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6th International Conference
Advances in Fusion & Processing of Glass
29th–31st May 2000
Ulm, Germany

Ductile High-Strength Platinum Materials for Glass Making

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Platinum and its alloys are used very widely in the glass industry because of their outstanding physical and chemical properties. Particularly advantageous properties of the platinum materials for this field of application are their high melting points, good oxidation and corrosion resistance against aggressive glass melts, negligible contamination of the glass melts because of the extremely low solubility of platinum in the melt, high mechanical strength at extremely high temperatures and good ductility, formability and weldability, together with the amenability to complete recycling. By using platinum alloys, the service lives of plant components can be greatly increased, and both the high quality of the glass melt and the achievement of precise dimensional and weight tolerances in glass products can be guaranteed. The most significant properties for the use of platinum and its alloys in the glass industry include stress-rupture strength, creep ductility, weldability and corrosion resistance.

Strengthening mechanisms: Solid solution or dispersion hardening

The use of pure platinum in the glass industry is very limited because of its low strength, particularly at higher temperatures. A significant increase in strength is achieved by alloying, but the only alloying elements which can be considered are rhodium, iridium and gold because they are not detrimental to the chemical stability of the platinum. The solid solution hardened alloys based on these elements, particularly the Pt-Rh alloys, have proven themselves in a wide range of applications throughout the glass industry. The substantial increase in the Young's modulus of

The investigations carried out at the University of Applied Sciences Jena during the development of the **DPH** materials were supported by funding from the Thuringian Ministry of Science, Research and Culture. The authors are responsible for the contents.

platinum achieved by alloying with rhodium is shown in Figure 1. A similar effect is observed on other strength properties. However, alloyed platinum is not suitable for melting high purity optical glasses and special glasses because the dissolution of traces of the alloying elements in the glass melts leads to deterioration of the optical properties. Platinum and its conventional, solid solution hardened alloys also show severe grain coarsening after long exposure times at high temperatures. As the grain size in these cases generally reaches the scale of the sheet thickness employed, the susceptibility to failure by corrosion along the grain boundaries increases greatly.

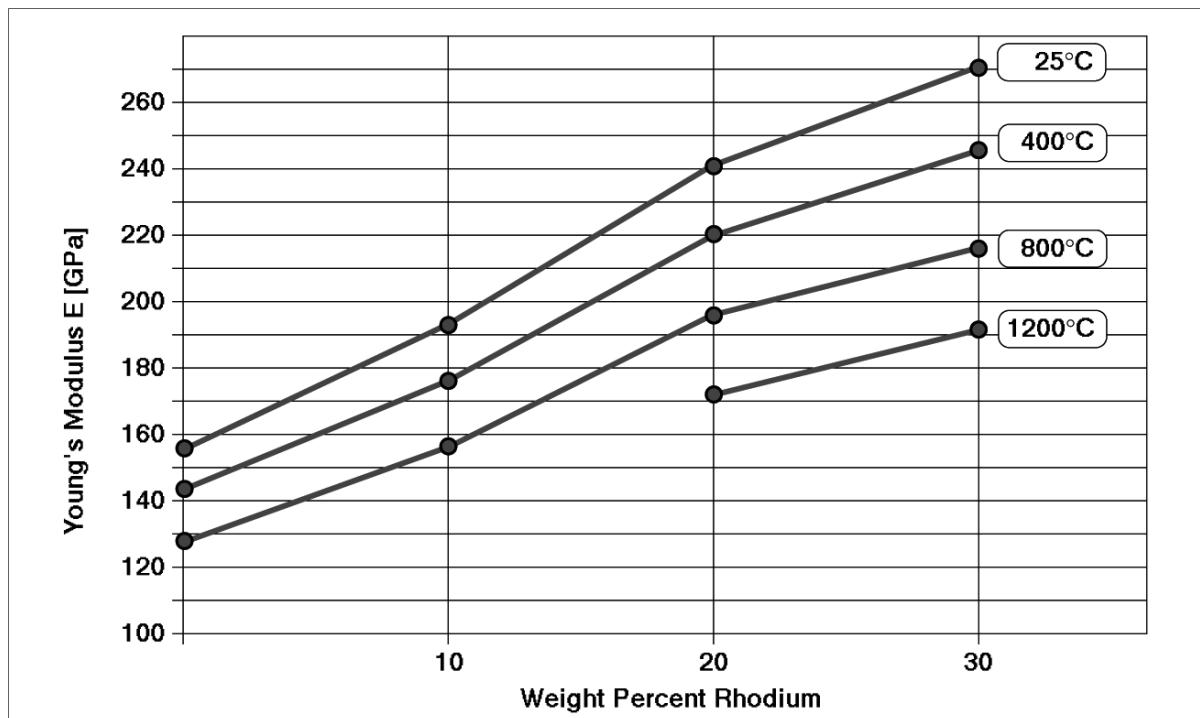
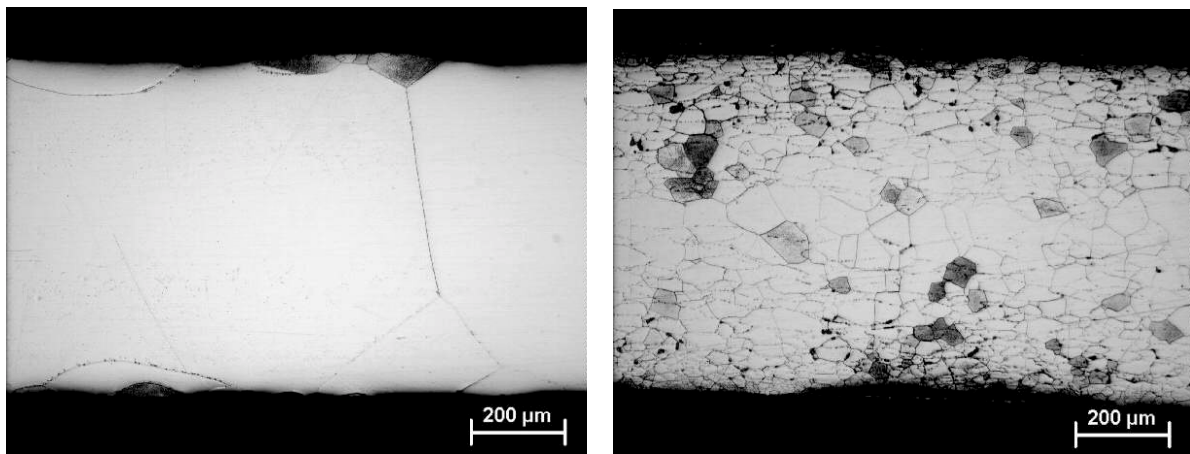


