Platinum in the Glass Industry

ZGS MATERIALS SUPPLEMENT CONVENTIONAL ALLOYS

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Platinum and its alloys have long been accepted as essential materials for the fabrication of equipment used in the glass industry. However the superior mechanical properties of the zirconia grain stabilised materials developed by Johnson Matthey have led to their successful utilisation for many of the most demanding applications; for others conventional platinum group metals and alloys are still preferred and both types of material are considered here.

The platinum group metals are characterised by high melting points combined with excellent chemical nobility. These properties are particularly useful in the glass industry which manufactures a multitude of end products. The range includes domestic glass as tableware or cookware, flat glass for windows, crystal glass for prestige domestic use, optical glass, radiation shields, and fibres for reinforcement and insulation, along with many others. Glasses in their most basic form are combinations of soda, lime and silica together with other modifiers and refiners, which melt at high temperatures to form aggressive liquids.

Platinum with a melting point of 1769°C is one of the most inert of the platinum group metals, and is suitable for applications at temperatures up to approximately 1450°C, although at these high temperatures softening due to grain growth reduces the materials' ability to withstand stresses and hence limits their 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 to about 20 per cent.

One disadvantage in the use of rhodium is that it tends to colour the glass yellow under certain conditions. This limits the applications of rhodium containing platinum alloys where high quality optical or crystal glasses are being manufactured. Pure platinum is therefore preferred in such high quality glass applications, even though the generally higher melting points of these glasses limits the service life of the platinum, due to grain growth and softening with time.

In some areas of the industry control of the glass flow rate is crucial to the success of a forming or processing operation. In such cases the tendency for glass to wet platinum surfaces results in adhesion and poor flow characteristics. To overcome such problems 5 per cent gold-platinum can be used, an alloy which can be described as non-wetting to molten glass. Although limited by a lower maximum operating temperature the use of this alloy has enabled increased glass flow control and improved operating efficiencies.

All conventional platinum group metals and alloys exhibit softening with time at temperature, and consequent reduction in ultimate strength due to recrystallisation and grain growth; in addition deformation occurs by creep. These factors limit the life of many fabrications so Johnson Matthey have developed a range of Zirconia Grain Stabilised (ZGS) platinum alloys which do not suffer from this undesirable loss of strength (1,2,3,4).

ZGS materials have a fine, evenly dispersed, discrete, second phase of zirconia, present throughout their matrix. These particles then slow down the processes of degradation

Fig. 1 During production of the discontinuous fibres used for heat insulation a steady stream of molten glass from an electrically heated feeder bushing is poured into a rapidly spinning basket. After hitting the base of the basket the molten glass is thrown outwards by the centrifugal force, forming fine fibres as it passes through the orifices in the cylindrical wall of the basket. The stream of fine fibres leaving the basket and then falling downwards under the force of gravity can be seen on the left-hand side of the illustration

Photograph by courtesy of Gyproc Insulation Limited

dramatically. They achieve this by pinning dislocation networks formed during thermomechanical processing, so inhibiting the movement of these dislocations to the grain boundaries. This process of dislocation movement is one of the steps that precedes grain boundary movement and competitive grain coarsening, leading to the removal of the highly anisotropic structure developed during the manufacturing operations. As a consequence, softening occurs and the ability of the materials to withstand stress with time at temperature is severely diminished. With ZGS materials microstructural degradation is effectively restricted, giving extended operating lives when compared to conventional platinum group metals and alloys.

