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Practical Experience with New Oxide Dispersion Hardened Platinum Materials

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Abstract

When platinum materials are used for structural components in the high-temperature range, for example in the glass industry and in space technology, extremely high thermal, mechanical and chemical loadings arise. Apart from the solid solution hardened alloys, dispersion strengthened platinum materials have also been well-known for a long time. However, these dispersion strengthened platinum materials show considerable problems during the manufacturing process. Especially after welding of components, crack formation is caused by the very poor ductility during the high-temperature use. This paper reports on a new class of **d**is**p**ersion **h**ardened platinum materials (Pt **DPH** materials). These materials, manufactured by Heraeus, have been the subject of a detailed programme of laboratory investigations and industrial trials. By means of the development of these materials, it is now possible to avoid the disadvantages mentioned above. After a short introduction describing the manufacture and structure of the new DPH materials the report gives comprehensive results on the examination of their improved high-temperature mechanical properties. The results of stress-rupture tests and tensile tests verify that the novel DPH materials display high hot strength, low creep rate and simultaneously very good ductility. The Pt DPH materials also show excellent properties even after welding, under cyclically changing temperatures, with notches and after corrosion exposure in aggressive glass melts.
Finally, test results from the use of these novel Pt DPH materials in analytical laboratories and in the glass industry are given.

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Keywords: Oxide dispersion hardened platinum materials; creep test facility; high-temperature tensile test; stress-rupture strength; creep behaviour; ductility; corrosion resistance in glass melt; industrial trial

Introduction

In spite of their high price platinum materials are used as high temperature materials in a wide range of technical applications because of their remarkable properties. The most important features are their good chemical stability, oxidation resistance and good mechanical properties at very high temperatures. Important fields of application are e.g. the glass industry and space technology. Platinum materials are used for instance in the nozzles of rocket engines which take satellites from the launch rocket up to the height of their service orbit or which are used to carry out orbital corrections. The platinum materials guarantee the temperature resistance and mechanical strength at very high temperatures which are required in these applications.

Platinum applications in the glass industry

Platinum and platinum alloys are indispensable high temperature materials for the glass industry. Important properties which predestine the platinum materials for this field of application are [1, 2, 3]:

- high melting point (over 1650 °C)
- good corrosion resistance against aggressive glass melts, gases and salts
- very little dissolution in glass melts and, therefore, negligible contamination of the glasses
- very limited pick-up of contaminants from the glass melt
- high mechanical strength and good ductility at extremely high temperatures
- good formability and weldability
- fully recyclable.

For applications in the glass industry the only elements that can be used to achieve solid solution strengthening are rhodium and iridium [4, 5], whereby the use of rhodium predominates. Gold is also used as an alloying element because it reduces the wetting of the platinum surface by glass melts, which can be important for certain applications in the glass industry and in glass-chemistry laboratories. The strengthening effect of gold is low and does not extend to the highest temperatures because of the relatively low melting point of this element. The use of less noble metals as alloying elements would be detrimental to the chemical stability of the platinum.

Nearly all high performance optical glasses are melted in platinum equipment. Originally, simple free-standing crucibles were used. Nowadays, processing systems are commonly used which consist of melting chambers that are joined by tubular platinum feeders. In contrast to the crucibles these systems permit continuous operation. Normally pure platinum must be used as the structural material because the alloying elements rhodium, iridium and gold dissolve more readily in the glass melts than platinum. This would lead to discoloration of the glass and thus to changes in its spectral transmission.

Outstanding purity, homogeneity and freedom from bubbles can only be achieved in glasses when the precious metal platinum is used. The use of ceramic refractories would lead to trace contamination of the glasses which in turn would reduce their transmission and could cause inhomogeneities in the glass. The glass melt can be much more intensively stirred in platinum melting systems than in ceramic vessels, thus permitting much better homogeneity and above all freedom from bubbles to be achieved in the optical glasses. In ceramic melting vessels the stirring would cause ceramic particles to be loosened by erosion resulting in contamination of the glass melts.

Because of the exceptional resistance of platinum materials to glass melts, which is exceeded by no other material, many important components made from these materials are used in combination with refractory melting furnaces in the manufacture of technical glass qualities, e.g. feeder systems (stirring cell, stirrer, plunger cell, plunger, feeder, orifice), bubblers, drain bushings and thermocouple thimbles. Furthermore, technical glass fibres are drawn through bushings which are made from platinum alloys. Figure 1 show some components of platinum materials manufactured for the glass industry by W. C. Heraeus, Hanau, Germany.

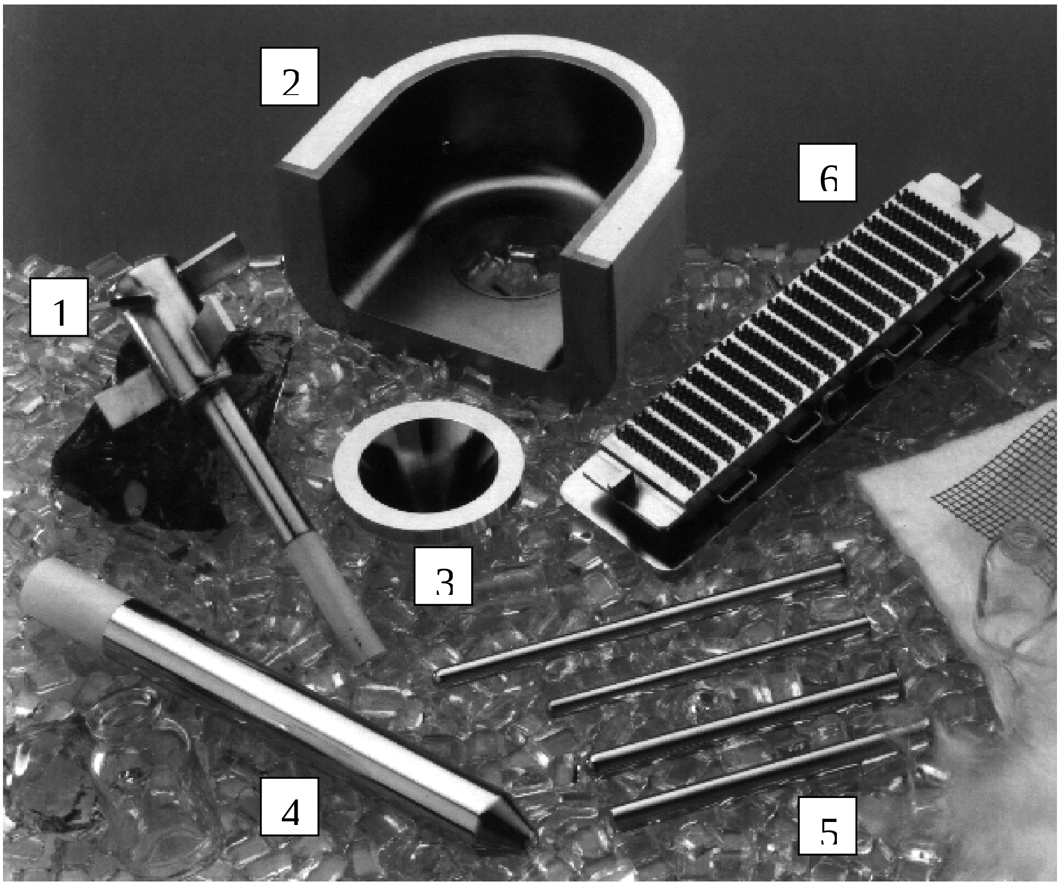


Figure 1: Components made from platinum materials for the glass industry

(1) Stirrer
(2) Spout bowl
(3) Drain bushing
(4) Plunger
(5) Thermocouple thimbles
(6) Bushing

At the high temperatures of application, up to c. 1600°C, platinum and its alloys have only relatively low mechanical strength and tend to show extreme grain coarsening which leads to a further loss of properties. Additionally even the noble metal platinum can suffer severe corrosion in aggressive glass melts. The extreme thermal, mechanical and chemical loading of platinum materials in the glass industry can lead to the premature failure of components. Therefore, the development of new platinum materials with greatly improved high temperature properties is essential. Oxide dispersion strengthened platinum materials (ODS platinum) have been available for many years. However, the previously known ODS platinum materials, which are produced by predominantly powder metallurgical routes, demonstrate the following decisive disadvantages:

- Difficulties in fabrication, in particular problems with welding.
  In the design of platinum components for glass melting, it is not possible to avoid the use of welding as a joining process. Insofar as the ODS platinum materials are weldable at all, one has to reckon with a substantial reduction in strength in the region of the weld. The strength can deteriorate to the levels in non-dispersion strengthened materials as a result of the coagulation of the dispersed oxide particles or their complete removal from the fusion zone.

