

Platinum-clad Equipment for Handling Molten Glass

THE MECHANISM OF FAILURE AT HIGH TEMPERATURES

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Under normal conditions platinum-clad molybdenum equipment used in the glass industry eventually fails because of a vapour phase reaction in which molybdenum is transferred to the platinum envelope across a partly evacuated void. In this article, based on a paper recently delivered at the joint meeting of the British Ceramic Society and the Society of Glass Technology in Sheffield in April, it is shown that metal transfer can be largely inhibited by keeping the partial pressure of oxygen in the interfacial volume at a very low level, and practical methods of achieving this objective are discussed.

Platinum-clad molybdenum apparatus is extensively employed for the industrial handling of molten glass, and at temperatures up to 1200°C can be relied upon for several months of useful service. Increased operating temperatures accelerate the breakdown process, however, and although platinum-clad molybdenum still represents the best combination of metals acceptable to the glass manufacturer for use above 1300°C, premature failures in this elevated temperature range tend to occur in a rapid and characteristic manner. Large distortions of the sheath occur at an early stage, the component develops a "blistered" appearance, and the eventual cracking and failure of the sheath leads to catastrophic oxidation of the molybdenum core.

Various explanations for such behaviour have been advanced. It is said, for example, that oxygen diffuses through heated platinum and that failure is caused because of the oxidation products which form at the platinum-molybdenum interface. An alternative mechanism involves the diffusion of molybdenum through the platinum so that the final failure process is caused by the weakening effects of internal oxidation on the grain boundaries of the platinum sheath.

An analysis of the gradually accumulating fund of information showed that neither of these postulated mechanisms accounted completely for the characteristics of actual failures. It was known, for example, that components in which the platinum had been metallurgically bonded to the molybdenum core tended to resist failure for longer periods at high temperatures than those in which the platinum cladding was not in intimate contact with the molybdenum. The blistering which preceded most failures implied the generation of considerable internal forces or pressures, and it also appeared significant that under industrial conditions sprayed alumina barrier layers, although marginally effective below 1200°C, had no significant effect on the process of breakdown at higher temperatures.

The investigation described below was undertaken to establish the true mechanism of failure as a preliminary to the development of generally improved techniques for cladding the refractory base metals with platinum.

Some preliminary tests on platinum-clad niobium were made to confirm that platinum was sufficiently impermeable at high tem-

perature to ensure effective oxidation protection over long periods of time. Niobium was selected for these tests because at 1400°C it takes oxygen very rapidly into solid solution. The increase in hardness thus caused provides a sensitive index of oxygen content and by this method it was hoped to obtain a quantitative measure of the rate at which oxygen diffused through the platinum envelope.

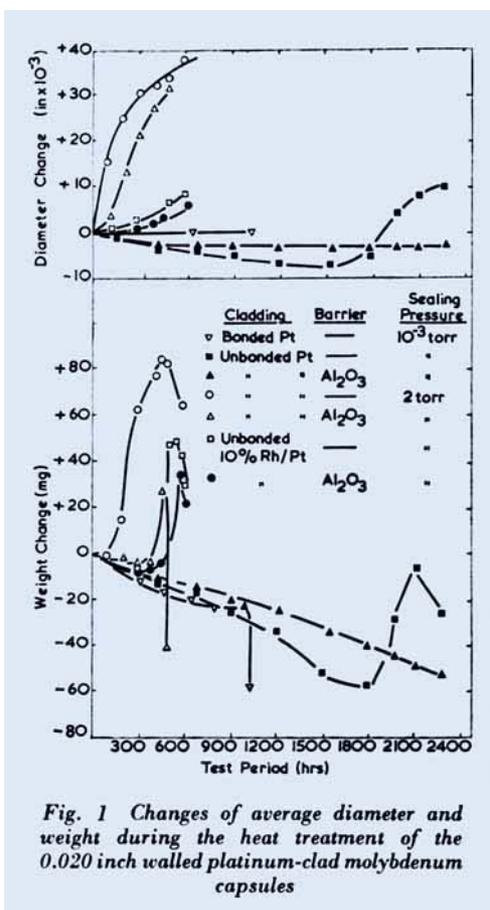
It was found, however, that niobium rods, when sealed up in platinum, softened appreciably even after the capsules were heated in air at 1400°C for over 300 hours. These results, and many others obtained with other specimens, confirmed that platinum, provided that it did not react with the core material, was for all practical purposes completely impermeable to oxygen at temperatures up to 1450°C.

