With this paper the authors would like to present first results of a joint research project being carried out in co-operation between the Engineered Materials Division of Heraeus, the University of Applied Sciences Jena and the University of Applied Sciences Giessen-Friedberg.

This project is focused on investigations into the influence of different high melting glasses on various platinum materials under different conditions. The overall aim of this project is to generate results intended to supply a basis for optimizing the selection of materials for glass fibre bushings.

The presentation is divided into the following points:

First, a short introduction about bushings and some general trends.

We will then review the materials for glass fibre bushings and the typical requirements they have to meet. These requirements concern, for example, the mechanical properties at high temperature and the wetting behaviour.

We will then introduce first results of our investigations on different bushing materials both in the initial state and after long-term tests in high-temperature glass melts.

Finally we will summarize the results and give an overview of further investigations planned for the future.

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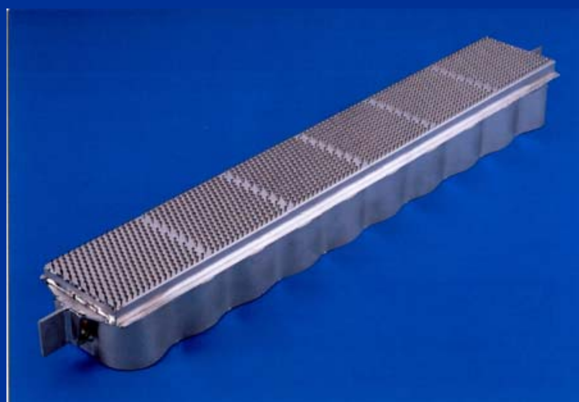
Introduction



glass fibre bushing of Pt-Rh alloy

glass fibre bushing in service

One of the most demanding applications for platinum materials is in bushings for the manufacture of endless glass fibres.

Bushings are more or less complex devices, containing a multiplicity of pressed or welded tips (the individual glass fibre nozzles). The pictures show a newly manufactured bushing and a glass fibre bushing in service.

With reference to the development of glass fibres, the following trends can be recognised:

1. an increasing market for endless glass fibres because short fibres are believed to be associated with a higher risk of causing cancer

and

2. an increasing market for endless high temperature fibres either made from glass or made of a natural mineral, for example, basalt.

Another trend is the increasing preference for larger fibre bushings for economic reasons.

These trends lead to requirements that can only be fulfilled by platinum materials.

The main requirements on bushing materials as a result of these trends are:

- improved high temperature strength, especially stress-rupture strength, and ductility
- a low creep rate
- excellent corrosion resistance, because some of high melting fibre materials contain high levels of impurities, for example iron and carbon
- very good weldability, because bushings are complex welded constructions
- and an optimized wetting behaviour.

Methods to increase high temperature strength of platinum materials are

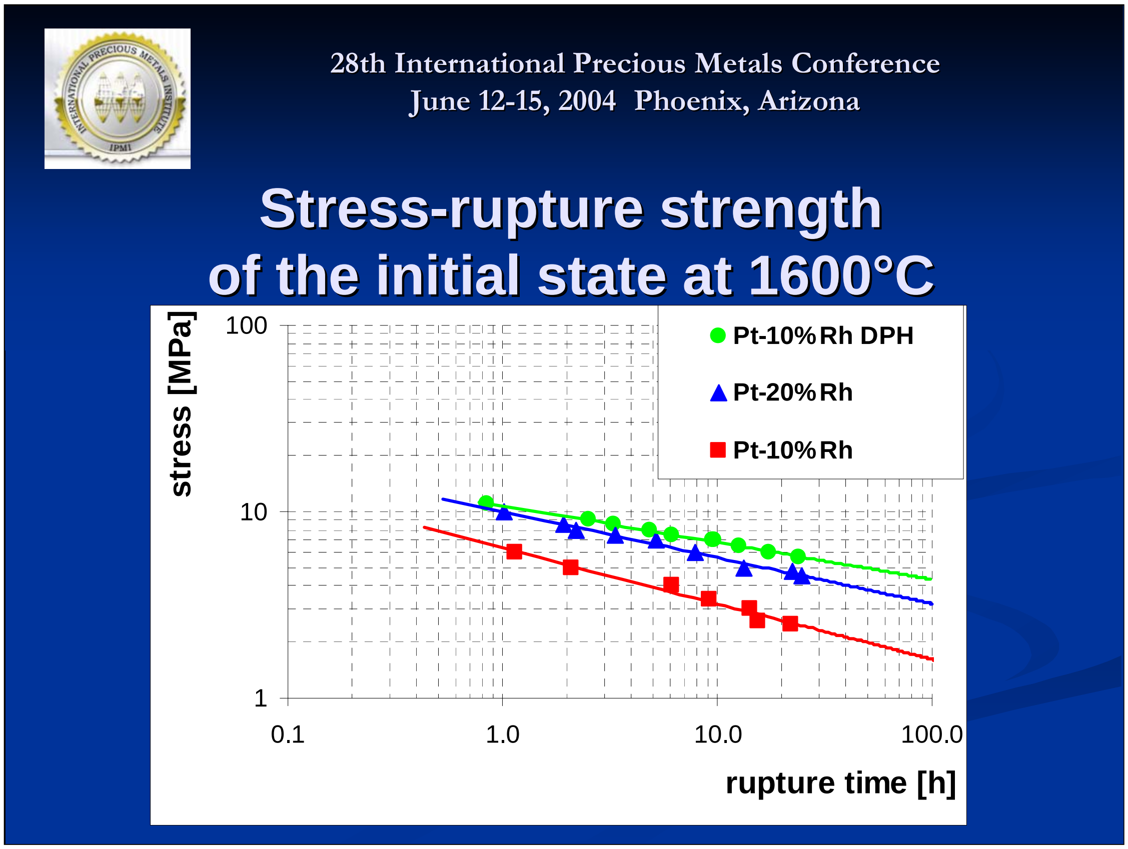
- solid solution hardening by alloying with 10% or 20% rhodium or
- oxide dispersion strengthening by adding or generating ZrO_2 and/or Y_2O_3