- Excessive brittleness and susceptibility to cracking
  The dispersion strengthening has so far resulted in a substantial reduction in the ductility of the platinum, so that the materials are unable to withstand stress concentrations caused, e.g. by rapid temperature changes or the thermal expansion when heating structures which are embedded in ceramic refractory.

As a result of these problems, previous ODS platinum materials have not been used in technical applications to the expected extent. Therefore, a new class of oxide **d**is**p**ersion **h**ardened platinum materials (Platinum **DPH**) have been developed by W. C. Heraeus in collaboration with the University of Applied Sciences, Jena, with the aim of overcoming the disadvantages mentioned above.

Manufacture and structure of the new Pt DPH materials

A completely new process was developed for the production of the Pt DPH materials. Oxidisable additions of the metals zirconium, yttrium and, in some cases, cerium are added to the platinum in elemental form during the melting process. The molten alloy is cast, as usual, to ingots. During the subsequent forming operations, the semi-finished products (typically sheets, tubes and rods) are subjected to an annealing process in an oxidising medium which leads to the internal oxidation of the platinum material. The internal oxidation leads to the formation of finely dispersed oxide precipitates from the alloying addition elements and the duration of the annealing process is adjusted to ensure that the reactive elements are essentially fully converted to oxide. W. C. Heraeus currently manufactures the materials Pt DPH, Pt-10% Rh DPH and Pt-5%Au DPH.

Figure 2 shows, for example, a metallographic section of the microstructure Pt DPH.

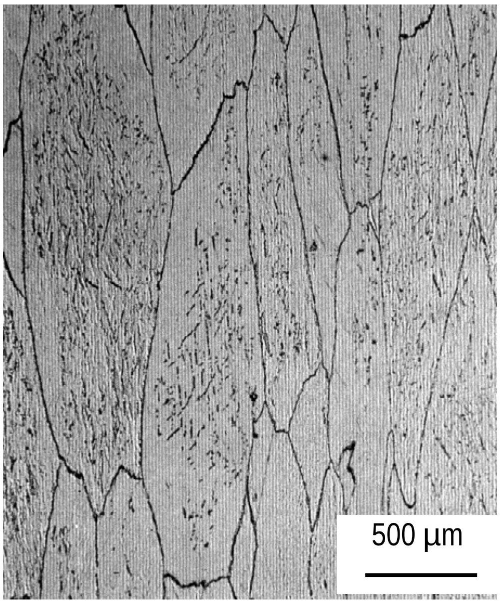
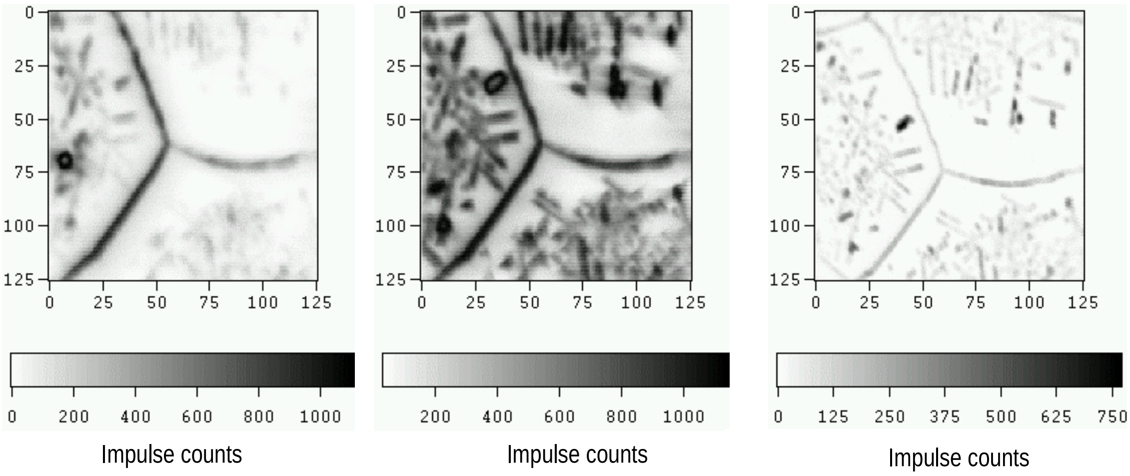


Figure 2: Optical micrographs showing structure of Pt DPH

The finely dispersed oxide particles in the matrix and at the grain boundaries can be clearly seen. In this case zirconium and yttrium were used as oxide-forming additions. An analysis of the oxide particles was carried out by secondary ion mass spectroscopy (SIMS) and further investigations by transmission electron microscopy. Figure 3 shows the element distribution as determined on Pt-DPH with SIMS [6]. The elements zirconium, yttrium and oxygen are present in the grain boundaries and in the precipitate particles in the matrix. It is therefore a mixed oxide of Zr-Y.



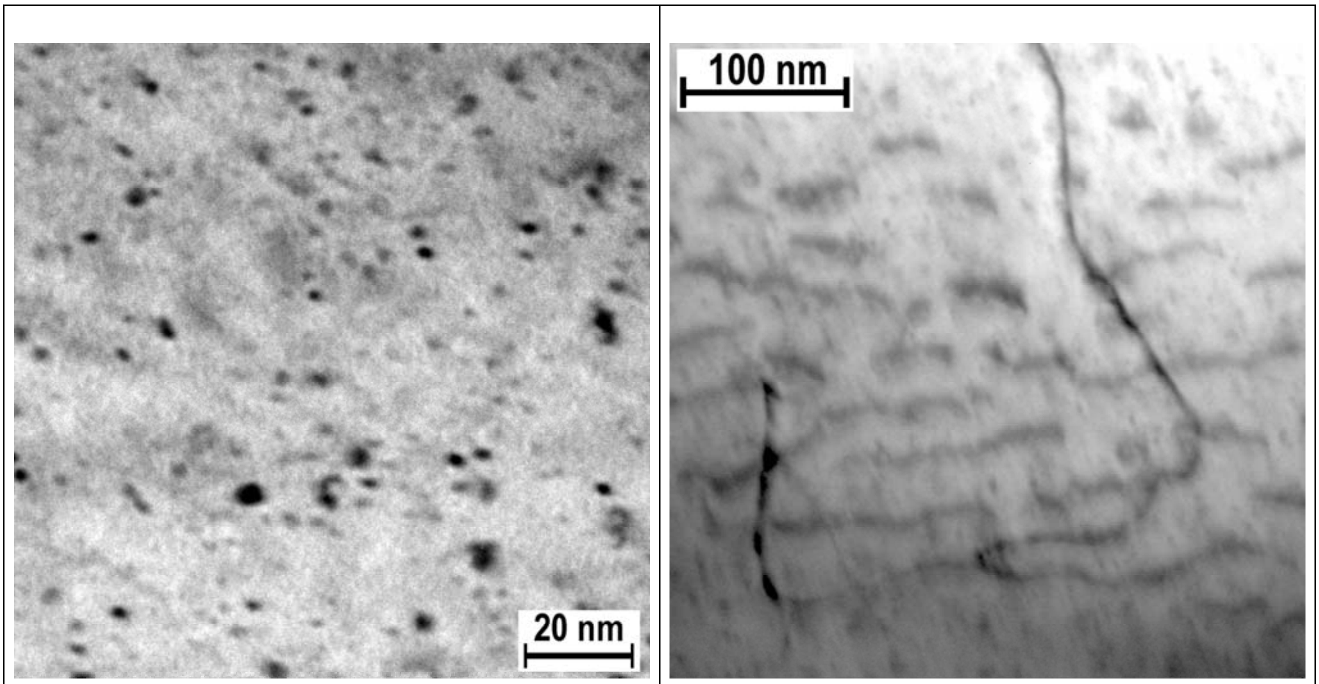
Y Distribution **Zr** Distribution **O** Distribution

Figure 3: Scanning SIMS micrographs showing the distribution of various elements in the material Pt DPH

The larger particles, which are already visible in the optical microscope, apparently hinder the movement of grain boundaries. The material therefore shows outstanding microstructural stability, i.e. it remains fine grained even after annealing at high temperatures and over long periods (c.f. Figure 19).

