Reduction of Platinum Corrosion in Molten Glass

THE INFLUENCE OF PHOSPHATE GLASS MELTS ON THE MICROSTRUCTURE AND RUPTURE TIME OF PLATINUM METALS

By Bernd Fischer
Faculty of Technology, Friedrich-Schiller-University, Jena, Germany

In order to ensure the high quality necessary for use in scientific instruments, most high-technology optical glasses are melted in platinum containers. In general, this noble metal has excellent corrosion and erosion resistance, as well as low solubility, when in contact with molten glass. Therefore the dangers of discoloration and reduction in optical transmission are low. Glass melts may be contaminated by the uptake of corrosion and erosion products if the glass is melted in ceramic materials. The use of platinum, instead of ceramics, for both containers and stirrers enables glass melts to be stirred more thoroughly and hence become more homogeneous. In this way a better quality and higher yields of glass are obtained. Even totally new glass systems which have superior optical properties, but which would attack ceramics very quickly, can be melted in platinum vessels and produced to extremely high quality. Generally, platinum or its alloys enables optical glass to be produced with high purity, homogeneity and the absence of streaks and bubbles.

The platinum used in the glass industry for melting pots, for coating melting vats, for stirrers and for other auxiliary equipment has to withstand high thermal and mechanical stresses. For many types of glass the process conditions are under close control and as a result the platinum apparatus has a very long service life. On the other hand during the manufacture of certain glasses elements such as phosphorus, lead, silicon and boron, arising from the decomposition of their compounds, form low melting point eutectics which may cause considerable corrosion of the metal. Nowadays there is an increasing tendency to melt even such glasses in platinum containers, since the required high quality glass often cannot be produced by melting in ceramic containers. Thus, it is necessary to study the basics of such reactions in order that they can be reduced, or avoided.

In the first part of this paper the corrosion of platinum during the melting of phosphate glass of a selected composition is discussed. Appreciable corrosion of platinum can be expected during the preparation of phosphate glass; therefore a study has been made of the corrosive action of the phosphate glass in order to develop procedures which would enable such glasses to be melted successfully in platinum crucibles. Reports of related work on the production of lead glass, barium crown glass and glass ceramics will follow.

Experimental Procedure

The composition of the phosphate-based batch was as follows: 60 per cent \( \text{Al(PO}_4\text{)}_3 \), 15 per cent \( \text{Zn(PO}_4\text{)}_2 \), 15 per cent \( \text{Mg(PO}_4\text{)}_2 \) and 10 per cent \( \text{BPO}_4 \). Cold drawn 99.9 platinum wire samples 1.5 mm diameter and 70 mm long were exposed for various times either to a melting phosphate batch or, in a long time exposure test, to a melt at 1370°C for up to 500
Fig. 1 The hot tensile strength and elongation to rupture of platinum is shown as a function of the time of exposure to a melting phosphate mixture, at a temperature of 1370°C, and to remelting phosphate glass lumps.

hours. Prior to testing the platinum was annealed for 2 hours at 1400°C to recrystallise and stabilise its microstructure. In the long term tests the samples were only put into the melt when it was in the form of a homogeneous phosphate glass. In this way it was possible to differentiate between the effects of the starting mixture and the actual melt upon the platinum. After exposure - at the same temperature - the hot tensile strength, elongation to rupture, and time to rupture of the samples were determined. The data given below are the average values from five measurements. The platinum samples were investigated further by light- and scanning electron-microscopy, electron microprobe, secondary ion mass spectrometry (SIMS) and X-ray diffraction analysis. For the creep tests specially developed apparatus was used which enabled data to be obtained at temperatures up to 90 per cent of the melting point of the sample, in the case of platinum at up to 1600°C (1, 2). In order to obtain the high testing temperatures, the samples were heated directly by an electric current. Regulating the power supply ensured a constant temperature despite changes in the electrical resistivity of the samples, resulting from a reduction of their cross-sectional area. Due to the temperature gradient along the sample, the holding clamps stayed significantly below the testing temperature. This apparatus has proved its efficiency over many years for testing high melting point metals at temperatures up to 2000°C; even higher test temperatures and various test atmospheres can be realised.

Results

The results obtained showed that the hot strength of platinum is reduced drastically as the phosphate batch starts to melt, but it does not change during long term exposure tests in the molten glass, even after long times. From Figure 1 it can be seen that the melting mixture reduces the hot tensile strength considerably in the first 15 minutes, and that the elongation to rupture is reduced to zero. This reduction in strength, and the embrittlement of the platinum are demonstrated even better by creep testing. As shown in Figure 2, the time to rupture of platinum at constant load, and its rupture elongation are reduced to zero by the melting phosphate batch after only 2 minutes; this means that the samples fail under load without any deformation taking place if they are cooled and then reheated to the test temperature.

