Progress in Platinum Group Metal Coating Technology, ACT™

COATED COMPONENTS IMPROVE THE GLASS INDUSTRY

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Refractory ceramics have long formed a vital part of the glass making and glass processing industries. Due to market pressures these industries are moving towards increasingly higher quality products and progressively improved plant efficiency. However, significant improvements to the refractory ceramics are difficult because of the range of properties which they are required to have. This second paper on ACT™ (Advanced Coating Technology) using platinum group metals, describes the latest developments and advantages conferred by ACT™ coatings to the various ceramic forehearth components.

An earlier paper on ACT™ coating technology explained the principles of its application and its potential uses for the glass manufacturing industry (1). It described the protection that could be achieved by using platinum coatings on nickel-based alloys, and gave details of the very earliest service performance of ACT™ platinum-coated tri-level thermocouples on ceramic substrates. The latest progress in ACT™ technology for ceramic thermocouples and for the very diverse refractory ceramic substrates which are used in the forming end of glass making furnaces, are presented here (2–5).

Materials in the Glass Industry

The glass industry provides a rigorous test for any potential containment material for molten glass. Ceramics perform the bulk of this service, and even though manufacturers of ceramics have been successful in progressively developing ceramics with improved properties they suffer limitations in use, so opportunities exist for materials that have higher levels of corrosion and erosion resistance; these are properties which the platinum group metals can enhance.

Platinum is relatively non-reactive with most glass melts and glass vapours at temperatures of up to approximately 1450°C. At the higher temperatures, however, the life of conventionally fabricated sheet metal platinum can be limited by grain growth, and therefore alloying with other platinum group metals may be beneficial. Alternatively, the use of grain stabilised materials substantially reduces the problems caused by grain growth. Johnson Matthey was the first to develop platinum group metals and alloys containing very fine, uniform dispersions of oxide particulates (6). The alloys, designated ZGS (Zirconia Grain Stabilised), are subjected to special processing during manufacture which, in combination with the oxide dispersion, promotes the formation of a high aspect ratio grain structure. Thus these alloys are extremely stable structurally, even at very high temperatures, and exhibit the highest tensile strengths, creep properties and general levels of durability of all comparable platinum group metals and alloys. Therefore ZGS alloys are eminently suitable for glass industry applications (7).

Cladding of Materials

By using sheets of platinum or platinum alloys, it is quite possible to fabricate furnaces, channels and consumables for glass processing (8).
Fig. 1 Standard assembly design for an ACT™ coated tri-level thermocouple assembly; the assembly length, coating length, coating thickness and coating material are selected according to customer requirements.

Indeed, for the highest quality glass products, such as optical and lens glasses, this is already done. However, capital cost is high because of the thickness of sheet that is needed, and may only be justified for the highest added-value products. A less costly method is to clad ceramic or molybdenum substrates with sheets of platinum group metals. In this way the amount of

Fig. 2(a) ACT™ 10 per cent rhodium-platinum coated mullite thermocouple sheath after being in service for 27 months in container glass. The coating has provided excellent protection to the underlying ceramic substrate.
(b) A traditional 10 per cent rhodium-platinum clad tri-level thermocouple sheath after service in container glass.
the platinum group metal employed is significantly reduced, while the strength and corrosion resistance of the component is maintained. However, there are limits beyond which the thickness of the platinum cladding metal cannot be reduced, without hindering fabrication or service requirements. To overcome this restriction Johnson Matthey introduced its ACT™ coating technology which allows coating thicknesses as low as 175 μm to be used.

**Thermocouple Assembly Design with ACT™ Coating Technology**

The first exploitation of ACT™ technology was for the protection of thermocouples used in the arduous service environments associated with the intrusive monitoring of glass temperatures in forehearths, or in melting furnaces (9). The early ACT™ system had been extensively investigated and analysed in tested and untested conditions before field trials on thermocouple assemblies were undertaken. Early field trials were performed in a forehearth for container making where the components were subjected to temperatures of up to 1200°C in flint, amber and green glasses successively, at times up to 1000 hours.