Generally, significant strengthening of the precious metal matrix can be expected when the dispersed oxide particles are very small (< 1 µm diameter) and are separated by only a small distance (≤ 10 µm). In this case they hinder the movement of dislocations in the matrix and thus lead to an increase in strength and to low creep rates [7, 8].

Investigations in the transmission electron microscope (TEM) showed very small particles (c. 2 – 10 nm diameter), which fulfil these conditions. Figure 4 shows these dispersed particles in a TEM bright-field micrograph and a dislocation line which has been bent into a U-shape by the hindrance of the particles in the new Pt DPH material.

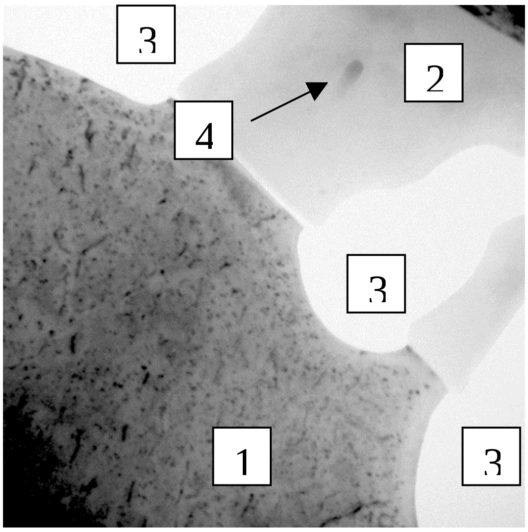


a) Very fine dispersed oxide particles

b) Dislocation structure caused by the fine dispersed oxide particles

Figure 4: TEM bright-field images of Pt DPH

Figure 5 shows larger oxide particles between two grains of platinum together with small particles in the platinum matrix by means of a further TEM bright-field image of Pt DPH. It also shows the EDX spectrogram of the larger oxide particle. The white areas in the figure represent holes in the very thin TEM foil. The identification of Zr, Y and O corresponds to the SIMS results and identifies the particle as a mixed oxide of zirconium and yttrium. The carbon and copper reflections in the spectrogram are caused by contamination in the electron microscope and by the sample holder.



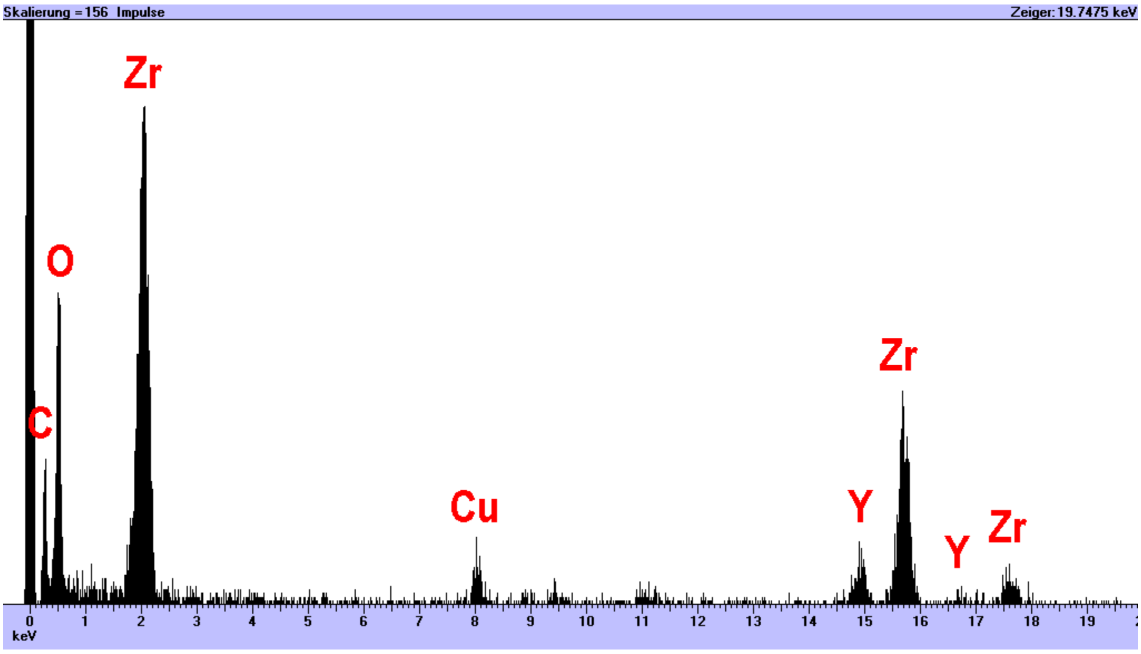
(1) Platinum matrix

(2) Oxide particle

(3) Holes in the prepared foil

(4) Point of interest (analysed)

a) TEM bright-field image



b) EDX spectrogram

Figure 5: TEM bright-field image and EDX spectrogram of Pt DPH

Test facilities for the determination of high temperature mechanical properties of metallic materials

The stress-rupture strength and the creep behaviour of high-melting metals (Pt materials, Rh, Ir, Mo, Re, W and their alloys) can be measured in our specially developed testing facility. This equipment permits measurements up to 3000°C either in air or under a protective gas atmosphere (for example argon-hydrogen mixture) [9-13].

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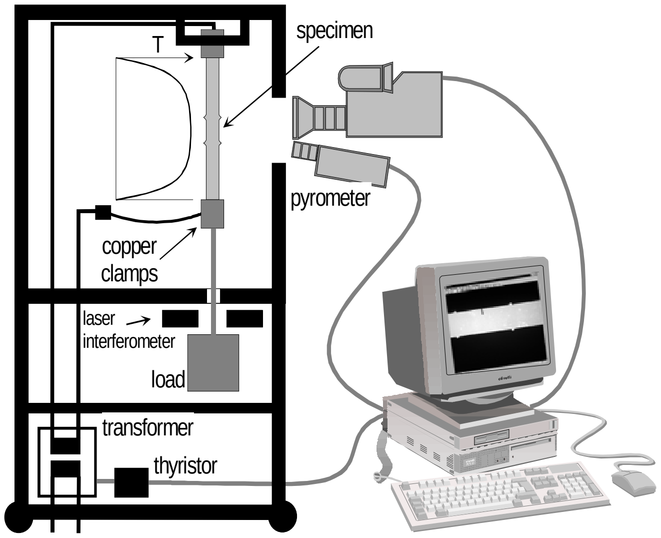

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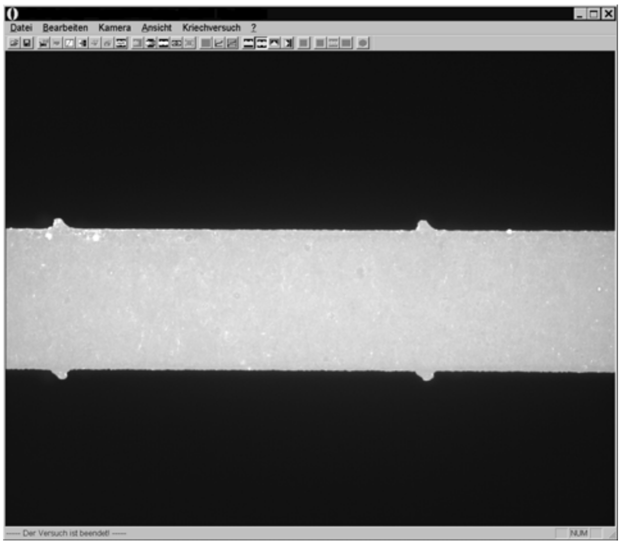