In this paper we will report on investigations on the

- solid solution hardened bushing materials Pt-10%Rh and Pt-20%Rh

and

- the oxide dispersion hardened Pt-10%Rh DPH made by Heraeus in Germany



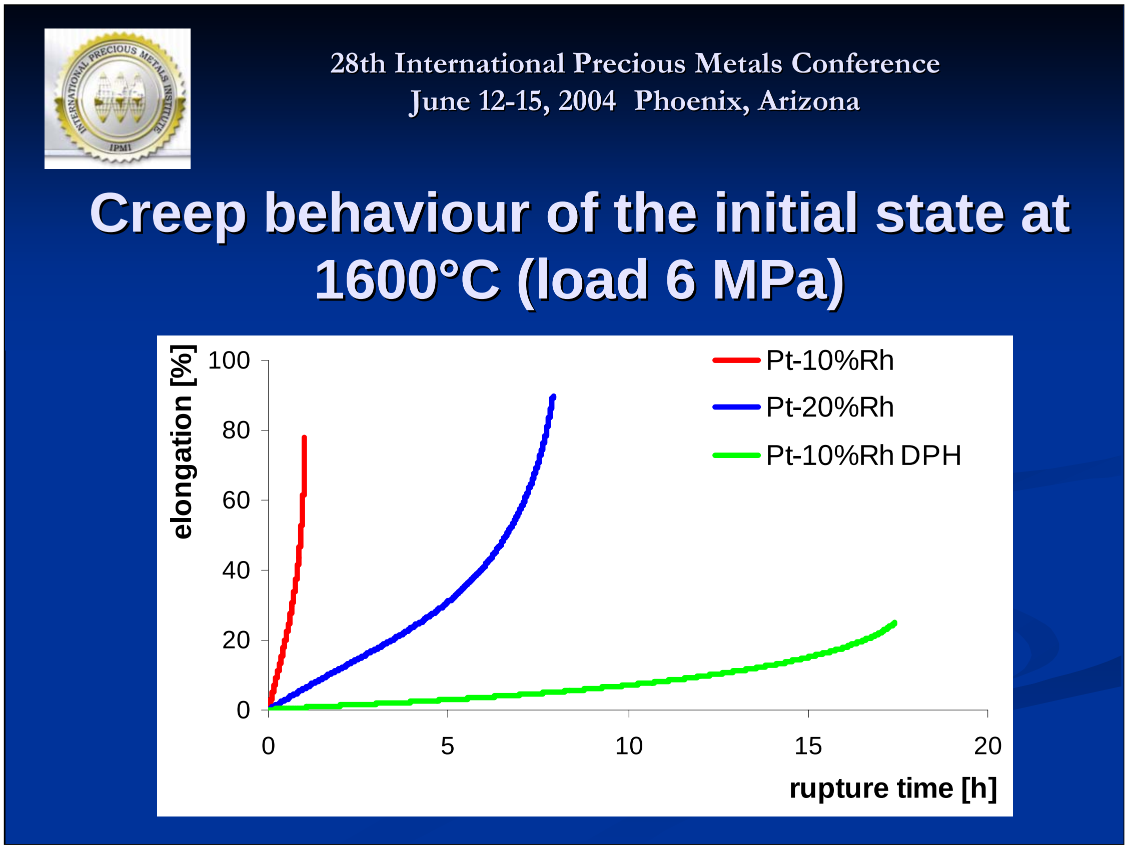
One of the most important properties of bushing materials is the stress-rupture strength at high temperatures.

The diagram shows stress-rupture curves determined at 1600°C in the initial state for the bushing materials investigated.

The comparison of the red and the blue lines shows the effect of solid solution hardening due to the increasing Rh content.

