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Overview of the high-temperature mechanical properties of Pt-alloys

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Owing to their excellent oxidation and corrosion resistance, Pt and its alloys are being used preferentially at elevated temperatures and in aggressive environments. For example, an important application field is the glass industry. Alongside the discovery of new potential application fields, the knowledge of material properties is essential for computer simulations, design configuration, process optimization, research and development or quality assurance purposes. Due to the importance for technical applications high-temperature properties have been investigated for currently available Pt-base alloys with ongoing improvements. For the determination of tensile creep test data up to 3000°C, including precise strain measurement, special experimental equipment has been developed at the University of Applied Sciences Jena, Germany.

An overview of the existing and newly obtained mechanical property data on pure Pt, solid-solution strengthened Pt-Rh alloy, oxide dispersion-hardened materials Pt DPH and Pt 10%Rh DPH as well as cutting-edge results on Pt-base superalloys hardened by intermetallic precipitates will be presented and discussed. Furthermore, some important application examples for the above mentioned Pt-materials will be given.

Introduction

Materials that withstand extreme thermal, mechanical and chemical conditions are required for many high-temperature applications. Pt-alloys are noted for their high melting points, thermal stability and thermal shock resistance as well as good corrosion and oxidation resistance. For several applications the good electrical and thermal conductivity of Pt are important facts. In terms of mechanical properties, Pt-alloys combine high ductility with creep strength. These properties make Pt-alloys interesting for applications in the chemical industry, space technology and glass industry[1,2]. For example, in the spacecraft industry Pt-materials are used to increase the heat resistance of rocket engine nozzles. The fabrication of high-purity optical glasses and glass fibres requires the use of tank furnaces, stirrers and feeders made of Pt, which can withstand high temperatures, mechanical loads and corrosive attack. Outstanding purity, homogeneity and absence of bubble inclusions can be achieved only in glasses with the precious metal Pt being used. In ceramic melting vessels the stirring would cause ceramic particles to be loosened by erosion, resulting in contamination of the glass melts and thus in worsening of optical properties, e.g. transmittance.

For the fabrication of technical glass qualities Pt-materials are used for many important components in combination with refractory melting furnaces, e.g. feeder systems (stirrer, stirrer cell, plunger, plunger cell, feeder, orifice), bubblers, drain bushings and thermocouple thimbles (Figure 1). Furthermore, technical glass fibres are drawn through bushings which are made from Pt-alloys[1].

While pure Pt has low mechanical strength at high temperatures, alloying with Ir or Rh increases stress rupture strength remarkably[3–5]. These solid solution strengthened alloys possess good ductility at high temperatures and can be welded. However, due to evaporation of oxides during annealing at temperatures above 1100°C in air, Pt-Ir alloys show relatively high mass loss. In contrast, the alloys Pt

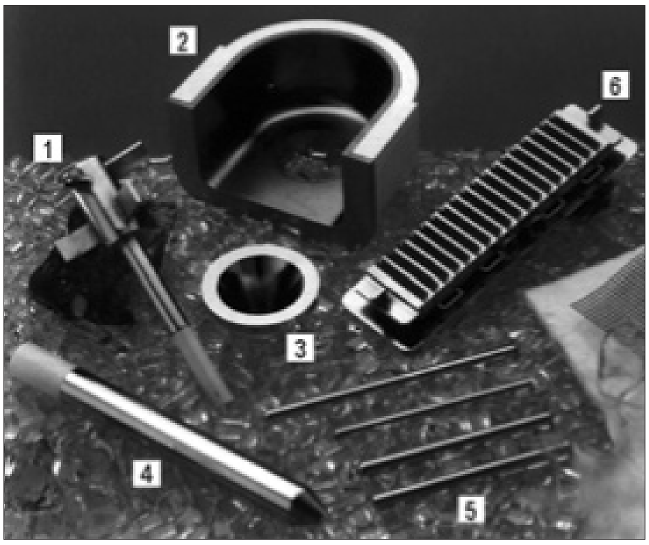


Figure 1. Components made from platinum for the glass industry: (1) stirrer, (2) spout bowl, (3) drain bushing, (4) plunger, (5) thermocouple thimbles, (6) bushing

10%Rh and Pt 20%Rh have a very low evaporation rate. However, grain coarsening of these solid solution strengthened alloys leads to a loss of properties that can result in premature failure of components.