As a complementary approach to this oxygen diffusion problem, platinum-clad molybdenum rods were heated in air, argon, vacuum and glass at 1400°C. Regardless of the test environment, the platinum sheath began to show signs of distortion after 20 hours at temperature. After a test period of 100 hours, the sheaths on all four samples were badly misshapen, and metallographic examination revealed extensive grain boundary cracking within the sheaths, and in the case of the specimen tested in air, gross internal oxidation of the intermediate alloy layers in the immediate vicinity of the cracked boundaries.

These preliminary experiments showed quite conclusively that failure was a manifestation of internal reactions within the composite itself, which were not affected, except possibly after the sheath had cracked, by the nature of the external environment. All of the subsequent tests were carried out in air, this being the most realistic test atmosphere from the practical point of view, particularly since weight measurements could then be used to determine, quite unambiguously, the point at which complete failure of the sheath had occurred.

Molybdenum rods were encapsulated in platinum envelopes which were evacuated and degassed as fully as possible at 1400°C and finally sealed off with residual gas pressures below 10^{-3} Torr. To simulate typical production conditions additional specimens were made in which the pressure of the interfacial volume was reduced to 2 Torr at 800°C and held at this level for about ten minutes before the envelope was sealed off by hammer welding. Both types of specimen were tested with and without a sprayed alumina barrier layer between the molybdenum and platinum, and for comparative purposes some of the capsules without alumina barrier layers were lightly hot swaged to bond the sheath to the platinum core.

After preparation as described above, the capsules were annealed in still air in a horizontal tube furnace for long periods at 1400°C.



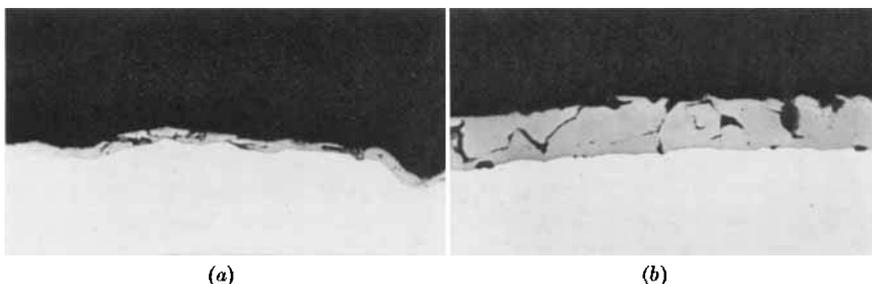


Fig. 2 Surface condition of molybdenum core at the time when increases of weight are first being detected. Specimens sealed with internal pressure of 2 Torr. Heated in air at 1400°C to produce weight increases of (a) 3 and (b) 31 mg. $\times 200$

It soon became apparent that the pressure of gas sealed up in the test capsule had a profound effect upon the rate of failure. Specimens sealed off with an internal pressure of 2 Torr failed after 400 to 600 hours at 1400°C and the alumina barrier layer had no beneficial effect.

Changes of Weight and Surface Effects

The dimensional and weight changes suffered by the test capsules during their periods of heat-treatment in air are summarised in Fig. 1. During the initial period of test, all specimens showed a steady decrease in weight due to loss of platinum from the sheath in the form of volatile platinum oxide. This period of steady loss was, however, at some stage superseded by a rapid increase in weight, inevitably followed by a rapid loss in weight. The onset of failure in loosely sheathed specimens was indicated first of all by a rapid increase in distortion, followed, after a short incubation period, by a similarly rapid change in weight.

The first increase in weight was taken to indicate the beginning of failure as it was at this time that the presence of molybdenum oxide could first be detected. The condition of the molybdenum core when examined at this stage is illustrated in Fig. 2, where the quantity of trapped solid oxides which account for the weight increases can be seen. It can also be observed how this trapped oxide increases in volume with time of heat treatment.

Ultimate catastrophic failure occurs when cracks or grain boundary defects in the platinum sheathing permit the molybdenum oxide to volatilise away as soon as it forms. The alumina interlayer did not retard the incidence of either effect when the capsules were sealed under a vacuum of 2 Torr. The external appearance of the low pressure capsules when