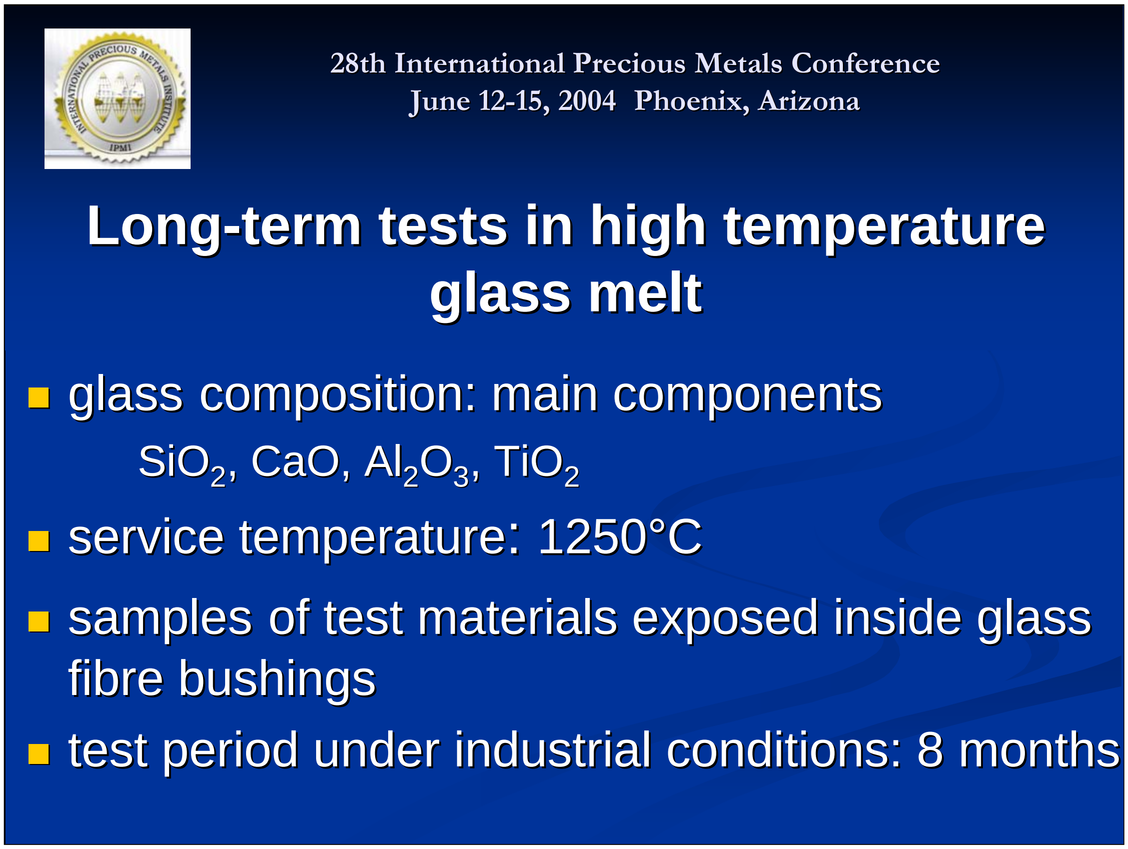
The oxide dispersion hardened alloy Pt-10%Rh DPH shows the highest stress-rupture strength over the whole time investigated.

Pt-10%Rh DPH demonstrates the smallest decrease in rupture strength with increasing rupture time compared with the other materials.



Creep curves measured at 1600°C for a load of 6 MPa in the initial state show significant differences between the materials investigated.

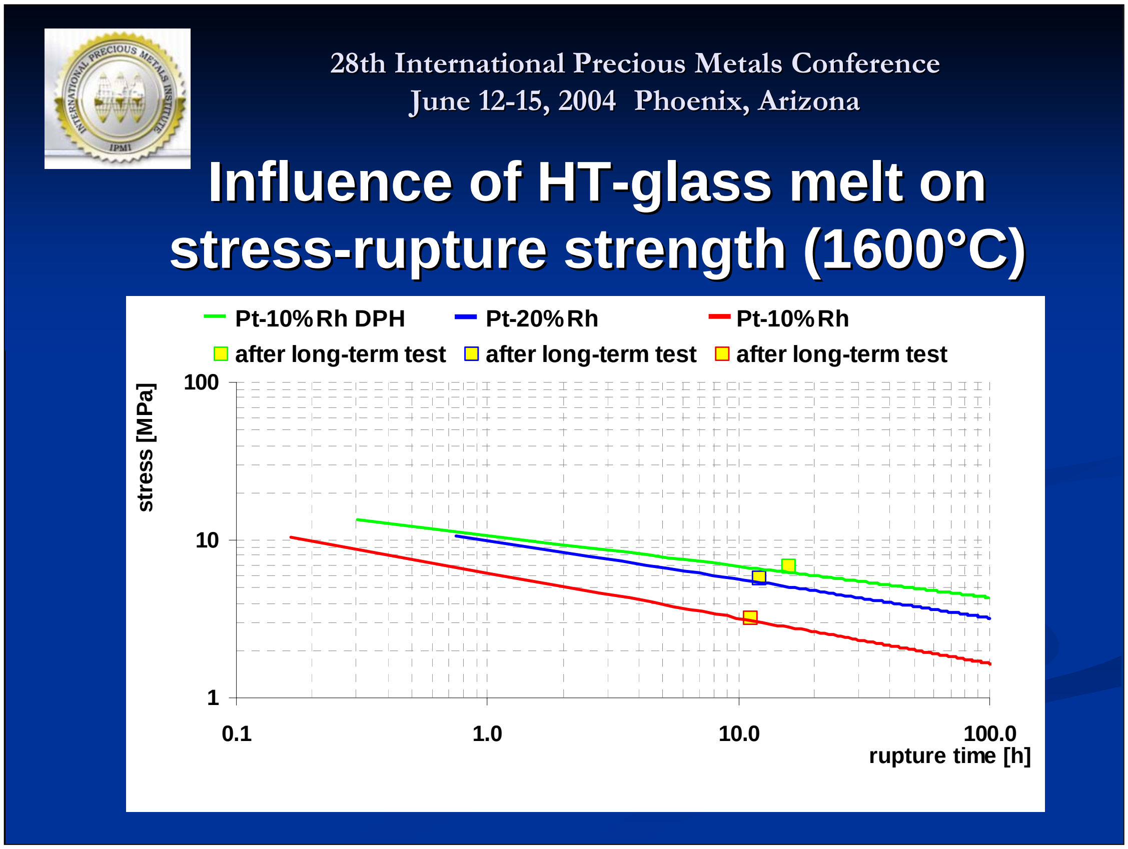
The solid solution hardened alloys demonstrate a very high failure strain but also a relatively high creep rate. Compared to that, the creep rate of the oxide dispersion hardened DPH material is very low (approx. 0.067 µm/s). This is a decisive advantage for these materials (more than 4 times lower than that of Pt-20%Rh). The failure strain of approx. 25% is more than acceptable for oxide dispersion hardened materials.



Long-term exposure tests were performed in a high temperature glass melt to obtain results showing its influence on the platinum materials investigated.

