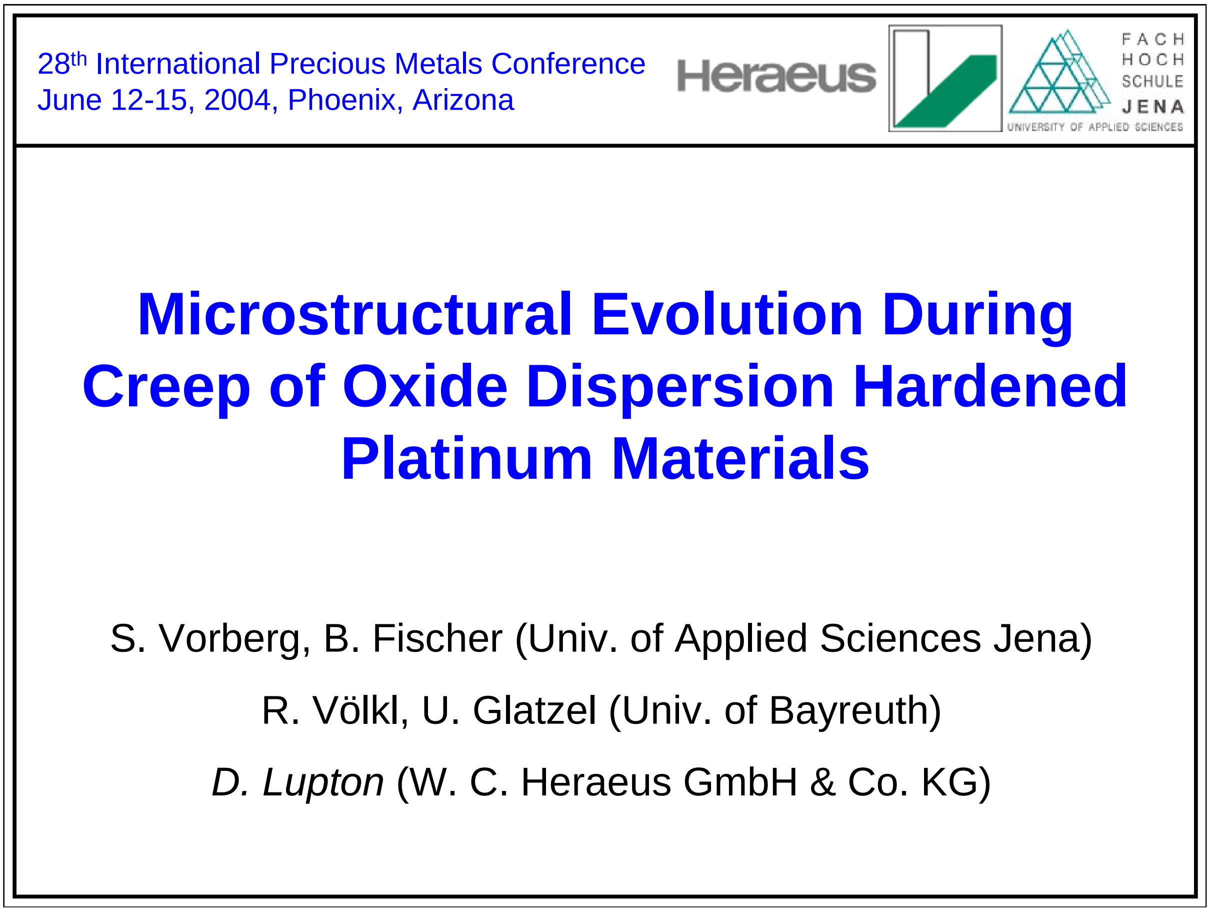


28th International Precious Metals Conference
June 12-15, 2004, Phoenix, Arizona

# Microstructural Evolution During Creep of Oxide Dispersion Hardened Platinum Materials

S. Vorberg, B. Fischer (Univ. of Applied Sciences Jena)
R. Völkl, U. Glatzel (Univ. of Bayreuth)
*D. Lupton* (W. C. Heraeus GmbH & Co. KG)

The present paper continues the series of presentations to IPMI Conferences over a period of nearly 10 years on the properties, applications and microstructures of high-temperature PGM materials carried out at the University of Applied Sciences Jena in collaboration with W. C. Heraeus in Hanau. Rainer Völkl, who was previously in Jena, has now moved with Uwe Glatzel to the University of Bayreuth. Völkl was, among other things, the initiator of the transmission electron microscopy (TEM) investigations described here, and his work is being continued and extended by Stefan Vorberg who is now in Bernd Fischer's department and is responsible for all the TEM micrographs in this paper.

The paper is divided into the following sections:

- Aims of Research
- Investigations
- Results
- Summary

## Aims of Research

Platinum and its alloys are used in the glass industry under high mechanical, thermal and chemical loadings.

Disadvantages of previous dispersion strengthened platinum materials:

- Processing problems
    - difficult or impossible to weld
    - loss of the strengthening effect in the weld
- Brittleness and notch sensitivity in service

➔ **Develop better dispersion hardened Pt alloys**

Platinum and its alloys – particularly with rhodium – are the only metallic materials capable of withstanding the high temperatures and oxidising conditions encountered in glass making and processing without also causing detriment to the glass. The platinum materials have to be fabricated into complex components which must then withstand severe mechanical, thermal and chemical conditions in service.

In the course of the last 30 years a number of oxide dispersion strengthened platinum materials have been developed which, similarly to their “cousins” the nickel ODS alloys, have considerably increased strength at high temperatures.

However, these platinum ODS materials, in common with the nickel and other ODS alloys, show significant disadvantages in fabrication and use compared with the conventional materials. They are, for example, difficult or impossible to weld in many cases, and the ODS strengthening effect is largely eliminated in the weld. Furthermore, they are prone to brittleness and notch sensitivity in service.