Another benefit of ZGS materials is that of improved resistance to intergranular 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. As a consequence, the critical intergranular crack length for failure is increased; this is shown in Figure 2. In summary, the use of ZGS alloys in the glass industry gives the following advantages:

(i) greater strength with time at temperature, and hence longer service life,

(ii) the ability to reduce cross-section (and hence initial cost) for a given level of stress,

(iii) enhanced resistance to intergranular corrosion,

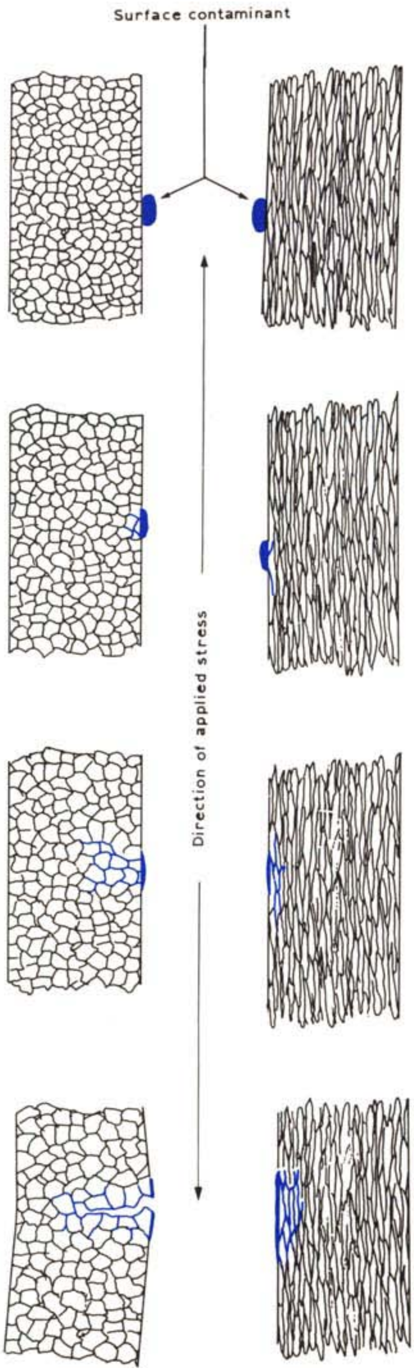
(iv) operation at higher service temperatures.

Zirconia grain stabilised versions of platinum, rhodium-platinum and gold-platinum alloys are used extensively in many areas of the glass industry.

Glass Fibre Production

The manufacture of continuous glass fibres requires the use of a platinum containing component called a "bushing". In essence, bushings are rectangular open topped boxes having bases with numerous precisely shaped orifices, called "jets", through which the fibres are drawn. In the process of glass fibre manufacture, molten glass or glass beads are fed from above into the bushing, heated to the operating temperature by direct electrical resistance heating, and then drawn through the jets in the baseplates. Individual glass fibres are combined to form roving which in turn can be woven into mat, and using a laying-up process and a resin binder large high strength fabrications can be made, for example car bodies. Chopped strands of roving can be added to a resin for use as a high strength moulding compound or for local reinforcement of glass rein-

Fig. 2 When both conventional and ZGS platinum and its alloys are subjected to high temperatures, of say 1400°C, while under stress, there is an opportunity for any surface contaminants to move into the material along grain boundaries. In the case of conventional alloys (left) the worked structure is replaced by equiaxed grains between which the impurities (shown in blue) can move readily, especially normal to the direction of the stress, so weakening the section. However, with ZGS materials (right) there is only very limited grain growth and the grains retain their elongate shape. Although the impurities again move along the grain boundaries the direction of movement is mainly parallel to the direction of stress, so the section retains its mechanical integrity for very much longer



forced plastics. Yarn which is produced from hundreds of filaments twisted together is usually processed into various kinds of cloth, tapes, sleeves, etc., and used for electrical insulation and pipe mouldings.

For the glass fibre producer the Noble Metals Group at Johnson Matthey has developed a proprietary process for the manufacture of baseplates with high precision and excellent metallurgical integrity. Using this process, some 5,000 baseplates have been produced in the United Kingdom and over 30,000 worldwide by Johnson Matthey associate houses.