The main components of the high temperature glass melt were SiO_2, CaO, Al_2O_3 and TiO_2.

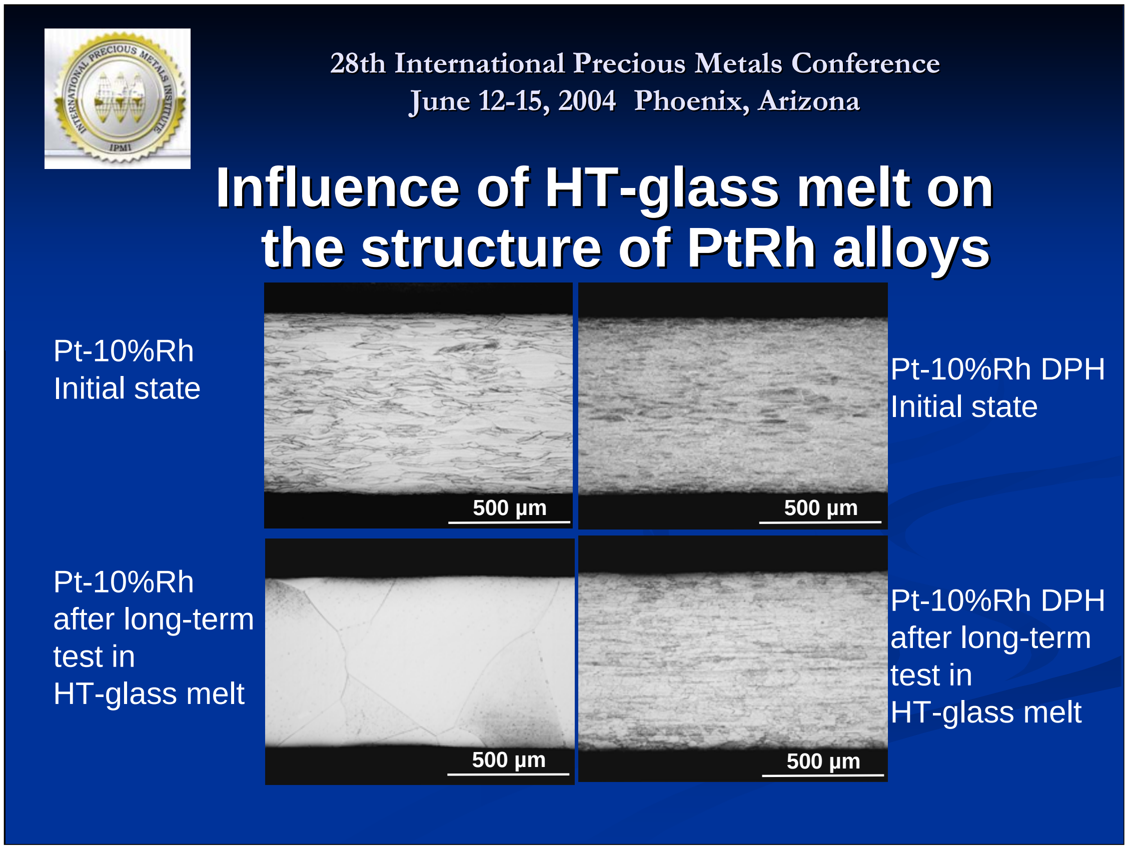
At a service temperature of 1250°C the samples of test materials were exposed for a test period of 8 months inside glass fibre bushings under normal industrial operating conditions.



This graph demonstrates the influence of the long-term exposure in the high temperature glass melt on the stress-rupture strength measured at 1600°C.

The red, blue and green lines show the stress-rupture curves in the initial state. The individual yellow squares are the averages of the rupture time measured on samples after the long-term exposure in the high temperature glass melt. The loads applied to these samples correspond to rupture times of 10 h for each material in the initial state.

Surprisingly, all materials investigated showed an increase in time to rupture after the long-term exposure. The effect is discussed below (page 13).