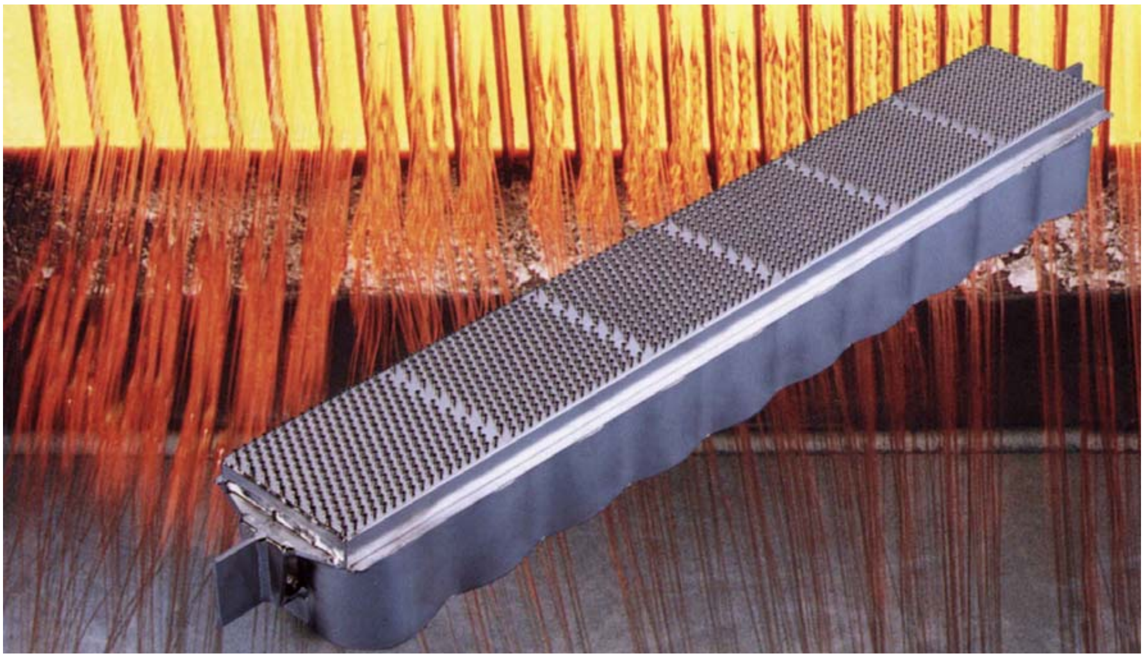
It was our aim, therefore, to develop an oxide dispersion hardened platinum material which does not show these disadvantages.

