

High Temperature Mechanical Properties of the Platinum Group Metals

STRESS-RUPTURE STRENGTH AND CREEP BEHAVIOUR AT EXTREMELY HIGH TEMPERATURES

By Bernd Fischer, Andreas Behrends and Dietmar Freund

Department of Materials Technology, Fachhochschule – University of Applied Science, Jena, Germany

and David F. Lupton and Jürgen Merker

W. C. Heraeus GmbH, Hanau, Germany

There is a constantly increasing need for metallic materials with melting points over 1700°C for use at very high temperatures. In contrast to the refractory metals: tantalum, niobium, tungsten, molybdenum and rhenium, which also have very high melting points, the metals of the platinum group, particularly platinum, rhodium and iridium, are characterised by outstanding chemical stability, oxidation resistance and resistance to many molten oxides. The platinum group metals are therefore ideal materials for using at high temperatures while undergoing simultaneous chemical attack and mechanical loading. However, for optimum effective employment of these metals, it is necessary to know their strength and deformation behaviour at extremely high temperatures. Data have therefore been collected from comparative investigations of platinum, platinum alloys, dispersion hardened platinum materials, rhodium and iridium, and the compilations are presented here.

The metals of the platinum group are essentially high temperature materials for the development of high technology products, used, for example, in small rocket engines and other areas of space technology, and in the manufacture of high quality glass and glass fibres. Indeed, many high temperature problems in space technology can be overcome by the use of platinum group metals. The nozzles of rockets which carry satellites from the launch vehicle to their service orbit or are used for positional corrections may be manufactured from platinum alloys. Capsules for radioactive power sources which provide space probes with electrical energy are made from iridium or platinum alloys (1, 2). In the glass industry, platinum and platinum alloys are used in glass melting equipment, such as in crucibles, tank linings, stirrers, spout bowls, plungers, orifice rings and thermocouple thimbles (3) as well as in bushings for glass fibre

production (4). One indispensable application of platinum alloys at elevated temperatures is in catalyst gauzes for the manufacture of fertilisers, cyanides and plastics (5).

Data on the mechanical properties of the platinum group metals at high temperatures are essential for their use in the above areas of application (6). Data are required to ensure that constant material properties are achieved by the production, in order to develop alloys with improved properties, and for the selection of appropriate materials and the optimum design of components.

Because of the creep processes which start to operate at high temperatures, the most important practical material property is the stress-rupture strength. Measurements were therefore taken at temperatures up to 2300°C.

The good stress-rupture properties of the platinum group metals, the strengthening effects of

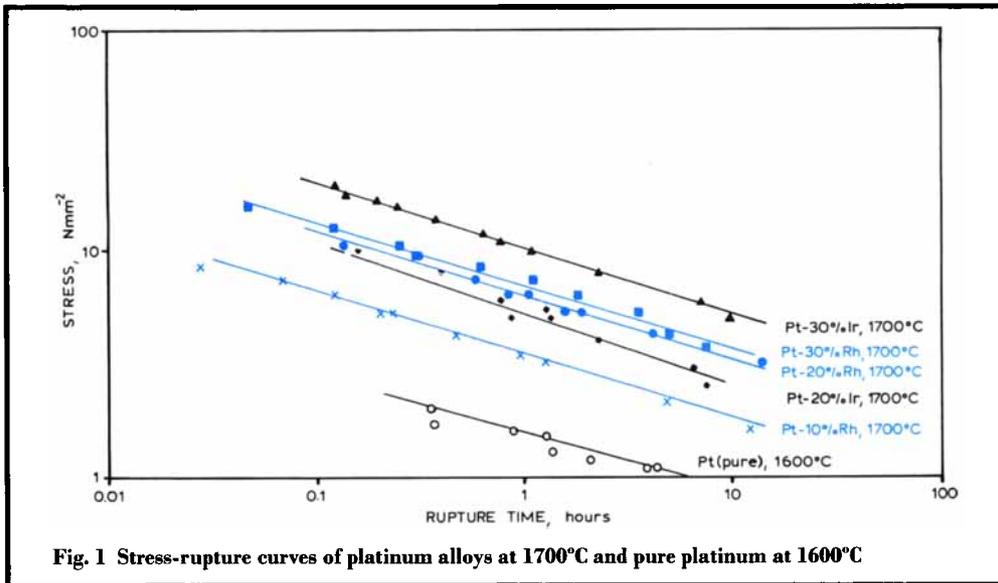


Fig. 1 Stress-rupture curves of platinum alloys at 1700°C and pure platinum at 1600°C

certain alloying elements and the possibility of using dispersion hardening in these materials have long been recognised (7–17). However, few investigations of these metals at temperatures over 1500°C could be found in the literature. Platinum is currently used in the glass industry at temperatures up to about 1600°C. To achieve even better quality in glass and to develop new special grades of glass, components made of platinum or platinum alloys are required which can operate at even higher temperatures. For temperatures at which platinum with its melting point of 1769°C can no longer be used, rhodium (melting point 1963°C) and iridium (melting point 2446°C) have to be employed, for example, in crucibles for pulling laser crystals from oxide melts and in components for space technology. Until now, these components had to be designed without knowledge of the high temperature mechanical properties of their constituent materials.