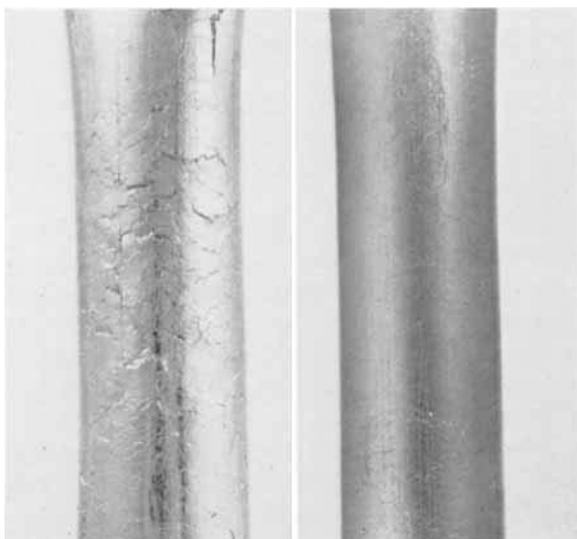


Fig. 3 External appearance of platinum-clad molybdenum test capsules after heating in air for 1091 hours at 1400°C. Left, originally sealed at 2 Torr; right, originally sealed at 10^{-3} Torr. $\times 4$

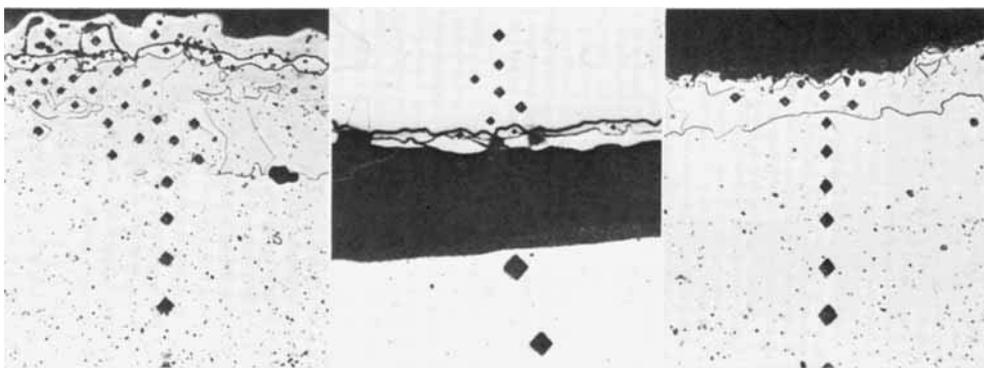


Fig. 4 Diffusion zone on the inner surface of a platinum sheath in which molybdenum was sealed with the internal pressure maintained at 2 Torr. $\times 200$

Fig. 5 Diffusion zone on the molybdenum core, obtained by heat treating a specimen sealed with the internal pressure maintained at 10^{-3} Torr. $\times 200$

Fig. 6 Diffusion zone on the inner platinum surface containing only platinum-rich phases. Sealed at 10^{-3} Torr, with an alumina barrier. $\times 200$

visually examined after 2300 hours at 1400°C suggested that the alumina barrier in these components had delayed ultimate failure by at least 500 hours.

The curves relating to bonded specimens show that the failure mechanism in this type of composite was somewhat different in nature. No dimensional changes were observed, and failure was catastrophic, announced only by a sudden decrease in weight. The most probable explanation of this type of failure is that the molybdenum had diffused completely through the cladding.

The surface condition of two specimens removed from the furnace after approximately 1100 hours at 1400°C is illustrated in Fig. 3. The extensive grain boundary sliding visible on the specimens sealed at 2 Torr is completely absent on the specimens sealed under a hard vacuum, and these illustrations emphasise the importance of sealing pressure on the mode of failure.

Internal Reactions

Metallographic studies were largely concentrated upon specimens which had been removed from the test furnace before the point of ultimate failure. In all specimens sealed up with an internal pressure of 2 Torr, considerable molybdenum deposits were found

on the inside of the platinum envelope. The constitutional relationships of the diffusion zones between molybdenum and platinum have already been described in some detail (1). The same range of phases can be detected on the section shown in Fig. 4, which illustrates the appearance of the inner surface of the platinum envelope after 1091 hours at 1400°C. The presence of a thick layer of sprayed alumina between platinum and molybdenum has had, in this instance, no inhibiting effect on the migration of molybdenum to the platinum.

Molybdenum migration was inhibited, however, by the simple expedient of sealing the capsules in a hard vacuum. The specimen shown in Fig. 5 was sealed off below 10⁻⁸ Torr and the alloying which has occurred is limited in extent and confined almost entirely to the molybdenum surface. Micro-analysis and micro-hardness measurements confirmed that no molybdenum had diffused into the platinum sheath. The failure which eventually occurred in thin-walled capsules sealed under such conditions was suspected to be a consequence of solid state diffusion in local areas where direct metallic contact occurred.