The method of baseplate manufacture requires the use of special equipment and tools of the highest precision and quality. This is necessary to ensure a high degree of bore concentricity. If concentricity is bad then thinning of the wall in part of the section will occur and in operation a hot spot will be formed. During fibre production the hot spot will lower the viscosity of the glass at that point and it may flow back up the outside of the jets. This leads to flooding of the baseplate, as glass flows among the jets, and prevents fibre production. Single baseplates with up to 2,000 jets and having widths up to 110 mm have been produced; using a modular construction far greater numbers of jets are possible. The jets can be aligned in longitudinal or transverse rows, and within each row the jets can be arranged in a rectangular format or with 60° offsets. Such

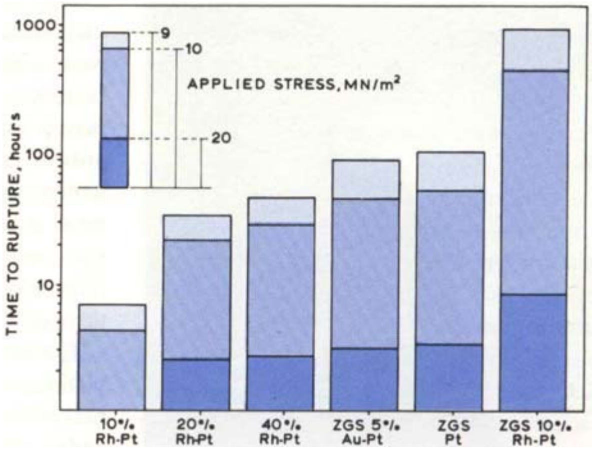


Fig. 3 Typical stress data for conventional rhodium-platinum alloys, and for the Johnson Matthey range of ZGS platinum alloys at 1400°C, showing the superiority of the zirconia grain stabilised materials

arrangements allow for logitudinal or transverse cooling fins, which may be nickel, palladium or silver. The jets themselves may have bore diameters from 1.1 mm up to 2.5 mm and lengths 2.25 times their bore diameters. Wall thicknesses may be as low as 0.25 mm while jets with thicker walls can be counterbored.

Baseplates manufactured from platinum and rhodium-platinum have been used for many years for the production of glass fibres having diameters in the range 25 to 10 μm. Below this the wetting of platinum by glass results in poor glass flow through the fine jets, and thus continuity and diameter are severely affected. Use of the non-wetting gold-platinum alloys has enabled fibres with diameters as fine as 6 μm to be produced economically and with bushing efficiencies in excess of 90 per cent. The use of ZGS platinum, rhodium-platinum and gold-platinum alloys has overcome one of the major operational limitations of a conventional bushing, namely baseplate distortion.

Since the development of ZGS materials bushing lives have increased by over 100 per cent, significantly improving the economics of fibre manufacture. Through the introduction of ZGS baseplates the use of high rhodium content alloys has become less necessary. Additionally, the higher strengths of the ZGS materials have enabled lighter bushing bodies, with thinner wall sections, to be used.

The latest development to improve bushing economics is the use of ZGS 5 per cent rhodium-platinum, which has superior mechanical properties to conventional 10 per cent rhodium-platinum. The reduced initial cost of the alloy, resulting from the lower rhodium content, has proved most acceptable as it has not reduced the life of the bushing.

By establishing a close relationship with glass fibre producers and working with them over many years, Johnson Matthey have gained considerable experience in baseplate and bushing manufacture. Johnson Matthey have now licensed their fabrication processes to glass producers in a number of countries.

