

Platinum in the Glass Industry

INVESTIGATING CONTAMINATION WITH THE ELECTRON PROBE SCANNING MICROANALYSER

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The modern glass industry is a major user of the platinum metals. When correctly used, platinum and its alloys are practically unaffected by continuous contact with molten glass but if reducing conditions are allowed to arise it is possible for reactions to occur which may lead to contamination. This article describes how such failures have been investigated in the Research Laboratories of Pilkington Brothers Limited and draws attention to the importance of avoiding reducing conditions in operation.

The platinum metals are used in large quantities by the glass industry, particularly in refining and processing optical glass for lenses and prisms. Optical glass to be used for instruments has to be of the highest quality in terms of freedom from colour and from ream or local regions of inhomogeneity. Many optical glasses are highly corrosive to refractories but platinum is practically unaffected and it is for this reason that it is used for the continuous melting and stirring of optical glass of the highest quality. Rhodium-platinum alloys are also used for special parts in the production of flat glass and for bushings in the manufacture of glass fibre.

In all these applications contamination of the platinum metals can occur in service, particularly if reducing conditions arise. This contamination drastically affects not only the life of the platinum unit but also leads to colouration of the glass, which is a serious

defect in the case of optical glass. In the examination of such contaminated platinum units the identification of the contaminant is vital to tracing its source and so to the elimination of the cause of failure. For this purpose electron probe microanalysis has been found to be invaluable. It is a relatively new analytical method initiated in France in 1951 by Castaing (1) who built the first practical instrument. The instrument has been developed further in this country by Dr Cosslett, Duncomb, Melford and Mulvey. Several descriptions of the instrument, now known as the electron probe X-ray scanning microanalyser, have been given in the technical literature (2), and only a brief description of the principles of the instrument need be given here.

A beam of electrons emitted from a heated tungsten filament in vacuum is accelerated under high voltage and focused by electromagnetic lenses into a spot less than one micron in diameter on the surface of a metallographically prepared specimen. When electrons strike the specimen, X-rays are excited, characteristic of each chemical element in the area being examined, which may be as small as one micron, and the emitted X-rays are analysed in a vacuum spectrometer. Quantitative analysis is made by rotating the crystal of the spectrometer to the Bragg angle appropriate to the characteristic radiation of the particular element, and the concentration is determined either from the peak plotted by a pen recorder or by reading the number of counts in a given time from a dekatron scaler. The peak or reading is

Fig. 1 Cracks in an electrically heated bushing in 10 per cent rhodium-platinum alloy. Metallographic examination revealed intercrystalline attack with signs of fusion of a contaminating phase (Fig. 2). The results of examination by the electron probe microanalyser are shown in Fig. 3



compared with that produced from a sample of the pure element or a standard of known concentration, and then converted to weight

per cent of the element detected, which can range from uranium (atomic number 92) down to magnesium (atomic number 12).

The electron probe can be made static so that a particular point or particle in the specimen can be analysed, or it can be made to scan the whole specimen. With the scanning technique an X-ray image is seen on one cathode ray tube which shows the distribution of a given element. This can be correlated with the electron image displayed on a second cathode ray tube alongside, the electron image closely resembling the optical image. Thus the distribution of an element can be correlated with the phases seen in the field of

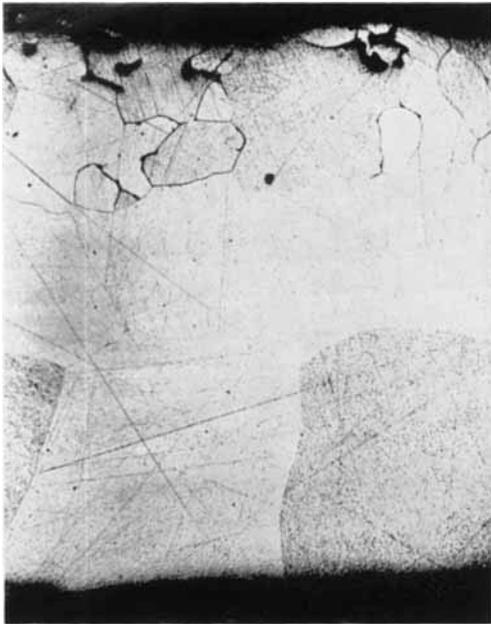


Fig. 2 Microstructure of the contaminated rhodium-platinum bushing showing intercrystalline attack and signs of fusion. ($\times 100$)

a microscope, and this is the feature so valuable to the metallurgist.

