Platinum Group Metals in Glass Making

An overview of the role of the pgms in the glass industry

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The platinum group metals (pgms) are characterised by their high melting points and resistance to corrosion. The glass industry most commonly uses platinum, platinum-rhodium alloys and, recently, iridium. These protect a variety of components and ceramic substrates used in glass manufacture from erosion by molten glass, including thermocouples, furnace and forehearth parts. This protection takes the form of a fabricated part or a coating applied to a substrate. Glass manufacturers use these pgm products to get financial benefits, such as increased output, reduced downtime, extended equipment life, shape retention of ceramic parts and fewer defects in the end product. Another important advantage is that pgms are recyclable: as with glass, precious metals can be recycled, melted and reused indefinitely. In addition to these advantages, a choice of pgm-based technologies is available to the industry and this flexibility ensures that both protection and metal use can be optimised.

Introduction

The platinum group metals (pgms) have been used for many years in the glass industry (1, 2). Due to their high melting points and superior resistance to corrosion, they are invaluable for protecting manufacturing equipment from attack by molten glass and corrosive vapours (1, 3). Although the initial cost of pgms may be high, they are fully recyclable and, depending on the product, 95% to 98% of the metal can usually be recovered and converted into revenue once the useful life of the component is over (4).

While there are many established products available to glass manufacturers, newer options with their own unique characteristics are being introduced to complement these. This article provides a brief overview of the use of pgms for glass manufacture, including typical materials, where they find application and the benefits they offer. It will also consider how pgm products are positioned to respond to more challenging requirements as the glass market evolves.

Common Alloys and Forms

Platinum-Rhodium Fabrications

Fabrications are self-supporting parts or linings that are usually made of welded sheets of platinum-rhodium alloys. Typically, between 5 wt% and 20 wt% rhodium is added to platinum to provide strength (3, 4), although alloys with 30 wt% rhodium are also available (5). Sheet metal, tubes and more complex assemblies such as stirrers (Figure 1(a)), feeder chambers, refiners or spout bowls constitute what are known as pgm fabrications. Fabrications or linings can withstand repeated thermal cycling, cracking of the ceramic substrate and exchange of contacting parts.

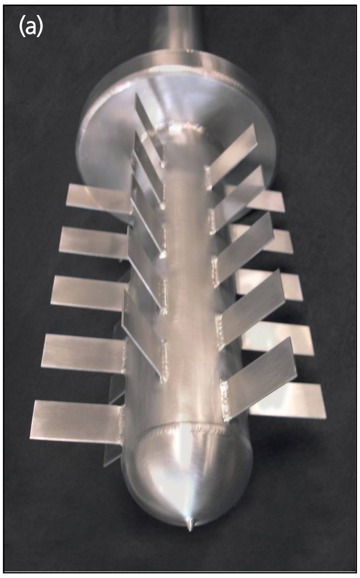
For the most demanding applications, platinum-rhodium alloys with dispersed zirconia particles can give fabrications increased mechanical strength and durability. Although only small quantities are necessary, the zirconia particles stabilise the grain structure of the alloy and improve its resistance to contamination (6). The general term used for these special alloys is 'doped' alloys, and they are also referred to as grain stabilised or dispersion hardened materials (3, 7).

Platinum and Platinum-Rhodium Coatings

The deposition of a thin layer of platinum or platinum with 10 wt% rhodium can be used for ceramic protection in the manufacture of all glass types, including soda lime, crystal, borosilicate, opal, solar and speciality glass, and is ideal for long runs with limited thermal cycling (8). Coatings range from 200 μm to 500 μm in thickness and rely strongly on the integrity of the ceramic substrate. The coating is applied using a low-temperature process that does not affect the substrate; hence, a minimal risk of damage to the component is involved. This makes coatings suitable for fused cast material which is sensitive to thermal shock. The coating process, usually carried out by plasma or flame deposition, is flexible and accommodates complex shapes (Figure 1(b) (4, 9)). Direct heating, where an electric current is passed through the pgm layer to heat the glass, is also compatible with this technology.