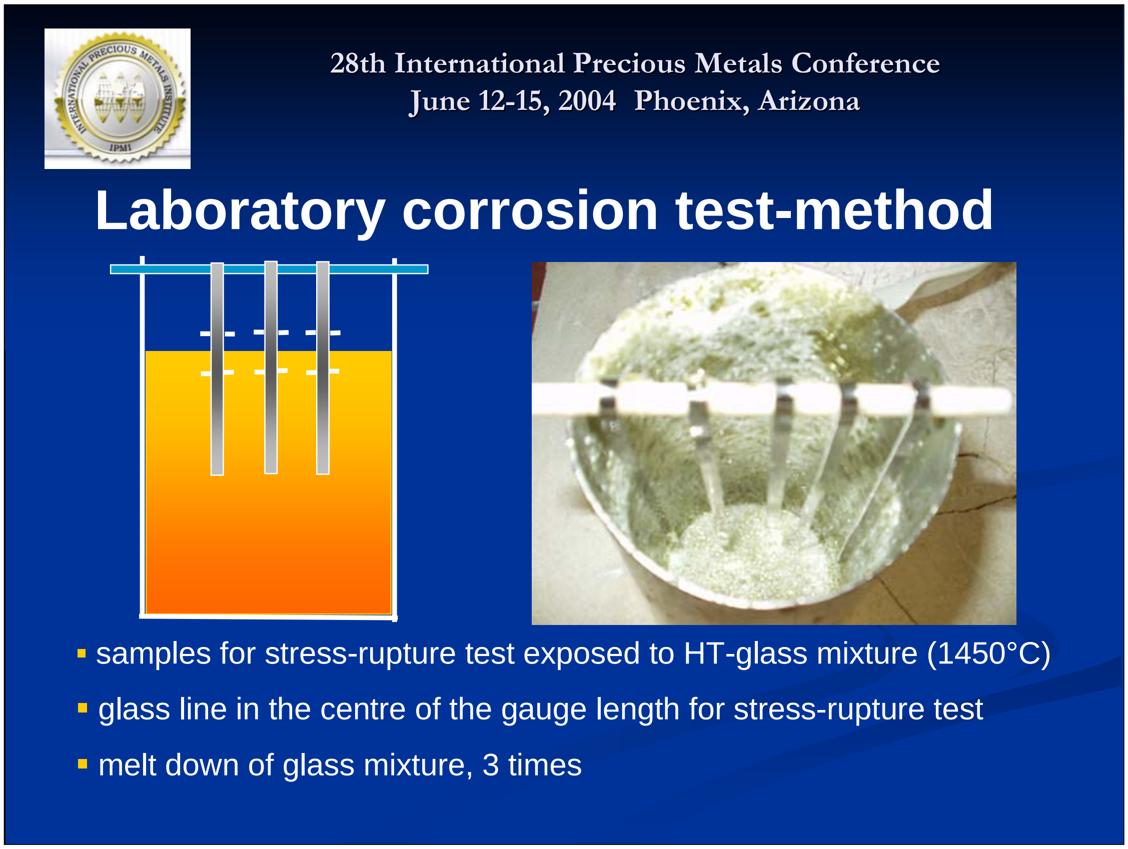


The influence of the long-term exposure in the high temperature glass melt on the structure of the test materials is shown in this picture.

The upper micrographs shows cross sections of Pt-10%Rh and Pt-10%Rh DPH in the initial state. No differences in the grain structure can be seen.

After the long-term exposure, the solid solution hardened Pt-10%Rh (the micrograph at the bottom left) shows significant grain coarsening. However, in the grain structure of the oxide dispersion hardened Pt-10%Rh DPH there is no difference to be observed after the long-term exposure compared with the structure of the initial state.

In contact with aggressive glass melts, the very fine grained structure of Pt-10%Rh DPH is advantageous in resisting corrosive attack.



Another method to test the influence of glass melts on the corrosion resistance of platinum materials is the exposure of samples during the melting down of a high temperature glass mixture.

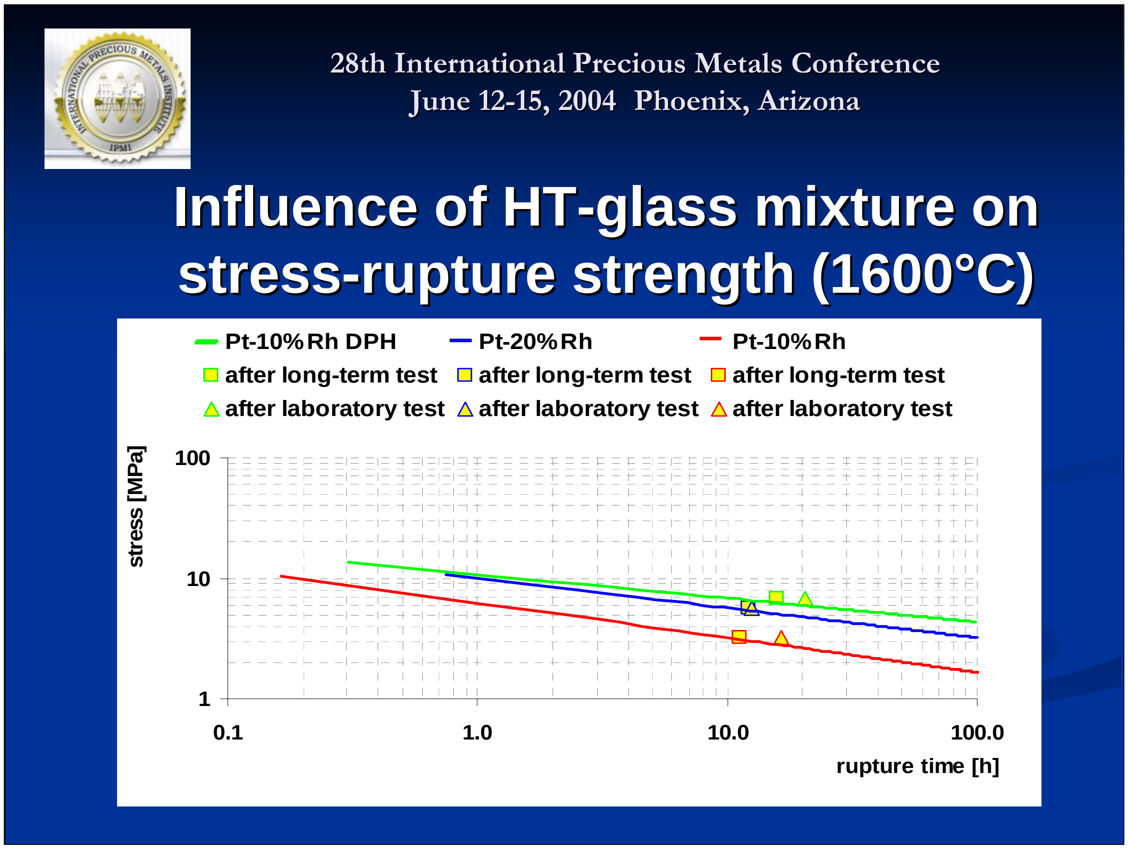
Platinum materials react very sensitively to the attack of glass mixtures during the melting-down procedure, as Professor Fischer and his co-workers from Jena found and published some years ago[1].

These laboratory tests were carried out in a crucible made of Pt-10%Rh DPH (picture above right).