Experimental Techniques

In the stress-rupture test, a load is applied to a sample of the material and the time to rupture of the sample is determined. The values of nominal stress are plotted against the time to rupture on a double-logarithmic scale to

obtain the stress-rupture curve; this normally approximates to a straight line.

As equipment for stress-rupture testing at extremely high temperatures was not commercially available, a special facility for testing high-melting metals was developed and built where:

- the temperature range of operation was 1000 to 3000°C;
- operation could take place under a protective gas environment if required, for example for iridium;
- creep curves could be determined and
- direct microscopic observations of the crystalline structure of the samples during the stress-rupture test were possible (18, 19).

Using this test facility, comparative investigations were conducted on various platinum, rhodium and iridium materials. The samples of platinum materials for the tests were in the form of strips, 0.5 × 3.0 × 120 mm, supplied from normal production of sheet from Heraeus. For tests on rhodium and iridium the materials were electron-beam melted, then rolled and cut into wire samples of size 1.0 × 1.0 × 120 mm. Comprehensive metallographic and scanning electron microscope (SEM) investigations of the microstructure, the surface structure and the fracture faces were carried out on the

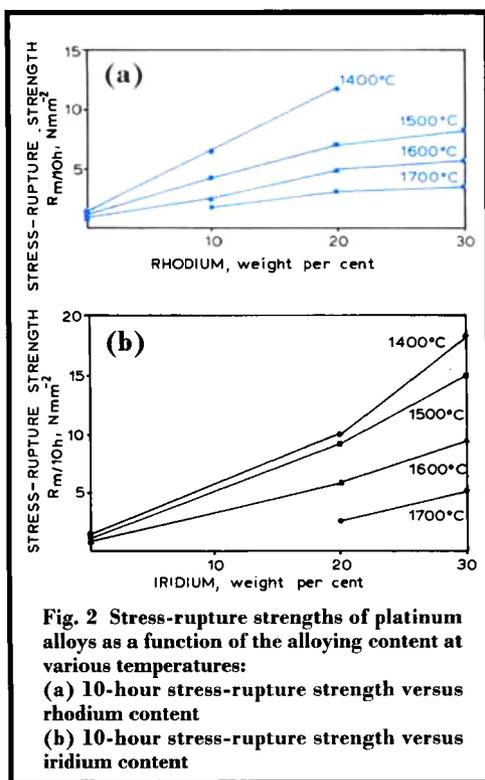


Fig. 2 Stress-rupture strengths of platinum alloys as a function of the alloying content at various temperatures:
(a) 10-hour stress-rupture strength versus rhodium content
(b) 10-hour stress-rupture strength versus iridium content

samples after testing, to obtain a better understanding of their behaviour during the test. The results of these investigations are summarised here with some examples.

High Temperature Properties of Platinum and Platinum Alloys

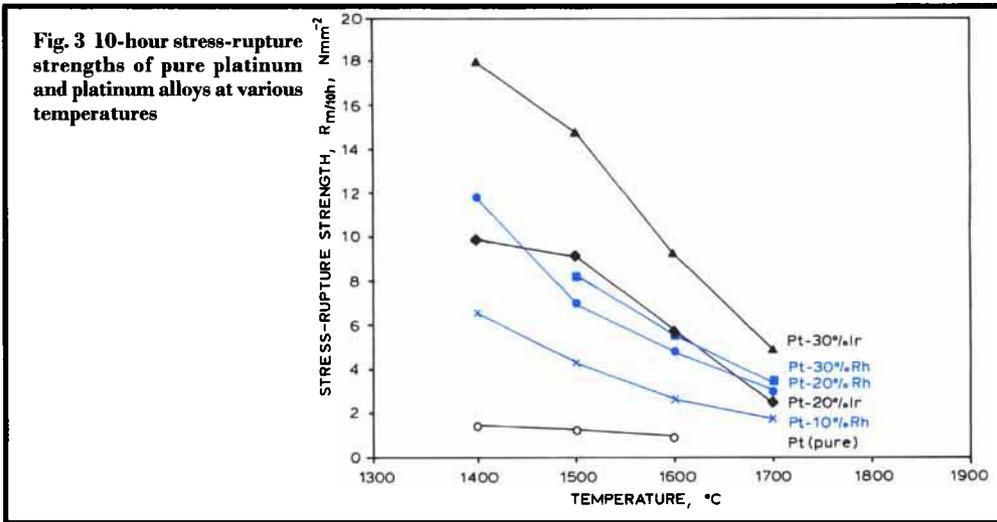
Stress-rupture curves at 1700°C for platinum alloys containing 10 to 30 per cent of rhodium and iridium and at 1600°C for pure platinum are shown in Figure 1 (20). The stress-rupture curve of pure platinum was included for comparison, because at 1700°C platinum can neither be tested in the stress-rupture apparatus nor used as a structural material. The individual values obtained showed an excellent degree of reproducibility and lie almost ideally on straight lines in the stress-rupture diagrams. By interpolation from the stress-rupture curve, it is possible to define the stress-rupture strength for a particular time, for example, for 10 hours, to facilitate comparison of different materials.

In Figure 1, it can be seen that solid-solution strengthening of platinum leads to an enormous increase in the stress-rupture strength. As would be expected, the effect increases with increasing amounts of the alloying addition. The alloys investigated have a higher stress-rupture strength at 1700°C than pure platinum at 1600°C.