Figure 1 Young's modulus of Pt-Rh alloys [1]

An increase in the strength of platinum can also be achieved by introducing finely dispersed oxide particles into the metallic matrix. In order to ensure the efficacy of the dispersion hardening up to the highest temperatures, the oxide particles must have adequate thermodynamic stability, a higher melting point than the matrix, and they must be insoluble in the matrix even at the highest temperatures. Zirconia and yttria have proved particularly suitable. Provided the particles are sufficiently finely distributed, they will hinder the movement of dislocations in the matrix, thus giving an increase in strength. The particles also restrict grain coarsening, permitting the stable fine-grained micro-structure of the platinum to be maintained after long-term high temperature use. Dispersion hardening can also be used to improve the high

temperature properties of the solid solution strengthened platinum alloys. Figure 2 shows the microstructure of dispersion hardened Pt-10%Rh **DPH** from Heraeus in comparison to conventional Pt-10%Rh after 10,000 h exposure in a glass fibre bushing (C glass) at 1200°C. The exceptional microstructural stability of the **DPH** materials provides the basis for high strength with very good ductility and excellent corrosion resistance at the very high temperatures used in the manufacture of high melting special glasses. In particular, it is possible to increase the refining temperatures in order to obtain glasses of the highest quality.



a) Pt-10%Rh (conventional)

b) Pt-10%Rh **DPH**

Figure 2 Pt-Rh materials after 10,000 h in C-glass at $T > 1200^{\circ}\text{C}$

Stress-rupture strength

In the stress-rupture test, a sample of the material to be tested is subjected to a constant tensile load at a predetermined temperature and the time is measured until the sample breaks. Although the test is, in principle, very simple, it is the standard basic test used in the development and characterisation of all high temperature alloys. A test facility specially developed at the University of Applied Sciences, Jena [2,3] permits the stress-rupture strength of metals to be measured at temperatures up to 3000°C. Figure 3 shows the schematic design of this facility. The sample takes the form of a rod, wire or strip which is clamped in copper grips at each end and heated to the test temperature by direct electrical heating. The hottest region of the sample is scanned with an infrared thermometer connected to a PID controller and thyristor regulator that adjust the heating current and ensure a constant test temperature. The sample is loaded by means of calibrated weights. The stress-rupture curve for a

specific temperature is determined by measuring the time to rupture of samples under various loads. When the load is plotted against the time to rupture on a double logarithmic scale, the stress-rupture curves usually take the form of straight lines. To simplify presentation of the results and to permit comparisons it is usual to quote the value for the stress which causes rupture of the sample in 10h, 100h or 1000h.