Platinum-Gold Fabrications and Coatings

Alloys of platinum with 5 wt% gold are used both in the form of fabrications and as coatings on ceramic substrates (10). They offer advantageous glass non-wettability characteristics, meaning that the surface tension of the molten glass in contact with the alloy surface is high and the glass will 'roll off' the surface rather than spread across it, but they are only suitable for lower-temperature applications (11). They can be doped with zirconia to increase strength (12), and in the form of fabrications are particularly relevant to platinum laboratory apparatus (PLA) and nozzle tips for glass fibre bushings. As a coating, platinum-gold protects orifice rings used in the container manufacturing industry, preventing the glass from sticking to, and solidifying on, the coated surface and so facilitating the removal of the ceramic part when it needs to be replaced.



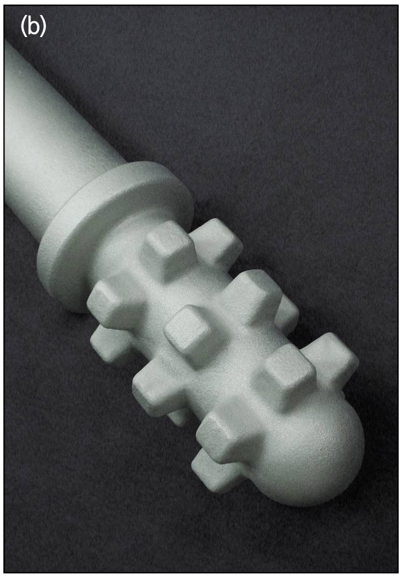


Fig. 1. (a) Fabricated stirrer for molten glass, made of platinum-rhodium sheet (design from Füller Glastechnologie Vertriebs-GmbH);
(b) A plunger, which oscillates vertically to repeatedly force precisely measured amounts of glass through an orifice ring (9), is ACT® coated with platinum-rhodium. ACT® is Johnson Matthey Noble Metals' advanced coating technology (4)

Advantages Offered by PGM Products

Suitable Technology for Each Application

In the 1990s, fabrications made with grain stabilised pgm alloys became less popular due to their higher cost of manufacture, but the early 2000s saw a revival in demand for these doped alloys as rhodium prices increased (13), making the conventional platinum-rhodium alloys comparatively more expensive to use. Due to their superior mechanical strength, doped alloys are now used extensively to replace traditional platinum-rhodium alloys with lower-rhodium equivalents, thereby reducing the investment in precious metal required (4, 14).

Also in the 1990s, the use of platinum coatings led to further benefits in terms of reduced pgm use. As they rely on the mechanical strength of the substrate (10), coatings use less metal overall and do not require the addition of rhodium for strength. However, fabrications continue to play an important role as their environmental resistance and robustness cannot always be matched by a coated ceramic substrate.

As an example, thermocouple assemblies can be protected from glass erosion or chemical attack using precious metal, either in the form of a drawn tube with one end closed or applied as a coating on an alumina sheath. Both types of thermocouple protection are proven to be durable and to withstand high-temperatures such as those found in the crown of the furnace. A coated protection (Figure 2(a)) minimises the amount of pgm required to protect the assembly against glass erosion and is a more cost-effective choice for less demanding applications, but a fabricated sheath (Figure 2(b)) will better withstand thermal cycling and in general be a more robust option under severe conditions. As every glass plant has its own unique characteristics, trials of various forms of protection can be undertaken to establish which technology is most suitable in each case.

Improved Glass Product Quality

It is possible to use unprotected, consumable ceramic parts in the forehearth section of a glass furnace. However, while their performance has improved progressively, problems which can affect end product quality may still be experienced (15). For example, dimensional stability and durability are two of the key requirements placed upon the feeder consumable set used in an automated feeding process for mass production of glass tableware and glass containers such as bottles (9, 16). Over time, corrosion of the ceramic leads to altered dimensions in the feeder parts (9, 16), causing variability in the finished product. However, the use of a protective pgm coating on the ceramic will ensure complete resistance against attack by molten glass, providing protection at the glass line and against corrosive vapour condensates, thus stabilising the forming process and allowing the formed shape to be more controlled and of consistent quality. In one case it has been found that the number of dishwashing cycles that glass tableware can withstand is more than doubled by using pgm in critical

