Almost every glass article in existence has been formed by cooling from a molten state (with the exception of the relatively tiny amount produced via sol-gel processing and similar routes). Molten glass is a difficult and challenging material to handle due to the extremely high temperatures required to melt and combine the glass constituents (typically 1400 to 1600°C) and to the highly corrosive nature of glass in this state. Further difficulties arise when glass is formed using automated production equipment. Over the last century or so these difficulties have been overcome and mass-produced bottles, windows, tableware and display screens, amongst many other items, are now taken for granted. However, the various pieces of equipment used to melt, distribute and form these glass articles all suffer from continual corrosion. The corrosion causes two major problems:

• First, corrosion has an obvious limiting effect on the lifetimes of the furnace and handling equipment used to melt and process the glass. For instance, some of the furnaces that produce the more aggressive glasses (such as fluoride opal glass for white tableware, or borosilicate glass for Pyrex® articles and LCD screens) need to be completely rebuilt every two years and this can cost tens of millions of pounds each time.

• Second, the products of the corrosion process (undissolved ceramic particles ('stone'), chemical inhomogeneities ('cord') or bubbles ('blister')) can cause defects in the glass which reduce its overall quality. While the occasional defect in a beer bottle may be of minor consequence, a single minute defect in a high-quality lead crystal item or LCD screen panel is completely unacceptable.

Materials for Glass Making

Platinum is one of the few materials that is relatively immune from the corrosive effects of molten glass. Its high melting point (1769°C) (1) and oxidation resistance at elevated temperatures make it the ideal material for handling molten glass. Ideally, the entire glass-contact surface of a glass furnace should be fabricated from platinum. However, the high intrinsic value of platinum precludes this as an option for the majority of glass producers. Therefore, this approach is confined to the highest-value and extremely-specialist production operations – that is, glass for flat panel display screens or glass for lenses of extremely high-power astronomical telescopes.

Instead, most sectors of the glass industry use platinum only for certain critically important items in the furnace. These items, protected by or manufactured from platinum, are subject to the most corrosion or have the greatest effect on the quality of the final product. In general, the extent to which platinum is used in a furnace is determined by a number of factors. These include the value of the product glass, the quality required of it and the corrosiveness of the molten glass. For example, a single LCD glass production line uses about 350 kg of platinum in the redistribution and forming sections and typically lasts only 2 to 3 years. In this application, the use of platinum components is vital to the final product quality, and the high value of the product justifies the investment. By contrast, the beer bottle plant mentioned earlier may require only a few hundred grams of platinum for the thermocouples used to control the glass melt temperature. The bottle production process would certainly benefit from the use of platinum but it is not a necessity for the final product and the high-volume, low-margin nature of the business makes using large amounts of platinum difficult to justify.

Platinum Fabrications

Traditionally, the platinum used in the glass industry is either fabricated to produce solid, freestanding components or is wrapped (clad) around...
ceramic or high melting-point metallic components. Both methods use rolled sheets of platinum alloy (for example, 10%Rh/Pt or 20%Rh/Pt, measured in wt.%), which are cut, formed and welded to the requisite shape. Extremely complex and sophisticated fabrications can be achieved using these processes.

However, with such a precious resource, optimisation of its use is essential and in order to minimise the amount of platinum the thicknesses of the platinum fabrications should be as small as possible. There is, however, a minimum thickness below which the sheet is not sufficiently strong to support itself and contribute its protective and/or containment function.

Platinum Coatings

An alternative technique, which utilises the beneficial properties of platinum in a far more efficient manner, is by thermal spraying a protective platinum layer directly onto the glass-contacting surfaces of the production equipment. This process, known as advanced coating technology, ACT™ (2), has the capability to render the

ACT™ Platinum Coatings

ACT™ platinum coatings are applied by a thermal spray deposition process. Platinum in wire or powder form is fed into an oxygen-propylene or plasma flame. The residence time within the heat source is carefully controlled to ensure that the platinum is melted without vaporising it. A compressed gas stream fires the molten droplets onto the surface to be coated. The droplets 'splat' on impact and solidify almost instantly. The large differential in thermal mass between the molten particles and the substrate means that the component normally experiences only a slight increase in temperature during the deposition process. A continuous feed of wire or powder ensures a uniform, even stream of thousands of droplets per second. Successive 'splats' build up to form the coating.

