Influence of high melting Glasses on selected Properties of PtRh Alloys for Applications in Glass Fibre Bushings

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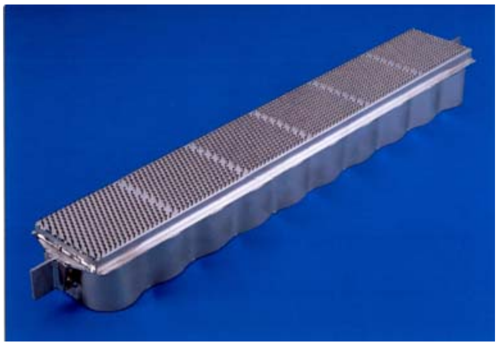
For the production of endless glass fibres, the use of glass fibre bushings made of PtRh alloys is necessary. The manufacturing process for high melting glass fibres in particular leads to simultaneous chemical attack and mechanical loading at extremely high temperatures.
The influence of these complex loadings on the stress-rupture strength and the creep behaviour of various PtRh alloys (conventional and oxide dispersion strengthened alloys) was investigated after contact with various glass melts. The investigations include both long-term tests under service conditions and laboratory corrosion tests. The investigations will be complemented with metallographic and fracture examinations in the SEM and microprobe analysis.
Furthermore, the fibre manufacturing process is influenced by the wetting of the bushing material by the glass melt. For this reason the wetting behaviour of the platinum materials in contact with the different glass melts was investigated as a function of the working temperature of the glass fibre bushings.
The results of the investigations provide a basis to optimise materials selection for glass fibre bushings.

Introduction

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). Fig. 1 shows a newly manufactured bushing with the lower, glass-exit side facing upwards and a bushing in service.

The demand for endless glass fibres is increasing because the competitive product, short glass fibres, are suspected to be carcinogenic. Moreover the trend is towards endless fibres made of high melting materials (glasses, minerals e.g. basalt) in order to be up to standard for more heat-resistant materials. Of course there is also a continuous demand for bigger bushings in order to increase the output of fibres. As a result of these trends the market for bushings is increasing. However, the requirements that can only be fulfilled by platinum materials are also increasing. The resulting main requirements on bushing materials 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 because this influences the quality and output of fibres



a)

b)

Fig.1: a) newly manufactured bushing of PtRh b) Bushing in service

In this context, the effect of the glass on the mechanical properties at high temperature and on the wetting behaviour of platinum alloys is a critical factor for their use as a bushing material. However, there are few investigations into the effect of glass melts on mechanical properties at elevated temperature. Investigations of the creep behaviour of Pt-7%Rh in air and different silicate melts (SiO_2, Al_2O_3, CaO, MgO) showed increasing creep rate with increasing iron content (10 - 20 %) [1]. The influence of phosphate glass on the thermal resistance of Pt-5%Au is discussed in [2]. Furthermore there are more investigations about the effect of glass on mechanical behaviour of bushing material at high temperatures [3-6]. Investigations of the wettability of platinum materials by glass have been published extremely seldom. In [7] the contact angle between different Pt alloys (Pt, Pt-10%Rh, Pt-5%Au, ODS-Pt, ODS-Pt-5%Rh, ODS-Pt-10%Rh, ODS-Pt-5%Au) and E-glass at 1200°C is described. In the current project the influence of high temperature glass on stress-rupture strength, creep and wetting behaviour of commercially available bushing materials was investigated. The results of the investigations provide a basis to optimise materials selection for glass fibre bushings.

Experimental

Both solid solution strengthened alloys Pt-10%Rh and Pt-20%Rh and additionally oxide dispersion strengthened materials Pt-10%Rh DPH and Pt-10%Rh ODS (adding or alloying with Y- and/or Zr-oxides) were tested. The influence of HT-glass (main components SiO_2, Al_2O_3, TiO_2 and CaO) on the stress-rupture strength and on creep behaviour of these PtRh alloys was investigated. The examinations include both long-term tests in a glass melt under service conditions and laboratory tests in a melting down glass mixture.

For the long-term test metal strips of the PtRh alloys were welded into bushings which were used in the fibre production process for the whole service life (8 months). Samples for the creep-rupture test (4 x 0.8 x 120 mm) were laser cut from the metal strips after disassembling the bushings.