Discontinuous Fibre

High quality fibres have a high recovery factor such that following compression during packing, delivery and long term storage, the mat will recover to its original thickness and give optimum heat insulation. This necessitates the use of a platinum or rhodium-platinum spinner basket, which is used in conjunction with a platinum group metal feeder bushing. The feeder bushing can be heated by electrical resistance, either directly or indirectly through the use of a rhodium-platinum coil situated around the orifice ring. The purpose of the feeder bushing is to provide a steady stream of glass of homogeneous composition and closely

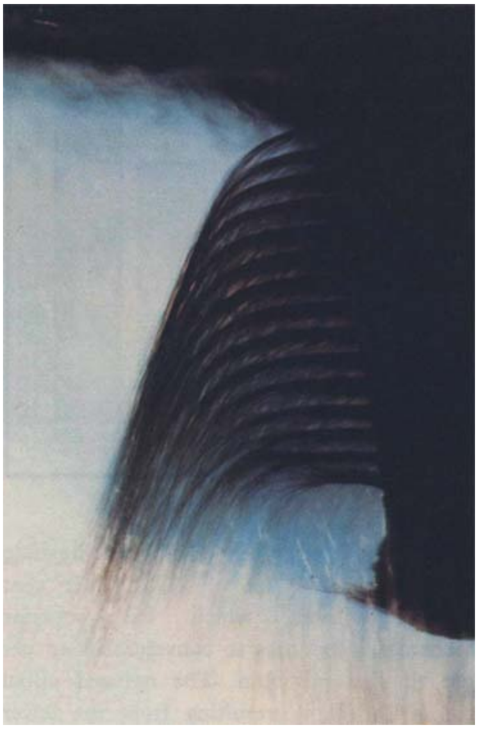


Fig. 4 By means of high speed photography it is possible to record the glass fibres leaving a spinner basket and then falling downwards, as gravity overcomes any residual centrifugal force
Photography by courtesy of Gyproc Insulation Limited

controlled viscosity, from the forehearth to the spinner basket.

Several different licensed methods of producing insulation fibre find applications throughout the world. The essentials of all these methods rely on a spinning basket between 150 and 600 mm in diameter whose walls contain accurately drilled orifices. Glass from the feeder bushing strikes the base of the spinning basket and is then thrown outwards and upwards whereupon it passes through the orifices due to the centrifugal force. The streams of fibres produced are then broken up either by a second rotating spinner or by an attenuating flame, depending on the process employed. Fibres of glass, typically between 9 and 25μm, then fall under gravity onto a conveyor belt where they are agglomerated through addition of a binder.

The use of platinum group metals for spinner baskets has been declining recently due to the use of modern high strength superalloys, which were introduced for economic reasons. However, the life of superalloy spinner baskets may be limited by erosion and distortion of the orifices, resulting in a reduction in the yield of dimensionally acceptable fibres. An improvement is achieved using a platinum-containing alloy, so most insulation fibre manufacturers do retain platinum group metal spinner baskets in their production lines.

Through the introduction of ZGS rhodium-platinum alloys the operating lives of spinner baskets have been improved significantly. The added strength helps to reduce bowing of the basket walls during service. ZGS rhodium-platinum feeder bushings similarly have been introduced where the combination of high strength and resistance to contamination has increased operating lives.

Optical Glass Production

Glass for use in optical applications must be of extremely high quality. In this case the quality determining factors are consistent homogeneity, a high degree of transparency and high transmittance of light.

Transparency is affected by coloration and bubbles, seed and blisters within the glass. Many of these problems were associated with the use of refractories within critical areas of the glass manufacturing process. Through the selective introduction of platinum into the key areas of melting, conditioning and forming, high quality optical glass can be produced.

Pure platinum and ZGS platinum are the preferred materials since, as stated earlier, the use of rhodium-containing alloys leads to coloration of the glass.

In the melting furnace, platinum is used for bubbler tubes, electrodes and, occasionally, as a lining material in small furnaces. Skimmer blocks which remove surface debris from the glass prior to conditioning are common, and consist of a refractory block clad with platinum sheet, typically 0.5 mm thick. However with ZGS platinum a typical cladding thickness could be only 0.3 mm, giving a significant reduction in the weight of the platinum employed.