The first commercial products were sheaths for tri-level thermocouples used for measuring temperatures at various depths in molten glass as it flowed down the forehearth. The advantage in using Johnson Matthey ACT™ for thermocouple sheaths, compared with conventional cladding, is that the standardised basic assembly design can be customised for assembly length, coating length, coating thickness and coating material, according to customer requirements, see Figure 1.

Mullite thermocouple sheaths should be used at temperatures below about 1400°C, primarily because they have better thermal shock properties than alumina. Although mullite may be used at temperatures as high as 1700°C, the environmental conditions in the melting zones of glass furnaces (where these temperatures may be approached) are often extreme. Therefore, for temperatures above approximately 1400°C an alumina substrate should be selected.

**Present Status of ACT™ Forehearth Thermocouples**

Forehearth thermocouples, and in particular tri-levels, are used to measure the glass temperature profile both across the width of the forehearth and in the glass depth. This allows total control over forehearth firing cycles, and thus provides controlled viscosity of the glass gob leaving the furnace. Control of viscosity is

<table>
<thead>
<tr>
<th>Country</th>
<th>ACT™ coating type</th>
<th>Glass type</th>
<th>Service life in months</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>6</td>
<td>Failure of uncoated Ni-Cr substrate</td>
</tr>
<tr>
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<td>10%Rh-Pt</td>
<td>Flint</td>
<td>27</td>
<td>Mechanically damaged; removed for examination</td>
</tr>
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<td>Amber</td>
<td>32</td>
<td>Still operating</td>
</tr>
<tr>
<td>Scandinavia</td>
<td>10%Rh-Pt</td>
<td>Fibre</td>
<td>28</td>
<td>Still operating</td>
</tr>
<tr>
<td>Holland</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>23</td>
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<td>Amber</td>
<td>12</td>
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<td>Flint &amp; amber</td>
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</tr>
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<td>Flint &amp; amber</td>
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<td>Platinum</td>
<td>Amber</td>
<td>17–19</td>
<td>Still operating</td>
</tr>
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Typical Service Lives for ACT™ Coated Mullite Thermocouple Assemblies in Glass Making Forehearths

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Fig. 3 Optical micrograph of a section through 10 per cent rhodium-platinum cladding after service in container glass. Note the high level of porosity within the structure of the cladding and the presence of glass between the cladding and the underlying substrate.

essential to ensure that the gob weight may be maintained within the tight tolerance band required, for example, in the production of glass containers by the NNPB (narrow neck press and blow) process.

ACT™ coated sheaths are already installed worldwide in numerous plants in full scale production. The success of the coating technology is demonstrated by the service lives, now in excess of 2.5 years, shown in the Table.

Comparison between ACT™ Coated and Traditional Sheet-Clad Assemblies

The second thermocouple assembly referred to in the Table entered service in May 1992 at PLM Redfearn’s Barnsley plant. Approximately 200 mm of its mullite sheath was coated with ACT™ 10 per cent rhodium-platinum to a thickness of about 200 μm, thickening to 250 μm at the glass line. The thermocouple ran continuously until its removal following mechanical damage during forhearth repair work in September 1994. It had been fractured during the repair work in the uncoated ceramic where it had rested within the forhearth roof.

The thermocouple assembly was visually examined, evaluated, fully destructively analysed and compared to a traditional clad tri-level thermocouple sheath with a cemented ZGS 10 per cent rhodium-platinum cladding that had been in service for several years in a forhearth at the same container manufacturer (10, 11). The cladding had an original thickness of at least 500 μm.

On visual examination the ACT™ 10 per cent rhodium-platinum coating, and particularly the portion that had been submerged in the molten glass, was found to be in excellent condition, see Figure 2(a). The traditional clad product also appeared to be good, Figure 2(b). However, further examination of the clad thermocouple assembly revealed a significant amount of pore development within the structure of the cladding, Figure 3. This degradation is serious since it would be expected to promote considerable mechanical weakening.

Alloy cladings are essentially separate structures from the underlying ceramic sheathing and are expected to have inherent mechanical strength. When the strength is compromised, as happened here, the integrity of the whole assembly must be at risk. A reduction in the mechanical strength of the component could result in thimble failure and loss, with consequential damage to the thermocouple element.