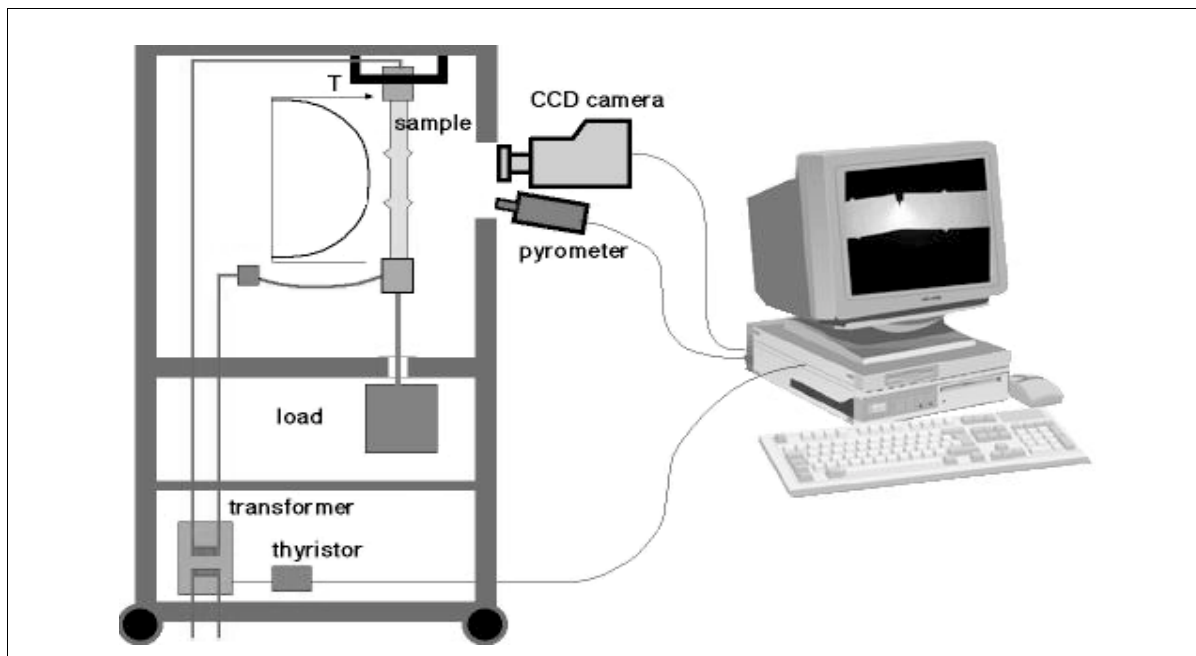


Figure 3 Stress-rupture and creep test facility (“Super Creep”)