Optical glass is conditioned to remove bubbles, seed and blisters, to ensure homogeneity of composition and to give close control of temperature, all of which are crucial to the quality of the product. The most common method of achieving these aims is through the use of a refining or fining system made from platinum. Generally tubular in section, the design of these items is proprietary information and varies from plant to plant. Following the signing of non-disclosure agreements with glass producers, Johnson Matthey have manufactured many such items.

At the forming stage in the manufacturing process secrecy again limits the amount of freely available information. However, platinum is used for flow control devices, stirrers and gobbing units, most of which are made of clad refractory.

In summary, the high quality of modern optical glasses results from significant use of platinum and ZGS platinum in key areas.

Crystal and Tableware Glass Production

Crystal glass generally relies upon the addition of lead oxide to give it high transparency, colour purity, a high refractive index and to increase its density. It is a combination of these factors which makes crystal glass such a desirable material for cutting and faceting in high quality domestic ware. In order to achieve consistently high quality, platinum melting, conditioning and processing equipment is now used throughout the industry. In many cases the low throughput of glass by crystal manufacturers dictates that batch melting techniques are used. In these types of operation large platinum crucibles, often up to 500 mm in diameter, are employed for the melting stage. The use of ZGS platinum has extended operating lives, increased resistance to attack from contaminants and in addition, in some cases, it has enabled the weight of the crucible to be reduced. Larger crystal glass manufacturers use small continuous furnaces and in these cases platinum linings are often used.

Conditioning in platinum finers is carried out in a similar manner to that for optical glass production. Again the objective is to produce glass for the forming operation that is homogeneous with respect both to composition and temperature, as well as being free from bubbles.

At the forming end a plunger operating above an orifice ring controls the size of the glass gob, and rotation of the plunger ensures constant temperature throughout the gob. The orifice ring is made from platinum and the plunger is generally a piece of refractory material clad with platinum.

In the case of tableware the use of platinum is generally confined to the forming end of the process where pressing or blowing takes place.

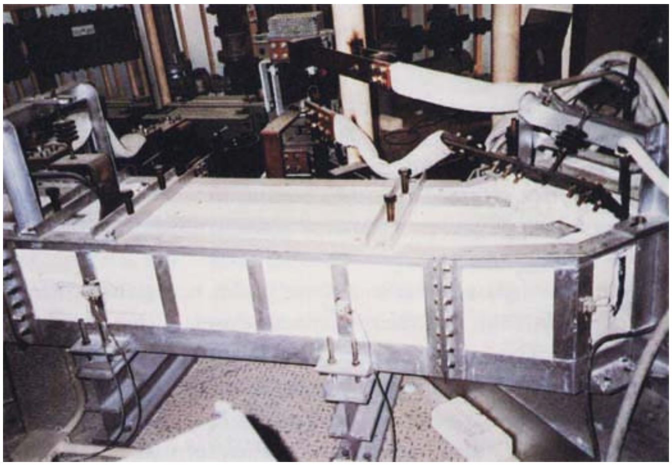


Fig. 5 With good insulation, direct electrically heated platinum forehearths provide an efficient means of producing consistently high quality optical glasses
Photograph by courtesy of EGLASSTREK GmbH