However, alloys with alloying additions of more than about 30 per cent are not generally used as structural materials because of problems that arise in their processing. Values for the stress-rupture strengths of alloys with 20 per cent rhodium and 20 per cent iridium do not differ very greatly, although the platinum-rhodium (Pt-Rh) alloy has a slight strength advantage. Increasing the alloying addition by a further 10 per cent leads to only a moderate increase in stress-rupture strength for the alloy platinum 30 per cent rhodium (Pt-30%Rh), whereas the platinum-30 per cent iridium (Pt-30%Ir) alloy shows a substantial strength increase, see, respectively, Figures 2(a) and 2(b). At a test temperature of 1700°C, for example, the increase in strength for Pt-20%Rh on addition of a 10 per cent increase in rhodium is only $\sim 0.3 \text{ N mm}^{-2}$ compared with $\sim 2.5 \text{ N mm}^{-2}$ for the Pt-Ir alloys, that is, the strength of these alloys is doubled. Similar relationships have been found in studies of high temperature elastic properties of these alloys (21).

In practice alloys with more than 20 per cent rhodium are rarely used because the increase in strength does not compensate for increased problems in fabrication. Care must also be taken in using Pt-Ir alloys with high iridium contents because they can become embrittled in service at intermediate temperatures due to the precipitation of primary iridium in the platinum matrix.

Figure 3 shows the 10-hour stress-rupture strengths as a function of temperature for pure platinum and the alloys over the temperature range 1400 to 1700°C. At all temperatures the Pt-30%Ir alloy has the highest strength. The stress-rupture strength of pure platinum even at 1400°C is lower than that of any of the alloys investigated at 1700°C. For all the alloys the relative decrease in stress-rupture strength

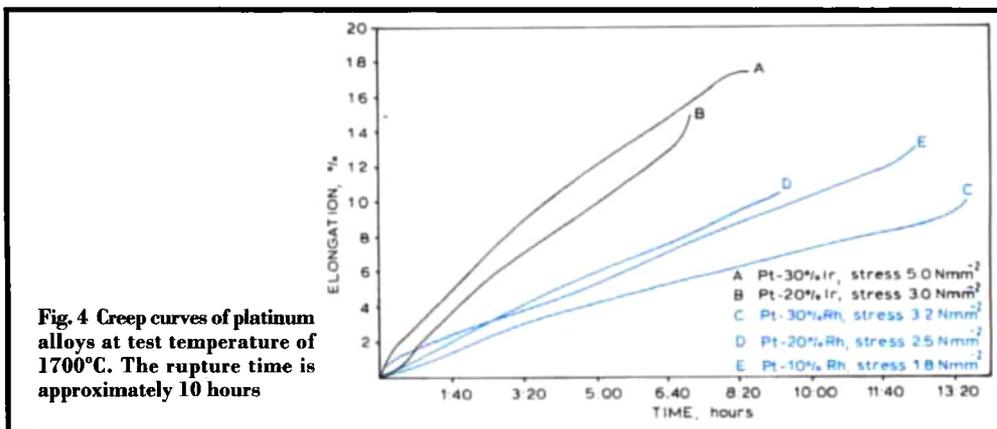


resulting from a temperature increase from 1400 to 1700°C is very similar. However, the strength of pure platinum, although low at all temperatures, decreases more slowly as the temperature is increased.

Using alloys at high temperatures under conditions of mechanical loading leads to a change in their dimensions by creep, that is by diffusion-controlled deformation processes that are time and rate dependent. Figure 4 shows creep curves of the platinum alloys investigated. The stress was selected for each sample so that a stress-rupture life of approximately 10 hours was achieved. The change in the overall length of the samples was measured as a function of

the testing time. The elongation values therefore relate to the nominal gauge length of 100 mm. However, because samples were direct resistance heated, only the central part of each gauge length reaches the test temperature and it is cooler near the grips. The true elongation in the central portion of the sample is therefore considerably greater than the values shown. In the secondary, steady-state range of creep, all alloys show similar creep rates in the range 2 to 5 $\mu\text{m s}^{-1}$.

The Pt-Ir alloys give higher values for rupture elongation than the Pt-Rh alloys. The Pt-30%Ir alloy, which has the highest stress-rupture strength, also shows the greatest elongation to



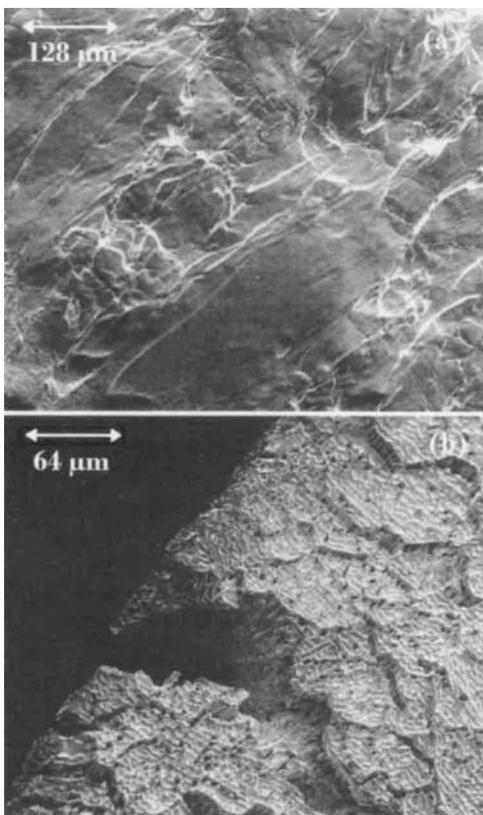


Fig. 5 Scanning electron micrographs of the surface near the fracture zone of Pt-30%Ir samples after the stress-rupture test:
(a) rupture time approximately 1 hour
(b) rupture time approximately 10 hours

fracture. It also demonstrates excellent ductility at very high temperatures, despite the very high level of solid solution strengthening and the tendency of this alloy to embrittlement at lower temperatures.