# Aims of Research

Heraeus

FACH HOCH SCHULE JENA
UNIVERSITY OF APPLIED SCIENCES

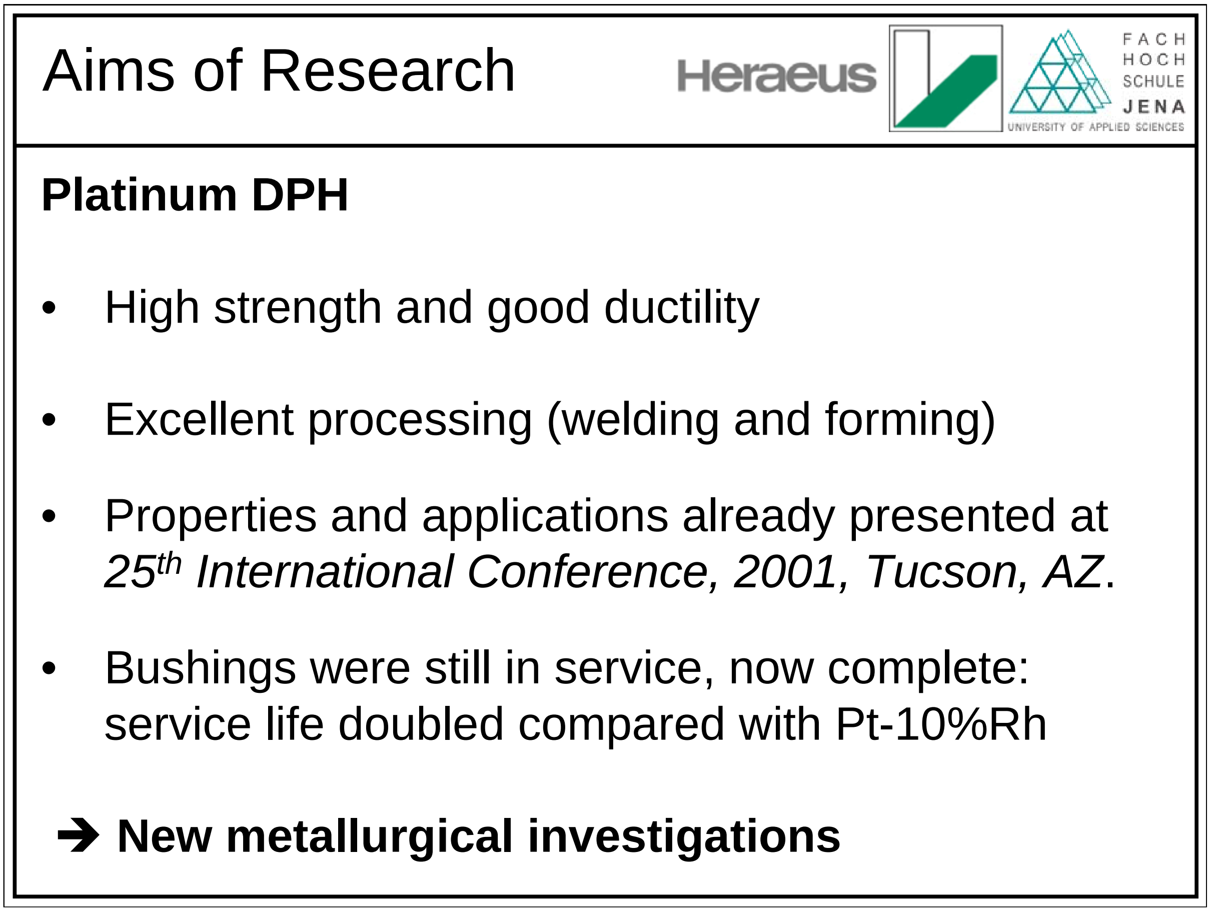
## Bushing



One of the most complex components used in glass processing is the glass fibre bushing. This is essentially a recipient for containing and homogenising molten glass which has a multiplicity (typically between 400 and 4000) of small nozzles or “tips” on a base plate. The glass fibres are drawn from the individual tips.
The bushing is normally embedded in a refractory cement and is electrically resistance heated to its service temperature, usually in the range 1200 – 1400°C. The interior of the bushing contains a diversity of elements which are required to homogenise the glass flow and give mechanical stability to the overall structure – and thus a large number of welds are required.

The mechanical stresses arising during the service of a bushing have been analysed in detail by Völkl et al.(1) who concluded that the highest loadings are thermally induced stresses. These lead, in turn, to creep strains which cause cumulative damage that can cause rupture of the structural elements. A structural material is therefore required which is capable of absorbing strain without cracking, i.e. it should have good ductility at the service temperature.

(1) R. Völkl, B. Fischer,R. Teschner, D. Lupton: “Finite element modelling of strains and stresses in platinum alloy bushings for textile glass fibre production”, Glass Science and Technology, 74 (2001), 142-151.



## Aims of Research

### Platinum DPH

- High strength and good ductility
- Excellent processing (welding and forming)
- Properties and applications already presented at *25th International Conference, 2001, Tucson, AZ*.
- Bushings were still in service, now complete: service life doubled compared with Pt-10%Rh

➔ **New metallurgical investigations**

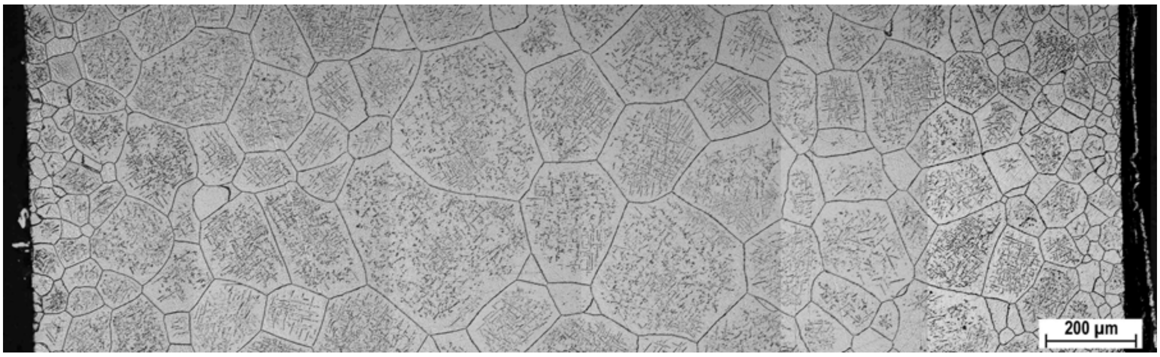
The result of our development work was the class of dispersion hardened platinum materials designated Pt DPH. These materials demonstrate a unique combination of high strength and good ductility under the conditions encountered in glass making and processing. They also have excellent processing characteristics – in particular, a degree of weldability and formability comparable to conventional non-dispersion hardened platinum materials.

The properties and applications of the Pt DPH materials were presented in detail at the 25th International Precious Metals Conference, 2001 in Tucson, Arizona. At that conference we reported on the excellent performance of bushings which at that time were still in service. These bushings have now been taken out of service after completing periods of operation of about 20 000 h, i.e. double the life obtained with similar bushings manufactured from conventional Pt-10%Rh.

In the meantime a considerable range of further investigations – in particular, using the transmission electron microscope, TEM – have been carried out on Pt DPH in order to understand better its unique properties.

# Investigations

- Melting (platinum with zirconium, yttrium)
- Rolling
- Annealing in oxidizing atmosphere
  - internal oxidation of zirconium and yttrium
  - dispersoids at grain boundaries and in the grains