For the laboratory tests in melting down glass mixture the samples were suspended from a ceramic bar positioned over a crucible and were heated at 1450°C. After 15 min the glass mixture was added for the first time, thus covering the lower half of the samples. The crucible was refilled with glass mixture every 20 min till the surface of the glass melt was in the middle of the gauge length of the stress-rupture test sample. Then the temperature was elevated to 1500°C and kept constant for 45 min. The corrosion exposure was carried out three times. Afterwards the samples were cooled down and cleaned in hydrofluoric acid.

The stress-rupture strength and creep behaviour of the samples which were obtained from the long-term exposure and the laboratory test were determined and compared to the results obtained in the initial state. The test method is described in [8-9].

Subsequently, metallographic and various micro-analytical investigations and examinations of the fractured surface with SEM were conducted in order to explain the effect of HT-glass on stress-rupture strength and creep behaviour of the bushing materials.

In addition the wetting behaviour of the PtRh alloys with HT-glass was investigated with a contact angle measurement device including a high temperature furnace up to 1700°C (fig. 2). The measurements were performed in the temperature range from 1000°C up to 1500°C with a heating rate of 10 K/min and temperature holds every 50 K for 10 min. At least three measurements were carried out for each PtRh alloy. One value of one measurement for a constant temperature results from the analysis of five images (fig. 3). The weight of the glass sample was about 0.15 g. The samples showed very smooth surfaces with an arithmetic average surface finish of approximately 0.01 to 0.02 µm.

Fig. 2: Contact angle measurement device with high temperature furnace (up to 1700°C)

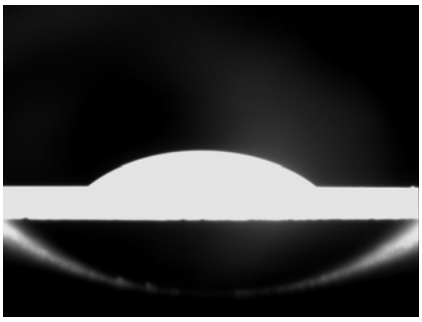


Fig. 3: Drop of HT-glass melt on Pt-10%Rh DPH at 1250°C

Results and Discussion

Stress-rupture Strength

One of the most important properties of bushing materials is the stress-rupture strength at high temperatures. Fig. 4 shows stress-rupture curves determined at 1600°C in the initial state for the bushing materials investigated. The comparison of the curves of Pt-10%Rh and Pt-20%Rh demonstrates the effect of solid solution hardening due to the increasing rhodium content. The diagram also shows the effect of oxide dispersion strengthening with the alloys Pt-10%Rh ODS and Pt-10%Rh DPH compared to Pt-10%Rh. The lines of the oxide dispersion alloys differ among each other due to their differing manufacturing process. The alloy Pt-10%Rh ODS, which is produced powder metallurgically, has lower stress-rupture strength than Pt-20%Rh. In contrast Pt-10%Rh DPH, which is manufactured by fusion metallurgy, shows the highest stress-rupture strength over the whole time investigated and demonstrates the smallest decrease in rupture strength with increasing rupture time compared with the other materials.

The effect of both long-term exposure in HT-glass and the laboratory test on the materials investigated is shown in fig. 5. The lines indicate the stress-rupture strength in the initial state. The loads applied to the samples after long-term test and laboratory test 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 contact with HT-glass. The reason for the increased rupture time both after the exposure in the melting down glass mixture and after long-term exposure in the HT-glass melt is due to the diffusion of oxide-forming elements coming from the HT-glass mixture.

Fig. 6 shows results of scanning SIMS (secondary ion mass spectroscopy) investigations on Pt-10%Rh DPH after laboratory test in HT-glass mixture and stress-rupture test at 1600°C with a load of 6.85 MPa. The measurement detected a homogeneous distribution of Al and Mg which had diffused into the sample. The investigations of the oxygen content of the bushing materials showed increased oxygen concentration due to the internal oxidation of these harmless elements. The Mg- and Al-oxides generated in this way influence the stress-rupture strength as if they were an oxide dispersion hardening addition.