Reaction of Platinum with Miscellaneous Substances (5)	
Substance	Results of reaction, and/or comments
Sodium or potassium carbonate, fusion mixture, alkali bifluorides, borax	Only very small losses occur during normal fusions
Sodium nitrite or nitrate	Up to 1–2 mg loss on fusion
Alkali chlorides, alkaline earth chlorides	Attack on metal above 1000°C, especially at air line
Alkali bisulphates	Attack occurs above 700°C
Magnesium pyrophosphate	Attack occurs above 900°C
Alkali oxides, peroxides, hydroxides, sulphides	When fused will rapidly attack platinum
Sulphuric acid, hydrofluoric acid, alkali hydroxides, sodium peroxide	Evaporations may be carried out with little loss
Hydrochloric acid	No attack if oxidising agents absent
Concentrated phosphoric acid or P_2O_5	Noticeable reaction on prolonged heating
Hydrochloric acid + oxidising agent (e.g. aqua regia)	Rapid attack
Fused cyanides	Platinocyanides formed
Selenium, tellurium, phosphorus, arsenic, antimony, lead, tin, zinc, bismuth, etc.	All attack platinum
Iron oxide, lead or bismuth oxides	Reaction occurs above 1200–1250°C
Air, nitrogen oxygen, oxides of nitrogen, bromine and iodine vapour, carbon dioxide	Negligible effect
Ammonia, sulphur dioxide, chlorine, volatile chlorides	These atmospheres cause attack on platinum
Hydrogen, carburetted gases or vapours, luminous gas flames, reducing gases	Encourage reduction of a wide range of substances at elevated temperatures. Must be avoided
Organic ignitions, coal	Burn off carbonaceous materials at as low a temperature as possible with access of air
More stable oxides, Al_2O_3, MgO, TiO_2, ZrO_2, etc.	Ignitions possible without attack
ZnO, Co_3O_4, NiO CdO and other reducible oxides	Ignitions should be carried out in oxidising conditions
Silica, silicates	Attack under reducing conditions above 1000°C

The supply of glass to a pair of shear blades is sometimes through a rhodium-platinum downdraw tube. This conditions the glass to some extent but also controls the flow to the forming machine.

The corrosive and erosive properties of glasses differ considerably with their composition. In the case of (heat-resistant) opal glass manufacture, extensive platinum cladding is necessary at the forming machine supply end of the forehearth. With other glasses, platinum cladding of refractory metals such as molybdenum is necessary only at or around the glass/air interface.

The use of a paddle plunger or a gobbing stirrer clad in platinum or rhodium-platinum is often used in high output operations. These include feeds to independent section presses or spinning machines used to produce tableware and stemware, such as wine glasses.

Temperature Measurement

In all sectors of the glass industry temperature measurement and control is of extreme importance. With temperature change, glass viscosity and flow rate can vary significantly and the subsequent control of glass forming and processing operations is impaired. Gob size and homogeneity are, for example, of prime importance in the production of crystal glass and precise temperature control is crucial in the control of these factors.

The use of standard alumina sheathed platinum-rhodium/platinum thermocouples for measuring furnace crown temperatures has been common for some time. However, the hot atmosphere above the molten glass often contains exhaust gases from combustion of the fuel and vapour phases from the batch, either of which can attack the alumina sheathing and affect thermocouple accuracy. This problem is compounded by the increasing number of special refractory materials used in furnace linings and by some of the more exotic glass additions which can be incompatible with alumina. The use of 10 per cent rhodium-platinum as a sheathing material over the alumina had proved to be successful in overcoming these problems. In the case of oil fired furnaces the presence of traces of sulphur-containing gases can lead to direct attack on platinum group metals, or to the reduction of refractory oxides which can then cause attack. The use of ZGS 10 per cent rhodium-platinum as a sheathing material has significantly reduced the number of failures due to contamination.

Measurement of molten glass temperature is an area where radiation pyrometers are used extensively. However, such systems only measure the temperature of the glass surface and as such only an approximation of sub-surface temperature and viscosity can be made. A far better temperature measurement and control arrangement is made possible by the use of immersion thermocouples in the furnace and forehearth. These assemblies contain multiple thermocouples which enable temperature to be measured at various depths within the glass. The temperature and aggressive chemical conditions require that these assemblies are sheathed below the glass line with a rhodium-platinum alloy.

ZGS 10 per cent rhodium-platinum is preferred for this use because of its excellent contamination resistance, and its ability to function at high operating temperatures. Additionally, the high strength of the alloy means that only thin sheaths, typically 0.5 mm thick, are needed to protect the alumina.

The use of ZGS 10 per cent rhodium-platinum has proved extremely successful even in the most chemically aggressive glasses, for example the amber glass which is used extensively for container manufacture.