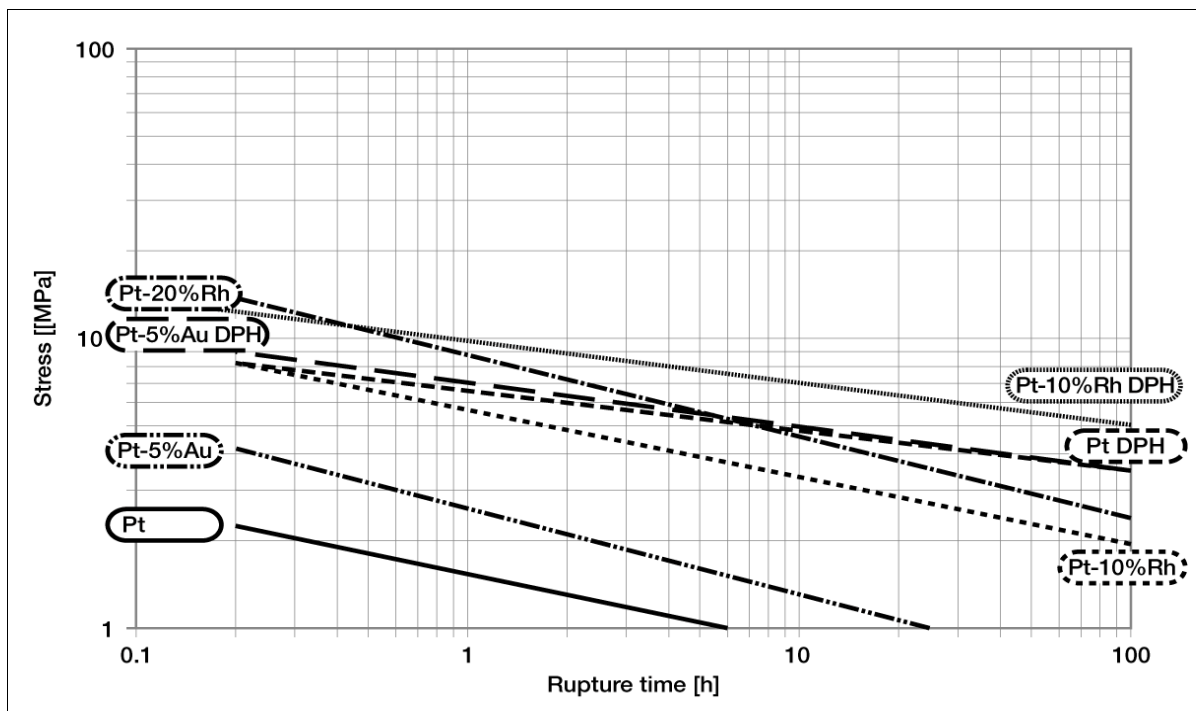


Figure 4 Stress-rupture curves for platinum materials at 1600°C

Figure 4 shows comparative stress-rupture curves for various platinum materials at 1600°C. The comparison between pure platinum and the non-dispersion hardened alloys shows the influence of solid solution strengthening on the stress-rupture properties. However, it is very noticeable that the dispersion hardened materials achieve significantly higher stress-rupture strengths. For example, Pt **DPH** demonstrates a higher stress-rupture strength than the solid solution strengthened alloy Pt-10%Rh. Another significant effect is the fact that the stress-rupture curves of the dispersion hardened materials show a slower decrease in rupture stress with increasing time than the conventional alloys. This means that the dispersion hardened materials have an even greater advantage relative to the conventional materials when they are used over long service lives such as are commonly required in the glass industry.

The main advantage of Pt-Au alloys is to be found in their reduced wetting by molten glass in comparison to pure platinum or other Pt alloys. The alloy Pt-5%Au is therefore widely used for crucibles, dishes, etc. for sample preparation in X-ray fluorescent analysis, but its use as a structural material in glass making is hindered mainly by its low strength. In view of the excellent high temperature strength of the dispersion hardened alloy Pt-5%Au **DPH**, which even exceeds the strength of the conventional alloy Pt-10%Rh, the use of this material can be seriously considered for load-bearing components in glass processing.

Creep strength, rupture behaviour and ductility

The creep and rupture behaviour of platinum materials can be assessed during the stress-rupture test with the aid of the creep curve. The stress-rupture test facility is fitted with a laser extensometer and an image processing unit to determine creep curves, i.e. the change in length of the sample as a function of time under load. By means of the laser system, the overall elongation of the sample is measured as a function of time during the stress-rupture test at constant temperature and load. Figure 5 shows creep curves for selected platinum materials at 1600°C and a stress of 3.5 MPa. A comparison of conventional Pt-10%Rh with Pt-10%Rh **DPH** demonstrates that the higher strength of the dispersion hardened material is reflected in the considerably longer life to rupture under the same load and the much lower

rate of elongation, i.e. creep rate, in the essentially linear range designated secondary creep. For example, the creep rate of Pt-10%Rh under the given conditions is decreased by an order of magnitude from 1 $\mu\text{m/s}$ to 0.09 $\mu\text{m/s}$ as a result of the dispersion hardening.