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<td>Fig. 6a: Schematic diagram of the equipment used to measure stress-rupture strength and creep parameters of metals at temperatures up to 3000°C</td>
<td>Fig. 6b: Image of a tensile specimen with shoulders recorded by *SuperCreep*</td>
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A schematic diagram of the equipment is given in Figure 6a. In order to achieve high test temperatures, the samples are heated by direct electrical resistance heating. Strips, rods or wires with a cross-sectional area of 1 - 5 mm² (Figure 6b) can be used as samples for the tests. The temperature is monitored by an infrared thermometer focussed on the centre of the sample and connected to a controller which adjusts the sample heating current via a thyristor regulator. The small measurement point of the infrared thermometer (0,3 mm diameter) scans the length of the specimen by means of a tilting mirror. The maximum value found is used for temperature measurement and control. The equipment design guarantees a constant maximum temperature throughout the test in spite of deformation of the sample. The load is applied to the sample by means of calibrated weights. The stress-rupture curve is determined by measuring the time to rupture of the samples at different loads and constant temperature. At the same time it is possible to record continuously the sample elongation, i.e. creep curves, with a laser scanning system or by observing it with a high resolution camera which is itself controlled by the program *SuperCreep* developed at the University of Applied Science for strain measurements by means of digital image analysis [12]. In this technique the distance between the two shoulders on each side of the specimen is continuously measured. This is the central portion of the specimen which has a uniform temperature. In this way it can be guaranteed that the measurement of elongation ensues without being influenced by the temperature gradient in the region of the ends of the specimen. The specimens, which have shoulders of only 0.3 mm radius, are laser-machined from sheet material. All creep curves presented in this paper were determined using the camera and the *SuperCreep* technique. Lower values for the elongation are registered when the laser-scanning system is used as a result of the temperature gradient over the length of the specimen.

In order to carry out tensile tests for the determination of yield points, tensile strength and failure strain at test temperatures up to 3000°C, a test chamber was built following the same principle and integrated into a conventional tensile-testing machine. In order to determine the tensile curve and the values for the technical yield point and the failure strain, the data from the software of the tensile testing machine (mechanical stress) and the *SuperCreep* program (elongation at constant temperature) are correlated with each other. All results given in this report were determined out on samples with a length of 120 mm, a width of 4 mm and a thickness of 0.8 mm.

High temperature mechanical properties of the new Pt DPH Materials

Figure 7 shows, for example, stress rupture curves of the dispersion hardened materials Pt DPH, Pt-10%Rh DPH and Pt-5%Au DPH in comparison to the conventional materials Pt, Pt-10%Rh and Pt-5%Au at1600°C.

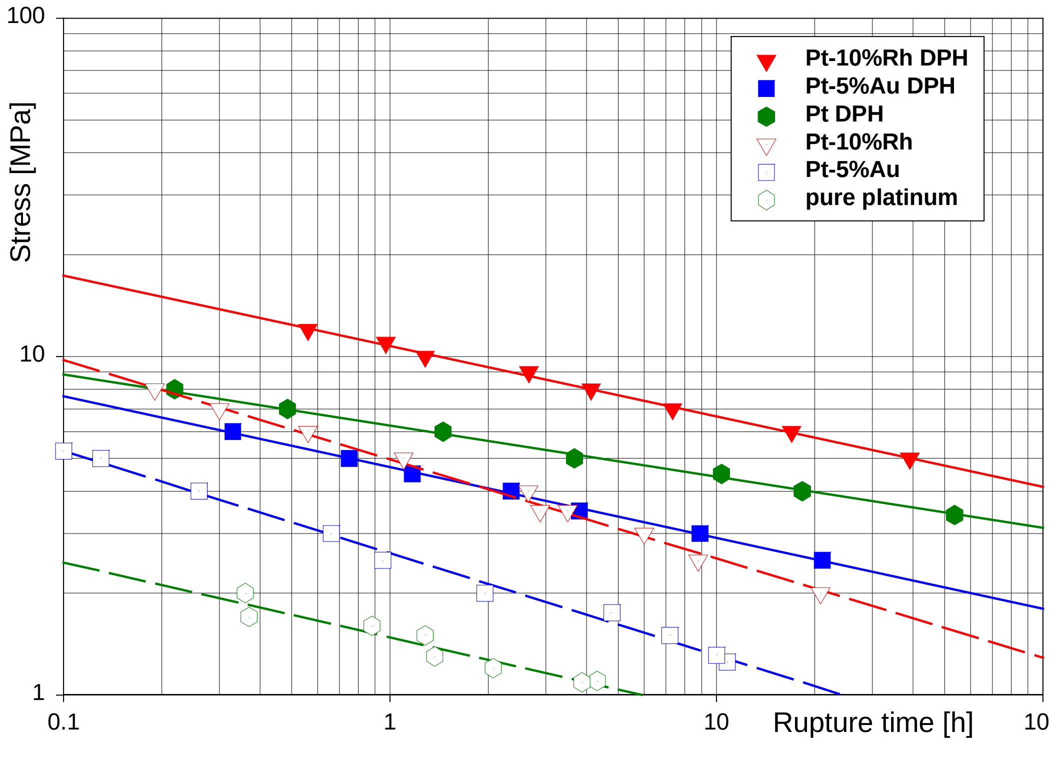


Figure 7: Stress-rupture curves of various platinum materials at 1600°C [14]

For the conventional materials, the solid solution strengthening of platinum by the alloying elements gold and rhodium can be recognised. The three oxide dispersion hardened materials show a considerable increase in strength relative to the corresponding conventional material. A comparison of the available test results at various temperatures in the range between 1200 and 1700°C has shown that the strengthening effect from the dispersed oxide particles increases with increasing temperature. Thus the new Pt DPH materials are predestined for use especially at the highest temperatures where the use of the conventional materials leads to particular difficulties.

Figure 8 shows, for example, the results of hot tensile tests on Pt-10%Rh DPH.

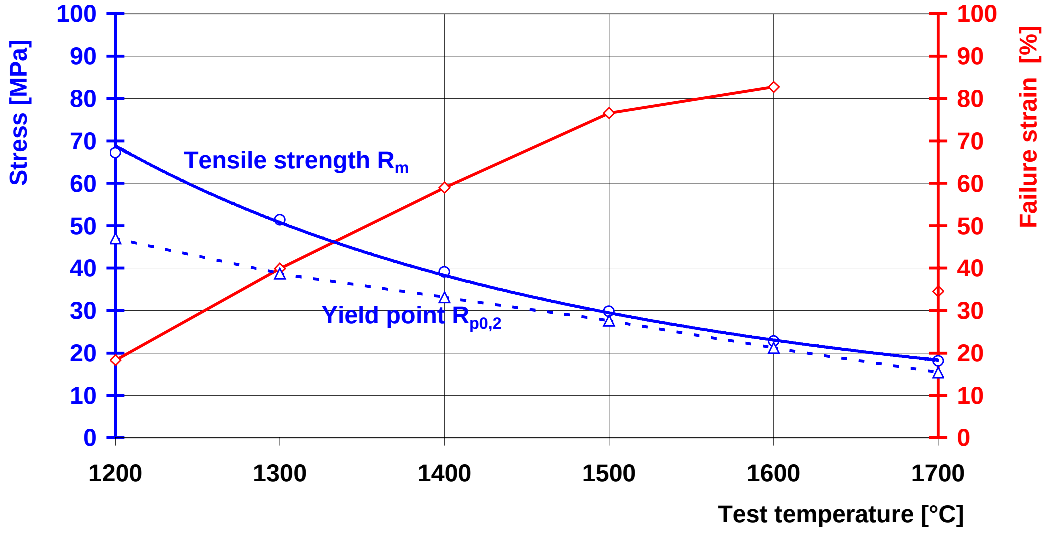


Figure 8: Tensile strength, yield point and failure strain of Pt-10%Rh DPH in dependence of test temperature

Besides the expected loss of strength and increase in elongation with increasing temperature, it is particularly significant that the new dispersion hardened platinum materials show relatively high rupture elongation values, i.e. good ductility. Depending on the alloy type and the temperature, the rupture elongation is between about 20 and 80%.

The fact that the new Pt DPH materials achieve their increase in strength without substantial loss in ductility is very significant for their industrial application. Otherwise, unavoidable thermal stresses would greatly increase the danger of cracking in components used in glass melting technology.

