CG IRIDIUM – Metal for the 21st century

Christophe Couderc, Paul Williams and Duncan Coupland, Johnson Matthey – Noble Metals, UK

Introduction

The objective of this paper is to present the history of PGM technologies in the Glass industry: from traditional platinum alloys fabrications to Grain Stabilised and Advanced Coating Technologies. These techniques will help us to understand why CG iridium could be a further advance in materials for glass applications.

Traditional platinum alloys fabrications for use in the glass industry

The platinum group metals (PGM) are characterised by high melting points combined with excellent chemical nobility. These properties are particularly useful in the glass industry. Platinum, with a melting point of 1769°C is one of the most inert of the platinum group metals. It is suitable for applications at temperatures up to 145O°C, although at these high temperatures softening due to grain growth reduces the material’s ability to withstand stresses and hence limits its service life.

The addition of rhodium, typically 10 weight per cent to platinum, produces a much stronger alloy which can be used under more highly stressed conditions, and with some gain in maximum operating temperature. However, the high initial cost of rhodium tends to limit its use as a platinum strengthener.

All conventional platinum alloys exhibit softening with time at temperature and consequent reduction in ultimate strength. This is due to recrystallisation and grain growth. These factors limit the life of many fabrications.

Grain stabilised platinum alloys fabrications

Johnson Matthey has developed a range of Zirconia Grain Stabilised (ZGS) platinum alloys, which suffer less from this undesirable loss of strength. ZGS materials have a fine, evenly dispersed, discrete, second phase of zirconia, present throughout their matrix. These particles slow down the processes of degradation dramatically. They achieve this by pinning dislocation networks formed during thermomechanical processing. With ZGS materials, microstructural degradation is effectively restricted, giving extended operating lives when compared to conventional platinum alloys. Another benefit of ZGS materials is that they possess a better intergranular resistance to contamination. This is achieved through retention of the high aspect-ratio grain structure, which provides a long and tortuous route for intergranular contaminants to travel. [1]

ZGS platinum and alloys were the successful results of a close relationship between suppliers and users. Since then, Johnson Matthey maintained these on-going relationships and continued generating PGM innovations for the glass industry. The goals were to increase the resistance to contamination and extend the service life of PGM fabrications. Another key objective was to help glass manufacturers to better manage their metal inventories and particularly reduce them. This was the idea behind the Advanced Coating Technology.

Advanced Coating Technology for platinum alloys

ACT®, the Advanced Coatings Technology was introduced to the glass market in 1993. It consists of a thin layer of platinum alloy deposited onto a range of ceramic substrates. It seeks to impart the properties of precious metals to non-precious substrates.

Applying platinum as a thin coating provides a more efficient use of the PGM. In general, coating thicknesses vary between 200 and 400 microns. Alloys are pure platinum or 10% rhodium-platinum. The addition of rhodium is not used to strengthen the coating, as the mechanical characteristics of the system rely on the ceramic substrate. It is required for applications running at higher temperatures, up to 1600°C instead of 1450°C for pure platinum. As with all platinum alloy products for use in the glass industry, the metal can be refined and recovered after use. ACT® Coatings possess superior grain growth resistance compared to traditional platinum claddings or fabrications.