For this reason oxide dispersion strengthened (ODS) Pt-alloys with improved high-temperature properties have been developed[6]. In these alloys small amounts of zirconium or yttrium oxides are finely distributed in the Pt matrix. By reducing dislocation mobility and stabilizing the grain boundaries these thermally stable oxides lead to an increase of stress-rupture strength up to about 1600°C. Conventional Pt ODS alloys are manufactured by complicated and expensive powder metallurgical (PM) processes[7–11]. However, these alloys show excessive brittleness and susceptibility to cracking. Due to the low ductility these materials are unable to withstand stress concentrations caused by thermal expansion during frequent rapid temperature changes. Furthermore, difficulties in fabrication, in particular a decrease in strength due to coagulation of oxide particles after welding, have impeded the use of these ODS platinum materials in technical applications so far[1]. W. C. Heraeus produces ODS Pt-alloys, so-labelled Pt DPH® alloys, in a melting process with subsequent internal oxidation. In these alloys the above-mentioned disadvantages are eliminated. Pt DPH alloys show good ductility, while the oxidation and corrosion resistance is comparable to solid solution strengthened Pt-alloys [12].

Another new group of Pt-alloys, the so-called Pt-base superalloys[13–18] possess even higher strength than solid solution and dispersion strengthened Pt-alloys at temperatures up to 1300°C. In these materials hardening is achieved by the precipitation strengthening mechanism that is known from Ni-base superalloys. The oxidation resistance of Pt-base superalloys is ensured by the formation of a thermally grown aluminium oxide layer.

For the development and application of Pt-alloys with further improved properties, precise measurements of high-temperature properties are necessary. The data obtained are especially important for design configuration and computer simulations. For the data determination, a special experimental set-up for creep tests at extremely high temperatures was developed.

Manufacture and microstructures of the new Pt-alloys

For the new Pt DPH materials small amounts of the metals zirconium, yttrium and, in some cases, cerium are added in elemental form to platinum during the melting process. In a following annealing process in air the material is internally oxidized. Thereby finely dispersed oxide precipitates are formed from the minor alloying elements. The annealing time is adjusted to ensure that the reactive elements are fully converted to oxide. The particles are thereby incoherently embedded in the Pt-matrix. Figure 2 shows a metallographic section of the microstructure of such a Pt DPH alloy. Within the grains and at the grain boundaries finely distributed oxide particles can be seen.

After casting of the new Pt-base superalloy $PtAl_{12}Cr_6Ni_5$ with a composition of 77 at. pct. Pt, 12 at. pct. Al, 6 at. pct. Cr and 5 at. pct. Ni, a homogenization heat treatment leads to a dissolution of dendritic areas and to a homogeneous distribution of the elements. During subsequent air cooling finely distributed intermetallic Pt_3Al-cuboids (called γ´) are precipitated coherently in the f.c.c. solid solution matrix (called γ)[13,18]. The Pt_3Al-particles are $L1_2$-ordered, have edge lengths of about 500 nm and a volume fraction of about 50%. The microstructure of these alloys (Figure 3) is very similar to that of the role-model, i.e. the Ni-base superalloys.

Creep testing facilities

The creep testing facilities[19] permit tests at constant load either in air or inert gas atmosphere at temperatures up to 3000°C. The schematic diagram of the set-up is given in Figure 4a. The specimen is gripped in clamps and heated by an electric current running through the sample. The load is