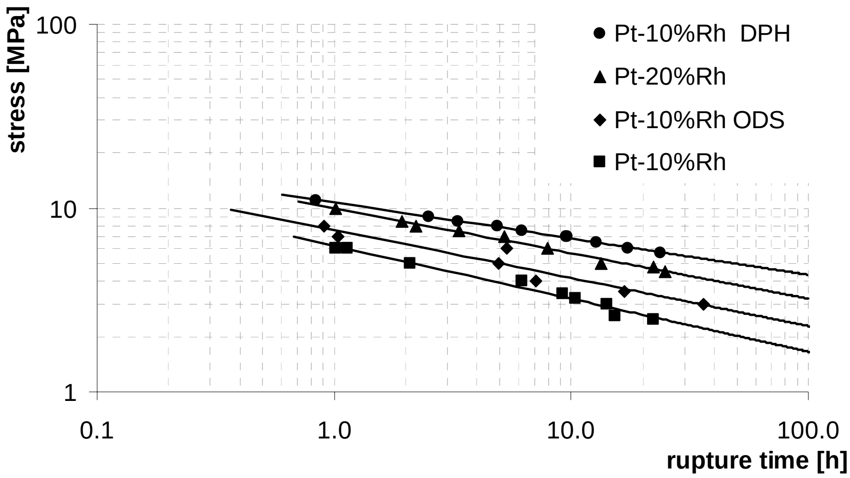


Fig. 4: Stress-rupture curves of bushing materials investigated at 1600°C

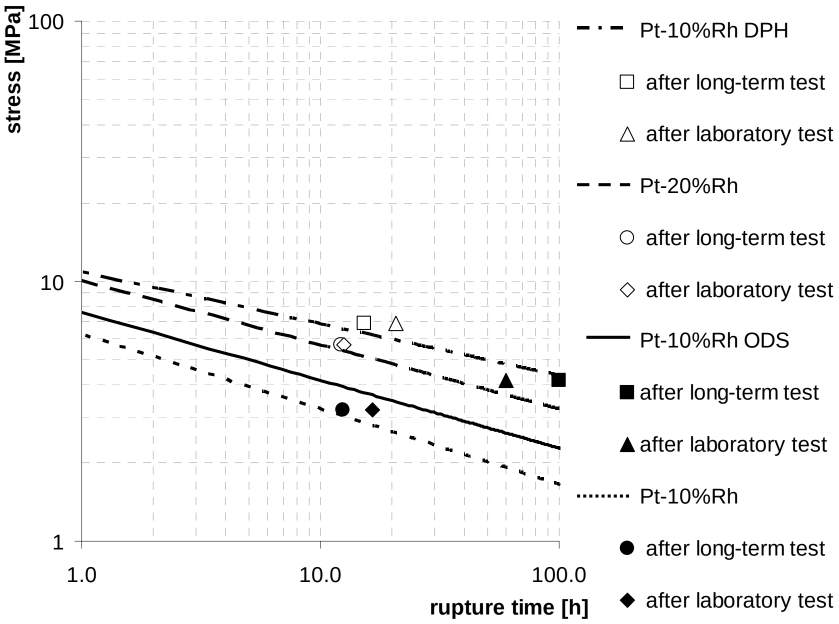


Fig. 5: Effect of HT-glass after long-term exposure and after laboratory test on stress-rupture strength compared with initial state of the bushing materials investigated at 1600°C

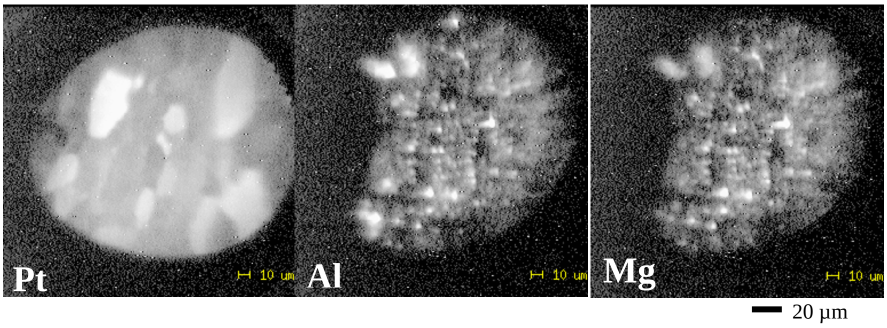


Fig. 6: Results of the scanning SIMS of Pt-10%Rh DPH after laboratory test in melting down HT-glass mixture and creep-rupture test at 1600°C