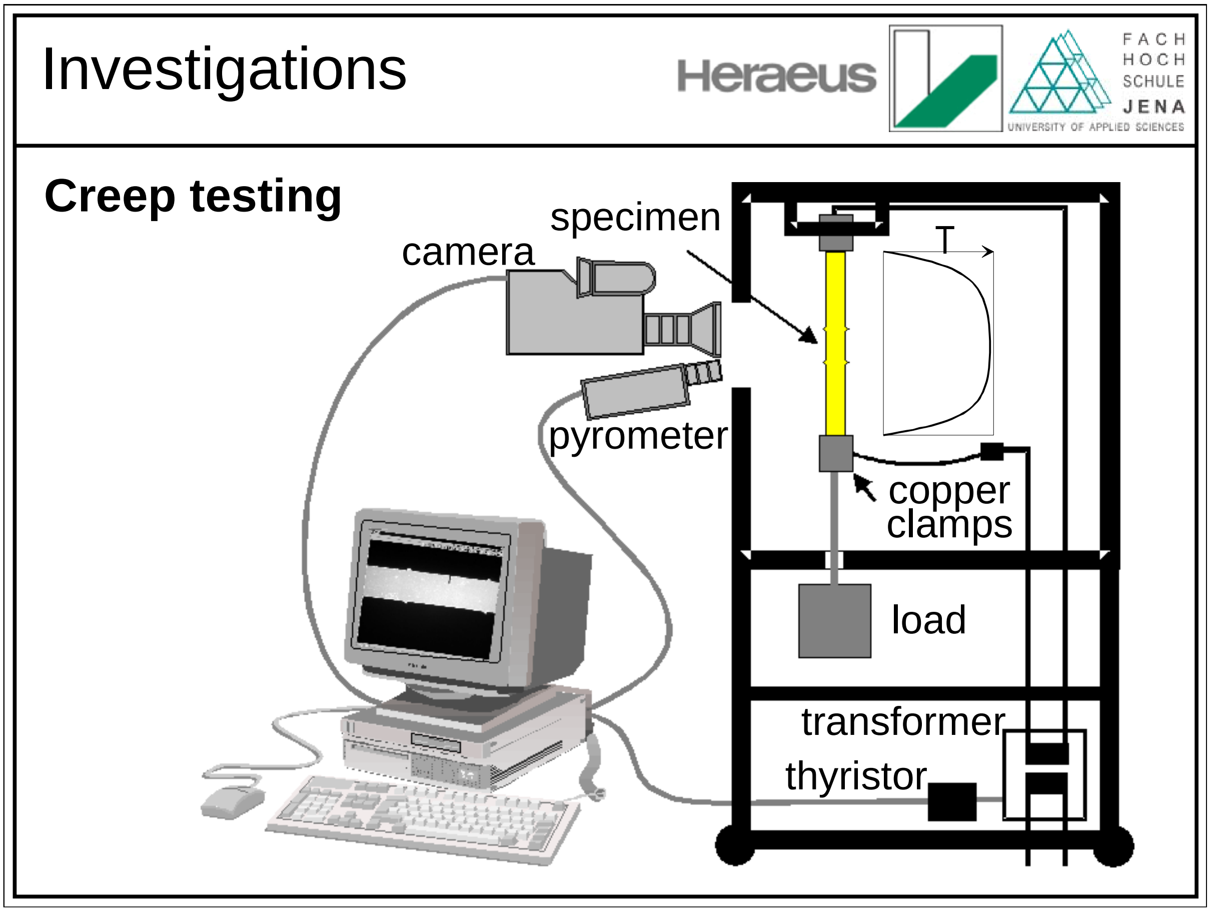


Let us first look at the special manufacturing process developed for the Pt DPH materials.

Platinum or a platinum alloy is melted under vacuum with small additions of reactive elements such as zirconium and yttrium and is cast to an ingot which is then rolled down to a slab. The slab is exposed to an oxidizing atmosphere which leads to the internal oxidation of the zirconium, yttrium, etc. resulting in dispersoids at the grain boundaries and in the grains.

The internally oxidized slab is subsequently processed further to the final product which has been shown in our earlier investigations to have the excellent mechanical properties characteristic of the Pt DPH materials.

However, the question remained as to how the oxide particles actually lead to the remarkable strength and why Pt DPH demonstrates properties that are highly advantageous compared with conventionally manufactured ODS materials.



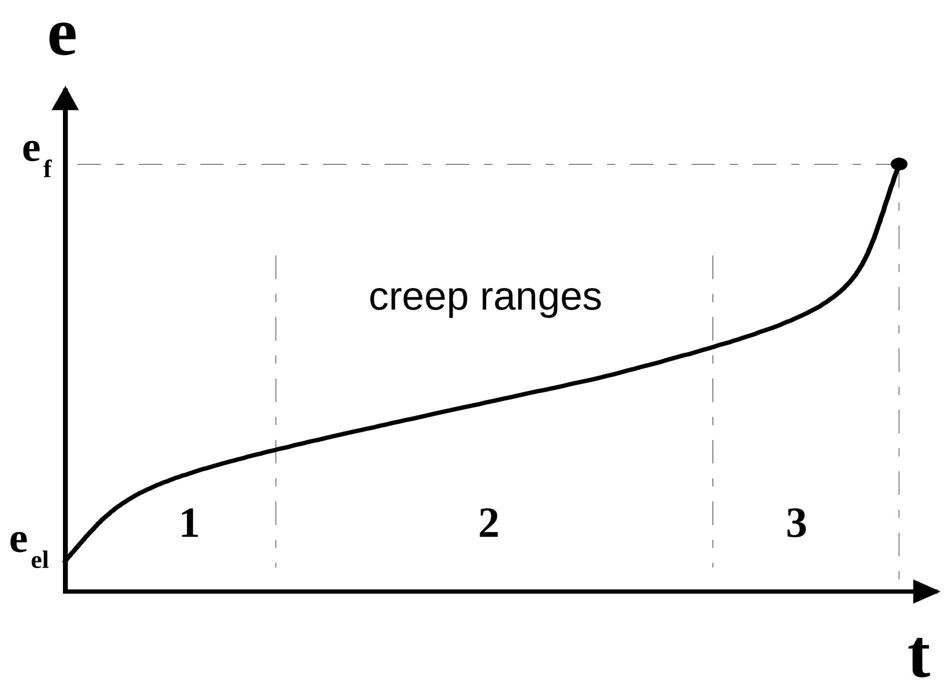
## Investigations

### Creep testing

The high temperature strength of metallic materials is determined using a technique specially developed by Bernd Fischer and his co-workers in Jena.

A specimen in the form of a strip or wire is gripped between two copper clamps and heated by electrical resistance to the test temperature. A load applied to the specimen causes creep deformation which is determined by means of the specially developed (SuperCreep) strain measurement technique based on continuous image analysis.

