When speaking about refractories, we must bear in mind the changes that take place continuously in this highly aggressive environment of glass furnaces. And this means that products used in the furnaces also need to be able to withstand the high speed of glass movement, improved furnace design and the extended life of furnace campaigns.

In this article P. Carlo Ratto discussed the developments of High Zirconia Fused Cast materials, and how the product might be evolved for the future.

When, almost 40 years ago, it was clear that a particular refractory lining niche, too large to be ignored, was still without a specific and optimized application, major fused-cast manufacturers and glassmakers started looking for a solution.

Among the primary bottlenecks in the glass contact refractory lining, throats have been (and generally still are) a critical weak point; just think that for a typical modern furnace producing 300 tpd for a campaign of 10 years, more than one million tons of hot glass moves at a relatively high speed in a throat with very few square meters of glass contact surface.

The traditional block lining of throats in soda-lime glass smelters was based on fused cast high-zirconia AZS (41 per cent) blocks. This application was fairly balanced with the application of low-zirconia AZS (32 per cent) in the sidewalls and pavers, when average furnace life was less than eight years and specific pull generally less than 2 tpd/sq.m.

However, with the intensive application of electrical boosting, improved furnace design, and the utilization of high-zirconia AZS (41 per cent) fused cast blocks for the entire sidewalls, campaign life has been exceeded by 10 years, with specific pulls of more than 2.5 tpd/sq.m. Under these boosted conditions (and other details such as glass temperature), all seriously increasing the corrosive stress of throat materials, what has been done to balance the life of throats?

Unfortunately, there was (and is) no univocal response to this understandable exigency. Throat cooling by means of conveyed air or water cassettes is effective to reduce leakage risks when the residual thickness of throat blocks is minimal but, in most cases, overcoating (some time multiple overcoatings) has been a common practice to extend throat life, progressively compro-
mising throat efficiency, since the glass intake point moves up too close to the glass surface with an excess of throat overcoating, bringing more polluted glass to the working end and, therefore, worsening the glass quality towards the end of the campaign.

The chrome move

One of the first effective solutions to this problem was the installation of chrome bearing blocks in critical positions, such as inlet beam and sleepers, covers. This regarded fused-cast chrome-doped AZS or aluminachrome and, more recently, the most effective isostatically pressed sinter chrome blocks. All these materials, at different degrees, have the advantage of not only having strongly improved corrosion resistance, but also maintaining the throat inlet profile unchanged and, therefore, maintaining throat efficiency for a much longer campaign lifetime.

Unfortunately, this great solution has one single but serious condition that indicates the inadvisability in a particular application niche. And here we’re speaking about glass discoloration due to traces of chrome in the produced glass, when dealing with extra-clear white glass and, particularly, when producing high-thickness items. It was the case of automotive lighting glass (now generally replaced by plastics) and it is the case of high quality tableware, decorative objects, white borosilicate tubing for medical devices and more.

Here we are, with the significant niche, orphan of a specific acceptable application.

Increasing the amount of zirconia in AZS fused cast, above the typical 41 per cent, has proven to be ineffective in terms of corrosion resistance, since already at 41 per cent the amount of corundum-baddeleyite pseudo eutectic is at a maximum and any further addition of zirconia only increases the presence of free Baddeleyite microcrystals surrounded by glassy phase. These crystals do not significantly contribute to the corrosion resistance, while they potentially increase the release of zircon stone defects. In fact, we must remember that resistance against soda-lime glass contact, for AZS fused cast, is solved by a so-called "passivation layer" that is none but a layer of high viscosity glass (high alumina, high zirconia) including a few primary zirconia crystals, adherent to the refractory like a skin. Alumina and zirconia are slowly dissolved through this passivation layer toward the matrix glass.

So, as a matter of fact, after experimental validation of these mechanisms, there was never an AZS refractory marketed at, say 50 or 60 or more per cent of ZrO2.

NEW ZR MATERIALS?

Molybdenum

Another way that was pursued to try to fill up the application niche, was the development of a new type of high zirconia (41 per cent) material, a so-called composite, with a Molybdenum pro-
file embedded inside the block, in strategic position, so that after corrosion of a thin layer of refractory, the metal is exposed to the glass (and not to free oxygen!) showing almost total corrosion resistance, keeping the throat profile in almost perfect shape. These blocks are theoretically a very elegant solution to the problem, since Mo metal is protected against “combustion” by the refractory in the heating up phases and then protected by glass contact, providing the glass covers the exposed Moly profile.

So, in spite of the high cost of these blocks, was this a universal solution for the critical application niche? Unfortunately, we must say no. In fact, moving from a theoretical to practical approach, we must observe that, unluckily, there are several “details” that can go wrong in the manufacturing of these special composite blocks, throat design, handling during furnace construction, and in furnace warm up. In a significant number of cases, glass did, in fact, infiltrate between the Moly profile and refractory body, with nasty consequence in terms of corrosion and glass defects. The inevitable consequence is that these types of blocks do not have a very widespread use and do not represent a final solution fitting the application niche.

So, here we are again, almost back at square one, with the application problem.

HZFC

It was about 40 years ago when a real invention was made in the domain of fused cast refractories, leaving the AZS range, producing a body that did not count on a passivation layer to resist glass corrosion. This was High Zirconia Fused Cast (HZFC), a composition around 95 per cent ZrO2, with lower silicatic glassy phase content compared to AZS and very low alumina content. The most important feature of this specialty product is the presence of monoclinic zirconia in the form of relatively large crystals in a very interlaced structure, with thin layers (cushions) of silicatic glassy phase between crystals.

This interwoven structure makes it impossible to release crystals at the glass-refractory interface.