Creep Behaviour

Regarding the creep behaviour in the initial state of the bushing materials investigated at 1600°C there are great differences between solid solution strengthened and oxide dispersion hardened PtRh alloys. In fig. 7 the creep curves of the materials investigated in the initial state are presented. These were determined with comparable loads at 1600°C. The solid solution strengthened alloys Pt-10%Rh and Pt-20%Rh demonstrate a very high failure strain but also a relatively high creep rate. Compared to these, the creep of the oxide dispersion hardened alloys Pt-10%Rh DPH and Pt-10%Rh ODS is very low (more than 4 times lower than that of Pt-20%Rh). The failure strain of Pt-10%Rh DPH of approx. 25 % is more than acceptable for oxide dispersion hardened materials. This is a decisive advantage for this material.

The influence of HT-glass on the creep behaviour of the alloy Pt-10%Rh DPH at 1600°C is shown in fig. 8. This figure shows creep curves of this alloy after both the long-term exposure in the HT-glass melt and the laboratory test in melting down HT-glass mixture in comparison with the initial state. The positive effect of the oxidized HT-glass components Mg and Al lead to a significant increase both in rupture time (as mentioned above) and in fracture elongation of the bushing material after glass contact (approximately 55 %). At the same time only the sample after long-term exposure in HT-glass melt shows a higher creep rate.

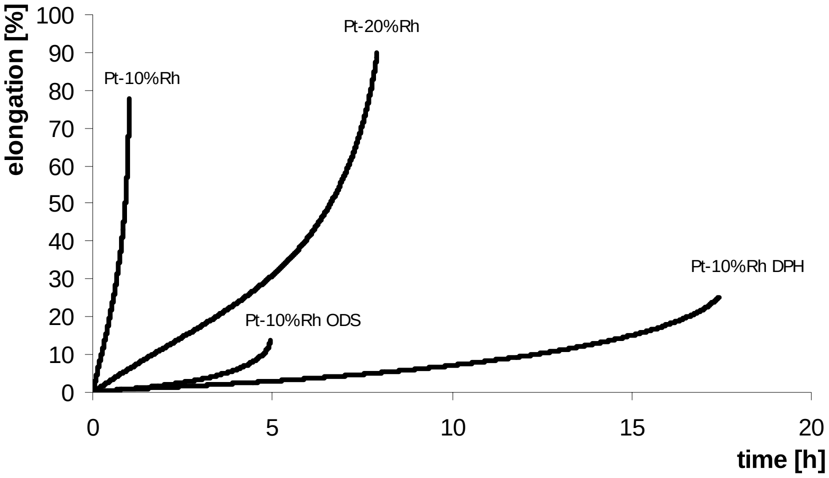


Fig. 7: Creep curves of bushing materials investigated in initial state at 1600°C and 6.0 MPa (except Pt-10%Rh ODS with 5.0 MPa)

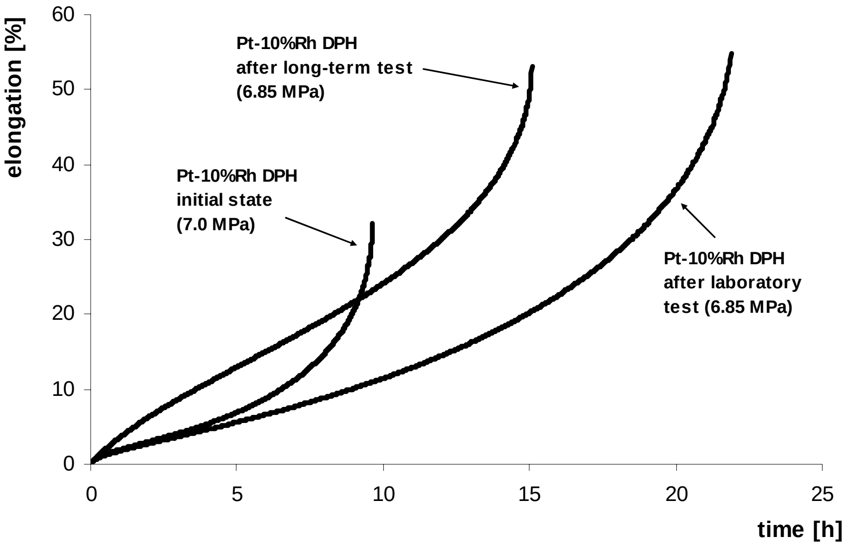


Fig. 8: Creep curves of Pt-10%Rh DPH after long-term test and after laboratory test (both 6.85 MPa) in comparison with initial state (7.0 MPa) at 1600°C