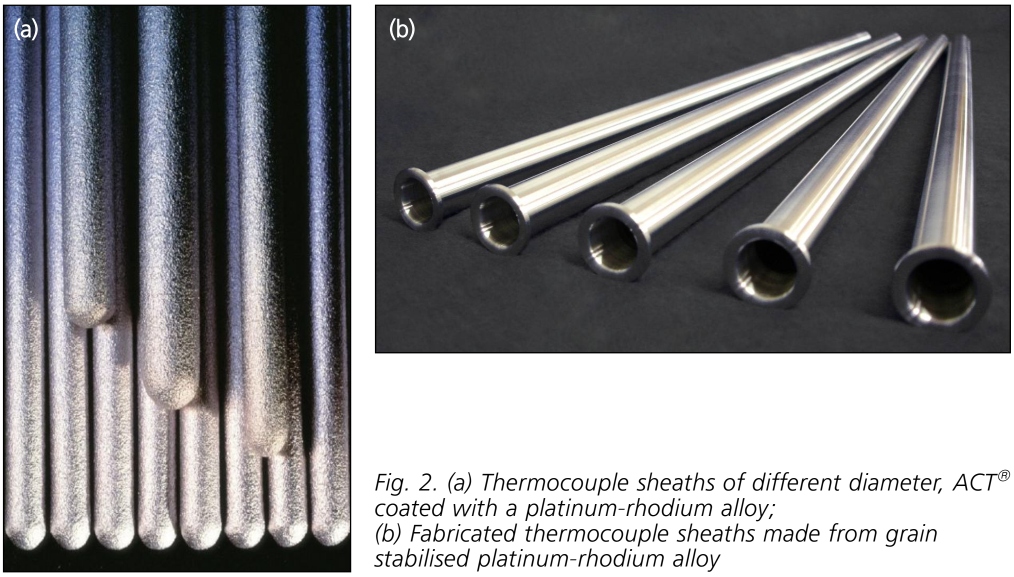


Fig. 2. (a) Thermocouple sheaths of different diameter, ACT® coated with a platinum-rhodium alloy;
(b) Fabricated thermocouple sheaths made from grain stabilised platinum-rhodium alloy

areas of the forehearth, because the occurrence of cords (visible streaks caused by differences in glass viscosity (17)) is minimised.

This could find particularly interesting application in supporting the glass container and tableware industries in their effort to move towards more sustainable products. Properly protected components could help reduce the final weight of glass bottles by allowing tighter tolerances and should help minimise the rejection rate, thus optimising the energy cost per unit produced.

Another problem encountered when using unprotected ceramic parts is contamination of the glass melt by dissolution of the ceramic (15, 16). This may also cause defects in the glass product (15, 16) and can be prevented by using pgm protection in the stirrer cell and on ceramic surfaces in the critical zone prior to forming (16). Protection on stirring components, in the form of a fabricated part or coating, further ensures that stirring efficiency is maintained and inhomogeneities in the batch are minimised.

For these reasons, the use of pgm coated or fabricated components is particularly beneficial in the manufacture of glass for specialist applications where quality is paramount, including solar glass, optical glass, vitroceramic (a glass-ceramic material used in many modern hobs or stove tops) and glass components for pharmaceutical containment (Figure 3).

Fig. 3. A Danner sleeve for the manufacture of glass tubing for pharmaceutical components is ACT® coated with platinum and then fully polished

Examples of components which benefit from pgm protection are mandrels in the tubing industry, tweels and lipstones for speciality flat glass, and chambers and refiners for crystal and optical glass.

Extended Furnace Life

Any measure taken to extend the life of a glass furnace potentially offers considerable return on investment. This objective is often achieved by protecting the furnace throat. Some glass manufacturers use bare fused cast ceramics, including chromium oxide blocks, to construct the throat, but further dimensional stability and durability may be required. These unprotected blocks could also be a source of contamination of the glass melt by dissolution of the ceramic (15). For other types of glass, such as borosilicate and opal glass, the throat can be protected with platinum-rhodium linings or molybdenum shields, although more cost-effective solutions are sought.

A platinum-rhodium coated throat can be more cost-effective than installing platinum-rhodium linings or fabricated parts (Figure 4). The technology is applicable to furnaces for all types of glass, including soda lime, crystal, borosilicate, opal and speciality glass. The average coating thickness varies between 400 μm and 500 μm, and a medium-sized throat requires between 15 kg and 20 kg of platinum or platinum-rhodium alloy which can be recovered at the end of the campaign (4).

Iridium in the Glass Industry

Iridium has been available in the form of sheet for many years. However, before the mid 1980s, production was difficult and quality was variable. Since then, it has become possible to supply high-quality, uniform sheet iridium, typically in thicknesses between 0.7 mm and 4 mm. This has been facilitated by improved melting equipment and processing techniques. These product developments were driven by the increasing global demand for iridium crucibles, which are used in the electronics industry in the temperature range from 1500ºC to over 2200ºC. Glass processing equipment tends to be more complex in shape than a simple crucible, however manufacturing capabilities have continued to develop and iridium can now be formed to meet these needs. There are still limitations but these can usually be overcome by design adaptations.