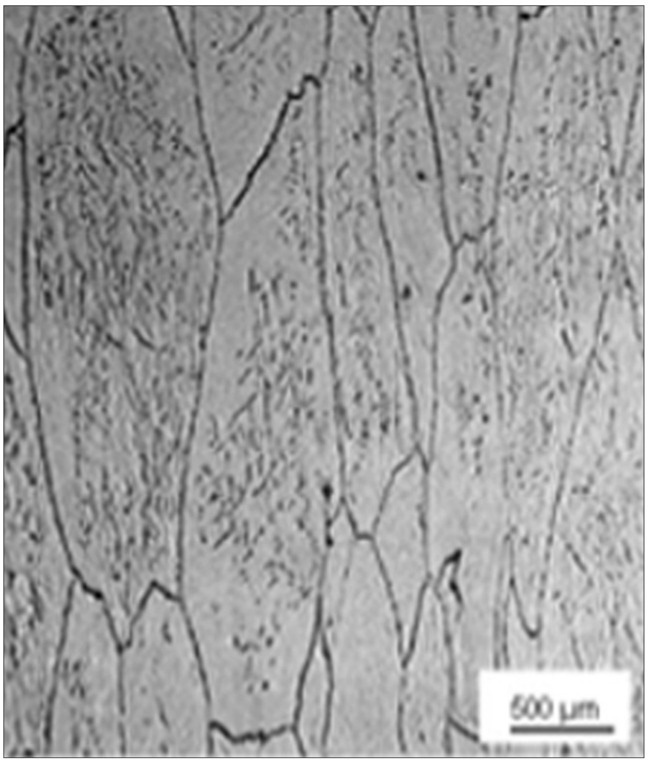


Figure 2. Optical micrograph showing the microstructure of internally oxidized Pt DPH

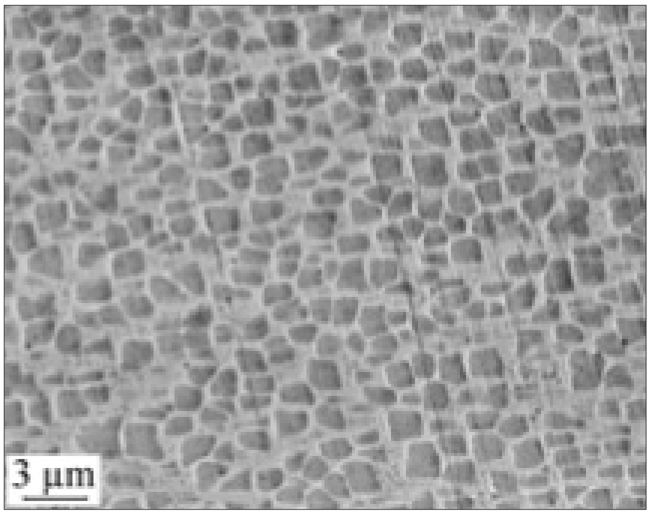
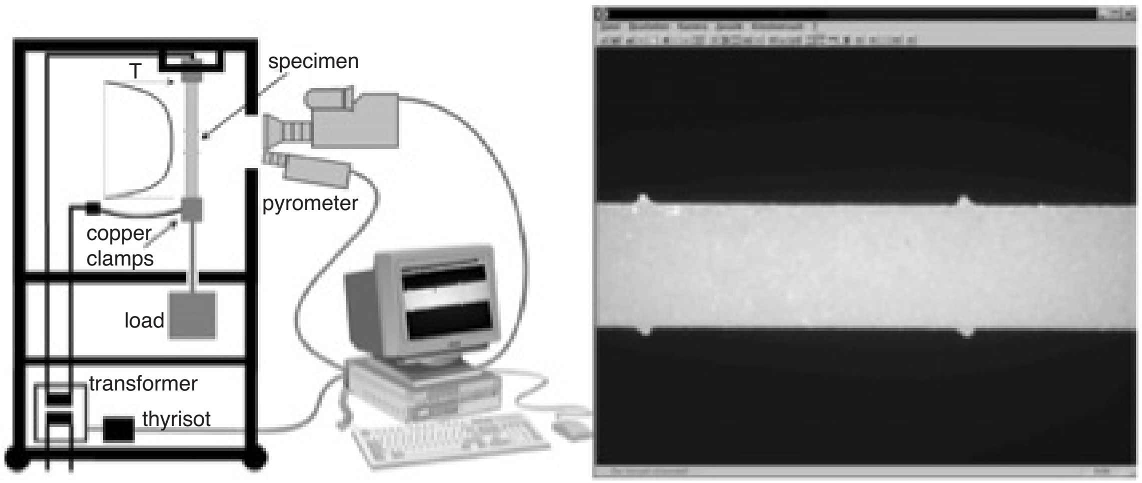


Figure 3. SEM micrograph showing two-phase γ/γ´-microstructure of Pt-base superalloy $PtAl_{12}Cr_6Ni_5$



(a) (b)

Figure 4. (a) Creep testing facility for tests at constant load either in air or inert gas atmosphere at temperatures up to 3000°C. (b) Screenshot of the software SuperCreep for strain measurements.