In comparison, ACT™ coated thermocouple sheaths are simple composite structures. They do not lose integrity in the same way as clad products since the mechanical strength of the platinum group metal coating derives from its intimate contact with the substrate sheath. The ACT™ coating had fully protected the underlying ceramic sheath from glass corrosion, even at the critical air/glass interface. It had performed successfully for 27 months in a molten glass environment, and could have continued in service.

The maximum service life of an ACT™ coated thermocouple assembly is therefore still
unknown, currently being 32 months operating in a forehearth in Scandinavia, as shown in the Table. Ultimately service life will be dictated by specific operating and environmental conditions.

**Development of ACT™ Technology for Forehearth Consumables**

The natural development of ACT™ coating technology was into forehearth consumables and these applications are achieving major success, as the following case studies illustrate.

Glass composition and chemical homogeneity are largely determined by control at the melting stage and during conditioning of the glass. However, the feeder of the forehearth is crucial for the effective manufacture of components and dictates the shape, weight, thermal homogeneity and compositional homogeneity of the glass gob from which the products are made. The introduction of foreign material or defects at this stage in the manufacture will almost certainly have a discernable and detrimental effect.
on the final product. Thus, the performance of the forming end components: spout bowl, plunger, tube and orifice ring, requires careful control.

For the more expensive and difficult glasses, the quality of the glass in the forming end has often been achieved by the use of components made of massive amounts of platinum group metals, and ACT™ coating technology is unlikely to replace all of this use. However ACT™ technology will enable manufacturers who presently produce lower quality optical and heat resistant glasses to upgrade their products and develop into other markets. For container makers the opportunities presented by ACT™ platinum coatings for forehearth consumables are described below.

**Spout Bowls**

The spout bowl is located at the end of the forehearth, see Figures 4 to 6. The glass flowing down the forehearth, which may be 1200 mm wide and 150 mm deep, is funnelled through a hole in the spout bowl into the orifice ring. Therefore the ceramic bowl, especially the leading edges of the basal hole, is subjected to extremely erosive and corrosive conditions due to the passage of high volumes of molten glass.

If erosion takes place it has a detrimental effect on the maintenance of gob weight control and in some product types defects, such as cord and stones, may be formed. Erosion can also make it impossible to close off the glass flow to allow the orifice ring to be changed, so the whole spout bowl has to be removed and replaced.

Changing the spout bowl is a major operation, requiring the glass in the forehearth to be “frozen off” while the old bowl is removed. Installing a new bowl takes the major part of a shift, and re-establishment of a flow of high quality glass may take several hours.

Thus, changing the spout bowl causes major downtime and production loss, and while it may be possible to schedule changes to coincide with other downtimes, the true cost can be very high. Clearly anything which can extend the intervals between changes, or improve the coincidence with other downtimes, must be beneficial. The following service experience of PLM Redfearn, Barnsley, illustrates that a spout bowl ACT™ coated with platinum can provide these benefits.

The alumino-silicate bowl, installed in May 1993, was in a forehearth used for green glass production. As can be seen in Figure 7, the bowl was partially coated only in the most critical region, that is, around the exit hole. No problems were reported at any time throughout its service, although by December 1993 there were concerns about cracks which had developed in the refractory substrate. While not causing leakage, under normal circumstances the cracks would have been sufficiently serious to indicate that the bowl might not survive until the next scheduled break for maintenance. In fact the ACT™ coating sustained the bowl for a further full year.

When the bowl was finally removed at a planned shutdown it had been in service for...
20 months. The area of the bowl carrying the ACT™ platinum coating was separated from the bulk of the ceramic and returned for examination.

The ACT™ coating was found to be intact over the major portion of the original surface, see Figure 8. The refractory substrate was in two pieces, resulting from cracks in the ceramic which had developed after only a few months of service. The regions of the coating that were not associated with any ceramic substrate cracking appeared to have performed superbly. In the areas where the ceramic had cracked the platinum coating had even maintained the profile of the original substrate surface, allowing the glass flow to be shut off.