# Investigations

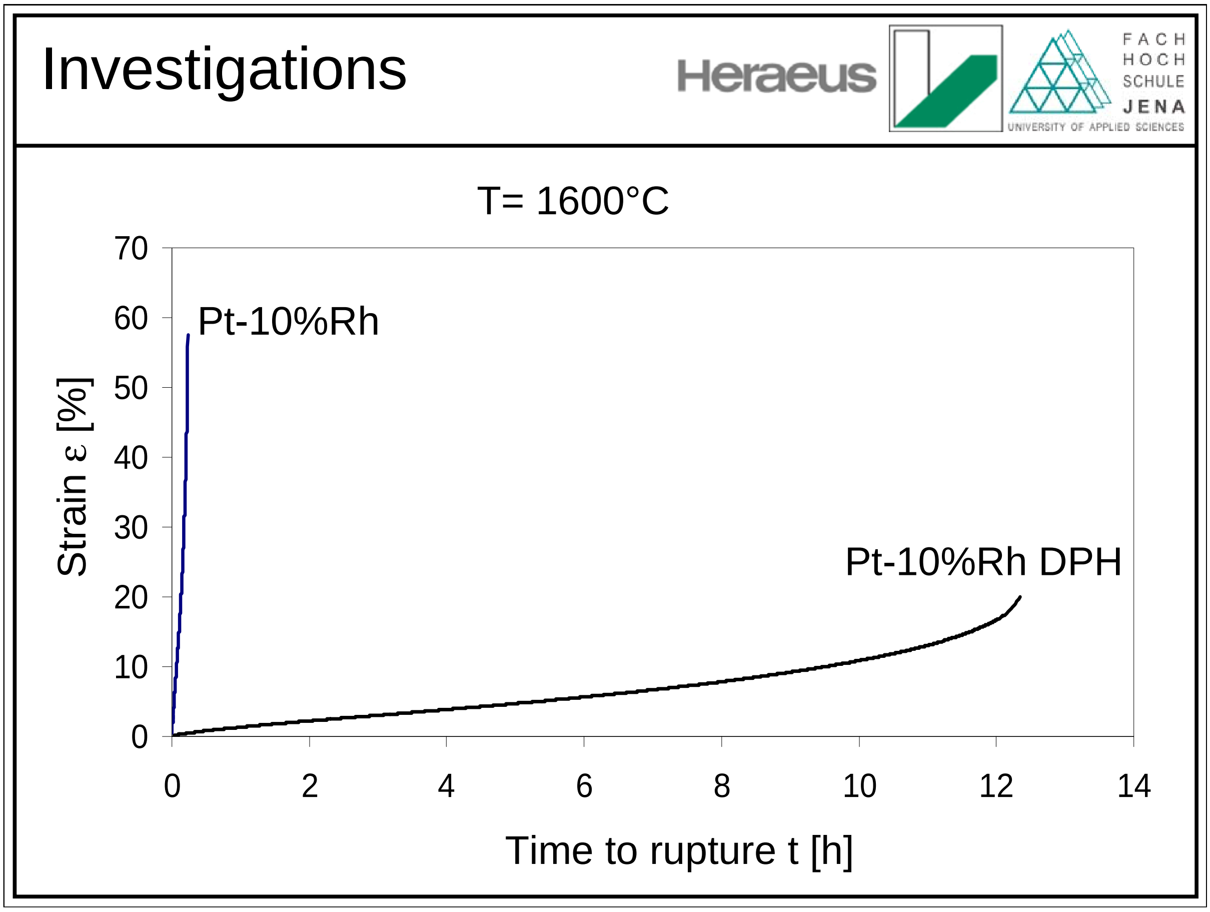


Most specimens tested demonstrate the classical creep curve of strain vs. time which is divided into three ranges:

**Primary:** In the primary creep range, dislocations are generated in the crystal lattice of the material leading to relatively rapid strain. However, as the density of dislocations increases, they interact with each other and with obstacles (e.g. precipitate particles) in the crystal lattice. This leads to a reduction in the strain rate generally known as work hardening.

**Secondary:** At elevated temperatures the dislocations can move past obstacles by time-dependent diffusion processes. In the classical theory of creep a steady state is established between the generation of dislocations and their annihilation by diffusion. This leads to an essentially constant dislocation density and a constant creep rate.

**Tertiary:** The diffusion processes cause pores to form at the grain boundaries, leading to an effective reduction in the load-bearing cross-section of the material. This effective increase in applied stress causes the deformation to accelerate until the specimen ruptures.