In contrast, during the long term exposure test in a phosphate glass melt, reductions in the hot tensile strength and the standing time are not observed during exposure times of up to 500 hours, Figure 3, provided that the amount of melt lost by vaporisation is replaced by the addition of glass pieces. If the replenishment is achieved by adding the phosphate mixture, however, the reactions on melting cause an appreciable reduction in the standing time but not
in the hot tensile strength. The values of fracture elongation behave accordingly.

Since the results of the long term exposure tests reveal the changes in the properties of the platinum better than the hot strength/rupture test, in later work only the former were studied.

Scanning electron microscopy investigations of platinum which had been annealed prior to testing showed that after the exposure test the fracture area displayed transcrystalline deformation, this is evident in Figures 4(a) and 4(b). During translation on the slip planes a shear lip (Scherslippe) formed in places where the metal finally fractured. The ductile metal showed appreciable reduction in cross-section in the fractured area.

After reaction with the melting phosphate mixture intercrystalline brittle fracture occurs, exposing crystal grain boundaries, Figures 4(c) and 4(d). At the edge of the samples the early stages of melting can be seen, Figure 4(e). The fracturing suggests the uptake of alien elements leading to a reduction in the melting point of the sample. Platinum forms low melting point phases and eutectics with many of the elements that are present in glass and this must be considered as the main reason for possible failure (3–5). In the platinum-phosphorus system a eutectic of platinum and Pt₃P₂ exists at 3.8 weight per cent phosphorus and a temperature of only 588°C, see Figure 5. At 6 weight per cent phosphorus the Pt₃P₂ phase forms; this starts to melt at 590°C.

As a result of metallographic and microanalytical investigations the following observations can be made about the reduction in the high temperature mechanical properties of platinum samples caused by the melting...
Fig. 4 Fracture surfaces produced by tensile creep testing of platinum samples in both the starting condition and after reaction with a melting phosphate mixture at 1370°C/4 min and showing:
(a) starting condition, general view showing transcrysalline deformation fracturing
(b) starting condition, shear lip (Scherlippe) on edge of sample
(c) intercrysalline brittle fracture following reaction with a phosphate batch
(d) intercrysalline brittle fracture on the edge of a sample after reaction with the melting phosphate mixture
(e) following reaction with the phosphate mixture the start of melting can be seen on the edge of the sample
phosphate mixture: if cold deformed platinum is recrystallised at a moderately high temperature a fine grained microstructure results, see Figure 6(a). In a high melting point glass melt a coarse microstructure forms in the platinum by collective recrystallisation, Figure 6(b). In this way detrimental alien elements can diffuse rapidly along the grain boundaries into the platinum. Coarse grains occurred in platinum which was in the as-annealed starting condition, as well as in samples which were exposed to the melting phosphate mixture or to the glass melt. The formation of widened grain boundaries, however, is only observed after exposure to the phosphate mixture, see Figures 6(b) and 6(c).

In samples that had been exposed to the melting mixture, the diffusion of phosphorus into the grain boundaries of the platinum was always detected. The line scan for phosphorus, Figure 6(d), the $^{47}/$PO/$^{+}$ secondary distribution image, Figure 6(e), and the mass spectrogram, Figure 7, all show the uptake of phosphorus at the platinum grain boundaries. The $^{47}/$PO/$^{+}$ ions occurred with $^{31}$P$^{+}$ in the mass spectrometric investigations, since primary oxygen ions were used. In Figure 7 the grain boundary area analysed is shown, together with the $^{47}/$PO/$^{+}$ secondary ion distribution. The mass spectrogram also reveals a series of alien elements and impurities, but it is necessary to bear in mind the high sensitivity of the SIMS method.

Following reaction with the mixture, phosphorus was the only additional element detected in the products that occurred on certain areas of the surface of the platinum. Figures 8(a) and 8(b) show, respectively, optical and X-ray images of such an area. By comparison with a standard, the phosphorus content was determined to be 5.3 weight per cent. This is in good agreement with the phase Pt$_{5}$P$_{3}$ shown in the phase diagram at 6.0 weight per cent phosphorus.

Additionally, on the surface there are areas that have been molten. These consist of a eutectic of platinum and a Pt-P phase. The photomicrographs Figures 9(a) and 9(b) show a solidified platinum eutectic particle at the edge of the sample. This particle would be liquid at the service temperature, due to the melting point reduction resulting from the uptake of phosphorus, and likely to drop into the liquid glass. In this way glass can be contaminated by minute platinum particles. Even in small amounts these may be harmful to the optical properties of glass. The uptake of phosphorus in eutectically solidified areas of the platinum has been confirmed by microprobe analysis, Figure 9(c), and by SIMS, Figure 9(d). No other contaminations were detected at a level exceeding that of the initial platinum. In the hot-stage microscope the start of melting of the Pt-P phase was found to be about 580$^{\circ}$C, Figure 10, which is in good agreement with the figure of 590$^{\circ}$C given for Pt$_{5}$P$_{3}$ in the phase diagram. At 630$^{\circ}$C droplets of the melt were clearly observed. Above this temperature some evaporation from the sample was seen, an indication of the relatively low thermal stability of the Pt-P phase. With further increases in temperature the molten areas within the material also increased.

