Malgré les progrès constants dans les cuves de fours de fusion, les gorges restent, dans beaucoup de cas, un point noir pour la durée de vie d’un four. Une attention particulière a été portée à la possibilité d’augmenter la durée de vie de cette partie du four, et ainsi de préserver sa fonctionnalité et son intégrité physique.

Différentes solutions de réfractaires ont été appliquées avec succès, mais aucune d’entre elles n’est éligible pour une large gamme d’application : les réfractaires au chrome (réfractaires électrofondus et iso-pressés) sont des options sûres pour une vie plus longue de la gorge, mais ils ne peuvent pas être utilisés lorsque les verres sont sensibles à la décoloration. Les électrofondus à haute teneur en zircone (HZFC) ne fonctionnent que pour les verres spéciaux, mais leurs performances ne peuvent pas toujours compenser le coût élevé dans certaines applications spécialisées en verre.

Sur le plan technique, une solution plus générale est l’utilisation d’habillages métalliques spéciaux. Parmi les métaux de transition, le premier à être utilisé pour les habillages et le sputtering a été le platine et les alliages platine, mais l’investissement financier élevé réduit le champ d’application à de petites portions des fours de fusion pou verres spéciaux. Le molybdène, à un prix bien moindre que le platine, est le meilleur candidat parmi les “métaux réfractaires” ; son utilisation est devenue possible après que des traitements plasma superficiels et des traitements thermiques très efficaces aient été mis en œuvre afin de protéger efficacement le molybdène qui s’oxyde rapidement et s’évapore dans l’air à des températures aussi basses que 600 °C.

Les gorges renforcées au molybdène sont actuellement disponibles avec deux approches techniques distinctes : un bardage métallique des blocs réfractaires critiques ou bien des blocs de composite électrofondus AZS-Mo où la feuille métallique est intégrée dans un bloc AZS à haute teneur en zircone. Les deux solutions technologiques ont en commun le risque défaillance. Pour une succession possible d’événements, le verre peut s’écouler derrière le film métallique, stagner dans le bloc réfractaire et ouvrir à terme une voie alternative à la WE.

Quelque chose peut et doit être fait pour réduire le risque de ce type d’”accidents”. Les utilisateurs doivent être conscients que jusqu’à présent cette situation reste un danger potentiel. Une attention importante aux détails dans la conception de la gorge, dans la manutention des blocs ou du revêtement, dans l’assemblage, ou encore dans l’échauffement doit être apportée de façon à minimiser le risque d’échec.

In spite of continued evolution in glass fusion tanks, in most cases throats have maintained the role of a bottleneck in the campaign life extension. Special attention has been paid to the possibility of increasing the life of this furnace section, preserving its functionality as well as the physical integrity, in order to match the wear of other furnace sections.

A few different refractory solutions have been successfully applied, but none of them have granted a wide range application feasibility; chrome refractories (fused cast and iso-pressed) are intrinsically safe options for a longer throat life, but cannot be used when glasses are sensitive to discoloration. High Zirconia Fused Cast (HZFC) only works for special glasses, while its performance premium cannot always compensate the high cost in some specialty glass applications.

A more general solution, on the technical side, is the use of special metal claddings; among transition metals, the first to be used for claddings and sputtering was Pt and Pt-alloys, but the relevant high financial investment reduces the range of application to small portions of furnaces smelting special glasses.

Molybdenum, being almost two orders of magnitude cheaper than Pt, is the best candidate among “refractory metals”; its use has turned into a real possibility after that
INTRODUCTION

Glass furnaces performance has undergone continuous improvement throughout the last century, increasing campaign life from a few months up to over ten years for container glass, and, fifteen for float. Within the same timeframe, specific pull has also increased by at least fivefold, bringing the glass furnaces’ combined efficiency to a huge progress in terms of tons of glass produced in a given campaign, for a given fusion surface. All this has been possible through furnace design evolution, application of new types of refractories (mostly fused-cast), fusion temperature increase and continuous development of fusion know-how.

Yet, during this process, throats have been, in most cases, among the most critical areas of the fusion tank, particularly for the oil/gas fired container furnaces. After the definitive success of AZS fused cast refractory in glass contact, throats have been almost invariably lined with AZS41 cavity free large blocks, in an attempt to balance the throat life with the rest of the furnace, trying to reduce any serious campaign life bottleneck; furnace designers and technologists have also optimized the throat geometry and position in various ways (e.g. recessed and sloped throat design), so as to reduce thermal and mechanical stress in the area.