When high vacuum conditions prevailed in the interfacial volume the presence of the sprayed alumina layer restricted the formation

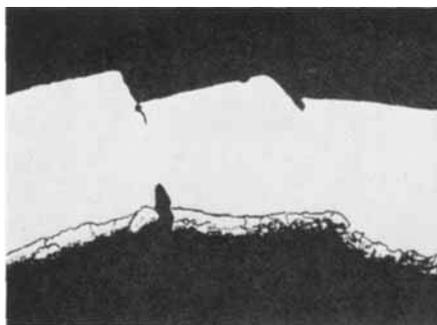


Fig. 7 Section through the platinum sheath of a specimen which had just begun to increase in weight. $\times 60$



Fig. 8 A grain boundary failure within the sheath of a specimen which was rapidly losing weight. $\times 25$

of the diffusion zone on the inner platinum surface. As shown in Fig. 6, this zone contained none of the molybdenum-rich phases.

Fig. 7 illustrates a section taken through a platinum capsule which was just beginning to increase in weight. The sheath has distorted considerably by grain boundary slip and cracks have formed from both the inner and outer surfaces. Under such conditions oxygen can obviously penetrate the sheath sufficiently rapidly to cause the oxidation effects shown in Fig. 2, where the trapped solid molybdenum oxide has not been free to escape.

After close examination of grain boundary cracking of this sort it becomes almost impossible to discount the possibility of direct although limited oxygen ingress through small cracks or fissures in other parts of the specimen. Oxygen diffusion through rapidly sliding grain boundaries must also be considered as a possible mechanism. Catastrophic failure occurs when the exterior cracks penetrate through to the diffusion zone and the molybdenum oxide then formed volatilises at a great rate. Fig. 8, a section through a control test specimen intercepted at this stage, shows the characteristic internal oxidation behaviour of molybdenum-platinum alloys.

Mechanism of Failure

The results described above show that failure occurs most rapidly in those components where the interfacial volume between the molybdenum core and platinum envelope

has been incompletely evacuated before sealing.

They indicate that under such conditions molybdenum migrates rapidly to the inside of the platinum envelope and that the dimensional changes and tensile strains resulting from the formation of these reaction layers cause ultimate failure of the sheath. Molybdenum transfer can be considerably reduced by keeping the pressure within the interfacial volume below 10^{-3} Torr. Under such conditions the direction of metal migration is reversed. Platinum diffuses to the molybdenum although the rate of transfer is very slow.

These simple relationships are complicated by the presence of the alumina barrier layer, which has no effect on metal transfer when the gas pressure is high, but appears to encourage the migration of molybdenum to platinum when the gas pressure is low.

This behaviour must obviously be interpreted in terms of vapour phase reactions as rapid metal transfer occurs even when the molybdenum and platinum surfaces are separated by a considerable void.

The metal vapours themselves are obviously not of critical importance within this context as transport is tremendously reduced under high vacuum conditions. The vapour pressure of platinum is, moreover, approximately twice that of molybdenum at 1400°C and, if any serious transfer occurred via metal vapour, we would have expected to find a

deposit of platinum upon the molybdenum core. As shown by our experiments, this occurred only under high vacuum conditions.

The vapour phase reaction most likely to be promoted by the presence of a residual gas pressure is one which involves volatile oxides. Molybdenum trioxide is such a volatile phase and it is interesting to speculate about the quantitative aspects of molybdenum transfer by this oxide.

The partial pressure of molybdenum trioxide within the interfacial volume will be directly related to the partial pressure of oxygen in the residual gases. Assuming the residual gas to be air, the partial pressure of oxygen at 2 Torr would be approximately 5×10^{-4} atmospheres, and molybdenum oxide vapours would be formed at pressures considerably higher than those of any metal vapours present in the system. It is reasonable to postulate, therefore, a mechanism in which oxygen reacts with the molybdenum to form a gaseous oxide from which the molybdenum is, in turn, extracted by the platinum to form intermediate phases and solid solutions in which the activity of the molybdenum is kept at a low level. Such a closed cycle would operate indefinitely on a very small quantity of trapped oxygen.

When the interfacial volume is well evacuated, the partial pressure of oxygen, and consequently that of the molybdenum trioxide produced, will be very low. Only the very dilute solutions of molybdenum in platinum would have sufficient affinity for the metal to extract it from the low pressure oxide vapours, and this would explain the absence of inter-

mediate phases in the envelope reaction layers in capsules containing alumina barriers which resisted failure for long periods of time.