Structure

The influence of HT-glass on the structure of the bushing materials investigated was also studied. There are significant differences between solid solution strengthened and oxide dispersions strengthened alloys. Fig. 9 shows the structure of Pt-10%Rh and Pt-10%Rh DPH. The initial state of both alloys has a deformed structure with a very small grain size. The long-term test in melting down HT-glass mixture led to grain growth of solid solution strengthened Pt-10%Rh. Pt-10%Rh DPH, however, still showed a fine grained structure after glass contact due to the oxide dispersion with Y- and/or Zr-oxides.

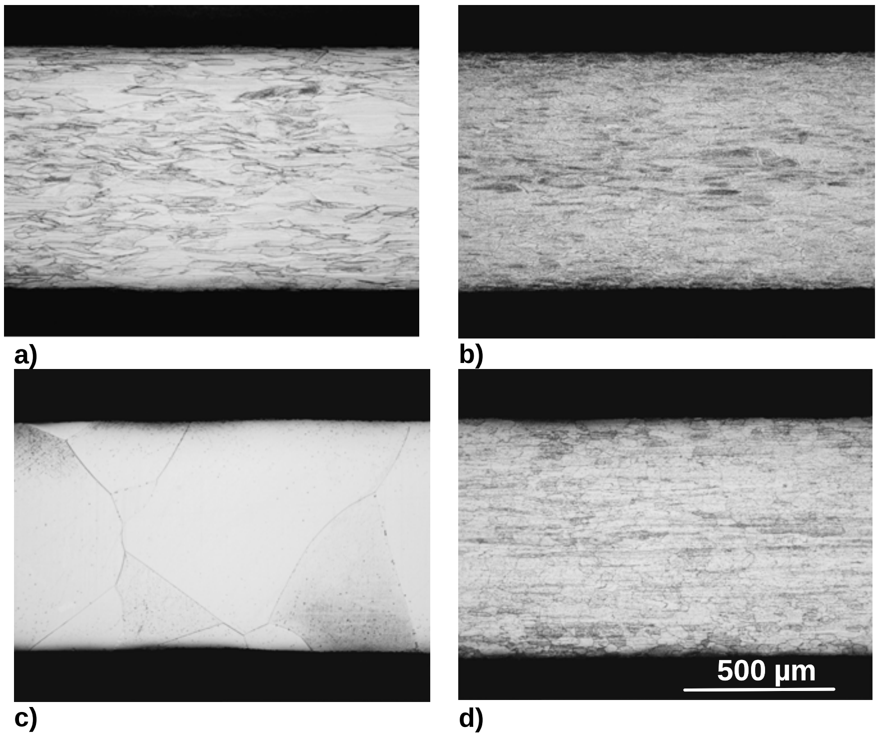


Fig. 9: a) Pt-10%Rh initial state b) Pt-10%Rh DPH initial state
c) Pt-10%Rh after long-term test in melting down HT-glass mixture
d) Pt-10%Rh DPH after long-term test in melting down HT-glass mixture

Wetting Behaviour

The assessment of the wetting behaviour was carried out by measurement of the contact angles of HT-glass melts on platinum materials as a function of the temperature (1000°C-1500°C). The contact angle of HT-glass melt on Pt-20%Rh as a function of temperature is shown in fig. 10. The diagram presents the values of each of the five measurements carried out. The significant decrease in the contact angle in the temperature range from 1000°C to 1150°C is a result of the melting down of the HT-glass sample. The slight variations of the contact angle for each measurement between 1150°C and 1500°C is attributed to measurement uncertainties. Consequently, no temperature dependence of the contact angle of HT-glass on the bushing materials investigated after melting down of the sample was observed.