Since Zirconia does not colour the soda-lime glass, these materials were looking promising to be applied in throats with the aim to balance high-zirconia-AZS sidewalls for high pull and long campaign life furnaces producing extra white glass.

But it did not take a long time to understand that the lack of a passivation layer formation (there is not enough alumina in the refractory) at the glass-refractory interface increased the dissolution speed of Baddeleyite crystals, particularly in applications like throat, where the glass speed (and therefore the renewal of the contact surface) accelerates this phenomenon.

As a matter of fact, the corrosion resistance of HZFC in contact with soda-lime glass, particularly in throat applications, did not significantly improve compared to traditional 41 per cent AZS. In some cases, the marginal advantage did not justify the very large difference in commercial price.

The bad news was that not even HZFC represented the most wanted wide range solution for the orphan niche application, and the game is still open for future improvements.

The good news was that a new product, with very peculiar characteristics was now available for applications other than soda-lime, and in the course of these 40 years this specialty has represented a very useful (if not essential) condition to enable the development of products that all of us use each and every day in several ways.

RESISTANCE ISSUES

The key factor for HZFC applications is based on the same facts that made it disappointing in terms of glass corrosion resistance: these materials do not generate any passivation layer at the glass interface, they do not have enough alumina to do so and the interlaced structure of their large Baddeleyite crystals make it very hard to strip out crystals, while the zirconia slowly dissolves in the glass, generating relatively large amounts of glass at very low zirconia pollution.
All these conditions are the basis for a refractory having extremely low potential of defects: no alumina cords, no cat-scratches, no primary/secondary zirconia stones, no Al/Zr knots (coming from the detachment of passivation layer shreds).

Amazing enough, this refractory was there, already before the marketing requirement revealed itself. The first relatively large volume application for these special fused cast refractories was, therefore, in CRT TV glass, particularly for glass panel production. For these items it is enough to say that one single defect in a piece (that can weigh a few kilograms) can easily lead to the rejection or declassing of a whole CRT. The premium in price of these HZFC refractories was, therefore, well justified by a substantial increase in yield of an extremely quality-demanding and expensive glass.

Unfortunately for the refractoryists who invested in developing HZFC (all the western players), the CRT market underwent a dramatic decline in just a decade, due to the advent of FPD devices.

Apart from some minor utilization in Borosilicate, the other significant application was, and still partially is, in lead crystal furnaces, particularly for electrical shelf furnaces, where HZFC products have been successfully installed in pavers (thanks to their resistance to downward drilling from Pb droplets), and partially successfully in tin-oxide (SnO2) electrodes holders. Once more, the decline of the high-quality houseware market in a generally depressed western economy, the competition of other non-glass items, caused a significant decline in these types of production, where quality was, once more, the driving force for HZFC application.

As often happens in our everyday lives, overcoming obstacles leads to new opportunities. The same consumable that caused the almost death of CRT opened the way for yet another extremely demanding type of glass or, to be more precise, to a relatively large array of special glasses, representing the substrates of different families of flat panel devices, ranging from our smartphones to computers, and large home-theatre television screens.

These substrates, based on different chemistries and different manufacturing technologies, have in common the extremely high demand for quality; and this requirement leads to the application of HZFC. As a matter of fact, these extremely thin special glasses can be produced with float-like or “fusion” technology by a few globalized companies, but basically all of them utilize HZFC in the hot end of their special manufacturing processes. Particularly in the “fusion” process, the smelting units are largely (if not exclusively) electrically powered and the special (aluminate) glass exhibits unusually high electrical resistivity. Among the various peculiar characteristics of HZFC, its high temperature electrical resistivity is lower than any AZS (typically half that of a high zirconia AZS) and can be close to the aluminate glass to be produced. Regular HZFC, therefore, could potentially become critical when installed in an electrically powered furnace smelting high-resistivity glasses.

**HZFC DEVELOPMENT**

The major western refractory makers producing HZFC have, in recent decades, been investing seriously in developing special versions of HZFC with high-
er electrical resistivity at working temperatures, basically working on glassy phase chemistry to reduce its electrical conductivity.

This has been not an easy task, and sometimes involved compromising other variables, particularly corrosion resistance, content of the glassy phase, thermo-shock resistance or dimensional stability at high temperatures.

As a consequence, due to the variable intensity of the problem (glass resistivity), answers to the issue have led to multiple optimized solutions, in other words, to the development of a family of high resistivity HZFC (or HR-HZFCn) products, tailor-made for specific customers.

Since there are different ways to play with the glassy phase to increase its resistivity, and because the relevant solutions are patented, the first manufacturers to do so followed the easier paths, while others have to struggle with more complex and sometime expensive ways to go.

For a few decades, HZFC and HR-HZFC have been a nice specialty market of relatively low volume but great profitability, providing a progressive recovery of the serious R&D investments.

In the very recent period, at least one Chinese low-cost player has started production of two types of HZFC, determining the beginning of commoditization for this latest profitable specialty.

Among myths and misunderstandings concerning HZFC, therefore, we can summarize:

- HZFC refractories are generally more resistant to glass corrosion: **WRONG**
- HZFC can be conveniently used for extra white soda-lime throats: **WRONG**
- The main feature supporting HZFC application is glass quality: **CORRECT**
- Regular HZFC can be used for all FPD support glasses: **WRONG**
- Special HR-HZFC is suitable for all high-resistivity glasses: **WRONG**

If we look at the history of fused-cast refractories like a novel embedded in the history of glassmaking, then HZFC has been, and is, some sort of a bizarre character, often looking for a proper allocation in the full picture, always struggling to fill up the best application niche.

People have been looking at this specialty with hopes that have been sometime frustrated, and yet this product has always been there, waiting to deliver the necessary performances to develop consumables that make our everyday life unique.