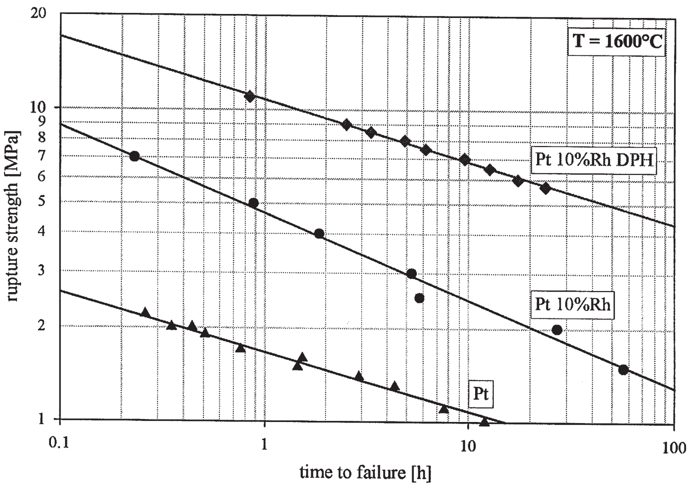


Figure 5. Stress-rupture strength curve of Pt and Pt-alloys at 1600°C

applied to the specimen by means of calibrated weights. Common dimensions of the specimens are 120 x 4 x 1 mm^3. The temperature in a zone 30 mm around the axial specimen centre is highest and nearly constant over the whole range. The temperature is monitored by an infrared pyrometer and the software LabView. Using the pyrometer signal, the heating current can be controlled and thus a constant temperature can be achieved. Lower temperatures at the clamps allow the use of cheap copper clamps. The middle part of the heated samples is observed by a high resolution camera that is connected to a PC with the software SuperCreep, a program that was developed at the University of Applied Sciences Jena. For strain measurements, SuperCreep continuously determines the distance between the markers attached to the specimens[19] (Figure 4b).

Results and discussion

Creep tests were carried out on pure Pt and three different Pt-alloys. The ODS alloy Pt 10%Rh DPH was developed by the company W. C. Heraeus in cooperation with the University of Applied Sciences Jena. The acronym DPH is the designation of W. C. Heraeus for their dispersion hardened alloys.

The stress-rupture curves for pure Pt, Pt 10%Rh and Pt 10%Rh DPH at a temperature of 1600°C are shown in Figure 5. Pure Pt has relatively low strength at that temperature. The addition of Rh in alloy Pt 10%Rh leads to a certain strength increase. However, the solid solution strengthening effect decreases with increasing temperature. Furthermore extensive grain coarsening during high temperature exposure leads to a drastic decrease in rupture time. Therefore a further increase in strength is achieved in the dispersion hardened alloy Pt 10%Rh DPH. The oxides are very stable and show very little solubility in the Pt matrix phase, even at high temperatures. The larger particles that are visible in Figure 2 hinder the movement of the grain boundaries. Therefore the microstructure remains fine grained even after annealing at high temperatures and over long periods of time. Within the grains small particles of less than 1 μm in diameter act as obstacles for dislocation motion in the metallic matrix[1]. This causes a further increase in strength and low creep rates.

Precipitation hardened Pt-base superalloys were recently developed in a joint project between the research groups at the University of Applied Sciences Jena and the University of Bayreuth in Germany. In these two-phase superalloys, dislocation movement is hindered by the coherent γ´-

particles precipitated in the γ-matrix[20]. However, due to the ongoing dissolution of the hardening γ´-phase at very elevated temperatures, the Pt-base superalloys are designed for applications up to 1300°C. Therefore the stress-rupture curves at 1300°C are plotted for Pt 10%Rh, Pt 10%Rh DPH and the Pt-base superalloy $PtAl_{12}Cr_6Ni_5$ in Figure 6. It can be seen, that the new Pt-base superalloy has higher stress-rupture strength than Pt 10%Rh and even Pt 10%Rh DPH.

Figure 7 shows the creep curves of Pt 10%Rh and Pt 10%Rh DPH at 1600°C. Both alloys show short primary creep, extensive secondary creep and subsequent ternary creep. An incubation period described by Hamada *et al.*[21] for pure Pt was not observed for either alloys. Although Pt 10%Rh shows high fracture strains of about 50%, the strength is relatively low. Compared to Pt 10%Rh the alloy Pt 10%Rh DPH has remarkably higher stress-rupture life.