The high fracture elongation of the Pt-30%Ir samples in the stress-rupture tests was accompanied by a very considerable degree of necking. After short test times slip bands could be seen on the surface of the material in the zone close to the fracture, some of which can be seen in Figure 5(a).

At longer test times, intergranular cracks, creep pores and superficial structures resulting from the selective evaporation of iridium were observed, see Figure 5(b). A certain amount of loss of iridium by evaporation in the form of

volatile oxides had no measurable influence on the high temperature mechanical properties at the test durations studied.

High Temperature Properties of Dispersion Hardened Platinum Materials

In a number of applications solid solution strengthening is insufficient, for example, when maximum mechanical stability is required at very high temperatures. The use of solid solution additions may also be limited for other reasons, such as, they have insufficient oxidation resistance or there is embrittlement of the alloy after exposure. In these cases the dispersion hardening of platinum materials can be used to its full advantage.

One example of this is the melting and processing equipment used for the manufacture of quality high grade optical glass, when it is not possible to use the Pt-Rh and Pt-Ir alloys discussed above. If trace quantities of the alloying elements dissolved in the glass melts it would be severely detrimental to the optical properties of the glass, causing discoloration of the glass and a reduction in the optical transmission. Less noble alloying elements cannot be considered for the solid solution strengthening of platinum in these applications because they would be detrimental to the corrosion resistance of platinum in the molten glass and the corrosion products would lead to even greater contamination.

Platinum used for melting equipment for optical glass must therefore be strengthened by other means. A strengthening effect can be achieved by the introduction of finely dispersed stable particles into the alloy matrix; this is known for other materials, such as the alloys of nickel, copper and aluminium. In order to ensure that the dispersion hardening is effective up to the highest possible temperatures, the dispersed phase must have a very high thermodynamic stability, a higher melting temperature than the matrix and must be insoluble in the matrix even at the highest temperatures. For this reason oxides are preferable to carbides and silicides. Furthermore, oxygen is harmless to platinum, in contrast to both carbon and silicon.

Oxides of zirconium and yttrium have proved particularly effective for the oxide dispersion hardening of platinum. Provided that the oxide particles are very small ($< 1 \mu\text{m}$) and the inter-particle spacing is also small ($< 10 \mu\text{m}$), the dispersion of particles will hinder the movement of dislocations in the matrix. During cold-working of the semi-products, high dislocation densities are created. These lead to a significant hardening of the material. The presence of particles at grain boundaries also hinders the movement of the grain boundaries at high temperatures and thus restricts grain coarsening. In this way, it is possible to achieve a stable fine-grained microstructure in the platinum which is maintained during long-term service at high temperatures.

The use of dispersion hardening is not limited only to pure platinum. It is also possible to increase the strength of solid-solution strengthened platinum alloys further, especially at very high temperatures. The development of dispersion hardened platinum and platinum alloys has permitted a substantial increase in the range of possible applications of platinum materials at high temperatures.

During the present work, platinum materials which had been dispersion hardened with zirconium-yttrium oxide particles were investigated (22). These materials are designated DPH here. High temperature properties were determined on dispersion hardened platinum (Pt DPH) and on the dispersion hardened alloys Pt-10%Rh DPH and Pt-5%Au DPH. The materials Pt DPH and Pt-10% Rh DPH are already widely used in the glass industry and many other fields where long term reliability is essential. They can be readily processed, and their good forming properties and excellent weldability, in particular, are important features in the manufacture of equipment and components.

The micrograph in Figure 6(a) shows finely distributed particles both in the matrix and at the grain boundaries of Pt-10%Rh DPH. The lower-magnification micrograph in Figure 6(b) shows elongated grains resulting from cold rolling of the sheet. After the stress-rupture test the microstructure has recrystallised, see Figure 6(c).