Other Glass Industry Applications

Two-ply glass tubing is used for the manufacture of low pressure sodium vapour lamps. Here a 10 per cent rhodium-platinum mandrel is used to bring a controlled thickness of sodium-resistant glass into contact with the outer glass at a predetermined rate.

In the aerospace industry limited use is made of glass which is coated with thin films of platinum and rhodium.

Conclusion

The platinum group metals and alloys possess chemical and physical properties which occur in unique combinations that make them particularly suitable for many applications in the glass industry.

As glass manufacturers have striven to improve the quality of their established products, to achieve economies in production and to satisfy the demand for new materials, the platinum suppliers have contributed improved fabrication techniques and alloys with superior properties. In particular the use of ZGS platinum and alloys has given improved service life, reduced metal inventories, and improved resistance to contamination, thus extending the applications for platinum in the glass industry. The continuing close relationship between suppliers and users will present further opportunities for progress to be made in glass production technology.

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A Study of Platinum Alloy Welds

THE EFFECT OF HYDROGEN CONCENTRATION

Considerable experience of the use of platinum alloys for glass-melting apparatus has now accumulated, and this shows that a key factor determining service life can be the integrity of the alloy in the proximity of welded joints. Brittle fracture of platinum alloys can result from contaminants entering the weld during fabrication or use, and a recently reported investigation by O. D. Smiyan, B. I. Shnaider, D. M. Pogrebiskii, L. A. Potapenko and E. I. Butkova of the E. O. Paton Welding Institute of the Ukraine SSR Academy of Sciences has considered the effect of welding technique on crack initiation and development (*Avt. Svarka*, 1986, **395**, (2), 10–12, 29).

The alloy used was platinum-20 rhodium-10 palladium-0.1 iridium-0.1 gold, in the form of a disc of 0.5 mm thick sheet which had been annealed for 30 minutes at 1000°C. Concentric welds were made by plasma micro-welding, either under an argon + hydrogen atmosphere or without a protective shielding, while the perimeter of the disc was held rigid. Microstructure, hardness and composition were examined and it was concluded that this alloy is highly resistant to crack formation during welding, that the use of the protective atmosphere does not affect the results, and that there is a relationship between welding sequence and the hydrogen distribution. Under unfavourable conditions the local hydrogen concentration can vary by more than 2:1, and may account for the reduced strength of some welded joints.

It is suggested that the formation of concentric welds, where the stresses are expected to increase as the diameter of the circular weld increases, is a convenient way of evaluating the weldability of a material.

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Solidification in Microgravity

Gravity induces significant disturbances in gaseous and liquid systems. These disturbances are manifested in the form of buoyancy, sedimentation, thermal convection and hydrostatic pressure. All these phenomena affect the solidification characteristics of liquid metals and alloys. By carrying out a solidification process in a microgravity environment, gravity-induced disturbances are virtually eliminated and the solid structures produced are unique in uniformity of composition and properties.

Undercooling experiments have been carried out on a number of refractory elements, including platinum, rhodium, iridium and ruthenium, in the free-fall microgravity ($10^{-6}g_0$; 1×10^{-5} Torr) environment of the drop-tube facility of the Marshall Space Flight Center by W. H. Hofmeister, H. B. Robinson and R. J. Bayuzick (*Appl. Phys. Lett.*, 1986, **49**, (20), 1342–1344).

Both platinum and rhodium achieved an expected cooling rate of between 17 and 20 per cent of their melting temperatures whereas iridium and ruthenium undercooled between 10 and 13 per cent. The latter effect was associated with heterogeneous nucleation caused by impurities. A high degree of undercooling on solidification is an important phenomenon in the production of amorphous, single crystal and metastable phase structures.

Clearly microgravity research is providing an understanding of material behaviour which will lead ultimately to new Earth- and Space-based products and processes. I.R.M.