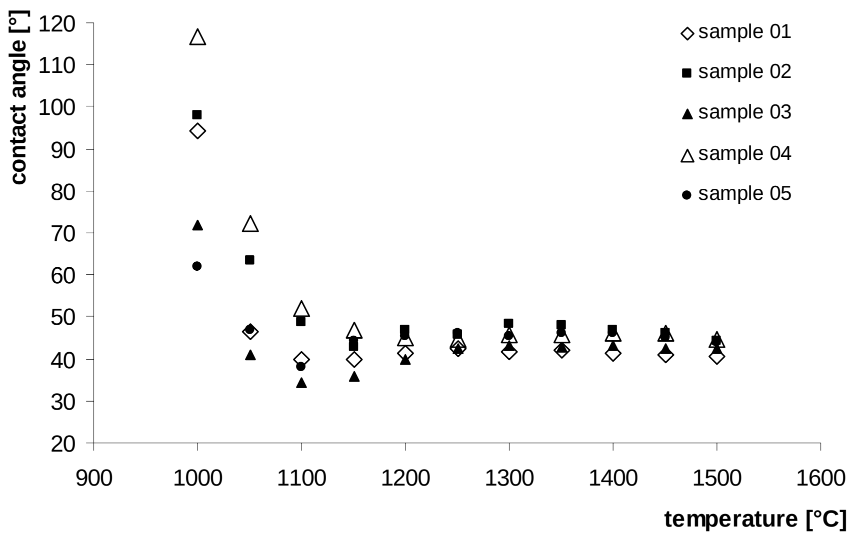


Fig. 10: Measurements of the contact angle of HT-glass melt on Pt-20%Rh as a function of temperature

A comparison of the contact angles of the bushing materials investigated is given for 1250°C in fig.11. The results of the solid solution strengthened alloys Pt-10%Rh and Pt-20%Rh indicate an increase in contact angle with increasing rhodium content of the alloy. In contrast the oxide dispersion hardened materials Pt-10%Rh DPH and Pt-10%Rh ODS show very small differences compared to Pt-10%Rh regarding the wetting behaviour. Consequently the influence of the dispersed Zr- and

Y-oxides in the PtRh-matrix on the wetting behaviour of the bushing materials investigated in contact with HT-glass is negligible. The results show typical values for the materials investigated in contact with glass melts commonly used for the manufacture of fibres.

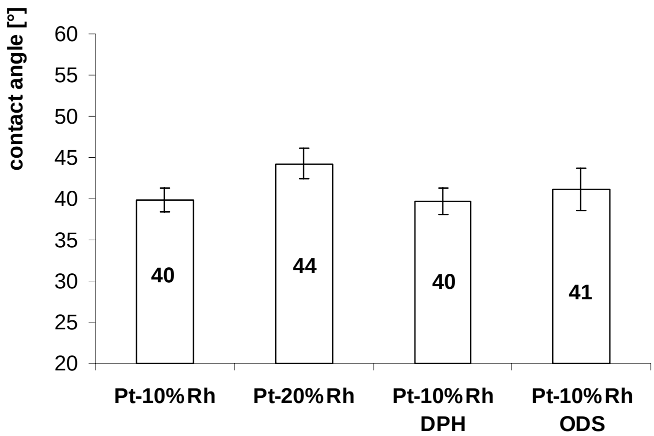


Fig. 11: Contact angle of the bushing materials investigated at 1250°C

Summary and Conclusions

Investigations into the effect of high temperature glass on commercially available bushing materials (Pt-10%Rh, Pt-20%Rh, Pt-10%Rh DPH and Pt-10%Rh DPH) were carried out. The results 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 HT-glass melt and the melting down HT-glass mixture. Furthermore Pt-10%Rh DPH shows excellent grain stability over long periods at the highest temperatures.
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 exposure in HT-glass. The samples have been “contaminated” by the harmless elements Al and Mg coming from the HT-glass melt. Internal oxidation of these elements has led to increased stress-rupture strength. Analytical investigations (scanning SIMS and measurements of the oxygen content) confirmed this assumption.

Practical trials on bushings made from Pt-10%Rh DPH show these to be fully comparable to those of the other platinum materials investigated.
Regarding the wetting behaviour there is a trend to increasing contact angle of HT-glass with increasing rhodium content of the bushing material. The oxide dispersion, however, does not have a definite influence on the contact angle of HT-glass.
Subjects of future work are investigations into 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 the temperatures up to 1700°C. The work will be complemented by metallographic and micro-analytical examinations using microprobe analysis and scanning SIMS together with fracture investigations (SEM).

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