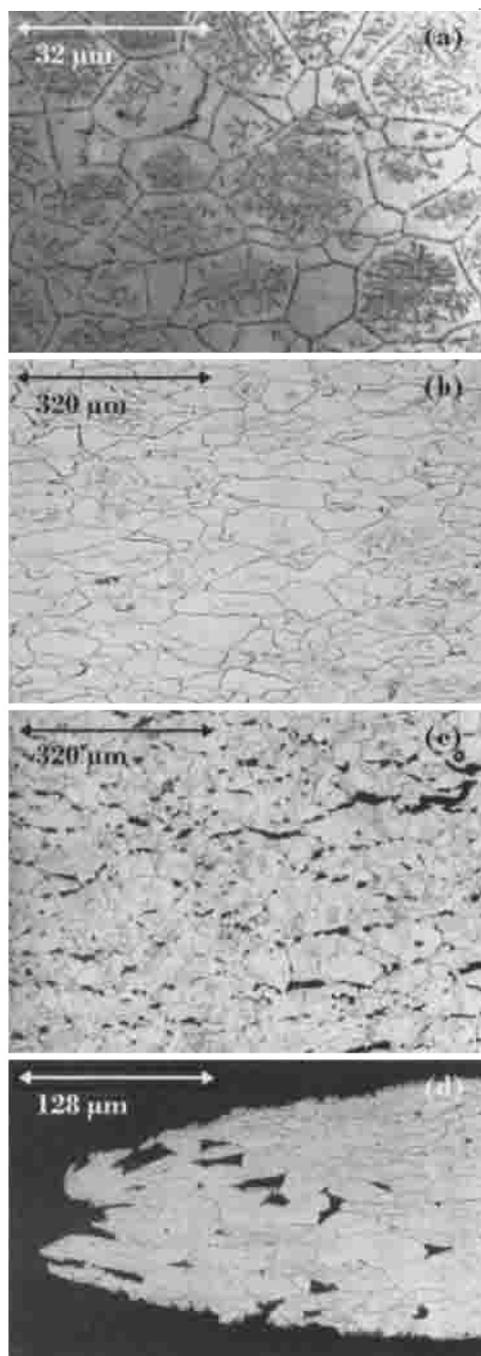
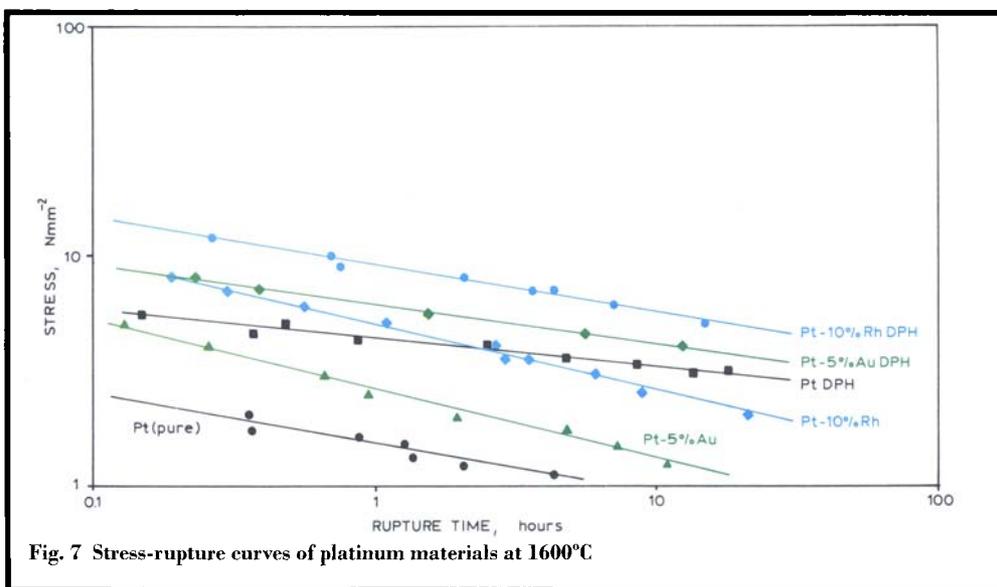


Fig. 6 Microstructure of Pt-10%Rh DPH:
(a) initial state
(b) initial state after cold rolling
(c) after stress-rupture test at 1600°C; tested for 8.87 hours; some way from fracture
(d) after stress-rupture test at 1600°C; tested for 8.87 hours; fracture with deformation



However, despite the high test temperature of 1600°C it has remained very fine grained. The severe deformation of the material, which largely occurs at high temperatures by grain boundary sliding, has resulted in numerous creep pores at the grain boundaries. This microstructure is much more favourable than that of the conventional alloy Pt-10%Rh in which similar conditions lead to a coarse microstructure with fewer, much larger pores at the grain boundaries. The dispersion hardened material has necked down substantially during the stress-rupture test, see Figure 6(d), which shows its good ductility. The severe deformation in the necked zone has led to a marked elongation of the grains.

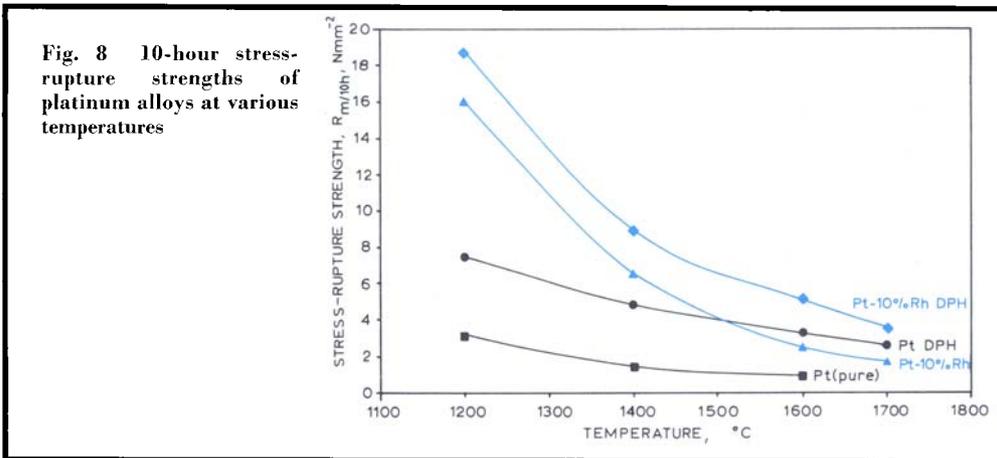
It is possible to control the stress-rupture strength of the dispersion hardened platinum materials by adjusting the content of the dispersed phase and modifying the production process. As would be expected, maximum strength is associated with a reduced level of ductility.