During glass melting, the decomposition of the Pt-P phase results from its low thermal stability and explains the presence of microscopically small particles of fairly pure platinum within the glass.

*Platinum Metals Rev.*, 1992, 36, (1)
Fig. 6 After recrystallisation and reaction with melting phosphate mixtures (1370°C/4 min) sectioned platinum wires show:
(a) fine grained microstructure following recrystallisation at 600°C
(b) coarse grained structure following recrystallisation and reaction with the phosphate batch
(c) following exposure to the phosphate mixture, scanning electron microscopy reveals an enlarged grained boundary
(d) the electron microprobe analysis line trace for phosphorus shows a build up of phosphorus at the grain boundary
(e) $^{31}$PO/$^+$ secondary ion-distribution photo (primary ions: O$_2^+$) again showing enrichment of phosphorus at the grain boundaries following reaction with the phosphate mixture
Finally, the formation of Pt₃P₃ by the reaction of platinum with the melting phosphate batch was confirmed by X-ray crystallography.

Discussion

Changes in the morphology of platinum were detected after the reactions involving the melting phosphate mixture (even though these were relatively short term), but not after testing in a phosphate glass melt. The results showed that during the heating and melting of a phosphate batch phosphorus is set free, as the element. This diffuses preferentially along the grain boundaries, especially into coarse grained platinum, causing hot shortness. Platinum forms a liquid phase with phosphorus which changes the mechanical properties of the platinum. Some areas of the platinum surface consist of a eutectic melt, part of which gets into the glass melt causing platinum inclusions.

Phosphorus can be produced easily by the reduction of compounds in the phosphate batch; additionally it is known that such reactions are catalysed by platinum. As can be seen from the thermogravimetric curves in Figure 11 the mass loss during heating in the presence of platinum is greater than it is in the absence of platinum. Furthermore, during the melting of metaphosphates phosphoric acid forms and this attacks platinum, also Pt₃P₃ may be produced.
Fig. 9 Areas on the surface of a platinum sample after reaction with a melting phosphate mixture (1370°C/4 min)
(a),(b) the eutectic melt consists of platinum (light coloured) and a platinum-phosphorus phase (grey)
(c) scanning electron microprobe line scan image of the eutectic for phosphorus
(d) $^{31}/PO^{+}$ secondary ion-distribution photo of the eutectic (primary ions: $O_{2}^{+}$), platinum-phosphorus phase (bright) and platinum (dark)

by a secondary reaction. Once the phosphate mixture is molten and phosphate glass formed the remaining phosphorus is tied up and no reaction with platinum will occur, providing that no other reducing agents are present. This explains the observation that in the long term
tests at up to 500 hours carried out with phosphate glass melts, no uptake of alien elements was detected even by the highly sensitive SIMS technique, neither was any change in microstructure observed.

Investigations with other batches and glass melts, which will be discussed in a later article, showed results comparable to those with the phosphate glass. Generally one may state that there are a number of chemical elements, including phosphorus, lead, arsenic, antimony, boron, silicon and bismuth, which when present at even low concentrations cause embrittlement and a reduction in time to rupture strength of platinum because of grain boundary cracking (5).

As long as these elements exist in the glass as stable compounds—generally as oxides—they do no harm. However, as soon as they occur as elements their diffusion into platinum takes place. In this way low melting point phases, eutectics or even peritectics form and influence

Fig. 10 High temperature photomicrographs of a platinum sample after reaction with a melting phosphate batch (1370°C/4 min). The melting of the platinum-phosphorus phase begins at about 580°C. A scanning electron microscope image after cooling to room temperature is also shown.
Fig. 11 Thermal analysis of the reaction of a phosphate batch with and without contact with platinum: (a) batch in contact with platinum wire, (b) batch without contact with platinum wire (heating rate about 6°C per min; atmosphere: stationary air; alumina crucible; sample weight 500 mg; sample loosely poured; substance for comparison, alumina)

Reducing Corrosion and Increasing Service Life

By making technological changes to the glass melting process the aggressive nature of the melt can be reduced and the working behaviour of the platinum improved.

The investigations on phosphate glass have shown strong corrosion of platinum by the melting batch, but no effect by the melt itself. Therefore platinum corrosion can be appreciably reduced if the reactions that take place during the heating and melting of the mixture are completed before the platinum is brought into contact with the batch. This may be achieved by presintering the batch before melting or by using premolten glass lumps.