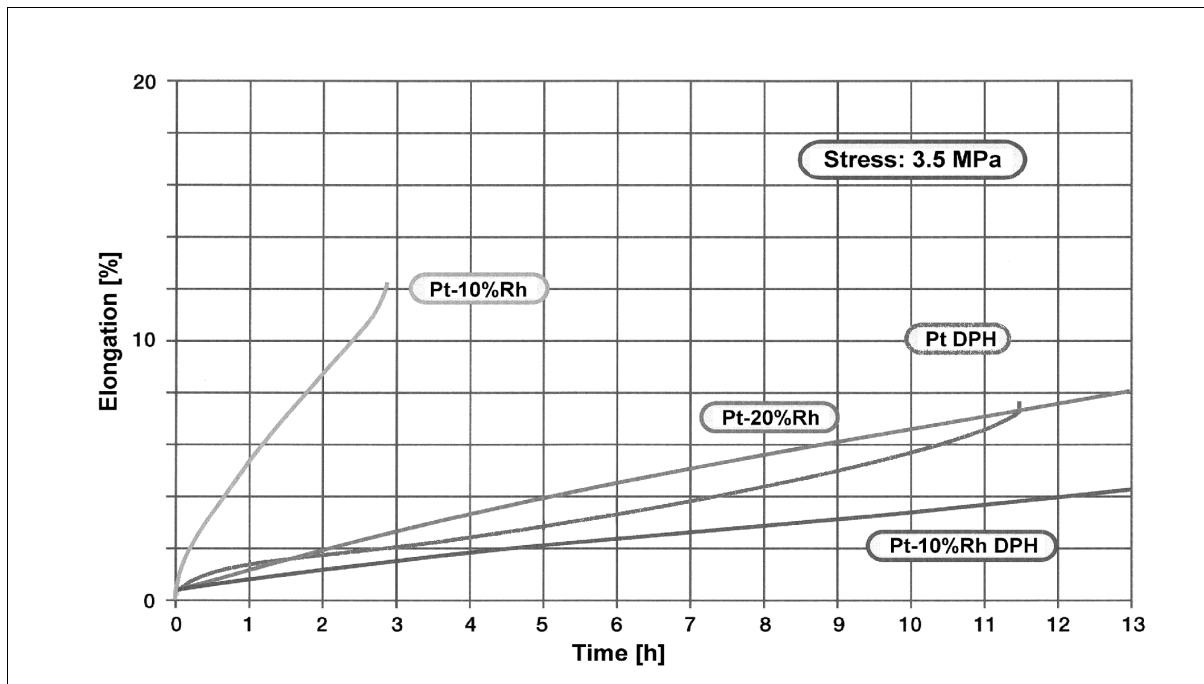


Figure 5 Creep curves for Pt materials (1600°C, 3.5 MPa, laser extensometer)

In addition to the increase in strength and reduction in creep rate by dispersion hardening, the ductility and the rupture behaviour of the dispersion hardened materials are very important. The rupture elongation given in Figure 5 relates to the overall length of the sample between the clamps, i.e. 100 mm. However, as the sample is heated by direct resistance heating, only the central portion of the sample (approx. 25 mm, see temperature profile in Figure 3) reaches the full test temperature. The percentage elongation in this region is therefore considerably greater. To determine the true rupture elongation more precisely, specially shaped samples were observed with a video camera during the stress-rupture test and the elongation was evaluated by means of continuous image processing [3]. Figure 6 shows the rupture elongation of conventional Pt-Rh alloys and dispersion hardened Pt-10%Rh materials determined by image analysis as a function of stress at 1450°C (“Super Creep” technique). A major disadvantage of most oxide dispersion strengthened platinum materials produced by powder metallurgical techniques is their low rupture elongation and their tendency to brittleness. The **DPH** materials