The ACT™ platinum coating on the critical section of the spout bowl had performed effectively. A very significant extension to its life had been achieved, and downtime, from one or more component changes, had been eliminated. The weakness, if any, lay with the refractory ceramic. The cracking could have presented a problem if the ACT™ coating had not been so stable and effective. In non-ACT™ coated ceramics, cracked areas usually erode more rapidly than the surrounding ceramic, and this accelerated erosion/corrosion would traditionally have
caused extreme variations in both flow andthermal distribution within the glass.

Investigations of the bowl have been undertaken and have provided guidelines for the selection of ceramic substrates.

**ACT™ Coated Feeder Tubes**

Unless protected, all ceramics used in glassmaking will begin to change dimensionally, due to erosion and corrosion, from the moment they come into contact with the glass. Stable components can be created by ACT™ coating with platinum or platinum alloys.

ACT™ coating of a tube requires a considerable quantity of platinum and in many circumstances, although full coatings are desirable, partial coatings can be satisfactory. A short coating over the bottom edge, terminating below the glass surface is very effective in maintaining efficient stirring and permitting closure to allow orifice ring changes. Some corrosion of the tube may occur at the glass/air interface, but in low corrosion glasses this may be tolerable. A partial coating may thus be very cost effective for many applications.

Several ACT™ coated tubes are currently in service and have been operating for long periods, in a variety of glass types. One stirring tube, examined after it had been in service in TV screen and tube glass for 12 months, was found to have edges which were as well defined as when it entered service.

From this observation and from destructive examinations, there are strong indications that the life of ACT™ coated tubes is as long as those expected for other forming-end components.

**ACT™ Coated Plungers**

Ceramic plungers are the easiest forehearth component to change, but are second only to the orifice ring in their contribution to the control of the final quality of the glass gob. Unprotected ceramic plungers change dimensionally due to the erosion and corrosion caused by the flowing glass. This progressive change must be monitored continuously to allow the plunger movement to be adjusted and so control the weight of the glass gob. While the newer continuous gob monitoring and feedback control systems significantly improve the gob weight control, an ACT™ coated plunger would enable even better control to be achieved.

**ACT™ Coated Orifice Rings**

The orifice ring is the final contact surface for the glass before the gob slides down the chute into the mould for forming. The orifice ring controls the dimensions and shape of the gob, and with the plunger and the tube it controls the weight of the gob. Ceramic orifice rings are made of alumino-silicate or zircon-mullite compositions. They provide adequate performance with respect to thermal shock resistance and erosion resistance, but only for limited periods of perhaps a few days to a few weeks. All unprotected ceramics suffer an initial major erosion followed by a steady state change, which causes the gob diameter and hence the gob weight to vary quite dramatically during service if almost-continuous adjustment of tube and plunger is not made.

However, users of ACT™ platinum-coated orifice rings report that both initial erosion and progressive erosion during use are totally eliminated, even for periods of operation lasting in excess of six months. One of the partially coated triple gob orifice rings shown in Figure 9 operated for over four months without any sign of dimensional change, and provided trouble-free operation limited only by loss of sealing against the underside of the spout bowl. The area of failure was not ACT™ coated, and replacements have been totally coated with an optimum amount of platinum. Many examples of ACT™ coated double gob orifice rings are in operation in the U.K. today. One container manufacturer has successfully operated these fully coated components for over six months.

It has also been found that an ACT™ platinum coated orifice ring of one diameter size can be used to produce a range of gob weights. Normally with unprotected ceramic orifice rings a number of diameters are required. One ACT™ coated diameter can effectively cover a range of diameters, which is explained by its stability. By careful selection of the median diameter and

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production scheduling, ACT™ platinum coating technology can be used for orifice rings in forehearts where both different sized containers and continuous runs of the same sized container are produced.

Operational benefits include improved control of the gob weight and a reduction in downtime caused by the need to change the ceramic orifice ring. Being able to maintain the glass flow between different sized containers also avoids the need to re-establish flow, which otherwise can often result in defects in the glass.

**Refractory Ceramics as Substrates**

While many refractory ceramics are available, current usage tends to limit the range employed within each zone of the glass melting furnace. At the forming end, for example, the choice is dominated by variants of alumino-silicate and zircon-mullite. The one selected is generally a compromise to provide the most appropriate combination of strength, thermal shock properties and corrosion resistance.