The thermal spray gun is controlled by a sophisticated multi-axis robot. The precise control of speed and motion obtainable ensures that even, reproducible coatings can be achieved. Coatings are applied in a purpose built coating booth which collects any 'over-spray' platinum, thus minimising loss of metal.

Correct preparation of the substrate material is vital to the integrity of the bond between substrate and coating. Great care is taken to ensure that the ceramic surface is in optimum condition to allow maximum adhesion of the coating. The substrate preparation methods allow the ceramic surface to be imperfect: minor defects can be rectified, but the number should be kept to a minimum.

The ACT™ platinum deposition process is being used here to apply a thin layer of platinum to a fusion-cast ceramic block which will cover glass delivery channels. Thermal spray techniques and sophisticated robotic systems ensure that the distribution of the platinum coating matches the carefully designated coating profile: for instance, two thicker (darker) bands of platinum can be seen on the upper surface.

The feeder chamber within a glass production unit. The chamber comprises a 'T'-shaped ceramic tube through which the high temperature molten glass flows from the melting area to the forming machines. In this chamber a rotating and reciprocating screw-plunger moves stirring the glass and forcing it into the moulds. The feeder chamber is the part of the system that most requires protection from the corrosive effects of the molten glass.

coated component virtually immune to the corrosive effects of the molten glass. The process is analogous to the cladding technique, where a base metal or ceramic component is protected by a platinum alloy sheet; however, the platinum is now strongly and intimately bonded to the substrate material. Rather than being a 'brick wrapped in metal foil', the component has become a composite structure. The platinum coating provides the corrosion resistance at the surface, while the substrate material provides the bulk properties, mechanical strength and shape. As the substrate now gives the system its strength, the platinum thickness can be reduced to the minimum required to ensure an impervious barrier layer and hence impart the necessary corrosion resistance. The thickness of the coating is typically in the range of 200 to 300 μm, compared to a cladding thickness of ~1 mm and above.

The obvious advantage offered by such coatings is that far less platinum can be used than in the traditional fabrication or cladding techniques. This reduction in platinum requirement also makes it feasible to use platinum in positions and applications that would not normally justify the investment of a fully clad platinum system.

**Lead Crystal**

The effectiveness of the ACT™ coatings can be illustrated by their use in premium-quality lead crystal production. High-quality lead crystal is a sector of the glass industry that has traditionally used significant amounts of platinum in the production process. Over the last six years, the glass industry has progressively adopted ACT™ coatings as the standard production route. The best examples of lead crystal tableware have always been produced to stringent quality standards. Recently, the growing trend for uncut or lightly cut crystal has raised these standards even higher. Defects in the crystal are more apparent when there are fewer cuts made, so the defect tolerance is much lower. In order to meet these high-quality requirements, crystal manufacturers are increasing the number of platinum or platinum-protected parts in the production line, especially in the delivery systems close to the forming zone.

**Delivery Systems**

The system that delivers the molten glass/crystal from the melting area to the forming machines is referred to as the feeder chamber. It normally comprises a ceramic 'T' shaped tube, the vertical section of which contains a rotating and reciprocating screw-plunger. This serves the dual function of homogenising the glass (stirring action) and forcing the correct amount from the chamber into the moulds (plunging action). For high-quality crystal production, the feeder chambers are either lined with platinum alloy claddings or are ACT™ platinum-coated on the internal surfaces. The quantity of precious metal required to do this is
obviously dependent on the size of the chamber. Typically, about 6 to 7 kg of platinum-rhodium alloy is used for the clad option and 2.5 to 3 kg of platinum for the coated version.

Pure platinum is rarely used for claddings or fabrications as it lacks the necessary strength when in the unalloyed condition. Therefore alloying additions are made to increase its strength. A common alloying addition for this purpose is rhodium, normally at 10 or 20 per cent. Rhodium is normally considerably more expensive than platinum and has recently cost more than twice as much (4). This has a significant effect on the cost of a platinum-rhodium alloy relative to pure platinum. However, because ACT™ coatings utilise the ceramic substrate to provide the mechanical strength of the system, pure platinum can be used as the coating material.