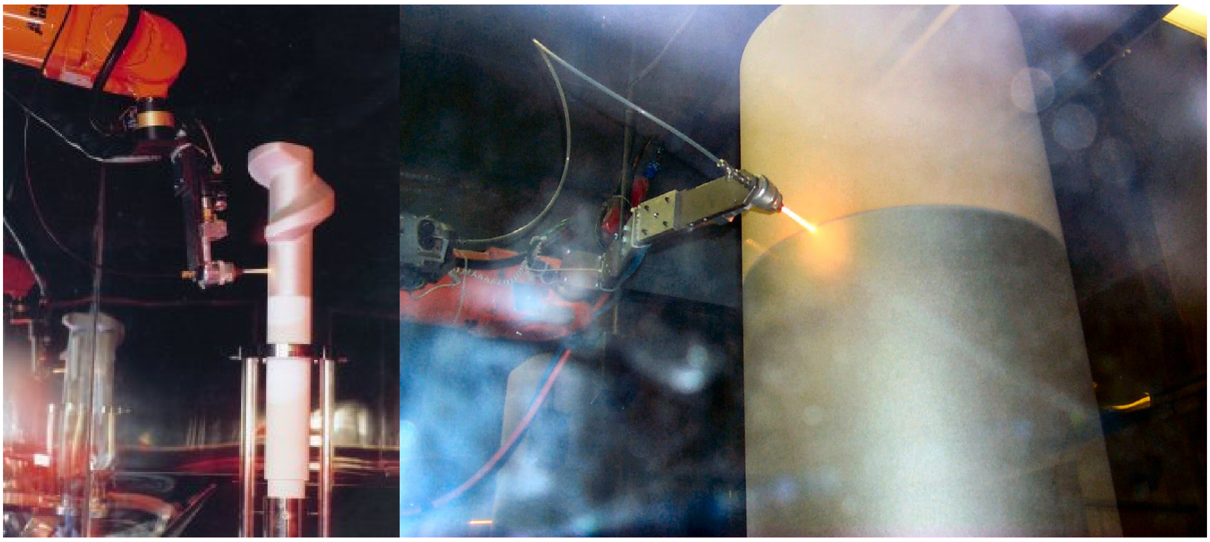

Fig. 1 Photos of ceramics being coated using Advanced Coating Technology.

During the manufacture of traditional sheet based products, the cold rolling of the sheet introduces an important deformation to the material, resulting in energy being stored in the structure. Figures 2a and 3a show the microstructure of such a material. This high-energy structure is useful at low temperatures. It makes a significant contribution to the strength of the material. At elevated temperatures, it provides a strong driving force for recrystallisation and grain growth. The rolling process also affects the atomic orientation of the crystal structure. It favours the merging of adjacent grains even when the level of residual energy has reduced. This eventually leads to large equiaxed grains that continue to grow until they span the entire thickness of the sheet with consequent reduction in material strenght.

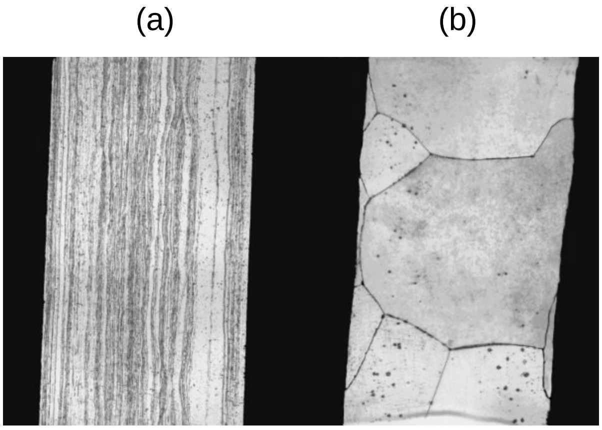

Fig. 2 Platinum sheet (a) before and (b) after heat treatment at 1250°C for 300 hours

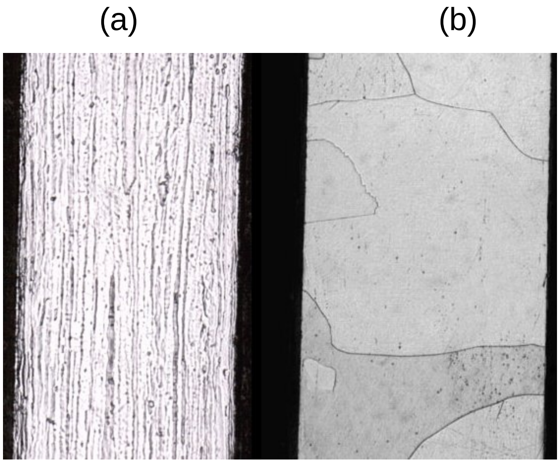

Fig. 3 10%Rh/Pt alloy sheet (a) before and (b) after heat treatment at 1250°C for 300 hours**.**