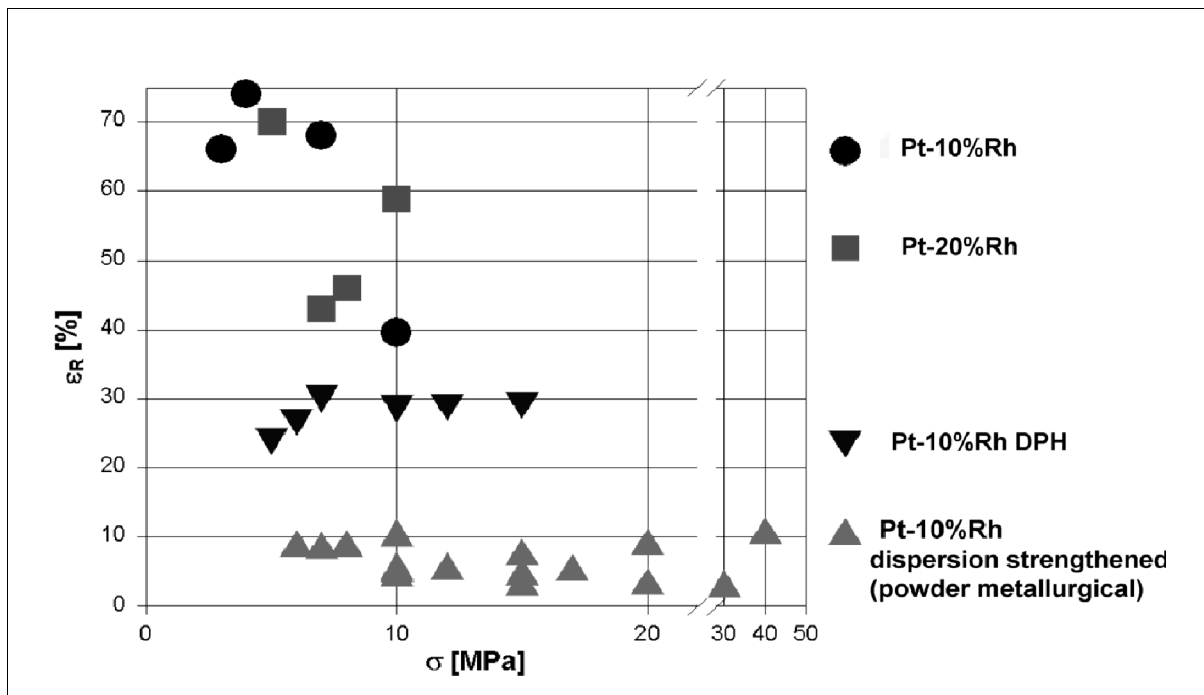


Figure 6 Rupture elongation of Pt-Rh materials at 1450°C with “Super Creep” (measurements performed at Fachhochschule Jena for SCHOTT GLAS, Mainz)

represent a completely new development in oxide dispersion strengthening. They are produced by melting, casting and forming. In a subsequent internal oxidation process, the oxide-forming elements are converted completely to an extremely fine dispersion of oxide particles, typically <5 nm [4]. The data in Figure 6 show that the rupture elongation of Pt-10%Rh **DPH** is considerably greater than that of the materials produced by powder metallurgy. Thus, the increase in strength achieved by dispersion hardening in Pt-10%Rh **DPH** relative to the conventional alloys Pt-10%Rh and Pt-20%Rh has not been gained at the cost of ductility.

Weldability

The conventional platinum materials commonly used in the glass industry can usually be fusion welded without difficulty. However, the welding of dispersion hardened materials is generally considered to lead to problems. During the fusion process in the welding zone the oxide dispersion agglomerates and separates out of the precious metal matrix. As a result, the pinning effect at the grain boundaries is lost and recrystallisation and grain growth can proceed without hindrance. For the same reason, the use of dispersion hardened weld filler material is not possible. The advantageous strength and corrosion properties of the oxide dispersion hardened

platinum materials are, therefore, not present in the areas of fusion welded joints. However, the DPH materials manufactured by melting and casting demonstrate a substantial advantage in weldability compared with the powder metallurgical materials. Figure 7 shows the 1000 h stress-rupture strength values of tungsten inert gas (TIG) welded joints of Pt-10%Rh **DPH** at 1450°C in comparison to both the unwelded material and the conventional alloys Pt-10%Rh and Pt-20%Rh. It can be