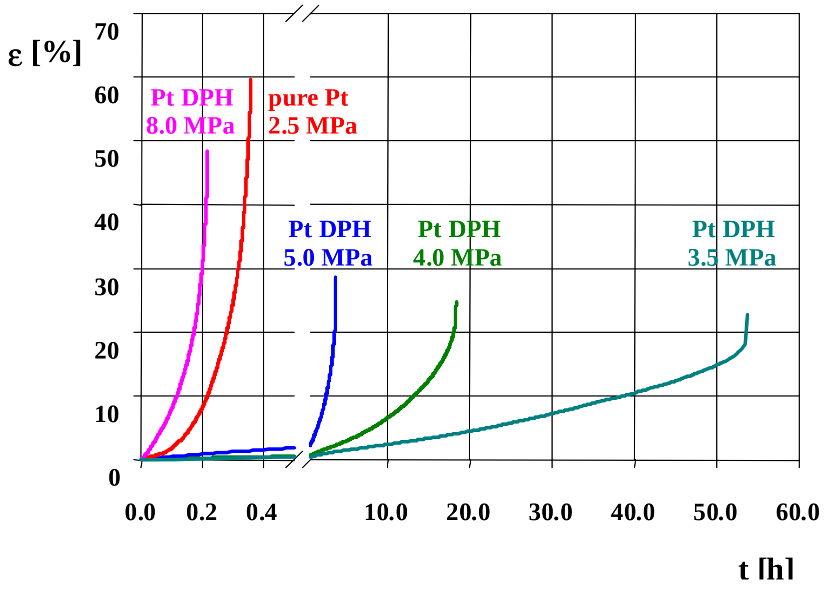


Figure 9: Creep curves of Pt DPH and pure platinum at 1600°C and various tensile loads

Figure 9 shows, as a further example, creep curves of Pt DPH in comparison to pure platinum at 1600°C. The rupture elongation of Pt DPH is almost 50% at a high test stress of 8.0 MPa and is thus not significantly lower than the value for pure platinum for a similar rupture time but at a much lower stress (60% at 2.5 MPa).

As Figures 9 and 10 also show, lower test stresses lead to a similar reduction in the rupture elongation for both materials. The rupture elongation values for Pt DPH are between 20 and 50 % and are comparable with those found for pure platinum. They are considerably higher than values determined on other dispersion strengthened materials [15,16].

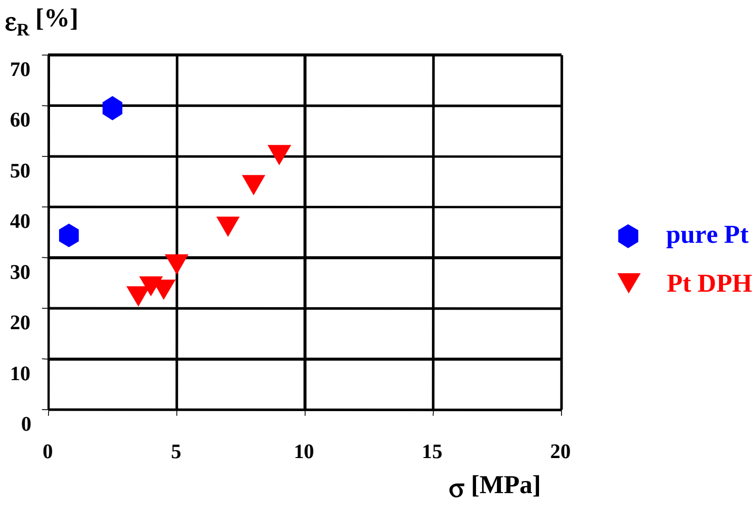


Figure 10: Fracture strains of pure platinum and Pt DPH at 1600°C

Figure 11 shows, for example, double logarithmic Norton plots of the stationary creep rates of Pt DPH and Pt-10%Rh DPH at test temperatures between 1200 and 1600°C in comparison with the conventional materials pure platinum and Pt-10%Rh. The stationary creep rates of platinum DPH materials are several orders of magnitude lower than for the conventional materials at the same temperatures and stresses.

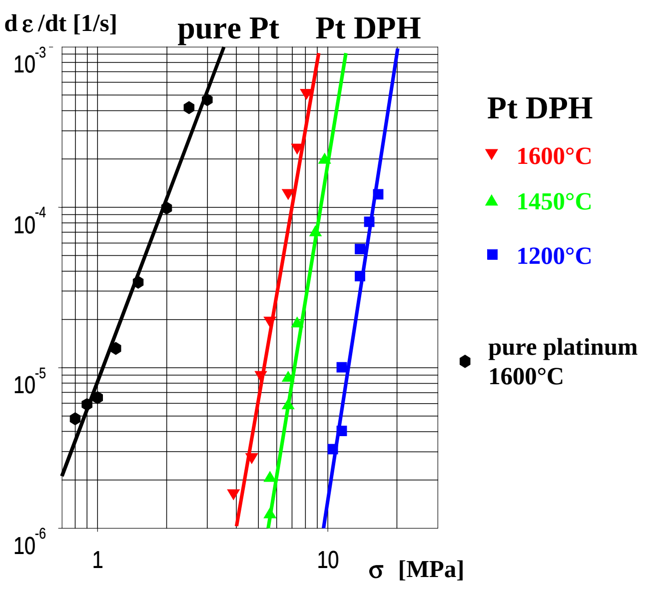


Figure 11: Stationary creep rate of Pt DPH at test temperatures between 1200 and 1600°C compared with pure platinum

The stationary creep rates of platinum DPH materials in the temperature and stress range considered can be fitted well with a Norton creep law:

Pt DPH:	$\dot{\varepsilon} = 0.26 \cdot \sigma^{7.3} \cdot e^{-343kJ/RT} \quad \left[1/s\right]$

The Norton exponent for Pt DPH (7.3) is almost double that for pure platinum (3.8). Very high values for stress exponents, as have been observed on various previously known ODS materials, indicate that relatively small changes in stress would lead to large changes in creep rate. Relatively small transient increases in load can then cause damage to components resulting in their failure. The increase in stress exponent observed on the new Pt DPH materials relative to the non-dispersion hardened materials is well below this critical value.

With the introduction of the new Pt DPH materials, the previous problems encountered in joining ODS platinum materials were successfully overcome. The new Pt DPH materials can be welded without any special measures using the standard TIG technique both with and without addition of filler metal. Surprisingly, the strength of the weld joints is not greatly reduced relative to that of the unwelded material. Furthermore, it is possible to use filler metal which contains the same oxidisable additions as the alloy. The weld zones of the welded structures can then be subjected to an oxidising annealing treatment, or the oxidation proceeds during the use of the component in air or in the glass melt. In this way welds can be achieved which have essentially the same high temperature mechanical properties as the unwelded material.

Figure 12 shows, for example, stress rupture curves of Pt DPH at 1600°C in different material and loading conditions. Relative to the unwelded starting condition, no reduction in the stress rupture strength is observed after TIG welding with filler material and subsequent internal oxidation annealing. On the contrary, a slight increase was found which is apparently caused by the thickening of the weld seam. During the high temperature use of structural components the loading conditions can be intensified by periodic temperature changes and by the presence of notches or small initial cracks. Therefore, stress rupture tests were also carried out with a periodic temperature change of +/-75°C every 2 minutes and further stress rupture tests on samples (4 mm wide) which had been notched to a depth of 1 mm on one side by means of a diamond wire (wire ∅ 0.17 mm).