But, with the unrestrainable increase of furnaces productivity, high performance AZS have been progressively installed in most glass contact areas, to the point that modern container furnaces are almost exclusively lined with AZS41 with reduced or no-cavity casting technique. This has made throats a more alarming critical area, sometimes a limit to the campaign life. Forced air cooling and even water cooling boxes have been applied to the external faces of throat blocks, particularly at the glass inlet edge, with some advantage and a number of risks. Another option has been the application of overcoating tiles to prevent glass leakage, typically at the glass inlet edge, when the throat erosion is getting critical: while this practice somewhat resolves the glass containment function, it clearly does not address the loss of throat functionality that occurs when the upper limit of the throat opening moves up due to corrosion, and more surface glass is sucked in the throat flow, moving to WE. It is obvious that reducing the criticality of a throat means maintaining, as long as possible, for the campaign life, its shape and integrity. Under this scenario, for those furnaces and applications having this severe problem (one typical example is the borosilicate for tubing), we must conclude that AZS fused-cast refractory have become critical in application, and something new must be done.

ALTERNATIVE REFRUCTORY OPTIONS

The first option proposed was a modified AZS fused-cast, supplemented with about 27% of Cr₂O₃, or alumina-chromium fused-cast with the same amount...
of eskolaite, but no zirconia and very little glassy phase. Both these castings have been utilized in throats, replacing the most critical blocks like facers and sometimes sleepers, with overall good performance: chromium based castings, generally, have proven efficient in maintaining throat shape and integrity for a longer campaign. (figure 2)

A remarkable further improvement came when, thanks to development of iso-pressing technology, large iso-pressed bodies became commercially viable and high-chrome blocks were shaped and fired with appropriate cycle under controled atmospheres; iso-pressed chrome blocks exhibit very low porosity and unparalleled textural homogeneity (to the contrary of fused cast blocks) and have a superior corrosion resistance in very stressed applications like weir (submerged, cross) walls, DH corners (under metal line!) and, of course, throats.

Unfortunately, there is an intrinsic limit to this application, due to the fact that Chromium is, among transition metals, one of the most powerful glass discoloring agents. Thanks to the great corrosion resistance, the leakage of chromium into glass is relatively limited and of course depending on the specific operational conditions; in very general terms, when only a throat (sleepers and covers) is lined with chrome bearing bodies under typical conditions for a soda-lime container, you might expect to find about 5 ppm of chromium under typical conditions; in very general terms, when only a throat (sleepers and covers) is lined with chrome bearing bodies under typical conditions for a soda-lime container, you might expect to find about 5 ppm of Cr₂O₃ contamination for the campaign life. Of course this figure will proportionally increase when chrome bearing refractories are installed in other sections, and particularly in the weir wall, where the glass contact area is extensive.

Of course, 5 or even 50 ppm of chrome oxide can be totally negligible for most soda-lime container glasses and for most glasses where chrome compounds are part of batch composition or pollution; this situation includes most bottle and jar production. Nevertheless, there is glass production where even a tiny chrome pollution cannot be accepted.

Examples are extra clear glasses for thick-body housewares and white borosilicate tubing for pharmaceutical applications. For these and other application niches, therefore, chromium bearing refractories are not a viable solution for throat reinforcement. Something different must be proposed.

When, a little more than thirty years ago, the high-zirconia fused cast refractories (HZFC) were developed, for a short time there was a hope that these materials, made of about 95 % ZrO₂+HfO₂, could have been a solution to the problem of reinforcing throats where chrome was not a viable option.

Unfortunately, it was immediately clear that HZFC refractories did not represent an answer for soda-lime glasses simply because the advantage in corrosion resistance was negligible or nil.

The apparent oddity is easily explainable by the observation that AZS corrosion resistance depends on the development of a “passivation layer” at the glass/refractory interface: this thick layer is mostly high viscosity glass saturated with alumina, coming from AZS composition. HZFC fused-cast refractories do not develop any passivation layer simply because they do not have important alumina content; therefore Baddeleyite crystals simply dissolve in the contact glass and its speed depends on the glass velocity tangential to the surface. Unfortunately, throats are possibly the highest glass velocity zone in a typical smelter.

Glasses other than soda-lime and special furnace designs have proven to be better candidates for HZFC applications; among these, electrical furnaces for lead-crystal, particularly in the bottom area have benefited from the low susceptibility to downward drilling and the very low tendency to yield defects to crystal; other type of glasses like fluorine opal and borosilicate have manifested mixed performances when HZFC was installed in throats and risers, since not in all cases the benefits/cost ratio was advantageous, considering the relatively high HZFC cost versus AZS41.