However, our experience with customers has shown that for most applications material with maximum ductility is preferred to material with the highest level of strength. The stress-rupture curves in Figure 7 and the following diagrams

refer to DPH materials which are optimised with regard to their ductility.

It is particularly interesting that all DPH materials have significantly greater stress-rupture strengths than the three conventional alloys. At the longer test times Pt DPH has a higher stress-rupture strength than the Pt-10%Rh alloy. It is significant that the stress-rupture curves of the dispersion hardened materials show a more gradual decrease in strength with increasing rupture time than those of the conventional materials. This means that the dispersion hardened materials show an even greater strength advantage when they are used for components with long service lives. The relatively short test times, which are dictated by the available testing capacity, are completely adequate to compare different materials. However, the design of components for use, for example, in the glass industry requires values determined over longer test times and such tests are currently in progress.

The main application for the Pt-5%Au DPH alloy is in the production of crucibles, dishes and other items for the analytical laboratory, where its stable fine-grained structure is of particular advantage along with its well known anti-wetting characteristics. This material has



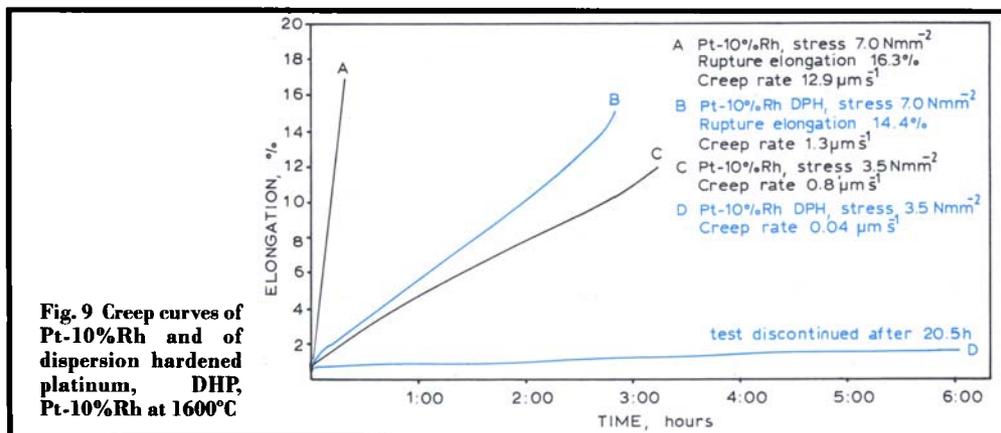
not yet achieved significant use in structural components for glass processing. However, as can be seen in Figure 7, the alloy also has interesting high temperature mechanical properties and its strength exceeds that of conventional Pt-10%Rh.

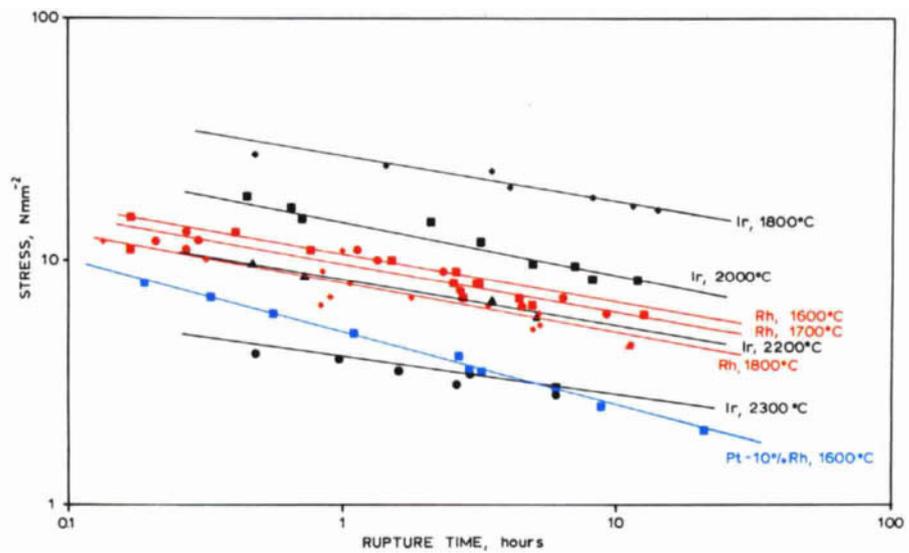
In Figure 8 is shown the 10-hour stress-rupture strength as a function of temperature for the dispersion hardened materials Pt DPH and Pt-10%Rh DPH in comparison to the conventional materials. The advantage of the dispersion hardened materials, especially at the highest temperatures, is quite clear. The temperature limit for the use of platinum materials, for example in the glass industry, is currently ~ 1600°C. However, Figure 8 shows that Pt-10%Rh DPH has a higher level of strength

than the conventional alloy even at considerably higher temperatures.

