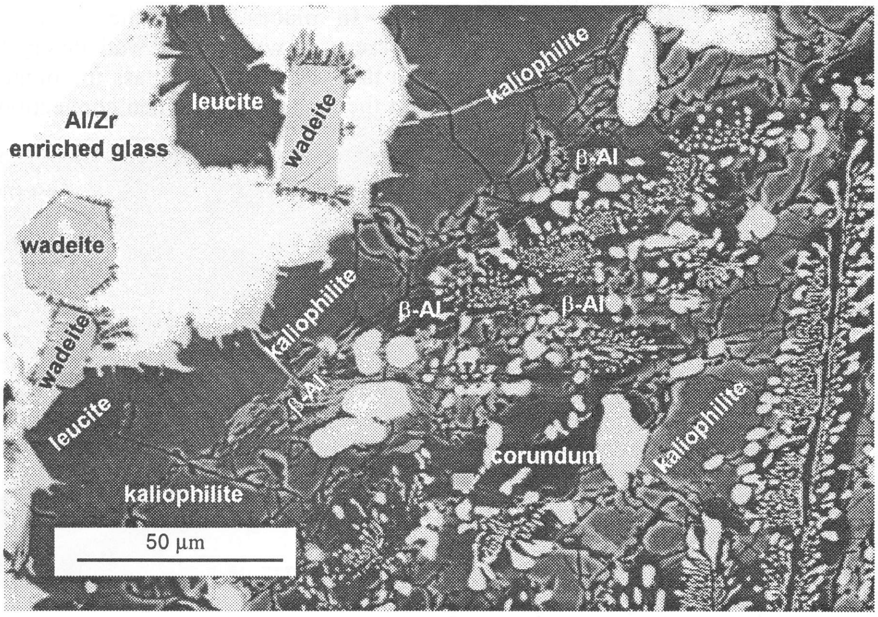
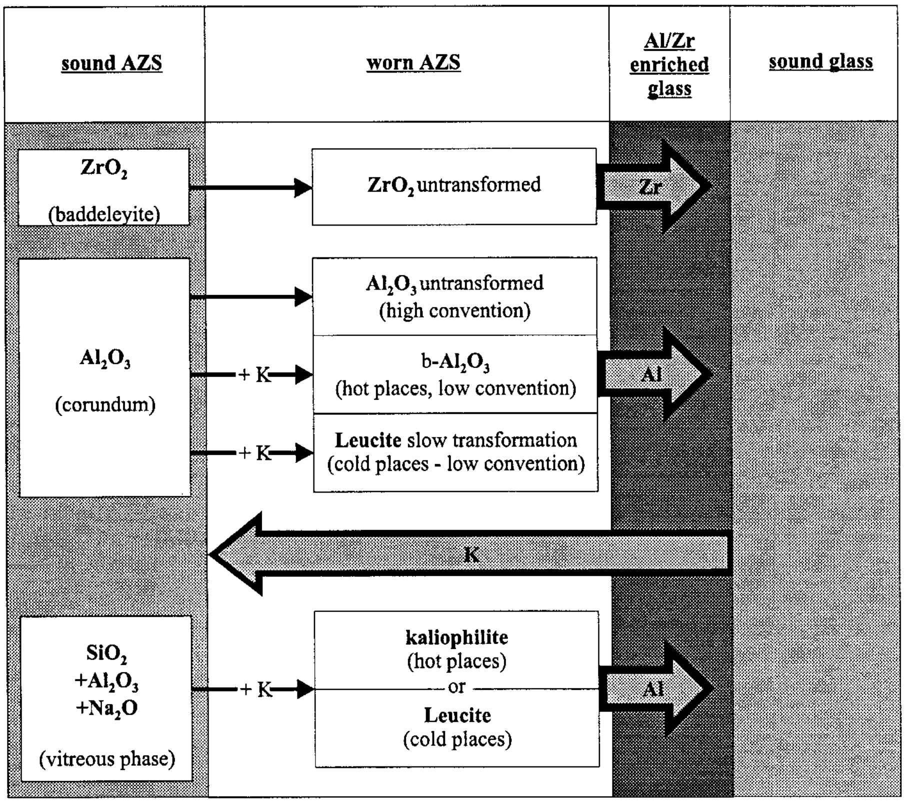


Figure 9. Section through an ER 1711 block in the melting area - crack showing crystals of wadeite - SEM, polished section, backscattered electron image.

Table 2. Mechanism of the corrosion of AZS fused cast refractories in contact with lead crystal glass.



The composition of the phases present in stones allows to trace them back to their source : kaliophilite in a worn AZS stone will show that it comes from the melting area. Beta-alumina in a worn AZS stone and / or wadeite in solution sacs will show that it comes from places with low convection currents.

CONCLUSIONS

The analysis of worn refractories in contact with glass is of major importance to trace the origin of defects in glass. This paper reports corrosion mechanisms for aluminosilicate and AZS refractories in contact with lead crystal glass in industrial conditions. Some chosen examples illustrate defects generated by this corrosion. Kaliophilite is found in hot places of the electric tank furnaces. Wadeite precipitates in Zr-enriched potash glass in low convection places. The corrosion of tin oxide electrodes leads to the production of tin potassium silicate.

Acknowledgement

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Submitted in English by the authors.

PŮVOD VAD SOUVISEJÍCÍCH S KOROZÍ ŽÁROMATERIÁLŮ V OLOVNATÉM SKLE

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Příspěvek popisuje mechanismus koroze žáromateriálů při tavení olovnatých obalových skel a některé vady spojené s touto korozí. Vzorky připravené z použitých žáromateriálů po demontáži pecí a různé vady skla byly zkoumány scanovací elektronovou mikroskopií.