If platinum protection of some form is not used, the molten glass will attack, corrode and dissolve the ceramic of the chamber, thus limiting its life. The products of the corrosion process (stone, cord and/or blister) are swept into the forming moulds and manifest themselves as clearly visible defects in the final product. Consequently, high-quality lead crystal producers regard platinum as a vital part of their production process and other producers are increasingly using it too.

**Heating Options**

The temperature of the glass/crystal as it is delivered to the forming moulds is a critical parameter in the production process. The glass temperature must be carefully controlled to ensure optimum viscosity and the correct cooling/solidification rate. The last stage in the production process at which the temperature can be controlled is when the glass is in the feeder chamber. The temperature is then typically around 1000 to 1200°C, depending upon the size of the glass article being produced and the actual glass/crystal composition.

There are two main methods of maintaining and controlling the temperature of the glass within the feeder chamber:

- One method that is used to maintain the temperature of the chamber, and hence the glass inside, is by wrapping external electrical heating elements around the outer walls of the ceramic.
This form of heating is known as 'indirect heating'.

- The second method, commercially known as direct heated platinum systems (DHPS®) (5), uses free-standing platinum alloy tubes welded together to form the ‘T’ section feeder chamber described before. These tubes contain and distribute the glass, and also control the temperature. Large electrical currents are passed through the platinum alloy, utilising the resistance/resistive heating effect to convert the electrical energy to heat. By using a control loop to adjust the current, the temperature can be precisely controlled.

The reason that two very similar but fundamentally different technologies continue to exist for this application is because each system has its own strengths and weaknesses and the crystal/glass producers choose the version that best suits their particular requirements.

Indirect Heating of Platinum Clad Systems

An indirectly heated ceramic feeder system, clad with platinum (alloy), will enjoy the excellent glass corrosion protection that platinum (alloy) offers. However, the chamber walls in the vertical section of the chamber can be subject to collapse due to suction from the viscous glass melt as the reciprocating screw-plunger makes the upward stroke. In order to combat this, the vertical section could be strengthened, but to be effective the amount of platinum (alloy) required would have to be significantly increased.

In addition, after prolonged exposure to the high temperatures of glass forming, grain growth of the platinum (alloy) microstructure can weaken the mechanical strength of the material to such an extent that the chamber ruptures.

With this indirect heating configuration, the response time is relatively slow as the heating elements are on the outside of the ceramic and the heat has to be transmitted through the body of the ceramic chamber. This method does not give the level of control that the direct heating option allows.

Indirect Heating of ACT™ Platinum Coatings

A ceramic feeder system that has been ACT™ platinum coated will similarly enjoy excellent corrosion resistance but will use a much smaller amount of platinum to do so. It will also utilise platinum rather than platinum-rhodium alloy. The excellent bond between the coating and the substrate removes the danger of suction collapse. Grain growth within ACT™ platinum coatings is minimal (6) and due to the support of the ceramic substrate is thus of much less consequence. However, the heating method has the same limitations in temperature control as the clad version, because in both these cases the heat source is on the outside of the ceramic.

Direct Heating of Free-Standing Platinum Fabrications

If the platinum cladding or liner is directly heated, the component providing the heating effect is in immediate contact with the glass. This results in a much more responsive system with an increased level of temperature control.

However, fabricated direct heating systems are subject to the same mechanical issues as the indirectly heated cladded version: suction collapse, large numbers of welds, grain growth, etc., and similar quantities of platinum-rhodium alloy will
also be needed. In practice, the choice is between just two of the above options. The majority of the indirect heating systems supplied to high-quality crystal producers are now ACT™ coated rather than clad. However, within the industry, there are still manufacturers who continue to choose fabricated direct heating systems because they feel that the precise temperature control offered by this system outweighs the advantages of the coated system.

**Power Coatings™**

**Combining the Advantages**

Power Coatings™ were developed in order to provide the advantages of both systems and eliminate the drawbacks. Power Coatings™ is a combination of the DHPS® and ACT™ coating technologies. An ACT™ platinum coating is applied to a ceramic substrate which is then directly heated in the same manner as the solid platinum fabrications used in the traditional DHPS® systems. As well as providing the beneficial features of both systems, it provides additional benefits such as increased responsiveness and high power capabilities.