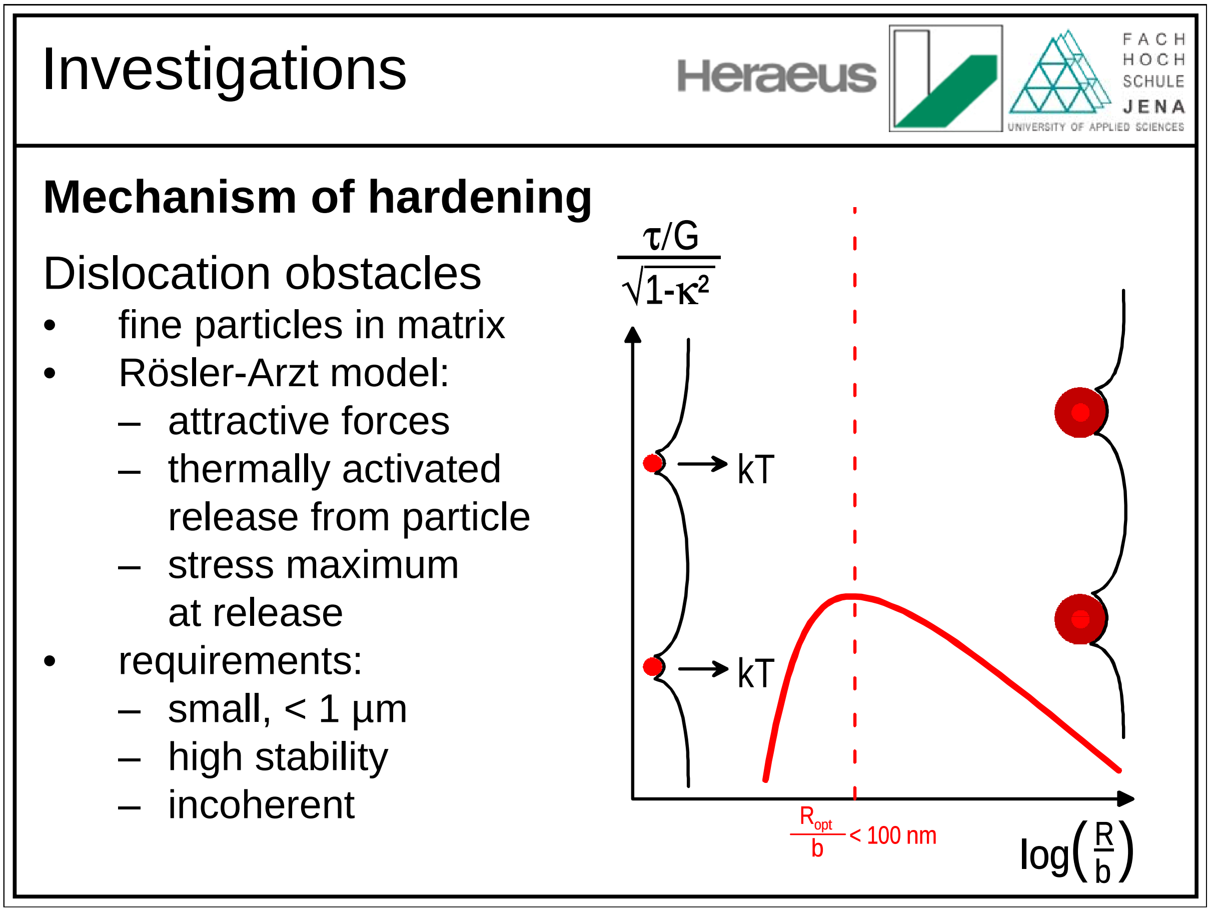


## Investigations

Different materials show very different creep curves.

The above diagram demonstrates the effect of the oxide dispersion on the creep rate of Pt-10%Rh at 1600°C. As can be seen, the creep rate is very substantially reduced and thus the life to rupture of the material is greatly increased.

The creep curves also show that, although the dispersion hardening causes a reduction in the ductility of the platinum alloy, the rupture elongation of over 20% can still be regarded as high with regard to all practical applications.



## Investigations

### Mechanism of hardening

Dislocation obstacles

- fine particles in matrix
- Rösler-Arzt model:
  - attractive forces
  - thermally activated release from particle
  - stress maximum at release
- requirements:
  - small, < 1 µm
  - high stability
  - incoherent

The mechanisms of hardening in oxide dispersion strengthened materials has been the subject of many studies over the last forty years. The most generally accepted model is that developed by Rösler and Arzt which is summarised in the diagram above.

Dislocations subjected to a shear stress in the lattice interact with fine particles. The particles exert an attractive force on the dislocation, thus hindering its further movement. The release of the dislocation from the particle is thermally activated and the stress reaches a maximum at the instant of release. This model requires that the particles should be small (< 1µm), thermodynamically and physically stable and should have an incoherent interface with the crystal lattice of the matrix.

The strengthening effect achieved by the particles is a function of their radius and the spacing between the particles. The optimum strengthening effect is found for particles with diameter < 100nm.

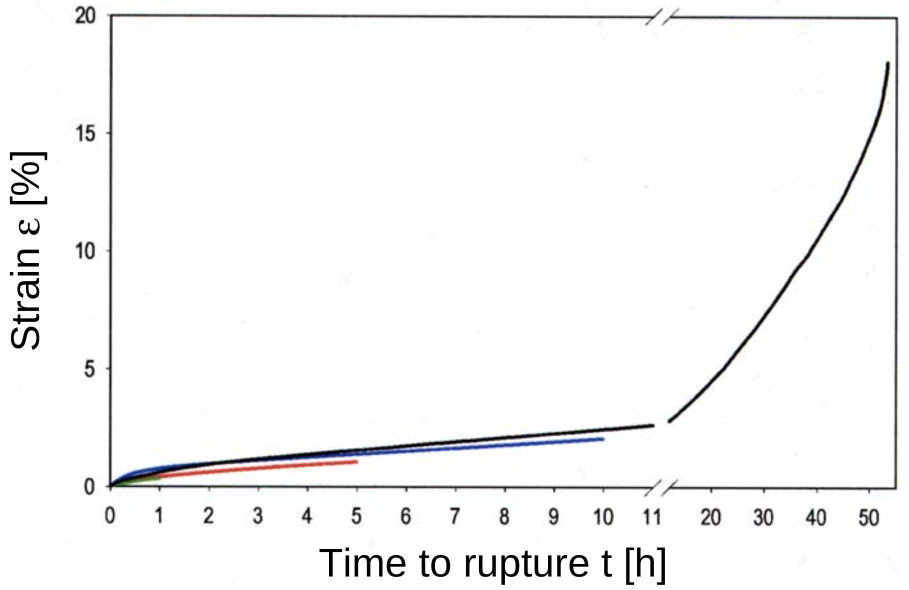
# Investigations

Heraeus

FACH HOCH SCHULE JENA
UNIVERSITY OF APPLIED SCIENCES

## Pt DPH creep tests

interrupted after 1h, 5h and 10h (1600˚C)



To improve our understanding of the creep processes in Pt DPH, specimens 0.8 mm thick were subjected to creep loading for different times at 1600°C.

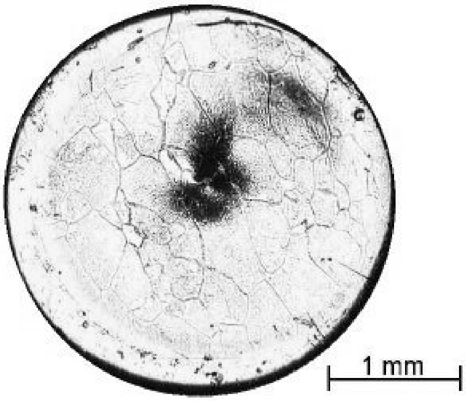
After creep times of 1h, 5h and 10h the specimens were removed from test. All specimens were in the secondary creep range, i.e. with constant creep rate. The specimens achieved 0.36%, 1.08% and 2.10% strain respectively, compared with the rupture elongation of 18.1% determined for material from the same batch.