The micrographs in figure 2 show the microstructure change in a platinum sheet, 350μm thick, when it was heated at 1250°C for 300 hours. The loss of the 'as-rolled' fibrous grain structure is a classic example of the process of recrystallization and grain growth. It affects rolled metals at elevated temperatures unless specific steps are taken to stabilise their structure. In the case presented, single grains have even grown to the full thickness of the sheet. It provides a significant point of weakness, as the platinum is very vulnerable to cracking along the grain boundaries. When fabricated from rolled sheet, rhodium-platinum alloys behave in a similar manner (see micrographs in figure 3). [2]

Finally, the diffusion of contaminants (eg: Pb, As, Sb, Sn, P) present in molten glass, can be exacerbated, as the progressive increase in grain size results in a corresponding decrease in the number of grain boundaries. The diffusion is thus concentrated and more serious.

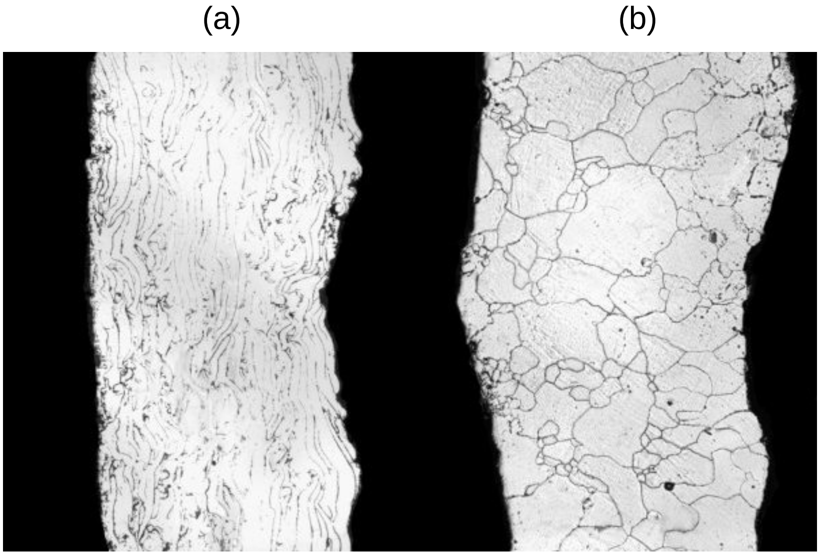

Fig. 4 ACT^{TM} platinum coating (a) before and (b) after 21800h (130 weeks) in service at 1200-1300°C.

The micrographs in figure 4 show an ACT® platinum coating (200µm thick) from a production component before and after service in glass for 130 weeks. The operating temperatures varied between 1200 and 1300°C. After this period, the coating retained several grains across its thickness. It is consequently less susceptible to grain boundary failure. The retention of micro granularity in aged ACT® platinum coatings is probably inherent to its as-deposited microstructure. The ACT® deposition process produces a relatively low energy structure with random orientation of the deposited grains. It probably removes a part of the driving force for grain recrystallisation.

CG iridium clad and fabrications for use in the glass industry

In many glass applications, ACT® platinum coatings are recognised as an effective solution to difficult glass industry problems. However, it cannot be assumed that it can always replace PGM fabrications or claddings. In fact, the two techniques complement each other. Fabrications continue to play an important role as their environmental resistance and robustness could not always be replaced by a coated ceramic substrate. The downside is the relatively high cost of the platinum and rhodium required.

The globalisation of the glass industry continues to reduce end-product prices, even while higher technical requirements are demanded. Therefore, new process solutions are needed. One aspect of this would relate to materials used in the process. Key characteristics would include very high temperature strength, excellent glass contact corrosion resistance and suitability for use under reducing conditions while lowering capital investment. A material with such properties would be invaluable to companies working in these aggressive new market conditions. This is where CG iridium fabrications or claddings have a role to play.