Examples of creep curves for Pt-10%Rh DPH, compared to the conventional alloy, are shown in Figure 9 for a test temperature of 1600°C and two test stresses. The higher strength of the dispersion hardened material produces a much longer time to rupture at the same stress and a much lower creep rate in the linear range of secondary creep. For example, the creep rate of Pt-10%Rh at 1600°C and a test stress of 7.0 N mm⁻² is reduced by a factor of ten (from 12.9 μm s⁻¹ to 1.3 μm s⁻¹) by dispersion hardening.

Structural components which are manufactured from the dispersion hardened material therefore show greater stiffness and resistance





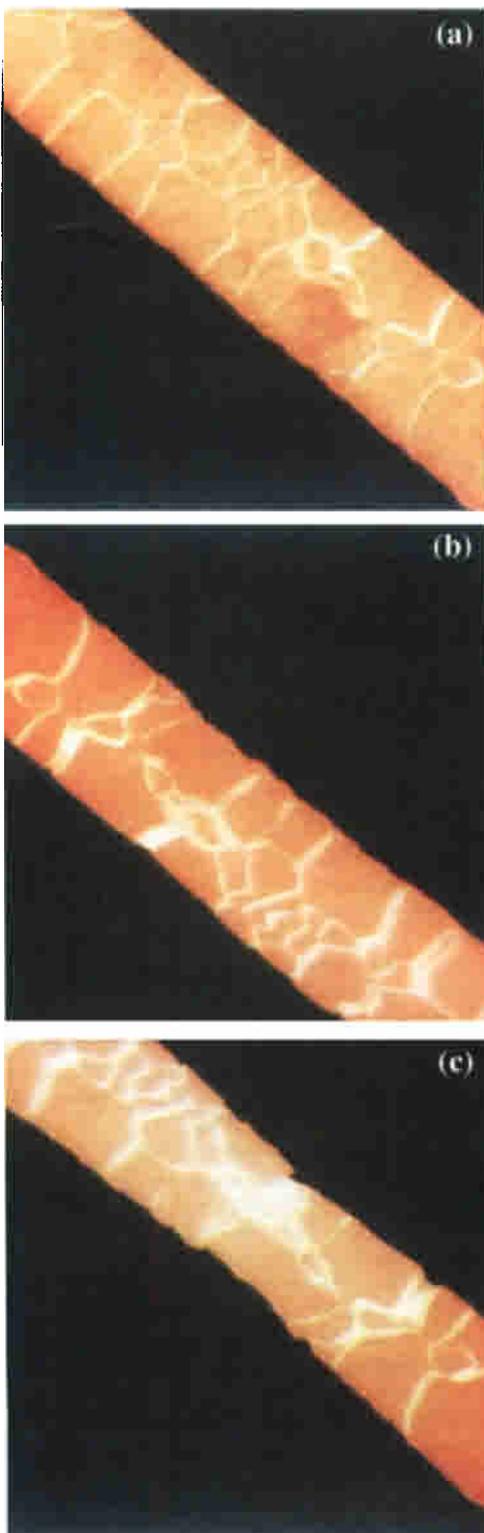


Fig. 11 High temperature images of an iridium sample 1 × 1 mm in cross-section during stress-rupture testing at 2000°C; stress: 19 N mm⁻²:
(a) at the start
(b) after 0.7 hour
(c) after 0.8 hour (10 seconds before rupture)

platinum materials in the welded state and after exposure to corrosive glass melts are currently being investigated and will be the subject of a subsequent report.

Acknowledgement

The investigations were supported by funding from the Thuringian Ministry of Science, Research and Culture. The authors are responsible for the contents.

References

- 1 T. G. George and M. F. Stevens, *J. Metals*, 1988, **40**, (10), 32
- 2 E. A. Franco-Ferreira, G. M. Goodwin, T. G. George and G. H. Rinehart, *Platinum Metals Rev.*, 1997, **41**, (4), 154
- 3 D. R. Coupland, R. B. McGrath, J. M. Evens and J. P. Hartley, *Platinum Metals Rev.*, 1995, **39**, (3), 98
- 4 J. Stokes, *Platinum Metals Rev.*, 1987, **31**, (2), 54
- 5 B. T. Horner, *Nitrogen*, 1997, (227), 33–38
- 6 J. W. Arblaster, *Platinum Metals Rev.*, 1997, **41**, (1), 12; *op. cit.*, 1997, **41**, (4), 184
- 7 G. Reinacher, *Metall*, 1961, **15**, (7), 657
- 8 G. Reinacher, *Metall*, 1962, **16**, (7), 662
- 9 G. Reinacher, *Z. Metallkd.*, 1962, **53**, (7), 444
- 10 G. Reinacher, *Metall*, 1963, **17**, (7), 699
- 11 A. A. Bourne and A. S. Darling, *Platinum Metals Rev.*, 1963, **7**, (2), 42
- 12 G. L. Selman, J. G. Day and A. A. Bourne, *Platinum Metals Rev.*, 1974, **18**, (2), 46
- 13 G. Reinacher, *Metall*, 1971, **25**, (7), 740
- 14 G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1976, **20**, (3), 86
- 15 S. Gärtner, D. Adam and W. Molle, *Neue Hütte*, 1979, **24**, (3), 103
- 16 B. Fischer, Dissertation B, Technische Hochschule Chemnitz, 1983
- 17 R. B. McGrath and G. C. Badcock, *Platinum Metals Rev.*, 1987, **31**, (1), 8
- 18 B. Fischer, H. Töpfer and R. Helmich, *East German Patent 245,576*; 1987
- 19 B. Fischer, D. Freund and D. Lupton, Congress Werkstoffprüfung 1997, Deutscher Verband für Materialforschung und -prüfung, Bad Nauheim, Germany, Dec. 3–4, 1997, Proceedings, p. 119
- 20 B. Fischer, D. Freund and D. Lupton, Proceedings of the 21st Int. Precious Metals Conf., p. 307, IPMI, San Francisco, U.S.A., June 15–18, 1997
- 21 D. F. Lupton, J. Merker and B. Fischer, 3rd European Precious Metals Conf., Florence, Italy, 17–19 September, 1997, Eurometaux, Brussels