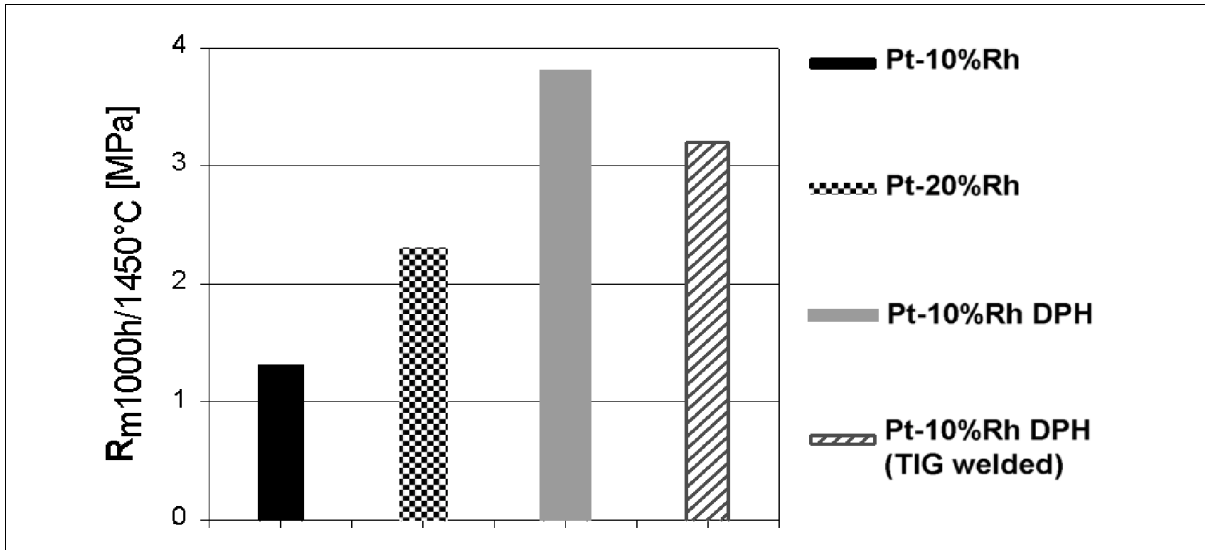


Figure 7 Influence of TIG welding on 1000 h rupture strength at 1450°C

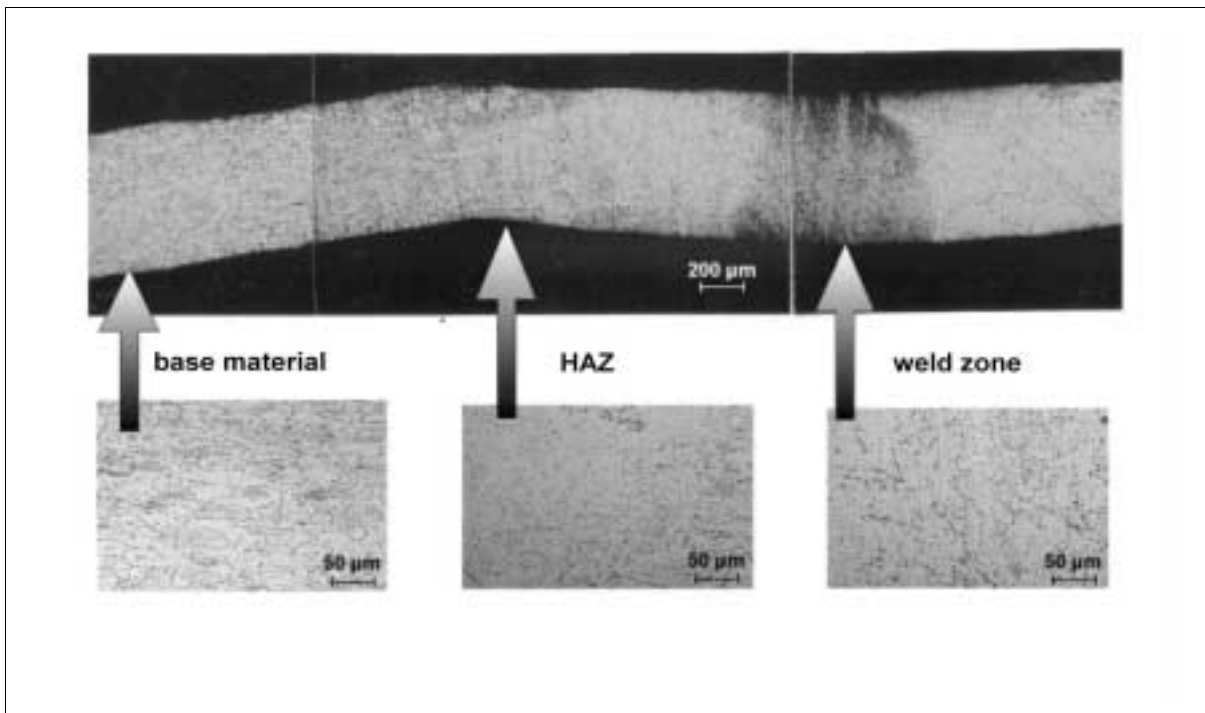


Figure 8 Microstructures in TIG weld of Pt-10%Rh **DPH** (HAZ=heat affected zone)

seen that the stress-rupture strength of welded Pt-10%Rh **DPH** joints is still very much higher than the strength of the unwelded conventional alloys.

The microstructure in the welded region (Figure 8) shows slight grain coarsening in the immediate fusion zone which is unavoidable when fusion welding techniques are used. However, dispersed phased particles can still be seen in the microstructure of the fusion zone. These are apparently sufficient to maintain a fine grained structure by pinning the grain boundaries. Even more remarkable, however, is the high stress-rupture strength after welding. We believe this to be a result of the extreme fineness of the oxide precipitates, thus minimising their tendency to agglomeration in the fusion zone.