Samples for stress-rupture tests were exposed to the high melting glass mixture at 1450°C. Each of the 3 melting down processes was stopped when the surface of the molten glass mixture reached the middle of the gauge length of the samples. At the end of each melting down process the temperature was increased to 1500°C for 45 min.

Subsequently the stress-rupture strength of the samples was determined at 1600°C.

[1] Fischer, B., "Reduction of Platinum Corrosion in Molten Glass", Platinum Metals Rev., 1992, 36(1), 14-25.

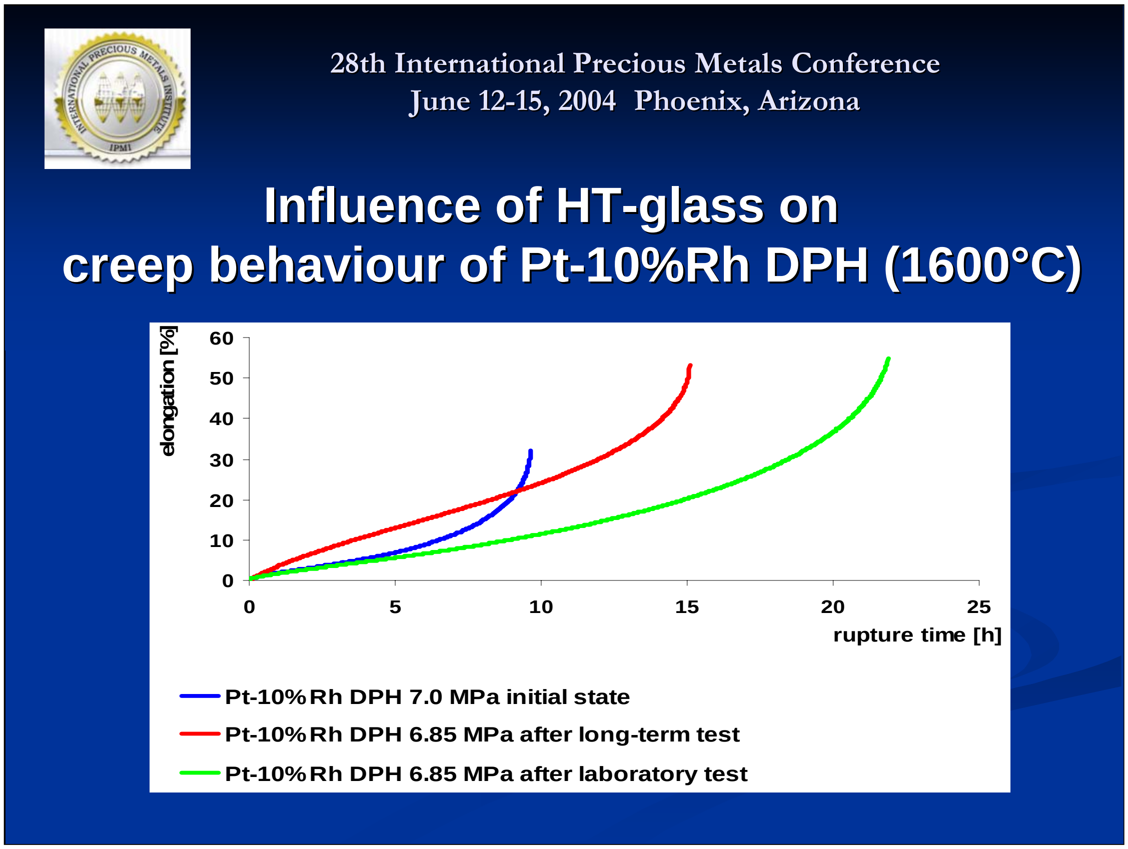


This diagram is based on that given on page 10 but shows the influence of the laboratory exposure to the melting down glass mixture on the stress-rupture strength at 1600°C in comparison to the long-term exposure in the high temperature glass melt.

The red, blue and green lines again show the stress-rupture curves in the initial state and the yellow squares give the averages of the rupture times measured on samples after the long-term exposure in the high temperature glass melt.

The individual yellow triangles are the averages of the rupture times measured on samples after the exposure to the melting down glass mixture. As in the diagram on page 10, the loads applied to the samples correspond to rupture times of 10 h for each material in the initial state.

All materials investigated again show increasing rupture times after exposure. Apparently the reason for the increased rupture time both after the exposure in melting down glass mixture and after long-term exposure in the high temperature glass melt is due to the diffusion of oxide forming elements coming from the glass mixture (e.g. Ca, Mg). Internal oxidation of these elements has led to increased stress-rupture strength. This assumption was confirmed by analytical investigations.