For industrial applications, high strength and good ductility, i.e. high rupture strains are required. Otherwise, unavoidable thermal stresses would increase the risk of cracking and fast disruption of components. Previous ODS Pt-materials[6] show only a very low rupture elongation of about 5% (Figure 8), the new Pt 10%Rh DPH has high strength and good ductility with fracture strains of almost 30%.

The creep rate for Pt 10%Rh DPH is highlighted for 1600°C and 7 MPa in Figure 9, and was generated from the respective creep curve in Figure 7. In the beginning the creep rate decreases rapidly due to work hardening of the material. The subsequent minimum of the creep rate represents the strength of the alloy. Then the creep rate increases slightly in the secondary stage of creep, and later on it increases strongly during ternary creep due to internal damage in the material.

The Norton plot is generated by plotting minimum creep rate against stress (Figure 10). Using a double logarithmic plot, the data points are situated on more or less straight lines. Their slope is equal to the Norton exponent n of the Norton creep law in Equation [1]:

$$\dot{\varepsilon}_{min} = A \cdot \sigma^n \qquad [1]$$

with A constant = f (temperature, material, state of the material)

σ stress in MPa

From Figure 10 the Norton exponent of Pt 10%Rh at a temperature of 1600°C was calculated to be n = 3.3, and A = 34. For pure Pt Völkl *et al.*[6] gave values of n = 3.8 and A = 10^{-5} at 1600°C and similar stresses.