Corrosion resistance

To obtain information on the corrosion resistance in the shortest possible time an accelerated corrosion test in hard crown glass was carried out as described previously [5], whereby the samples were exposed during the repeated melt-down of the glass constituents at 1400°C in order to increase the intensity of corrosive attack. The damage induced by the corrosive exposure was evaluated by determining the

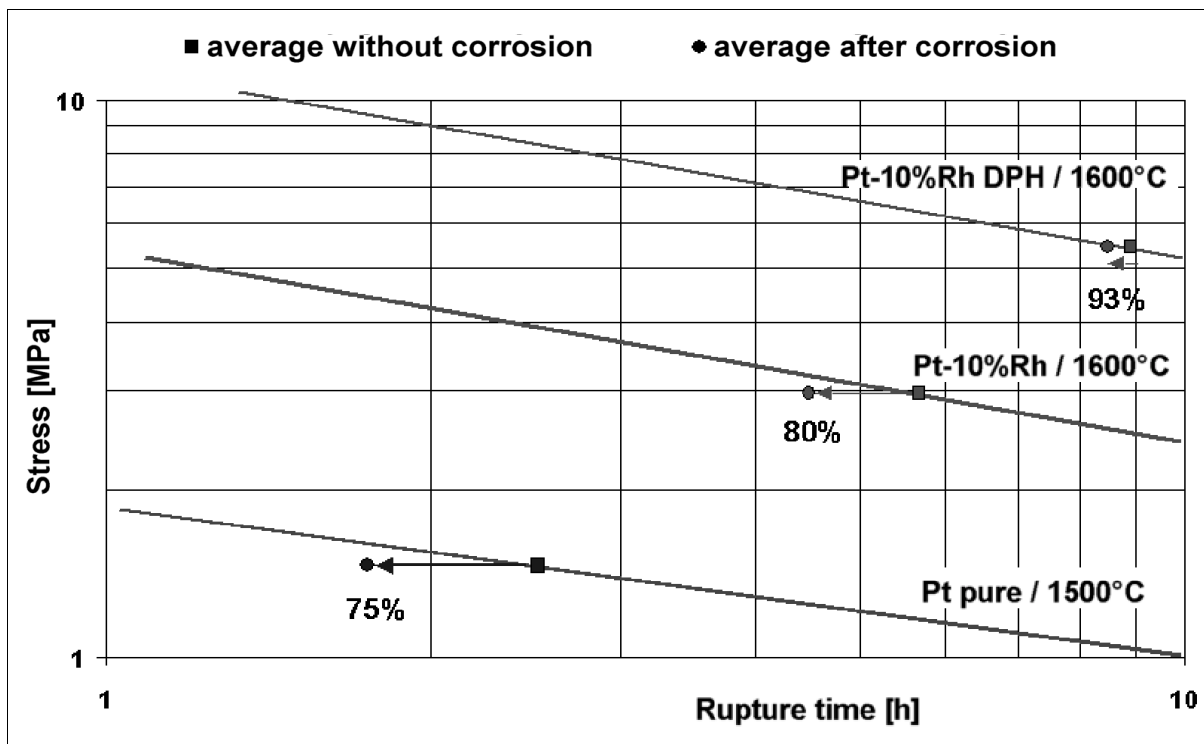


Figure 9 Influence of glass corrosion on rupture life of Pt materials

percentage reduction in rupture time in stress-rupture tests. Figure 9 shows the influence of corrosion on the time to rupture of Pt, Pt-10%Rh and Pt-10%Rh **DPH** at 1600°C. The reduction in strength of only 7% for Pt-10%Rh **DPH** is considerably less than the loss of strength observed in the conventional platinum materials. Welded Pt-10%Rh **DPH** showed the same proportional reduction in time to rupture as non-welded Pt-10%Rh. This is even more remarkable when one considers that the time to rupture of welded Pt-10%Rh **DPH** is a factor of ten higher than that of non-welded conventional Pt-10%Rh at the same load. Investigations of the creep behaviour after corrosion show no reduction in the rupture elongation, i.e. the ductility of the material is maintained [5].

Summary

The use of platinum materials is essential to guarantee continually high glass quality and very long service lives of processing equipment. Besides pure platinum, a wide range of conventional solid solution strengthened platinum alloys and oxide dispersion hardened platinum materials are available to meet the high mechanical requirements in every field of application. Especially with the development of the **DPH** platinum materials, which are produced by melting, casting and internal oxidation, Heraeus has succeeded in creating a class of materials characterised by good high temperature strength, excellent ductility and low creep rates. In view of their outstanding corrosion resistance and weldability, these materials are excellently suited to the most severe service requirements in the glass industry.

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