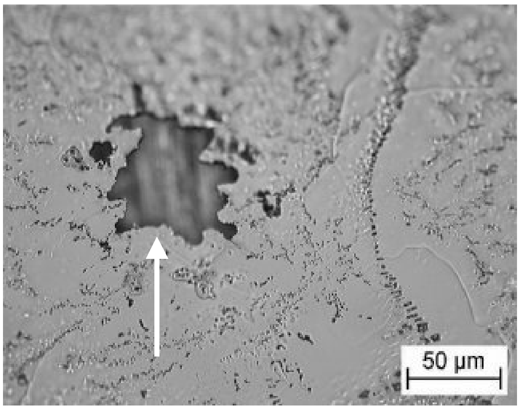
The specimens therefore offered the possibility of studying the development of dislocation structures over a significant part of the secondary creep range.

# Investigations

## Preparation for Transmission Electron Microscopy

- punch slices 3 mm diameter
- grind to thickness of about 100 µm
- dimple to thickness of about 15 µm
- electrochemical polish with KCN





Samples were taken from the creep specimens described above and from the same material in the initial state and were prepared for examination in the TEM.

First, discs of diameter 3 mm were punched out of the specimens and ground down to a thickness of about 100 µm.

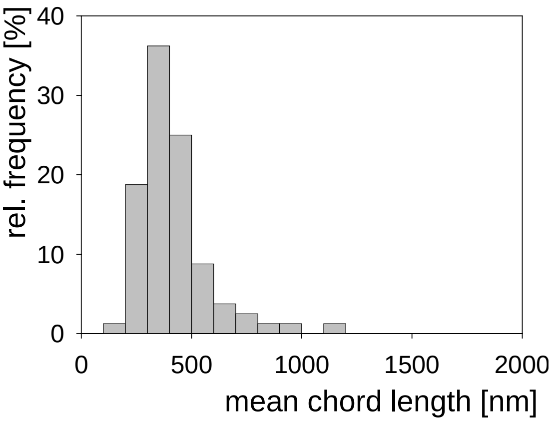
The discs were then “dimpled” until they had a thickness of about 15 µm approximately in the centre.

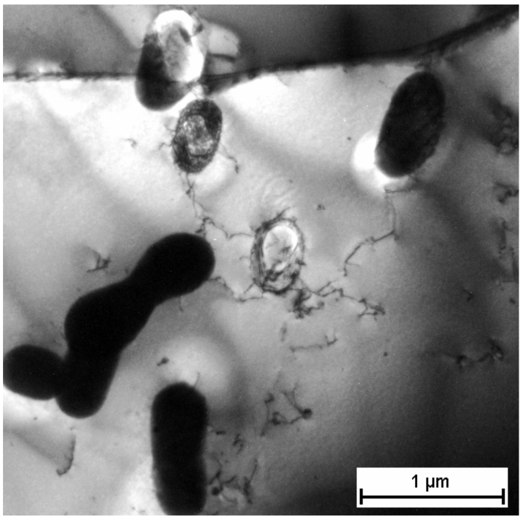
Final thinning was carried out by electrochemical polishing with KCN solution until a small hole developed.

The areas around the edge of this hole are suitable for examination in the TEM provided they have a thickness of not more than about 100 nm.

# Results

## Initial state





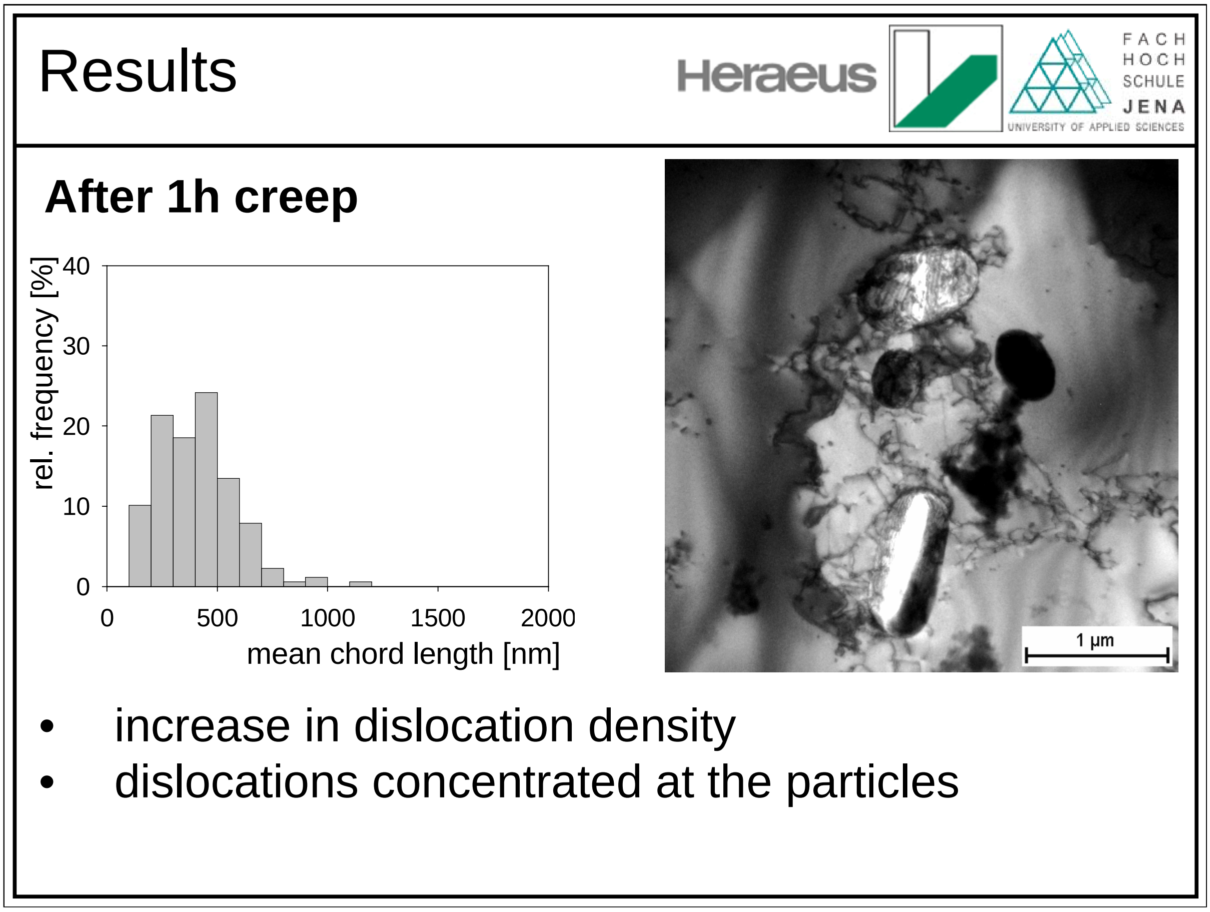
- low dislocation density
- dislocations concentrated at the particles