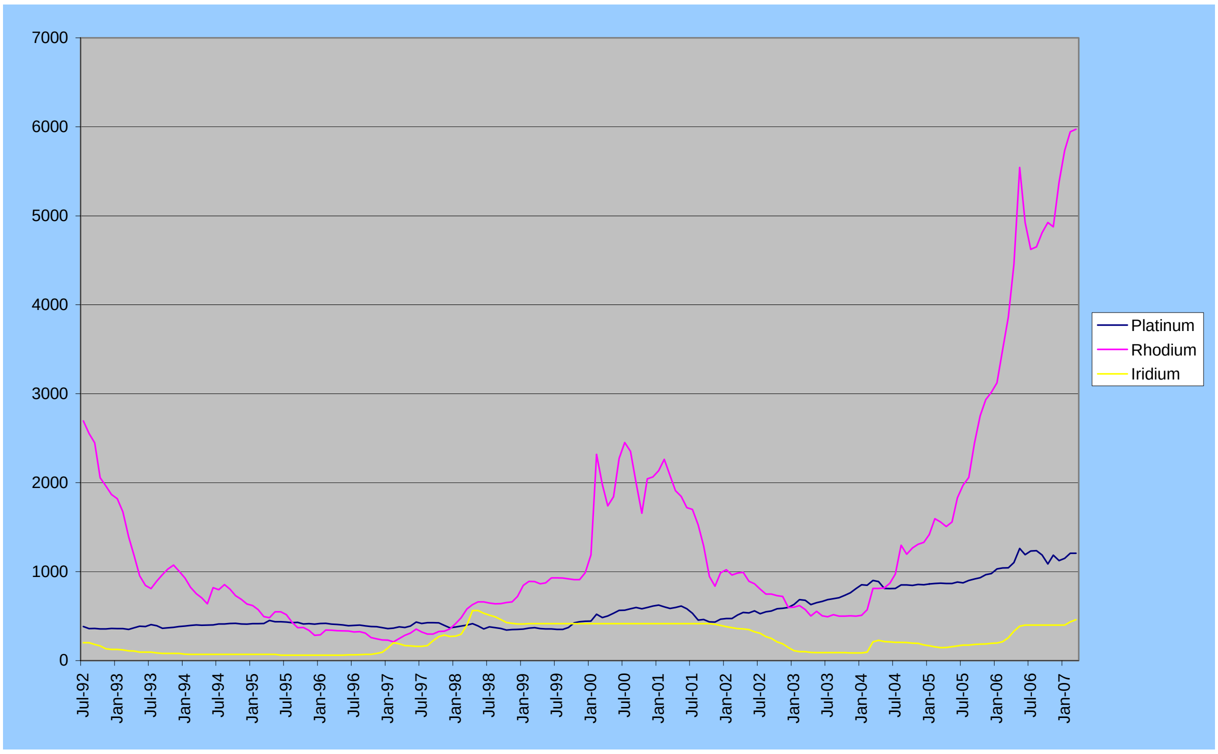

Fig. 5 Price in $ of platinum, rhodium and iridium per troy oz, monthly average

Iridium is one of the platinum group metals. Like platinum and rhodium, it is recyclable but more affordable (see figure 5). Glass manufacturers wishing to reduce their precious metal inventory, increase their return on assets or improve the quality of their product should consider this metal option.

Iridium has been available in the form of sheet for many years, however, before the mid 80’s production was difficult and quality was variable. The yield of finished sheet was as low as 15%. Nowadays, improved melting equipment and processes allow sheet iridium of 0.7mm and 4mm thickness with uniform properties and high quality to be routinely manufactured. The process is efficient and reproducible, giving rise to acceptable high yields of finished product. These product developments were generated by the increasing world demand for CG iridium crucibles, which are used in the electronics industry in the temperature ranges from 1500°C to over 2200°C. Such temperature cycles may last from days to weeks and require rapid transitions between low and high temperature. Crucibles of this type are sometimes expected to have lives of several years of almost constant usage, in mildly oxidising atmospheres.