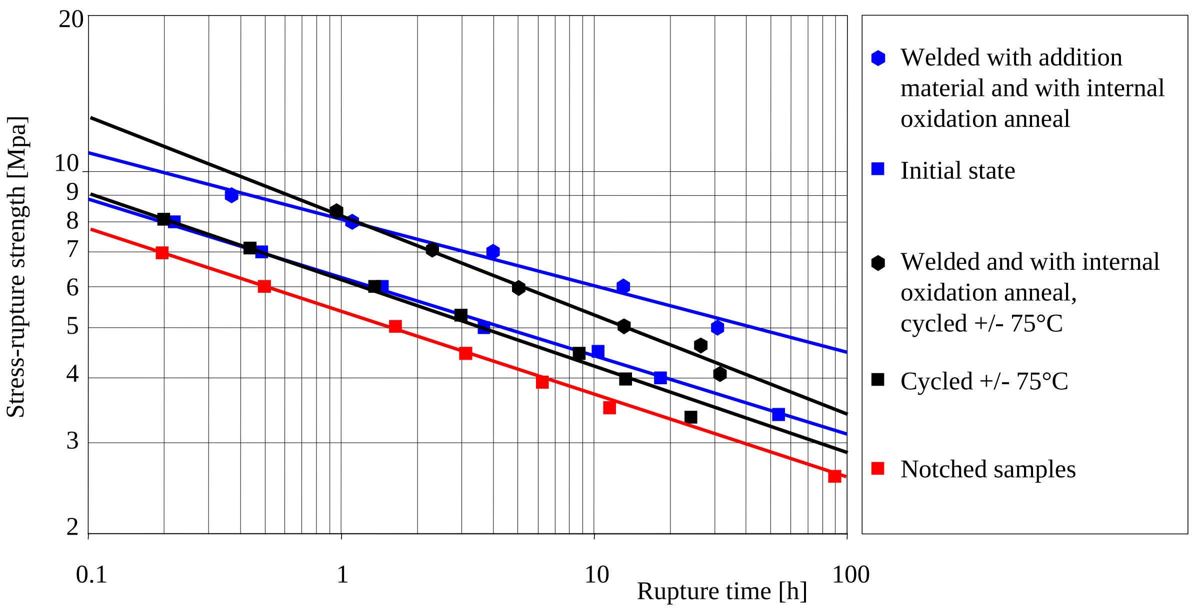


Figure 12: Stress-rupture curves of Pt DPH at 1600°C in various conditions

As Figure 12 also shows, the stress rupture strength of Pt DPH in the initial state and after welding is only reduced to a very small extent by the temperature cycling of +/- 75°C. Furthermore, it can be seen that the stress rupture strength of Pt DPH is only slightly reduced by the presence of a notch. The new material is insensitive to temperature changes and to the presence of notches.

Figure 13 shows creep curves of Pt DPH at1600°C and a constant load of 7 MPa in various material and loading conditions. It can be seen that the periodic temperature changes have hardly any influence on the rupture elongation (c.f. curves 1 and 3), whereas the notches cause a substantial reduction in ductility, as would be expected (curve 5). In the welded condition, both with and without temperature cycling (curves 2 and 4), the rupture elongation (25%) is still remarkably high, although a significant reduction relative to the initial state has occurred.

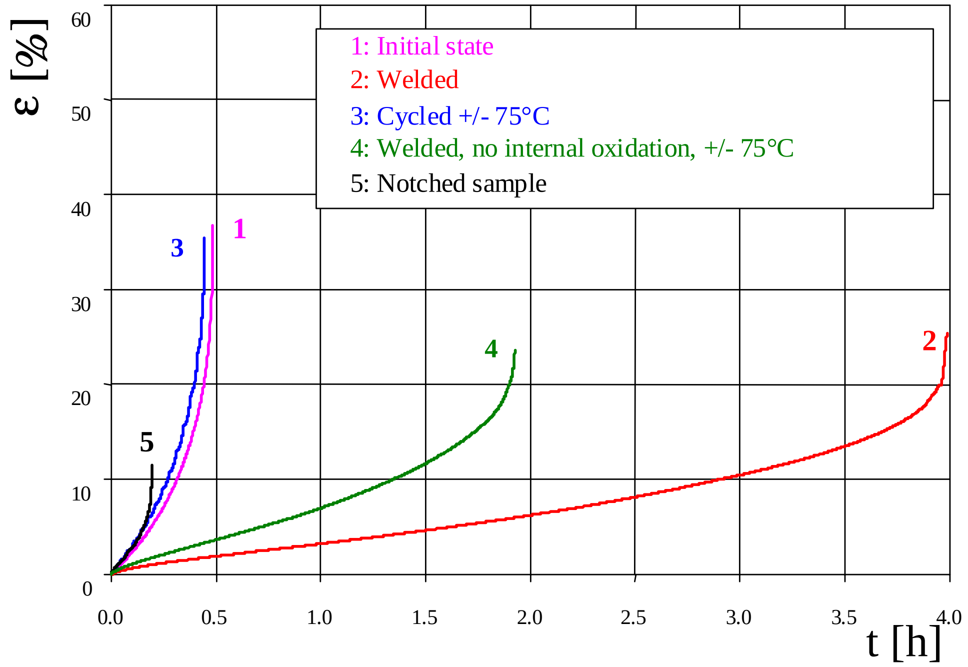
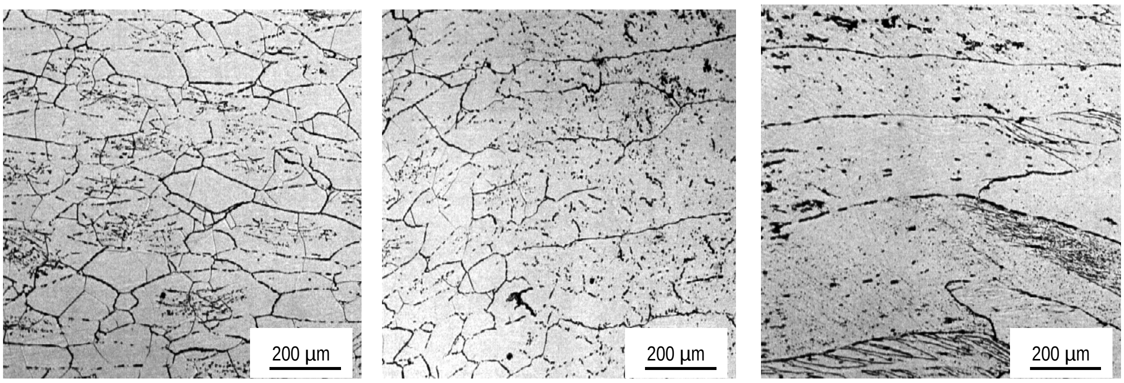


Figure 13: Creep curves of Pt DPH at 1600°C in various conditions at 7 MPa

Figure 14 shows the microstructure of the weld in Pt DPH (TIG welded with addition material and oxidation anneal). A degree of grain coarsening at the edge of the heat affected zone and particularly in the weld cannot be avoided, but even here the presence of the finely dispersed oxide precipitates ensure the good high temperature mechanical properties of the welded material. Similarly positive results have been obtained for the other new materials Pt-10%Rh DPH and Pt-5%Au DPH in the welded condition and under the influence of temperature cycling and with notches.



Base material

Heat-affected zone

Fusion zone

Figure 14: Microstructure of the welded zone of Pt DPH after second internal oxidation

Comparison of the high temperature mechanical properties of Pt DPH material with previously known ODS platinum materials

Comparative stress rupture tests were carried out on Pt-10%Rh DPH and on three oxide dispersion strengthened Pt-10%Rh materials (ODS¹, ODS², ODS³) from different manufacturers in various material conditions [16]. Figure 15 shows, for example, the stress rupture strength for 1000h test time and Figure 16 shows creep curves at 1450°C in the initial state. The figures also show the corresponding results for the conventional materials Pt-10%Rh and Pt-20%Rh.

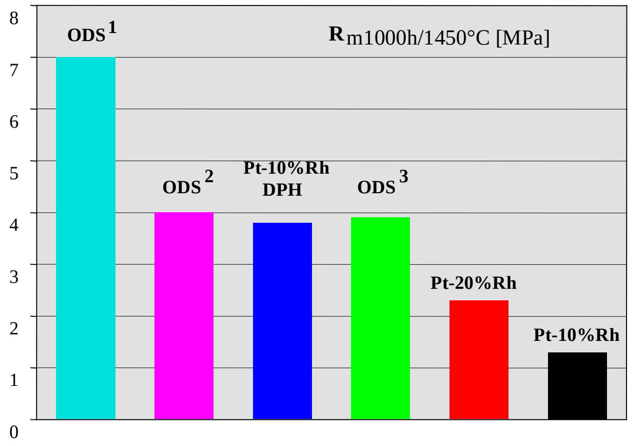


Figure 15: 1000 h stress-rupture strength of several platinum alloys at 1450°C

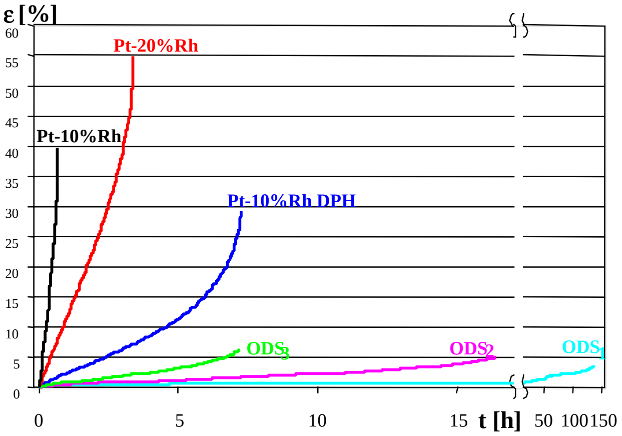


Figure 16: Creep curves of several platinum alloys at 1450°C

All four oxide dispersion strengthened Pt-10%Rh alloys have a significantly higher stress rupture strength than the conventional alloys Pt-10%Rh and even Pt-20%Rh. The material ODS¹ is distinguished by its particularly high stress-rupture strength whereas the other three oxide dispersion strengthened alloys have approximately the same stress-rupture strength. However, a major advantage of the new dispersion hardened material Pt-10%Rh DPH is apparent from the creep curves: its rupture elongation is still very high, i.e. 30%. In contrast, the materials ODS¹ to ODS³ show only very low rupture elongation values of about 5% and thus have only a low ductility.