An example of this correlation is given in the following case. Molten glass from a furnace flowed into an electrically heated bushing of 10 per cent rhodium-platinum alloy maintained at 1250°C, and issued as a ribbon of glass from a rectangular slot at the base of the bushing. After a time a leak developed in the side of the bushing. The glass flow was stopped and the bushing removed for examination. Two cracks were seen as shown in Fig. 1. The alloy was brittle near the crack and a metallographic examination of a transverse section revealed intercrystalline attack with signs of fusion of the contaminating phase, as shown in Fig. 2.

The etched microstructure, at high magnification, of the intercrystalline contaminating phase is shown at the top of Fig. 3. There appear to be two constituent phases, one etching dark at points 2 and 4, and the other etching light at points 1 and 3. The photograph immediately below shows the electron image of the same area in the X-ray microanalyser. The similarity to the optical image is readily seen. The X-ray images show the distribution of arsenic, platinum and rhodium in the respective photographs towards the bottom of Fig. 3. No contaminant other than arsenic was detected, so what were the two phases seen in the optical and electron image? Quantitative analysis of the dark phase at points 2 and 4 gave the result:

Arsenic	20 per cent
Rhodium	20 per cent
Platinum	50 per cent

and of the light phase at points 1 and 3 as:

Arsenic	20 per cent
Rhodium	45 per cent
Platinum	35 per cent

Thus both regions were alloys of arsenic-rhodium-platinum, but the light etching region was considerably richer in rhodium than the darker, more readily etched alloy. Arsenic both embrittles and lowers the melting point of rhodium-platinum and this

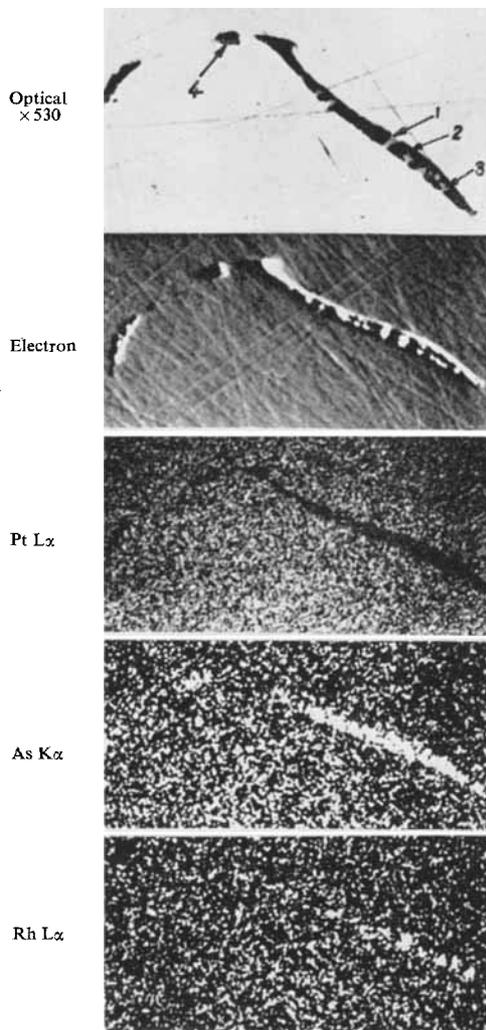


Fig. 3 Examination by X-ray microanalysis of the contaminant phase in the rhodium-platinum alloy bushing. Arsenic, reduced from arsenic oxide present in the glass, was shown to be the cause of contamination

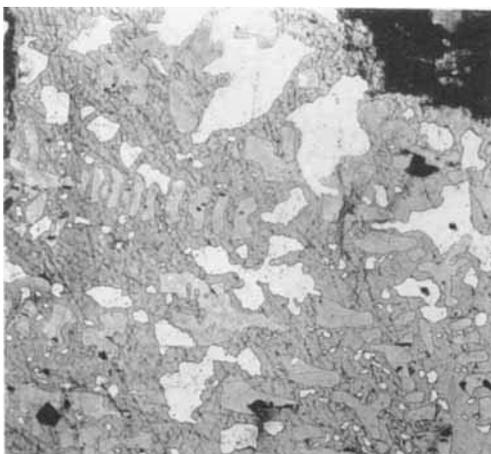
was the cause of the leak. When arsenic is present in a glass it is normally there in its oxide form. In this instance the arsenic oxide was reduced locally by molybdenum used as electrodes for the electrical melting of the glass and the free arsenic so formed alloyed with the platinum of the bushing.