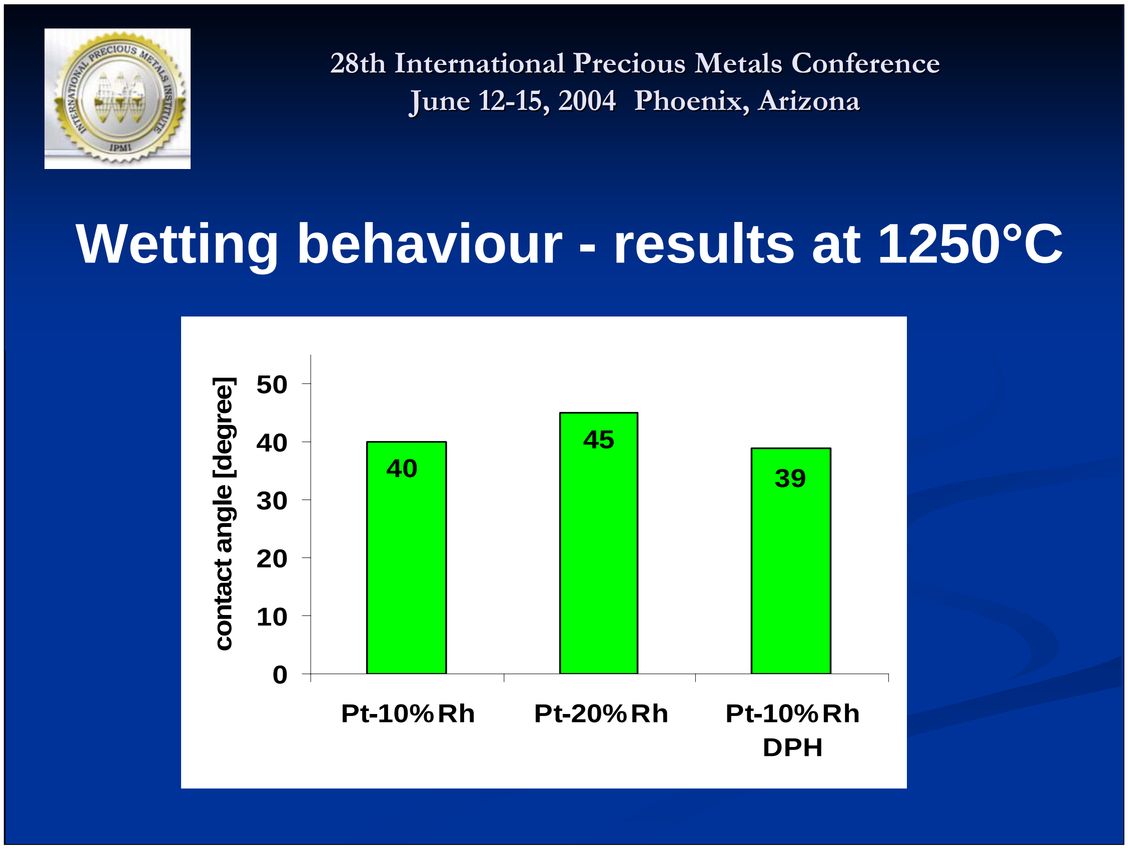
This figure shows creep curves measured on Pt-10%Rh DPH investigated after both the long-term test in the HT-glass melt and the laboratory test in melting down HT-glass mixture in comparison with the initial state.

In common with all other materials investigated, Pt-10%Rh DPH shows a significant increase both in rupture time (as mentioned above) and fracture elongation after both the long-time exposure (8 months) in the HT-glass melt and the exposure in the melting down glass mixture.

The assessment of the wetting behaviour was carried out by measurement of the contact angles of glass melts on platinum materials as a function of the temperature.

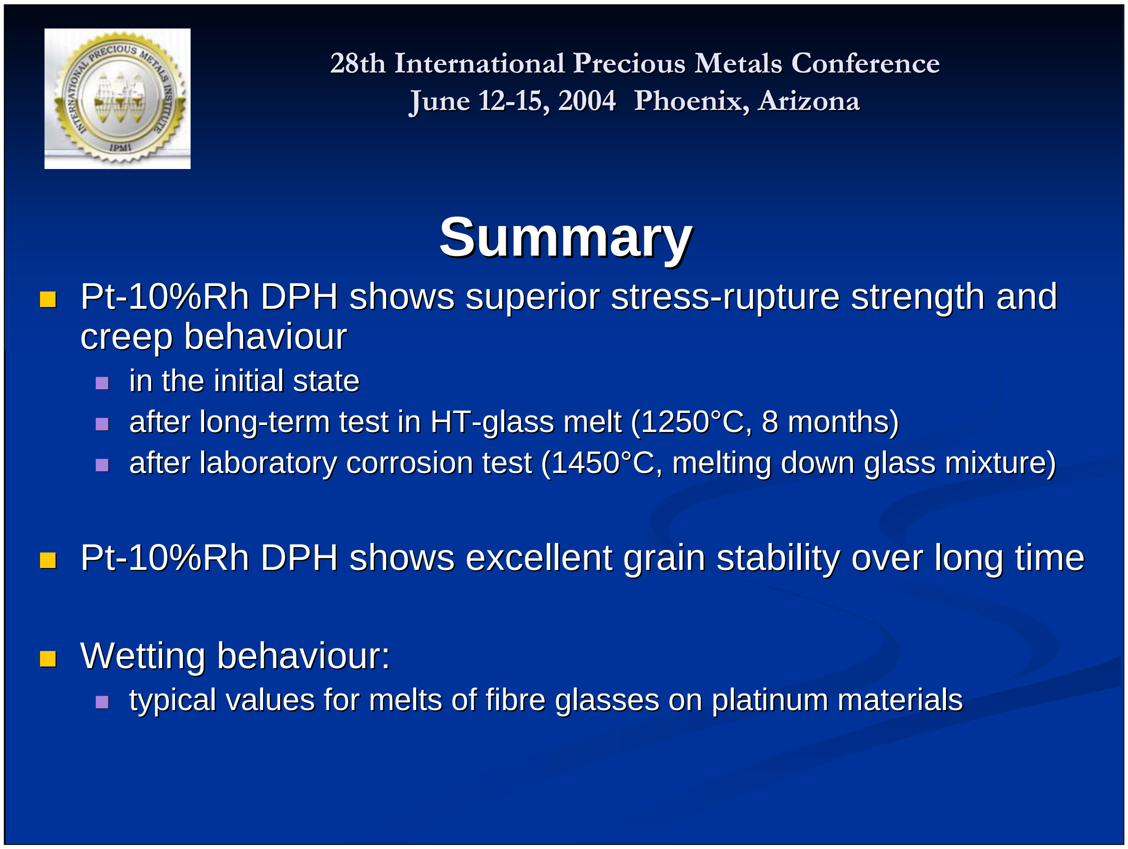
The picture on the left shows the measurement device. It performs measurements of contact angles at temperatures up to 1700°C by means of an optical system.