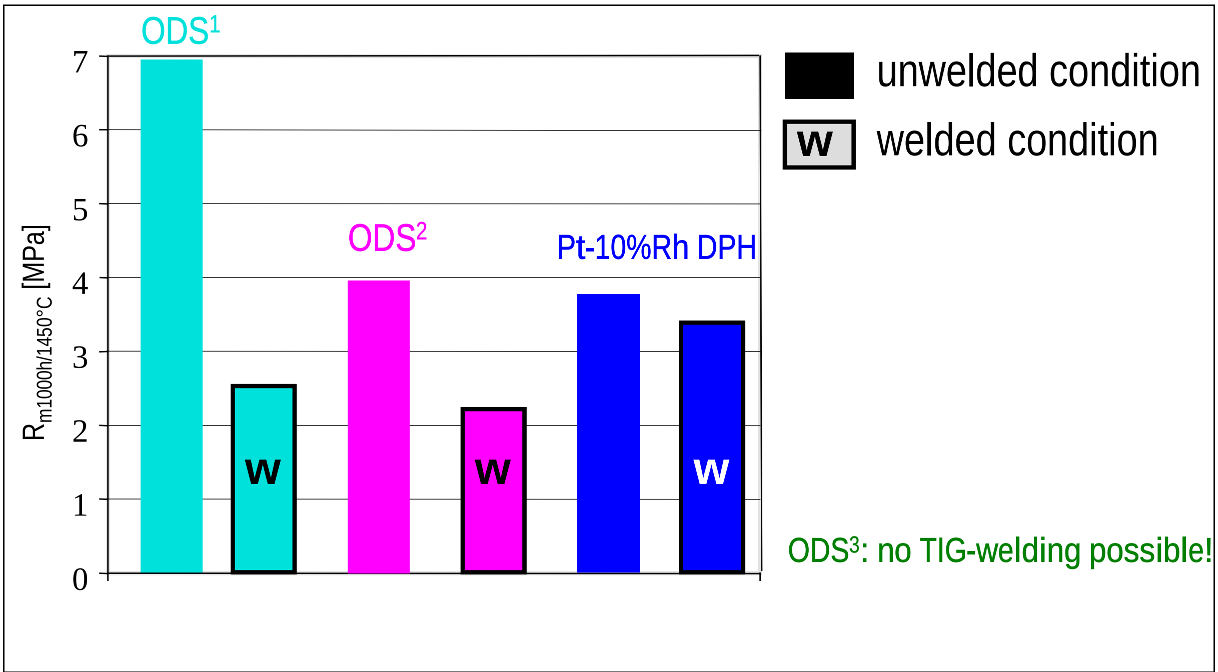


Figure 17: 1000 h stress-rupture strength of oxide dispersion hardened platinum materials at 1450°C in the welded and unwelded conditions

Figure 17 shows the change in the stress rupture strength for 1000h test time at 1450°C resulting from TIG welding using the same parameters for the four oxide dispersion strengthened Pt-10%Rh alloys. Firstly it should be noted that the material ODS^3 could not be TIG welded. The alloy ODS^1 with the highest stress rupture strength in the initial state experiences an extreme loss of strength as a result of the TIG welding. The new material Pt-10%Rh DPH experiences, however, hardly any loss of stress rupture strength after TIG welding (here without using oxidisable filler metal). The stress-rupture strength in the welded state is an essential property for the use of materials in the glass industry. After TIG welding Pt-10%Rh DPH has the highest stress rupture strength of all four materials investigated. Its rupture elongation in the welded state is also many times higher than that of the other materials.

Corrosion resistance of the new Pt DPH materials in molten glass

Firstly, comprehensive laboratory investigations were carried out to determine the influence of both molten glass and the melting process of glass batch on the new platinum DPH materials and their high temperature mechanical properties. For these investigations glasses were used which are known to be aggressive to platinum, i.e. hard crown glass and lead glass. The principles of the testing procedure have already been described in [17, 18].

Elements such as Si, Pb, P, As, Sb, B, etc. from the glass batch and molten glass can diffuse into the platinum materials preferentially along the grain boundaries. These elements form low melting point phases and eutectics with platinum and therefore have a strongly detrimental effect on the mechanical integrity of the material. The platinum materials become embrittled and the stress-rupture strength is reduced.

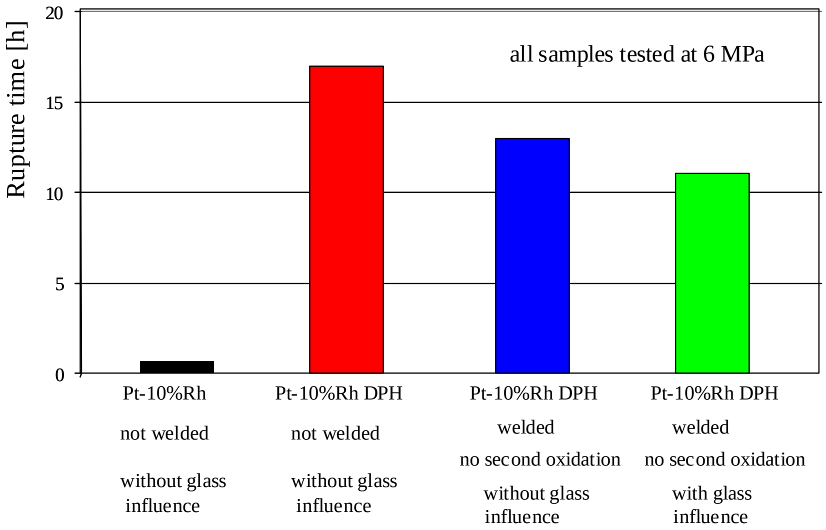
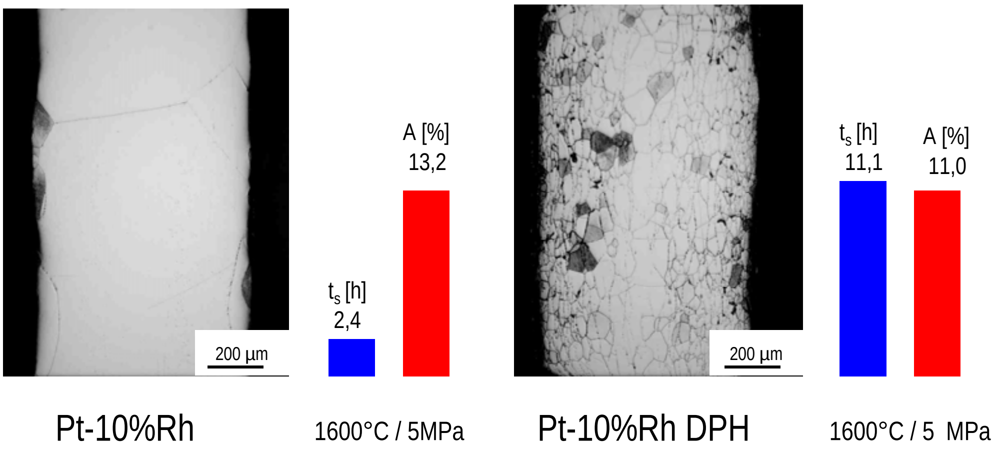


Figure 18: Influence of corrosion (hard crown glass) on the rupture time of several Pt-10%Rh materials at 1600°C and 6 MPa stress

Figure 18 shows the stress rupture life of Pt-10%Rh materials in various conditions determined under defined test parameters (1600°C / 6MPa). The rupture life of Pt-10%Rh DPH is reduced slightly relative to the material in the initial state by TIG welding without subsequent internal oxidation annealing. When TIG welded samples of Pt-10%Rh DPH are exposed to hard crown glass batch during the melting-down procedure a further reduction in the rupture time is observed. However, the decisive point is that the rupture life of Pt-10%Rh DPH in the TIG welded state and after exposure to the glass melt is still several times greater than the rupture life of conventional Pt-10%Rh in the initial, untreated state.