Of course, glass processing equipment tends to be more complex than a simple crucible. Fortunately, manufacturing capabilities have continued to develop and CG iridium can now be formed to meet these needs. There are still limitations but these can usually be overcome by small design adaptations. [3]

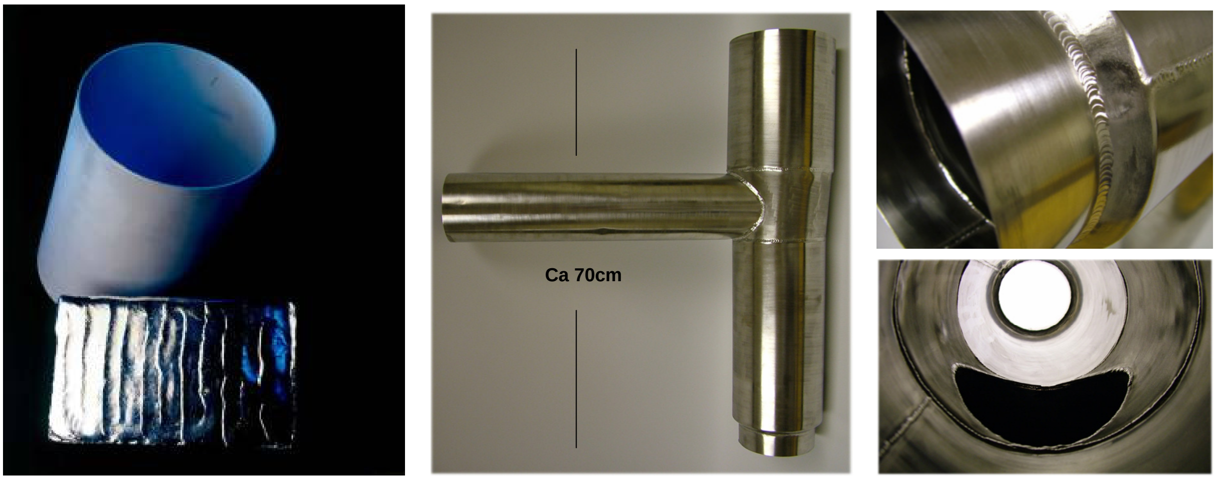

Fig. 6 CG iridium crucible (left) and chamber (right) made by Johnson Matthey.

CG iridium has an excellent strength and creep resistance. The stress rupture curve for several PGM alloys are shown in the figure 7. The y-axis shows the applied stress needed to promote failure in tension in 100 hours. The x-axis shows the influence of temperature. Platinum, shown as the dark blue line, exhibits a moderate resistance to stress even at temperatures as low as 1300°C. Alloying with rhodium increases the strength, and further gains are possible using the ZGS (zirconia grain stablised) versions. Such materials are potentially usable up to 1600°C. CG iridium stress rupture properties are significantly superior to all other alloys presented in this chart and open a new range of working temperatures up to 1800°C or even 2000°C.