The temperature control achievable within a chamber that has Power Coatings™ is extremely precise. To monitor the temperature, thermocouples are embedded in the ceramic immediately adjacent to the coating. These supply accurate temperature data to the computer control loop that automatically adjusts the power applied to the coating, thus controlling the temperature. The power applied is from a low voltage, high current (AC) source. The connection to the coating is made via specially-designed power distribution flanges which ensure an even current distribution around the chamber.

The temperature profile within the feeder itself can be specified by careful design of the coating thickness over the interior of the chamber. The heating effect of any section of the feeder chamber will be determined by the resistance of the coating in that section. The resistance is controlled by the geometry of the individual sections and by the thickness of the applied coating. By careful variation of the coating thickness, a constant heating profile can be obtained over varying chamber dimensions.

The heated coating is in direct contact with the glass and its temperature is constantly monitored. This provides a very responsive feedback loop that allows accurate temperature control. Tolerances of ± 0.5°C at operating temperature ranges of 1000 to 1200°C are currently being achieved.

Accurate temperature control provides control over the viscosity of the molten glass. Having accurate control of the glass viscosity, particularly at the point it is delivered to the moulding machines, is a key benefit to an automated glass manufacturer. For automated production, a critical operational parameter is the variance in the weight of the discrete quantities of molten glass (gobs) that are delivered to the moulding machines to form individual glass articles. This parameter is referred to as 'gob weight variance'. If the viscosity is under control then the gob weight can be controlled by careful regulation of the screw-plunger stroke. Ideally, the gob weight variance should be as close to zero as possible. The variance in gob weight that has been obtained with existing
A view looking down into a Power Coatings™ chamber during initial heat-up. No glass is present in the chamber at this point; the glow is from the platinum coating. The chamber is running at about 1200°C and this temperature was achieved with power being applied only to the coating. No other heat source was required.

Power Coatings™ systems, such as that used by Crystalex, Nový Bor, Czech Republic, is less than 0.2 per cent. This tightly-controlled delivery weight contributes towards the increased quality of the product and to a reduction in the rejection rate by ensuring that the correct weight of glass is consistently transferred to each mould, thus facilitating smooth, efficient operation of the glass forming machines.

There are now four standard designs of feeder chambers that use Power Coatings™. The chambers have volumes ranging from 8000 to 24,000 cm³ and are able to deliver glass at temperatures up to 1400°C. These chambers are suitable for dealing with the existing range of daily pull rates and gob weight delivery requirements for the vast majority of current indirectly and directly heated feeder systems.

Conclusion

Glass technology is one of the oldest manufacturing technologies. While using almost the same basic constituents now, as in the earliest times (for ornaments and utensils) the technology of production has advanced to the stage where manufacturers are able to produce perfect flat glass, lenses and display screens. Modern developments in the materials of production have contributed to this advance, and with the efficiency and accuracy available with Power Coatings™ technology, even more predictable outcomes are possible.

References
1 www.noble.matthey.com/pdfs/English/37.pdf
3 Taken from: www.noble.matthey.com/product/detail.asp?id=2
4 www.platinum.matthey.com/prices/
5 www.eglass.de/

The Author

Paul Williams is the Product Specialist for ACT™ coatings and platinum fabrications for the glass industry at Johnson Matthey Noble Metals, Royston. He has worked with the glass industry for the last six years, was involved in developing Power Coatings™ technology, and now Power Coatings™ and ACT™ products.

Electrically Induced Phosphorescence

When the voltage applied to a poly(para-phenylene) ladder-type polymer being tested for LED use was switched off, a team of researchers in Germany and Austria (J. M. Lupton, A. Pogantsch, T. Piok, E. J. W. List, S. Patil and U. Scherf, *Phys. Rev. Lett.*, 2002, 89, (16), 167401) saw a long-lasting pink phosphorescent glow (λ ~ 600 nm) instead of the expected, but shorter lasting, blue-green fluorescence (λ ~ 450 nm). Very low concentrations (~ 80 ppm) of Pd atoms left over from the process catalyst and bound to the polymer backbone are thought to be responsible for this new effect.

Large numbers of dark long-lived triplet states generated in the polymer by the electrical excitation may diffuse thermally through the polymer film until they encounter a Pd site where they decay as phosphorescence.