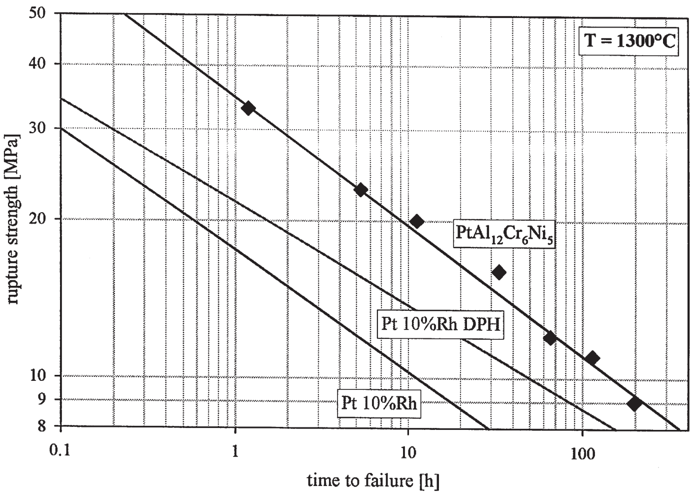


Figure 6. Stress-rupture strength curve of different Pt materials at 1300°C

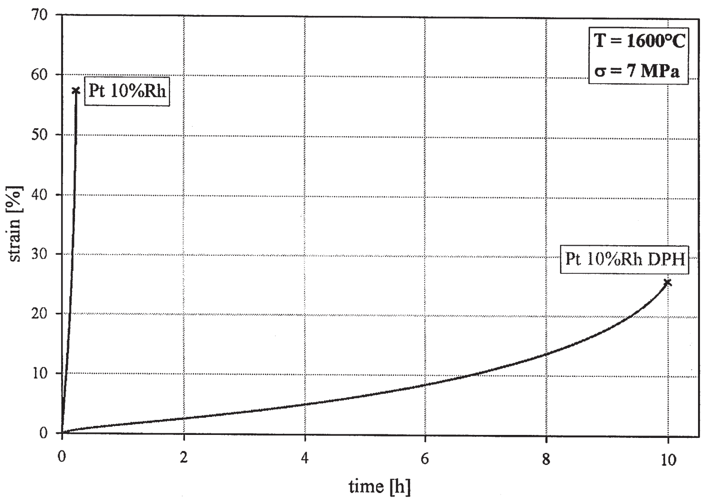


Figure 7. Creep curves of Pt 10%Rh and Pt 10%Rh DPH at 1600°C, σ = 7 MPa

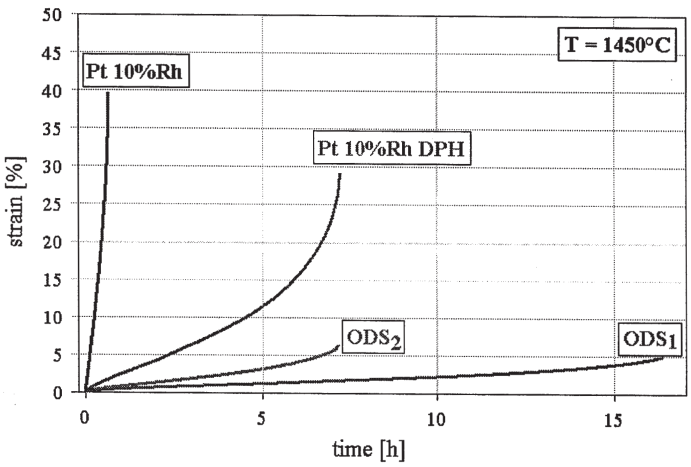


Figure 8. Creep curves of several platinum alloys at 1450°C

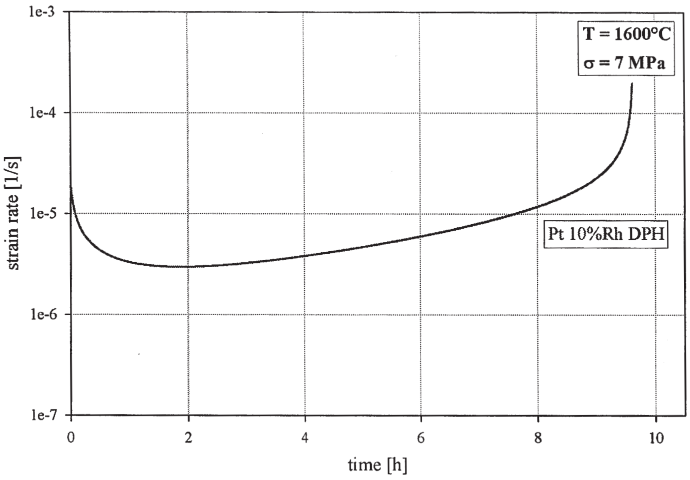


Figure 9. Creep rate of Pt 10%Rh DPH at 1600°C, calculated from the creep curve in Figure 7

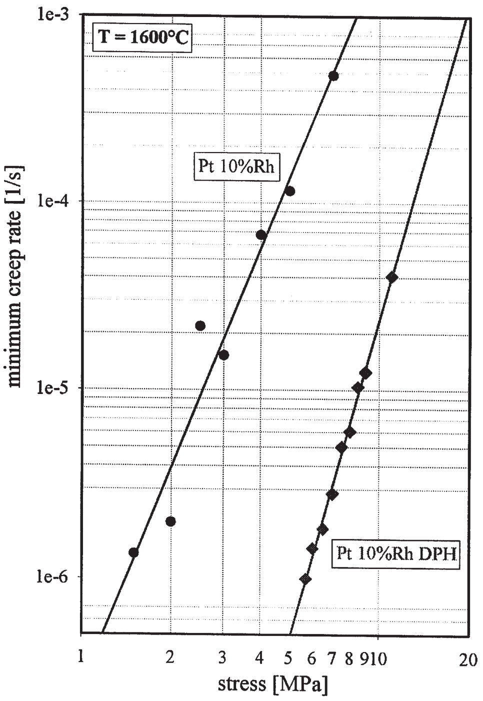


Figure 10. Norton plot of Pt 10%Rh and Pt 10%Rh DPH at 1600°C

The Norton exponent of the new precipitation-hardened superalloy $PtAl_{12}Cr_6Ni_5$ was determined to n = 3.6, as shown in Figure 11.

These low Norton exponents for pure Pt, Pt 10%Rh and $PtAl_{12}Cr_6Ni_5$ are typical for the viscous-drag controlled creep of single-phase solid solution alloys. However, the low value of the two-phase Pt-base superalloy $PtAl_{12}Cr_6Ni_5$ could be also explained by the observed intergranular fracture mode in the creep deformed samples. This points to a certain brittleness and weakness of the grain boundaries. Investigations are in progress to stabilize the boundaries by adding grain boundary strengthening elements. Thus, higher Norton exponents and creep life are expected.