ACT™ technology creates a special relationship with the ceramic substrate; the coatings are enhanced by high quality refractory substrates, but can be diminished by poor substrates. At the forming end, the ACT™ coating beneficially modifies the corrosion resistance of the composite structure. Thus, the choice of refractory substrate becomes easier, particularly when fully coated, and selection based on mechanical strength and thermal shock resistance becomes possible, and the compromises needed to select a ceramic are reduced.

In fact ceramic substrates can now be reassessed, perhaps enabling alternative ceramics which have some inherently valuable property, but which have been unusable for reasons such as coloration, to be chosen. Optimised refractory ceramic substrates, compatible with ACT™ coating technology will yield composites having far higher capabilities, such as longer service lives, than currently used materials. Such issues are now being studied.

The quality of the surface finish of the refractories used for ACT™ coating is important. It is not unusual to find pores and gas holes on the surface of a ceramic. In order to develop a surface coating with high interfacial integrity, a pre-coating preparatory stage may be required if the initial quality is poor. This pre-processing is clearly undesirable and refractory ceramic manufacturers must be encouraged to supply materials with the improved quality of surface finish that is now needed.

**Conclusions**

Current trends require glass manufacturers to produce better quality products, and are forcing them to improve efficiency. With brittleness, poor thermal shock resistance, high porosity and poor corrosion/erosion resistance inherent in primary refractory ceramic containment
materials this could present insurmountable difficulties. While cladding, relying on metal strength achieved by using sheets of platinum group metals over refractories has been beneficial for long periods of service, the metal requirement is high and therefore expensive.

New ACT™ coatings effectively combine the best features and properties of both ceramics and platinum group metals, and give the operational durability and efficiency required by the glass industry. ACT™ platinum coating of forming-end ceramics has demonstrated major potential for improving glass making operating practices. It has highlighted the benefits possible in control of gob diameter, shape and weight, and has brought stability to the forehearth operation. Major reductions in downtime now provide higher productivity and lower manufacturing costs.

ACT™ platinum coating for tri-level thermocouple sheaths is now a major world-wide product. Trials that have been undertaken on forehearth forming-end consumables have demonstrated the wider applicability of ACT™ coating technology, from which glass makers are now benefiting. It is anticipated that ACT™ coatings will find increased use in glass furnaces as the best combined features and properties of ceramics and metals are sought. These developments will require the integration of technologies, notably those of the ceramicist, the metallurgist, the glass technologist and the furnace builder to ensure that the maximum benefit is gained by customers and manufacturers.

References

3 Canadian Ceramic Society, 92nd Annual Meeting and Convention, Montreal, Canada, 20th to 22nd February 1994
5 Johnson Matthey PLC, *European Patent* 93/300,823B
10 Internal Johnson Matthey Report, Nov. 1994
11 Internal Johnson Matthey Report, Dec. 1994

### Ruthenium Improves Corrosion of Stainless Steel

Duplex stainless steels containing typically chromium, nickel, molybdenum and nitrogen, and having approximately equal volume fractions of austenitic and ferritic phases in their microstructure, are used in aggressive chemical and marine environments where high corrosion resistance is required, such as in heat exchangers, desalination plants, food pickling and mine waters. However, there is always a demand for improved corrosion resistance in these steels to cope with increasingly severe environmental conditions, and much work has been done to meet this. In particular, it is known that small additions of the platinum group metals improve corrosion resistance in stainless steel (1). Similar improvements have been observed after adding platinum group metals to duplex stainless steels with low-chromium contents, but no research had been done on the effects of adding platinum group metals to high-chromium duplex alloys.

Now, research from South Africa, involving immersion in sulphuric acid and electrochemical measurements, has shown that the addition of just 0.28 per cent of ruthenium to duplex stainless steel: iron-29 per cent chromium-14 per cent nickel-3 per cent molybdenum can increase the corrosion resistance of the base alloy by improving the hydrogen evolution efficiency and by inhibiting anodic dissolution (2). Adding ruthenium moved the corrosion potential towards more noble values. As the nitrogen content in these alloys was extremely low, in order to obtain the desired microstructure the nickel content was higher than usual; this additionally benefited the observed corrosion resistance.

References