Another case was interesting in that the contaminating constituent is rarely encountered in flat glass manufacture although it

Fig. 4 Failure of an electrically heated 10 per cent rhodium-plated alloy bushing by puncture and cracking at heavily contaminated areas. Again, investigation by means of the electron probe microanalyser revealed the source of contamination--- in this case silicon



occurs more often in bottle glass production. This involved an experimental melt of glass flowing into an electrically heated cone shaped bushing with a cylindrical spout made of 10 per cent rhodium-platinum alloy maintained at 1200°C. Leaks developed resulting in molten glass dribbling down the side of the platinum alloy cone, and the bushing was removed for examination. Two leaks at the base of the cone were found and the tubular spout had cracked as shown in Fig. 4. Fused metal from the punctured areas had flowed down the outside of the tube, leaving a wake of alloy with a rippled surface terminating in a fused blob. Metallographic examination of



a transverse section showed heavy contamination of the rhodium-platinum by a grey dendritic phase as seen in Fig. 5. The specimen was put in the microanalyser and one arm of the dendrite was examined. The electron image at high magnification is shown in Fig. 6a. X-ray microanalysis revealed silicon as the contaminant, the X-ray image showing the distribution of silicon in the dendrite is given in Fig. 6b. The correlation with the electron image is readily seen.

It also appeared that the centre of the dendrite had a lower silicon content than the outside layers. Fig. 6c shows the relative concentration of silicon along the path of the scan, shown as a white line in Fig. 6a, through the section of the dendrite. There is little silicon in the matrix of uncontaminated rhodium-platinum alloy, but as soon as the dendrite is reached the silicon content rises sharply, falling a little in the middle then rising again for the outside edge and finally

Fig. 5 Microstructure of a rhodium-platinum bushing heavily contaminated by silicon. The grey areas are silicide of rhodium-platinum, the white areas uncontaminated rhodium-platinum. ($\times 150$)

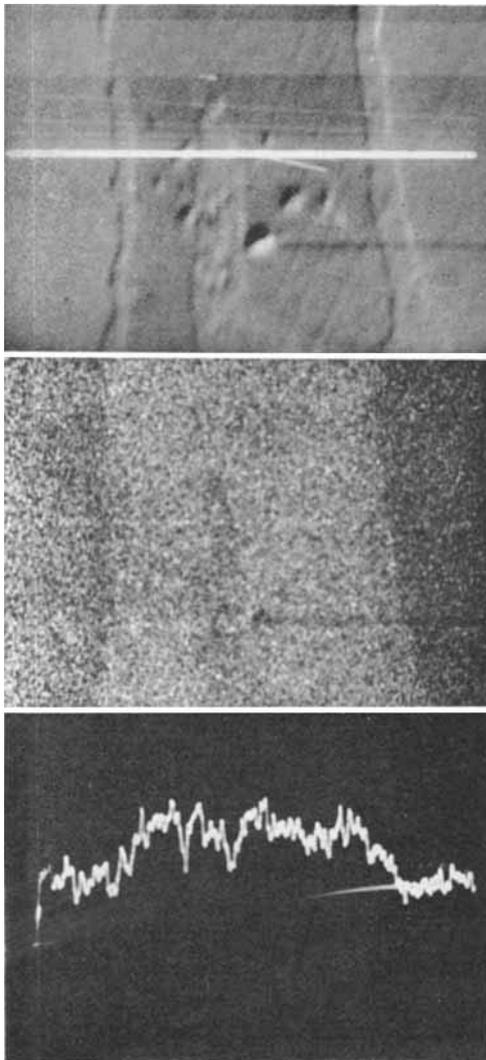


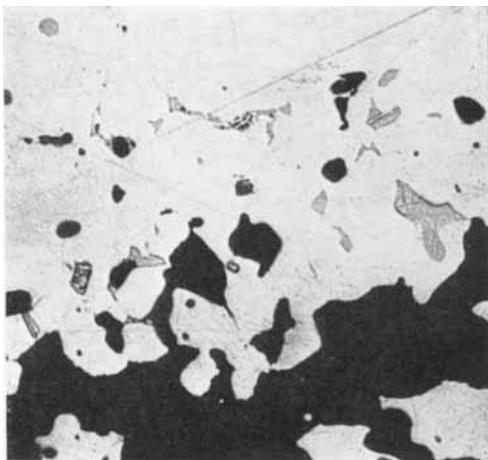
Fig. 6a (top) Electron image of dendrite showing line of scan ($\times 800$); 6b (middle) X-ray image of Si K α showing distribution of silicon ($\times 800$); 6c (bottom) Si K α distribution of silicon along line of scan of Fig. 6a ($\times 800$)

A third example illustrates the great value of the X-ray microanalyser to the metallurgist. The special need to ensure complete homogeneity in optical glass requires that the molten glass must be adequately stirred prior to casting. This stirring may take place at temperatures from 1000 to 1300°C or even higher, depending on the viscosity of the glass which in turn is dependent on its composition. For this purpose a material with high hot strength at these high temperatures is necessary and at the same time it must be resistant to corrosion by molten glass. Molybdenum is very suitable for hot strength and has a high melting point, but it can colour glass owing to slow solution under strongly oxidising conditions, and moreover it forms an oxide which volatilises rapidly in air at about 700°C.