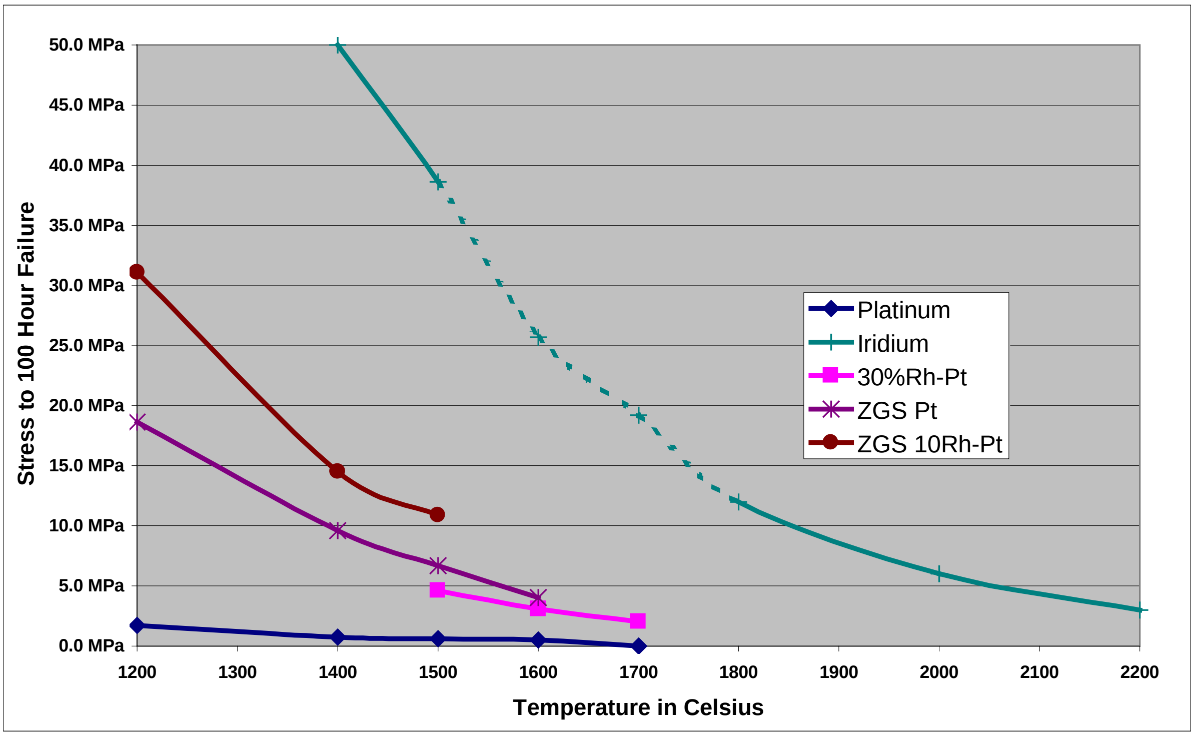

Fig. 7 100 hours stress rupture data

Platinum has issues when used in contact with molten glass under reducing conditions whereas iridium performs exceptionally well. The only downside for iridium is that it has oxidation properties that are less good than those of platinum and its alloys. There are some parallels with the oxidation properties of the refractory metals, although not to anywhere near the same degree, with iridium beginning to show appreciable oxidation as the temperature rises above about 1000°C. Since the oxidation rate is relatively slow, this phenomenon is manageable and no parallel should be made with the catastrophic oxidation rate of molybdenum.

At the beginning

After 1 hour at 1000°C

After 2 hours at 1000°C

Fig. 8 Oxidation of molybdenum (left) versus CG iridium (Right)

A small pellet of molybdenum (on the left) and a small pellet of CG iridium (on the right) were placed in air into a furnace at 1000°C. After one hour in these conditions, the CG iridium has slightly darkened but any dimensional changes are negligible, whilst the molybdenum piece (on the left) has visibly shrunk. Both pieces were returned to the furnace for a further hour. The molybdenum losses are clearly noticeable. After 2 hours in air at 1000°C, about 1/3 of the molybdenum pellet weight is lost. The experiment shows that iridium is far superior to molybdenum in an oxidising environment. However, in order to achieve the desired longevity in service, it is important that some protective measures be implemented at temperatures above 1000°C in air.

When dealing with CG iridium fabrications or claddings, a protective atmosphere can be engineered. Experience shows that CG iridium performs well in nitrogen, argon and reducing gas mixtures. Alternatively, a physical barrier could protect it. Figure 9 shows the results of a patented protection system, tested at 1600°C and potentially viable up to temperatures of 1750°C. This system has clearly protected CG iridium and reduced oxidation to a negligible level, making this no longer a life-determining factor for the material.