Thermal analysis of the phosphate mixture, Figure 11, in the temperature range 850 to 940°C showed an endothermic reaction, with a maximum at 920°C, during which the mixture did not change. When operating below these temperatures no sintering reaction was observed. Above 920°C a very porous low strength body was formed, while at still higher sintering temperatures the porosity decreased.

Based on thermal analysis and other experimental observations a sintering time of 2 hours, at temperatures of 920, 960, 1000 and 1050°C, was selected for the pretreatment of the batch. The sintered material produced in this way was broken into pieces and used for corrosion tests, as was material which had not been pretreated.

In a melting mixture that had not been...
pretreated the time to rupture and the elongation to rupture of platinum during tensile creep testing was quickly reduced to nearly zero. In contrast, a melt from a batch which had been presintered at 920 to 1050°C had no effect on the mechanical properties of the platinum, this is shown by the data in Figure 12.

During lump remelting the batch is first premelted in a ceramic pot then, after it has been cooled and broken into pieces it is finally melted in a platinum container. Figures 1 and 2 show that premelted phosphate glass lumps have no detrimental effects on the high temperature mechanical properties of platinum. Platinum samples subjected to tensile testing after contact with molten sintered phosphate glass or with lump melted glass failed in a transcrystalline manner, as did platinum in the as-received condition. The uptake of alien elements and related metallographic structural changes were not seen in platinum which had been in contact with melts prepared from sintered mixtures or glass lumps.

Thus by presintering the batches or by using lump remelted material the corrosion of platinum is greatly reduced. Since the glass melt or the raw glass does not affect the platinum a continuous melting process can be set up. In this case the untreated mixture is first melted in ceramic containers, then in the second stage the melt is treated in platinum containers only.

In this way glass can be made from mixtures containing elements normally too aggressive to be brought into contact with platinum ware, while glass which is usually processed in platinum ware can now be produced to a higher quality. Thus it is now possible to produce phosphate glass of improved quality using platinum containers.

**Platinum with Improved Properties**

The former Forschungsinstitut für Nichteisenmetalle in Freiberg, Sachsen (Freiberger NE-Institute GmbH) developed a dispersion hardened platinum known as DVS-platinum (8). This was made from foils produced by rolling an alloy of platinum containing 0.3 to 0.5 per cent zirconium, the foils then being annealed in an oxygen-containing atmosphere. A number of foils were then welded together by compression at high temperatures, and the final “sandwiched” sheet was made by cold and hot rolling this layered structure.

DVS-platinum has a fine grained structure...
with small embedded particles of zirconium dioxide, Figure 13. This kind of structure produces excellent resistance to grain growth at high temperatures and an appreciable increase in the time to rupture strength. It may be welded, but as welding is done by adding pure platinum the welds constitute weak points.

The corrosion resistance of DVS-platinum has been tested in phosphate glass. For these tests a specially prepared and treated phosphate batch of similar composition to those discussed earlier was used. In one series of long term tests approximating to a practical application iron and powered sugar (for reduction) were added in order to test the DVS-platinum under extreme conditions. Iron is known to be an element which causes intercrystalline oxidation in platinum, thus reducing its hot strength; the liberation by reducing agents of elements harmful to platinum has been considered above.

The results of these long term tests are shown in Figure 14. It is apparent that DVS-platinum exhibits a much greater time to rupture, and reasonable elongation to rupture, even if one considers that the load on DVS-platinum is 20 N (2 kg/mm²), five times greater than the 4 N of pure platinum, even without contact with glass (Figure 14). For pure platinum the time to rupture and the elongation to rupture are both lowered significantly by the action of the melting batches and by the aggressive phosphate glass which contains iron and a reducing agent. Under identical conditions, however, the effect on the properties of DVS-platinum is rather small.

In contrast to pure platinum, for DVS-platinum no appreciable grain coarsening is observed. After exposure to the phosphate mixture and to a phosphate glass melt a small amount of corrosive attack is seen at a few places on the rim of the samples, Figure 13(c). The uptake of alien elements is never observed. DVS-platinum not only exhibits a better long time to rupture strength but because of its stable fine grained microstructure and the coverage of grains by zirconia it also possesses a higher resistance to corrosion.

Acknowledgement

The author wishes to thank Professor Dr. Ch. J. Raub, Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, for encouraging discussions and for translating this article into English.

References

1 B. Fischer, H. Töpfer and R. Helmich, Silikatechnik, 1984, 35, (11), 329
3 G. Reinacher, Glastech. Ber., 1975, 48, (11), 221
5 B. Fischer, Diss. B, TH Chemnitz, 1983
8 S. Gartner, D. Adam and W. Molle, Neue Hütte, 1979, 24, (3), 103
9 D. Adam and S. Gartner, East German Patent 120,385; 1976