Very high values for Norton exponents of about 30, which were observed in previous oxide dispersion strengthened materials, indicate that relatively small increase in stress would lead to large change in creep rate. Components made of these materials are thus very susceptible to crack and damage during peak demands in mechanical load. The observed Norton exponents n = 7.3 for Pt DPH and n = 4.5 for Pt 10%Rh DPH at 1600°C[6] are well below the critical value.

Summary

Creep testing facilities for tests at extremely high temperatures up to 3000°C in air or protective atmosphere

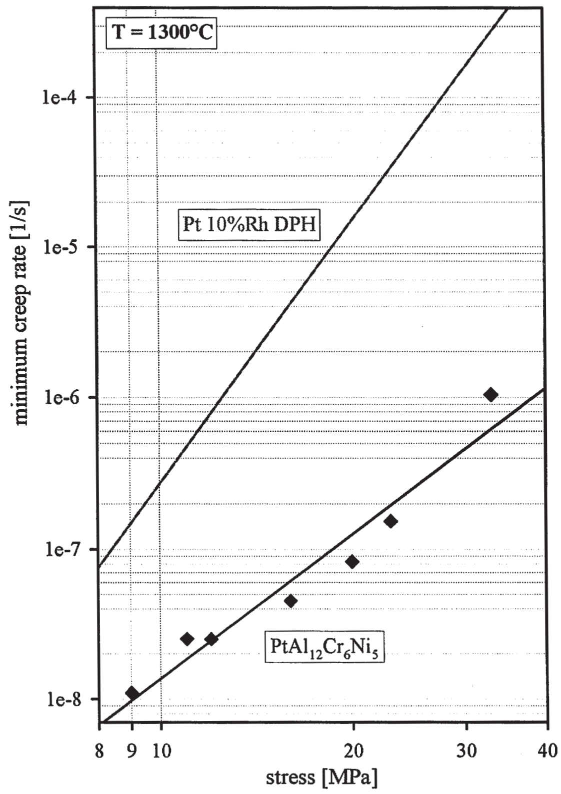


Figure 11. Norton plot of Pt 10%Rh DPH and $PtAl_{12}Cr_6Ni_5$ at 1300°C

were described. Ohmic heating of the specimen allows very high heating rates. The temperature is monitored by a contactless method using an infrared pyrometer. Due to a special geometry of the specimen temperature gradients can be minimized and a constant temperature can be realized in the measuring area with an accuracy of ± 3°C. Contactless strain measurement is carried out with a high resolution camera and digital image processing. The sophisticated temperature control and strain measurement techniques permit the use of small samples.

Investigations on Pt 10%Rh and Pt 10%Rh DPH at 1600°C and $PtAl_{12}Cr_6Ni_5$ at 1300°C reveal these alloys to creep according to the Norton power law. Compared to pure Pt, solid solution strengthening (alloy Pt 10%Rh), and the more oxide dispersion strengthening (alloy Pt 10%Rh DPH) lead to a significant strength increase. Because the new precipitation-hardened Pt-base superalloy $PtAl_{12}Cr_6Ni_5$ has higher strength at 1300°C than Pt 10%Rh and Pt 10%Rh DPH, Pt-base superalloys are regarded as very suitable for applications in this temperature range. For higher temperatures up to 1600°C the new Pt 10%Rh DPH alloy is superior. Compared to conventional ODS platinum materials, which are produced via the powder metallurgy route, in the new Pt DPH alloys previous problems were successfully overcome. Pt DPH alloys can be welded without any special measures using the standard TIG technique, and the strength of the weld joints is hardly reduced compared to the base material[1]. Thus, welded constructions for applications at very high temperatures can be manufactured from the new Pt DPH materials, which have displayed both high creep strength and ductility.

It is worth mentioning that crucibles and dishes of the Pt DPH materials showed in all cases considerably better handling properties than the previously used equipment made from non-ODS Pt-materials. By the replacement of bushings previously made from Pt 10%Rh by the new Pt 10%Rh DPH materials, the total service life could be almost doubled. This corresponds to a reduction in total costs by more than 30%, based on producing of bushings, installing, repairing and for time of shut down. Furthermore, process quality, the fibre quality and yield as well as the production rate could all be maintained. The improved mechanical strength also enabled the reduction of the thickness of sheets used in the bushings and thus in weight by 8.7%.

For the development of special glass that cannot be processed at 1600°C, the new Pt 10%Rh DPH material allows continuous operation at 1700°C without any problems. This has to be regarded as a strong benefit.

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