In conclusion, the high zirconia fused cast was really successful in specialty glass application, mostly thanks to the low tendency to generate defects (initially to the declining CRT TV glass and today in the expanding LCD glass production), but has not been a substantial help in improving throat resistance to corrosion.

REFRACTORY METALS AS VIABLE ALTERNATIVES

So, what today are the remaining options for balancing wear of highly stressed throats (as well as other critical areas), when chrome refractories cannot be used?

For a long time, platinum/rhodium alloys cladding has been installed in specific areas of furnaces, such as fiberglass forming bushings as well as spout, plungers, tubes, delivery orifices and other forming devices in special items like high quality mechanical crystal. In
several cases, when possible, the cladding was replaced by metal sputtering, to obviously reduce the amount of precious metal used. In spite of the perfect stability, resistance to molten glass attack and to oxidation, and despite the high recoverability of the metal (usually better than 95 % in weight), the very large investment per unit of surface protected has always limited this application to very special cases and where small surfaces have to be shielded.

The major limit for a Pt-alloy cladding has been the scarce mechanical characteristics at high temperatures and the relatively low temperature of fusion, besides the obvious cost factor.

More recently, another special group of transition metals has been considered for the very special characteristics; refractory metals properly said are Tungsten (W), Molybdenum (Mo), Niobium (Nb), Tantalum (Ta), Rhenium (Re). These metals share some common characteristics, such as their extremely high melting points (above 2400 °C), their strength and high-temperature stability. Several applications exploit these properties: tungsten lamp filaments operate at temperatures up to 2800 °C, and molybdenum furnace windings withstand 2000 °C. However, a problematic cold “fabricability” and a very poor resistance to oxidation at high temperatures are handicaps for these special metals.

Molybdenum, thanks to its outstanding thermomechanic and electrical characteristics, as well as its resistance to molten glass corrosion at high temperatures, was a perfect choice for electrodes used in boosting as well as all-electrical smelters. Mo in electrodes has been, for a long time, the standard application, besides Tin Oxide in lead crystal and some other special glasses.

With this remarkable “reference”, and thanks to its relative low cost (1 Kg of Mo costs only a bit more than 10 g of Pt), Molybdenum was a great candidate for refractory blocks cladding but, for quite a while, the main application problem was its sensitivity to oxidation in environmental conditions; as a matter of fact, this metal oxidizes (and sublimates) rapidly, in air, at just above 600 °C and cannot obviously withstand a furnace warm-up process when, at temperatures up to 1000 °C and for several tens of hours, refractory surfaces are exposed to free oxygen, before being covered by smelted glass. Several patents have been deposited for the usage of moly claddings or moly piping in special glass smelters (example borosilicate), where the metal was protected by inert gas purging before glass fusion temperatures, but the risk associated to these practices has been limiting the practical applications to selected proprietary processes Molybdenum cladding and AZS-Mo composite refractories have found more application chances fol-
following the realization of a patented protective plasma coating (and subsequent annealing) that proved to be very effective in protecting Mo from oxidation for extended periods of time, to the point to guarantee stability for 5000 hours at 1200 °C and 50 hours at 1600 °C. These performances are well above the demand for heating-up a furnace with protected-Moly cladding in throats or other critical areas. The same plasma coating (with Si and B) has proved effective for another application, called AZS-Mo composite, that has been developed and marketed by leading fused cast manufacturers in recent decades.

**MOLYBDENUM CLADDING AND AZS-MO COMPOSITES**

These are two different technologies to exploit the same fundamental properties of Molybdenum, as said above, the extreme resistance to high temperature, glass corrosion and good mechanic properties at operational conditions. Moly cladding consists of metal sheet armor, of typically 6-10 mm thickness, profiled to cover the glass-contact refractory surfaces of the furnace section to be protected (i.e. the throat). Since workability of this metal is not good, complex shapes are generally done jointing and screwing simpler components with moly hardware. All metallic surfaces are plasma coated with protective layer and annealed. In case of throat cladding, armor is generally made of a front plate (covering the cover block, sleepers and partially adjacent blocks), an inverted-U tunnel connected to the front plate (protecting sleepers and covers for all the throat channel length) and one or more “fins” or flanges normally connected to the front plate, which are to be inserted between refractory blocks and therefore anchor the whole cladding to the refractory set up. As we will see, the main concern related to these applications is the difficulty to make the rigid metal cling to the refractory assembly, the need to have the refractory working surfaces ground flat, and to ensure that during furnace warm up (and subsequent dilatations with almost inevitable minor block movements) these perfect fitting conditions are maintained.