Developments in Emission Control Technology

The main "Congress and Exposition" of the Society of Automotive Engineers (SAE) takes place in Detroit each Spring and smaller meetings are also held. One such meeting was the 1998 "International Fall Fuels and Lubricants Meeting and Exposition" held in San Francisco, October 19th to 22nd, 1998. Some 306 papers were presented to 1163 participants and a selection from sessions on the aftertreatment for petrol and diesel engines are reviewed here.

Plasma Technology Plasma is formed when very high voltage is applied across a zone through which exhaust gas flows. A variety of often novel chemical reactions is induced which might be useful in destroying pollutants. The papers presented probed fundamental questions. Siemens (982428) used dielectric barrier discharge devices in diesel exhaust gas to show that non-thermal plasma oxidation of NO to NO₂ is unfortunately favoured over dissociation to nitrogen and oxygen! Addition of ammonia in the presence of a Selective Catalytic Reduction catalyst brought about NO_x reduction at 100°C. A related contribution from Lawrence Livermore National Laboratory, Northwestern University and Engelhard (982508) reported that SO₂ is not oxidised under conditions where NO₂ is formed. This could be useful in situations where sulfate formation is detrimental.

Three-Way Catalysts (TWCs) Ford (982549) reported on hydrocarbon (HC) conversion efficiencies over Pd-only, Pt/Pd/Rh, Pd/Rh and Pt/Rh formulations during stoichiometric and rich operation. Their Pd-only and Pt/Pt/Rh catalysts had higher HC efficiency than Pt/Rh or Pd/Rh catalysts, the conversion efficiency for ethyne was > 98% for Pd-based catalysts, and > 96% for methyl *t*-butyl ether (MTBE) with all catalysts. MTBE and formaldehyde emissions from a warm engine were concluded not to be environmentally significant. Concentrations were given for the ten most abundant HCs in fuel, exhaust gas and post-catalyst gas and, with the exception of methane, there was significant reduction of already low HC levels over the catalyst. This paper has data for conversions for 154 HCs over aged Pt/Pd/Rh catalyst. Toyota (982706) described work on thermal deterioration of Pt/Rh TWCs and found that oxygen storage capacity depends on Pt metal particle size.

The complexity in providing On-Board Diagnostics compliance and low emissions was

evident in papers from Hyundai (982551) and Engelhard (982553). The former included evaporative and catalyst requirements, while the latter focused on development of ULEV catalysts, and included geometric surface area and heat capacity effects on catalyst light-off. The influences of substrate cell structure and catalyst configuration were emphasised by Corning, Johnson Matthey, Daimler Chrysler, and Southwest Research Institute (982634). There is advantage in having high cell density (high geometric surface area) during cold start; low thermal mass is important, and square cross-section cells are better than triangular ones. The viability of thin wall substrate in terms of processing necessary for incorporation into exhaust systems was confirmed by Corning (982635); thermal shock properties can be better than with conventional products. Emitec (982633) reported that conical metal substrates give enhanced gas flow over the main catalyst, and provide improved light-off due to heat cascade.

Lean-Burn Gasoline Engine Aftertreatment

Contributions from Daimler-Benz, Johnson Matthey, Chalmers, Leuven and Strasbourg Universities (982592) described the use of an absorber to trap NO_x, and intermittently recycle it back to the engine. A second paper (982593) focused on trap materials for this application. With appropriate formulations NO_x-traps can be regenerated in-situ in lean-burn gasoline or diesel engine applications. A major problem is sulfation of the trap components, which leads to performance deterioration. Renault (982607) found that temperatures of at least 600°C were needed for complete regeneration of a development NO_x-trap.

Two-Stroke Engine Aftertreatment

Exhaust emissions from 2-stroke engines contribute to urban pollution in developing countries. Because of high HC levels, exotherms during oxidation can increase gas temperature to 900°C. In addition, low oxygen content limits CO/HC oxidation under some conditions, and so HC steam reforming and reaction of CO with steam (water gas shift reaction) are important in the design of 2-stroke catalysts. ICT and Degussa (982710) reviewed these requirements and their achievement by thermal stabilisation of wash-coat components, appropriate selection of active metals and maintaining ceria surface area under rich ageing conditions.

M. V. TWIGG