Specimens of Pt-10%Rh and Pt-10%Rh DPH were exposed for 10 000h to molten C-glass at about 1200°C in a bushing during the production of glass fibres. As Figure 19 shows, the microstructure of conventional Pt-10%Rh has become extremely coarse grained.



By way of exception, the fracture strain in this case was measured by means of the laser extensiometer

Figure 19: Microstructure, rupture time and failure strain of Pt-10%Rh and Pt-10%Rh DPH after 10 000 hours exposure to a C-glass melt at approx. 1200°C

The size of individual grains corresponds to the thickness of the sheet. Elements which are detrimental to platinum can then diffuse rapidly along the grain boundaries into the interior of the material. Pt-10%Rh DPH has, in contrast, remained fine grained, thus offering greater resistance to the diffusion of impurities into the bulk of the material. In stress-rupture tests under the same conditions (1600°C / 5 MPa), the samples of Pt-10%Rh DPH still showed a considerably longer time to rupture (11.1h) than conventional Pt-10%Rh (2.4 h). The rupture elongation of Pt-10%Rh DPH (11.0%) was not significantly less than that of conventional Pt-10%Rh (13.2%). As before, the ductility of Pt-10%Rh DPH was good.

Practical trials in the glass industry

Components manufactured from the new Pt DPH materials were subjected to intensive practical trials in a glass analytical laboratory and in the production of glass fibres and special glasses in the glass industry. The results are summarised in the following sections.

- Glass analytical laboratory

For the chemical analysis of glass and raw materials, laboratory equipment made of platinum materials is essential to withstand the high working temperatures required and the presence of aggressive chemicals. In comprehensive series of tests, crucibles and dishes of dispersion hardened Pt DPH and Pt-5%Au DPH were tested in comparison to conventional, non-dispersion hardened Pt and Pt-5%Au.

Crucibles of Pt DPH and Pt were used for comparison in carrying out both aqueous and fusion preparations of glass analysis samples and in laboratory scale melting of various glasses. In these trials a number of sample materials and preparation additives were used which are typical for analyses in the glass analysis laboratory and for glass melting experiments. Some of these substances contained elements which are very critical for platinum, e.g. lead and phosphorus.

Melting crucibles and casting dishes of the alloys Pt-5%Au DPH and Pt-5%Au were used in the preparation of fused buttons of various glasses which were intended for subsequent chemical determination by X-ray fluorescent chemical analysis. In this standard practice of the glass analysis laboratory, the gold addition to platinum is necessary to reduce the wetting of platinum by the molten glass and thus to facilitate the release of the solidified fused buttons from the platinum dishes.

The results can be summarised as follows:

Crucibles and dishes of the Pt DPH materials showed in all cases considerably better handling properties than the previously used equipment made from non-dispersion hardened Pt materials. As a result of the hardening they have greatly improved mechanical stability at high temperatures. Less deformation occurs, especially in the hot condition. When the previous crucibles and dishes are gripped with tongs they are easily deformed along the rim. The use of a thicker wall to reduce this effect would cause excessively high costs.

In glass melting and aqueous sample preparation, slightly lower platinum losses were found for the dispersion hardened materials than for the conventional materials. The fused buttons can be more readily released from the casting dishes of dispersion hardened platinum material. This is a result of the better mechanical stability and a relatively low degree of adhesion because of the much reduced attack of the platinum surface.

- Glass fibre production

Trials were also carried out on glass fibre bushings manufactured from the new dispersion hardened alloy Pt-10%Rh DPH. The bushings used previously are made from the non-dispersion hardened alloy Pt-10%Rh and have an average "partial operating period" of 1200h. After this time the production has to be interrupted because the operational characteristics of the bushings, in particular the yield and fibre quality, have deteriorated as a result of the reaction of the molten glass with the surface of the platinum. In the actual "tips", i.e. the actual glass fibre drawing nozzles, the platinum is attacked significantly by the rapid flow of molten glass. The bushings have to be dismantled, deglassed and cleaned, resulting in non-operational periods and repair costs. After the cleaning process the bushings can be reinstalled and taken back into operation. Several cycles of this type are repeated until a total average operating period of 10 000 h is reached. The bushing must then be scrapped.

The results obtained on the new bushings of Pt-10%Rh DPH can be summarised as follows:

The "partial operating period" could be increased from 1200 h to the current value of c. 2000 h. The bushings have already completed several cycles and are still in service at the time of writing.

The bushings have now reached an operating period of c. 15 000 h, already representing an increase in service life of 50%. The current quality of the fibres and the stability of the drawing process indicate that the total service life will be considerably longer.

In spite of the significantly longer operating cycles when using bushings of the new platinum DPH material, the process quality, the fibre quality and yield and the production rate could all be maintained, whereas a small reduction in the energy required per kg of glass fibres was observed.

As a result of the improved mechanical strength of the new platinum DPH material, it was possible to reduce the thickness of sheets used in the bushings. Based on an original total weight of the bushing of 9 200 g, the weight of precious metal could be reduced by 800 g, corresponding to 8.7%.

The higher mechanical stability and improved corrosion resistance of the new Pt-10%Rh DPH material in molten glass also reduce the need for weld repairs after deglassing at the end of each "partial operating period". Based on the currently typical total service life of Pt-10% Rh bushings of 10 000 h, the amount of platinum filler metal required for repairs would be reduced by about 30%.

The increase in the partial operating periods and total service life for the bushings gives substantial economic advantages. The following costs are reduced:

- manufacturing costs for replacements of unserviceable bushings
- dismantling and assembly, deglassing and cleaning after each "partial operating period"
- repair welds
- down-time for dismantling and assembly
- insulating materials (the bushings are mounted in refractory insulating material).

The 50% increase in service life which has already been achieved on the bushings that are still in service corresponds to a reduction in these costs of 18.8% based on the total service life of the bushings. The cost reduction will be still greater if, as expected, the total service life is significantly longer than that achieved so far.

- Drain crucibles for special glass production

In a further range of industrial trials drain crucibles were manufactured from the new dispersion hardened platinum alloy Pt-10%Rh DPH and tested in the production of special glasses. The aim of the trials was to increase the working temperature of the molten glass above the present 1600°C, which can be achieved in conventional Pt-10%Rh crucibles, in order to improve the quality of the glasses and to manufacture special compositions which cannot currently be melted. New developmental special glasses cannot in some cases be melted at 1600°C, or in other cases their viscosity is not sufficiently low to allow them to be prepared with the required low bubble content by intensive stirring.

The drain crucibles were tested in continuous operation with an alkali-aluminosilicate glass and an alkaline earth aluminosilicate glass. The melting temperature was increased in steps of 25°C starting at 1600°C. Continuous operation was still possible at 1700°C without any problems. However, after a fairly long period of operation at 1725°C a crack formed in the wall of the crucible causing its destruction. The safe operating limit of the crucible is therefore 1700°C.

The increase in the possible melting temperature from 1600 to 1700°C has a strongly beneficial influence on the glass quality. After melting at 1650°C a special glass for use in micro-mechanical applications still contained c. 100 bubbles per gram with a diameter less than 0.2 mm. This is unacceptable. However, at a melting temperature of 1700°C this glass could be produced completely free from bubbles.

Summary

The platinum DPH materials represent a new class of materials with significantly improved properties. Welded constructions for applications at very high temperatures can be manufactured from them which have display both high strength and good ductility together with resistance to temperature cycling, corrosion resistance and low notch sensitivity. The platinum DPH materials are thus superior to previously known ODS platinum materials. They have already proven themselves in the glass laboratory and in industrial applications.

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