The colouration of glass and the oxidation can be overcome by coating the molybdenum stirrer with platinum or with rhodium-platinum alloys. However, difficulties arise at high temperatures owing to diffusion of molybdenum into the platinum to form a brittle zone which eventually causes fracture

dying away in the matrix of the uncontaminated rhodium-platinum. Silicon readily alloys with rhodium-platinum to form a fusible eutectic of platinum and rhodium-platinum silicide. This accounted for the fusing of the rhodium-platinum alloy at the locally heavily contaminated areas, the fused alloy then running down the tube. The associated cracking is due to the brittleness of platinum silicide.

Fig. 7 Platinum contaminated by arsenic as shown by the pale grey areas. The black areas are glass inclusions ($\times 200$)



of the platinum cladding under stress. In one example of a platinum clad molybdenum stirrer, the cladding had burst and glass had run in. Metallographic examination of a transverse section cut from the platinum cladding showed a pale grey phase occurring as discrete particles and at the grain boundary, as shown in Fig. 7. Particles of glass were intimately mixed and embedded in the embrittled platinum so that it would have been impossible to eliminate all traces of glass from a sample for analysis by optical spectrograph. Since the glass contained arsenic oxide, arsenic would have been reported by this method of analysis. Arsenic certainly would embrittle platinum but a particle of glass containing arsenic (as oxide) by itself would not. The X-ray microanalyser was brought into action on the polished and etched section and by pin-point analysis the round metallic phase and grain boundary contaminant were identified *in situ* as arsenic. There was now no doubt that the arsenic revealed by this analysis was the contaminating phase in the platinum, and not the arsenic oxide present in the closely adjacent glass particles. Here again the local reduction of

the oxide of arsenic present in the glass to arsenic by the molybdenum of the stirrer led to contamination of the platinum cladding after it had burst and allowed molten glass to come into contact with the molybdenum.

There are many other applications to which the electron probe microanalyser has been put. Diffusion studies of metal into glass, as well as metal into metal; identification of metallic inclusions in glass; variation in homogeneity in glass, and the variation in composition of extremely thin weathering bands in ancient glass, have been revealed. The technique of X-ray microanalysis in the fields of mineralogy and biology are being developed, but its outstanding usefulness in being able to analyse minute areas of the microstructure of metals as seen under the microscope is of immense value to the metallurgist.

References

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- 2 X-ray Microscopy and X-ray microanalysis: Proceedings of Second International Symposium, Stockholm, 1960. Edited by A. Engström, V. E. Coslett, and H. H. Pattee, Elsevier Publishing Co, 1960

Novel Isotope Technique in Nitric Acid Plants

TRACING METAL LOSSES FROM PLATINUM ALLOY GAUZES

A significant factor in the economics of nitric acid production is the loss of rhodium-platinum from the gauzes employed in the ammonia oxidation converters. These losses are particularly important in high-pressure plants, where they may be more than ten times as high as in low or atmospheric pressure plants.

Karel Akerman and co-workers at the Institute of Nuclear Research, Warsaw, have described a series of experiments carried out in a nitric acid plant at Tarnow, Poland, aimed at tracing the whereabouts of the platinum alloy lost in operation (*Przemysł Chemiczny*, 1964, 43/6, 306). A platinum gauze containing 2 per cent iridium was neutron activated in a reactor until it contained an activity of approximately 280 mC resulting

from the formation of Ir¹⁹². This isotope has a half-life of 74.4 days and proved much more suitable for the experiments than the shorter lived isotopes Ir¹⁹⁴ and Pt¹⁹⁷ that are also formed. The latter were eliminated from the irradiated gauze by storing it for two weeks before use.

The activated gauze was placed with other rhodium-platinum gauzes in the converter, and the plant operated for thirty-eight days. Activated platinum alloy that had been lost from the gauze was traced throughout the plant with a scintillation counter and the various dust deposits located. It was found that the rate of loss was highest shortly after start-up of the plant and that a good estimate of the dust filter efficiency could be obtained.

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