AZS-Mo composite blocks are special fused cast blocks, normally AZS41, that contain, inside the block one profiled moly sheet that lies several millimeters under the working (hot) surfaces of the fused cast block. To manufacture these composites, the metal sheet is positioned inside the sand mold by ceramic suspensions and then the block is poured, embedding the metal shield inside the block. Throat critical composite blocks are designed in order to leave, after corrosion of the initial millimeters of refractory, most of the throat stressed surfaces shielded by metal.

The feasibility of these composites is based, among other factors, on the low thermal expansion coefficient of moly, that is rather close to the average value of AZS refractories, though it obviously does not include the well known zirconia transition flex.

The main concern in this technology is to ensure the appropriate grip between refractory and moly and to prevent cracking (and potential spalling) of the thin refractory layer above the metal during block annealing and machining or during furnace heat-up; to reduce the latter risk, critical (inserted) surfaces are often covered with a thin insulating fiber panel (glued) to reduce thermal stress in the first stages of tank warm-up. The panel will eventually dissolve in the initial glass.

**INTRINSICALLY SAFE APPLICATIONS?**

Since Molybdenum has proven resistant against a wide range of glass compositions and physical conditions, can we say that the two approaches to moly reinforcement are the final solutions to the throats wear balance for chrome-sensitive glasses? In my opinion, the answer, unfortunately, is not “yes”. Both technologies share the same bug, that is the lack of intrinsical safeness. In fact, both technologies share “accidents” with a common factor that we can depict so: sometimes, glass infiltrated behind the armor, then through cavitation infiltrated deeply between metal and refractory blocks to the point to get to the end of throat channel and eventually created alternative communication between fusion tank and WE.

The glass moving through this erosion path was heavily polluted with refractory corrosion products, blisters, knots, and contaminated directly the WE or riser, with almost no chance to digest.
When this happened, glass quality was deeply compromised with all the imaginable consequences. In most of these accidents the moly shield was intact and on site, so almost invariably the protective (anti oxidation) treatment worked well; simply the glass found its way behind the armor. In the case of metal cladding it is not hard to imagine that, as a consequence of bad clinging of the front plate, glass infiltrated laterally when only one horizontal flange was used. As said, several factors can harm the front plate clinging, most of them related to job quality and other variables hard to control. Surely, the use of connected horizontal and vertical flanges, inserted in the joints relevant to cover and sleeper blocks, would largely reduce the risk of glass infiltrating behind the armor, forcing glass to go round the fins in a much colder zone of the assembly and therefore freezing the cavitation process. In the case of AZS-Moly composite blocks, since joints between normal and composite (as well as composite-composite) blocks are not protected (metal only start millimeters under surface), it is possible that glass infiltrates typically the horizontal joint of the cover block and finds its way behind the moly sheet, reproducing the above described mechanism. We could debate forever why sometimes it happens and fortunately most times it does not. Also here, erratic causes related to work quality, as well as overall design factors can make the difference. To improve the safety of the application, fused cast manufacturers should extend the profiled metal sheet insert into the joint face a bit more, increasing its edge curling. This will increase the labyrinth effect, therefore forcing glass to infiltrate colder zones of the refractory, on its way behind armor. As said, for moly cladding as well as AZS-Moly composites, this is what I call “not an intrinsically safe solution”.

**IN CONCLUSION**

Up to now, there is no better solution in cases when chrome refractories cannot be used and throats are critical to the campaign life. Molybdenum cladding and AZS-Moly inserted fused cast blocks are viable solutions, but suppliers and glassmakers must recognize that there is a risk associated to these applications. In case of accidents, the potential damage is much bigger than the value of the application; in extreme cases a furnace can undergo premature shut down and the throat replaced, due to heavily compromised glass quality. Extreme attention to details in design, set up, erection, warm-up, must be paid to reduce the risk of accidents that, unfortunately, will remain. This, until the next “intrinsically safe” technological innovation will become a reality.

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**Figure 6.** Depending on a number of factors hard to control, it can happen that glass infiltrates behind Mo armor and cavitates into refractory, with severe glass quality impairment.

**Figure 7.** Molybdenum cladding with connected horizontal and vertical anchor fins represents a significant improvement to reduce glass infiltration risks.