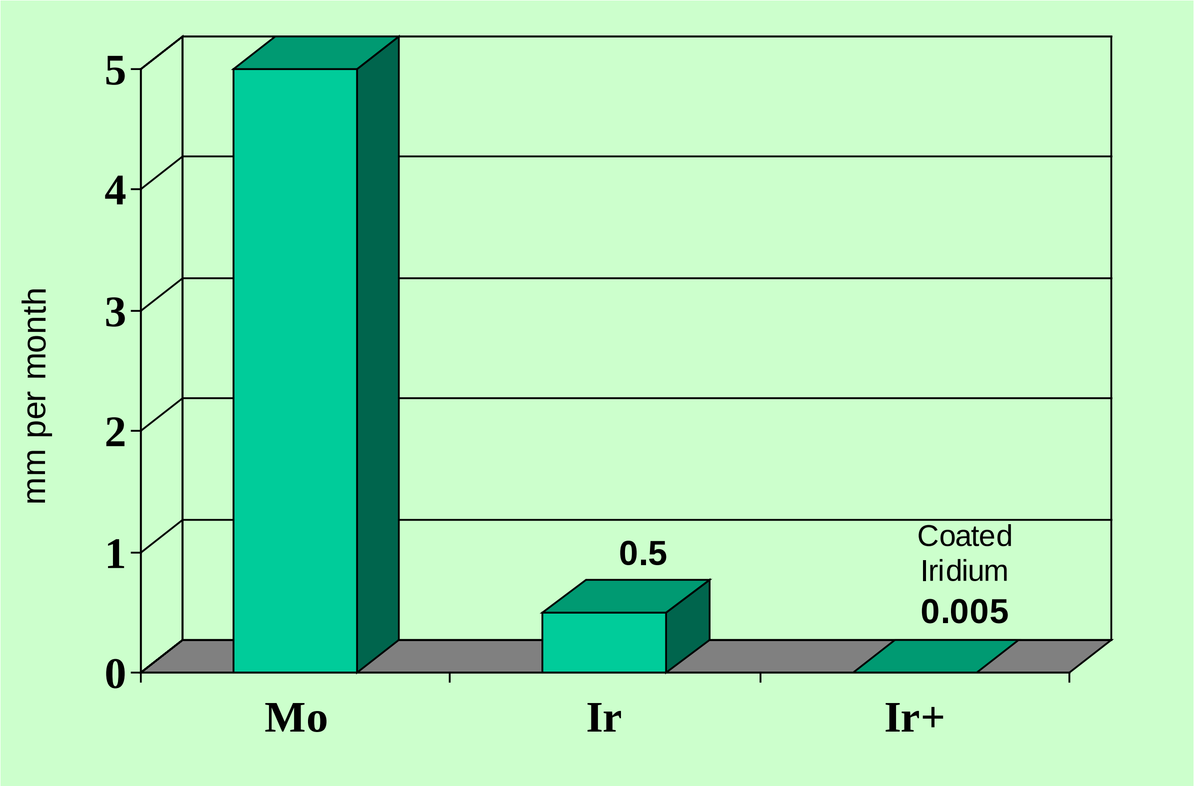

Fig. 9 Molybdenum, CG iridium, coated CG iridium metal loss at 1600°C in Air

Conclusion

CG iridium is formable into complex shapes, has excellent strength and creep resistance and is more affordable as a precious material than platinum or rhodium-platinum alloys.

CG iridium must now be considered as a containment material for molten glass, including for temperatures beyond the normal range of rhodium-platinum alloys.

References

[1] J. Stokes, Platinum in the glass industry, ZGS Materials supplement conventional alloys, Platinum Metal Review, 1987

[2] Paul Williams, Duncan Coupland, Mark Doyle and Jackie Jenner, Grain growth resistance of thermally deposited ACT® coatings

[3] Duncan Coupland, Beyond platinum alloys in the glass industry, technical paper, Glasstec 2006, Germany

JM

Johnson Matthey

Christophe Couderc , Precious Metal Products Division, Noble Metals, Orchard Road, Royston, Hertfordshire, SG8 5HE, phone: +44 (0) 1763 253910, fax : +44 (0) 1763 253313, e-mail : Coudec@matthey.com, www.noble.matthey.com