The picture on the right shows a drop of high temperature glass melt on a sample of Pt-10%Rh DPH at 1250°C as an example of this technique.



The results of the contact angle measurements are given in this figure.

The comparison of contact angles measured on Pt-10%Rh and Pt-10%Rh DPH does not demonstrate a significant difference. The results show typical values for the materials investigated in contact with glass melts commonly used for the manufacture of fibres.

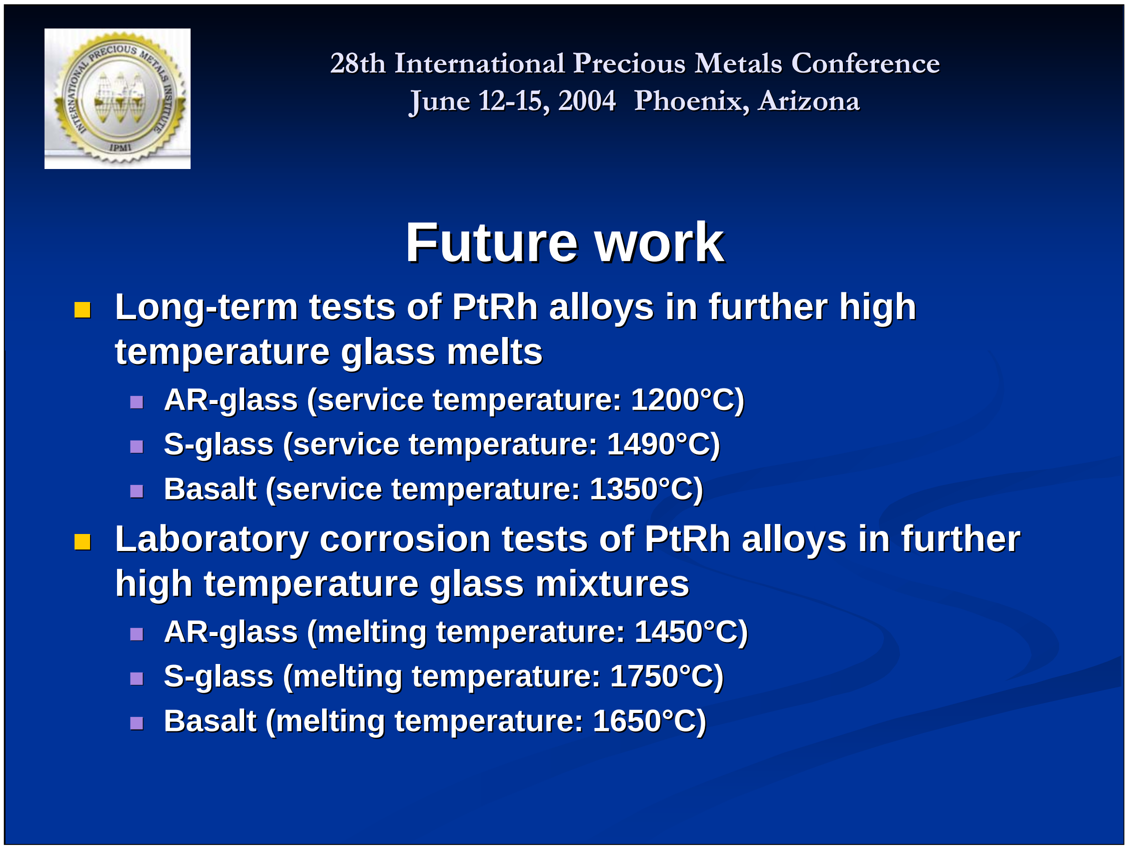


The results of the investigations indicate that the oxide dispersion hardened alloy Pt-10%Rh DPH shows superior stress-rupture strength and creep behaviour not only in the initial state but also after exposure in the high temperature glass melt and the melting down glass mixture. Furthermore Pt-10%Rh DPH shows excellent grain stability at the highest temperatures over long periods.

Neither exposure in the high temperature glass melt at 1250°C over 8 months nor exposure in the melting down glass mixture leads to a decrease in stress-rupture strength. All materials investigated show increasing rupture times after long-term exposure. Obviously the samples have been "contaminated" by harmless elements coming from the glass melt (e.g. Ca). Internal oxidation of these elements has led to increased stress-rupture strength. Analytical investigations confirmed this assumption.

Practical trials on bushings made from Pt-10%Rh DPH in contact with a C-glass melt at a slightly lower temperature (1200°C) led to significantly longer (double) total service lives.

The wetting behaviour of the oxide dispersion hardened Pt-10%Rh DPH is fully comparable to that of the other platinum materials investigated.



Subjects of future work are investigations on the influence of further high temperature glass melts on platinum materials. Both long-term exposure trials and laboratory corrosion tests up to the highest temperatures are planned in melts and mixtures of alkali-rich glass, special high temperature glass and basalt.

In addition to the exposure trials, the work will be supplemented by investigations of high temperature properties, in particular

- stress-rupture strength and
- creep behaviour

We also intend to determine the contact angle of the glass melts investigated in contact with the PtRh alloys at temperatures up to 1700°C . The work will be complemented by metallographic and microanalytical examinations using microprobe analysis and scanning ion mass spectroscopy together with fracture investigations.

We would like to thank Carolin Scheckenbach for the contact angle measurements and the metallographic examinations. We are also grateful to Torsten Schurig and Erik Hartmann for the measurement of stress-rupture strength and performing the creep tests.

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