The somewhat anomalous role of the sprayed alumina barrier layer must also be considered. As would be expected, this permeable layer had little effect upon the vapour phase metal transfer process when gas pressures were high. Under hard vacuum conditions it seems evident that the alumina must have acted as an oxygen source, and as mentioned above, limited, although detectable, alloying occurred at the inner platinum surface. The ability of platinum to reduce alumina under vacuum conditions has recently been established (2), and such reduction processes would inevitably release enough oxygen to promote molybdenum transfer.

Under high vacuum conditions with no alumina present, platinum transferred to the molybdenum. This direction agrees with the relative metal vapour pressures of platinum and molybdenum. In spite of the molybdenum transfer and diffusion which occurred in the presence of alumina, the effective molybdenum concentration above the inner surface of the platinum was insufficiently high to promote the formation of the molybdenum-rich intermetallic phases, and no distortion of the sheath took place. These experimental findings provide a strong clue to the reason for the more satisfactory behaviour of platinum-clad molybdenum components at lower temperatures, since it is now known that at temperatures below 1325°C the molybdenum rich ϵ phase can no longer exist in the diffusion zone (1).

Effect of Zirconium Additions upon the Life of Molybdenum clad with 0.020 in. thick layers of Pure Platinum at 1400°C in air

Core	Barrier layer	Average Life (hours)
Molybdenum	—	460
Molybdenum + 0.1 per cent zirconium	—	1200
Molybdenum + 0.5 per cent zirconium	—	2000
Molybdenum + 0.003 in. of sprayed zirconium	Stabilised ZrO_2	>2300

Non-Volatile Oxides

Since the mechanism of failure had been shown to involve a volatile oxide of molybdenum, experiments were made to confirm that improved results could be obtained by using niobium as a core, this metal having an oxide of low vapour pressure (3).

Specimens sealed with an internal pressure of 2 Torr exhibited lives which were 2 to 3 times as high as those which would be expected from similar specimens containing a molybdenum core. The results obtained on loosely encapsulated specimens did, in fact, confirm the beneficial effects of low vapour pressure oxides as the evidence for vapour transport of niobium to the platinum sheath was very limited indeed. Failures in the main were caused by diffusion which occurred where the sheath and core were in direct metallic contact.

The violent bursts caused by the accumulation of niobium oxide in the failure area were rather more spectacular than those in platinum-clad molybdenum, however, and niobium was found to have other disadvantages which would restrict its application as a core material for platinum-clad apparatus

in the glass industry. Any failure which occurred would have serious effects upon both the glass and the glass tank refractories and few barrier layers can be envisaged which would be completely inert with respect to both niobium and platinum at high temperatures. For this reason attention was concentrated upon the problem of ensuring that the residual gas pressure in the platinum-clad molybdenum apparatus was kept at a very low level. A convenient way of achieving this desirable objective is to use zirconium as a getter (3).

The results of some tests in which the zirconium was added to the molybdenum core as an alloying constituent and as a sprayed deposit are presented in the table. This shows that lives in excess of 2300 hours at 1400°C can be obtained even when the platinum sheath is only half a millimetre thick.

References

- 1 G. L. Selman, *Platinum Metals Rev.*, 1967, **11**, (4), 132
- 2 A. S. Darling, *Metals and Materials*, 1968, **2**, (1), 28
- 3 Johnson Matthey B.P. Application No. 17306/66

Properties and Uses of Palladium

Palladium: Recovery, Properties and Uses, by Edmund M. Wise. Pp. xii and 187
Academic Press, New York and London, \$11 (102s.)

Although it is probably better known for its catalytic uses and its selective transmission of hydrogen, palladium, the cheapest of the platinum metals and the second most abundant, has an unusual ability to form workable alloys with an extremely wide range of other metals. For this reason palladium has a number of commercial uses in the electrical contact field, in special purpose brazing alloys and in dentistry and jewellery, and these applications are all dealt with briefly in the present volume. Perhaps the most valuable part of the book to the metallurgist, however, is the lengthy compilation of binary and ternary equilibrium diagrams that forms the longest chapter, in each case full properties of the alloys being given as far as they are established.

Palladium plating is also of growing interest, particularly in the telecommunications field, and several suitable electrolytes are described in a short chapter on this subject, but it is a little unfortunate that the obsolescent tetrammino-palladous nitrate bath (giving matte deposits) is featured and that no reference is made to the diammino-palladous nitrite bath yielding bright deposits.

Although the title of the book includes the word "Recovery", little or no reference is made to the mineralogy, extraction or refining of palladium, while the substantial output from South Africa also escapes mention.

A final chapter contributed by P. N. Rylander surveys the many types of reactions in which palladium serves as a catalyst.

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