Like platinum and rhodium, iridium is recyclable; but, with a substantially lower metal price (13), it is

Fig. 4. A furnace throat, ACT® coated with a platinum-rhodium alloy. The throat is constructed from fused cast ceramics (in this case ER 1711 RT (40% ZrO_2) from Saint-Gobain SEFPRO): the surface of these materials is laser drilled prior to coating to ensure a strong, uniform adhesion of the coating

more affordable upfront. Iridium has higher mechanical strength than grain stabilised platinum-rhodium alloys and excellent creep resistance (6). However the real advantage it offers is that it can be used under mildly reducing conditions, where platinum and its alloys may be subject to contamination and subsequent failure (18). Iridium can also be used at temperatures up to 2000ºC in air but, unlike platinum-rhodium, it may require some oxidation protection, as above 1000ºC it begins to show an appreciable degree of oxidation (6, 19). Iridium fabrications and linings therefore complement existing platinum-rhodium technology, and pgm solutions are now available for use in both oxidising and reducing environments. More information on iridium for glass manufacture can be obtained by contacting the author by email at: christophe.couderc@matthey.com.

Outlook

The globalisation of the glass industry continues to reduce end-product prices, even while higher technical specifications are demanded of manufacturers. Key characteristics that will increasingly be required of pgm technologies for the glass industry will include high-temperature strength and excellent glass contact corrosion resistance, with lower upfront capital investment. Many technologies that have been used for decades in the glass industry are still well suited to present needs. Others have responded less well to current economical conditions and technical requirements, but may still play a role in the future of the glass industry. These established products will be complemented by the new discoveries that continue to be made in the application of the platinum group metals to high-temperature and corrosive environments, ensuring the continued importance of these metals to industries such as glass manufacture.

References

1 E. Preston, *Platinum Metals Rev.*, 1960, **4**, (1), 2
2 E. Preston, *Platinum Metals Rev.*, 1960, **4**, (2), 48
3 D. F. Lupton, J. Merker, B. Fischer and R. Völkl, 'Platinum Materials for the Glass Industry', IPMI Precious Metals 2000: 24th International Precious Metals Conference, Williamsburg, Virginia, USA, 11th–14th June, 2000
4 Johnson Matthey Noble Metals, Markets and Industries: Glass, and datasheets contained therein: http://www.glass.noble.matthey.com/ (Accessed on 28th June 2010)
5 B. Fischer, A. Behrends, D. Freund, D. F. Lupton and J. Merker, *Platinum Metals Rev.*, 1999, **43**, (1), 18
6 C. Couderc, P. Williams and D. Coupland, *Glass*, September/October 2007, 24
7 J. Stokes, *Platinum Metals Rev.*, 1987, **31**, (2), 54
8 C. Couderc, *Glass Int.*, November 2009, **32**, (9), 32
9 E. Ingram, R. Ramey and G. Stark, *Ceram. Ind.*, September 2007, 34
10 D. R. Coupland, *Platinum Metals Rev.*, 1993, **37**, (2), 62
11 G. L. Selman, M. R. Spender and A. S. Darling, *Platinum Metals Rev.*, 1965, **9**, (4), 130
12 A. E. Heywood and R. A. Benedek, *Platinum Metals Rev.*, 1982, **26**, (3), 98
13 Platinum Today, PGM Prices: http://www.platinum.matthey.com/pgm-prices/price-charts/ (Accessed on 28th June 2010)
14 R. B. McGrath and G. C. Badcock, *Platinum Metals Rev.*, 1987, **31**, (1), 8

15 N. S. Prakash, *Glass Int.*, September 2009, **32**, (7), 43

16 D. R. Coupland, R. B. McGrath, J. M. Evens and J. P. Hartley, *Platinum Metals Rev.*, 1995, **39**, (3), 98

17 GlassOnline, Illustrated Glass Dictionary: http://www.glassonline.com/infoserve/dictionary/ (Accessed on 28th June 2010)

18 R. C. Jewell, *Platinum Metals Rev.*, 1964, **8**, (4), 122

19 H. Jehn, R. Völker and M. I. Ismail, *Platinum Metals Rev.*, 1978, **22**, (3), 92

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