The micrograph on the right shows the structure of the Pt DPH material in the initial state. A grain boundary can be seen near the top of the micrograph. The oval shapes are oxide particles and the fine black lines are dislocations.

The bar chart on the left shows the mean chord lengths measured across the visible particles. (Relatively large particles with a chord length > 2000 nm were commonly found on grain boundaries but were omitted from the evaluation of the particle size.)

The average chord length of the particles is approximately 400 nm.

The dislocation density in the matrix is low. However, most of the dislocations were found to be associated with the oxide particles. This suggests that the dislocations have been generated as a result of the difference in thermal expansion coefficient between the particles and the platinum matrix.



## Results

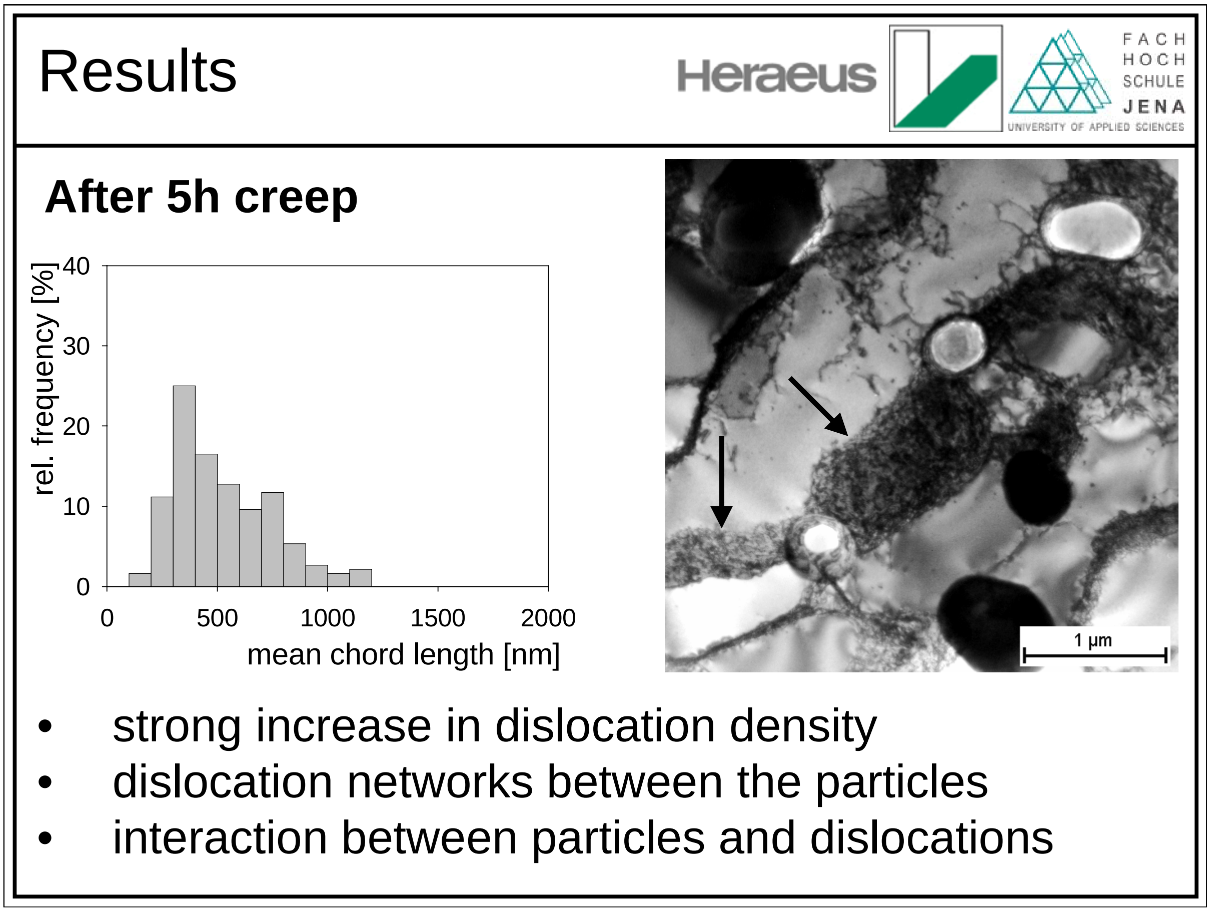
### After 1h creep

- increase in dislocation density
- dislocations concentrated at the particles

After creep deformation for 1 h the oxide particles showed no significant change relative to the initial state.

However, a significant increase in the dislocation density could be observed. This would be expected because, as described above (page 7), the dislocation density increases throughout the primary range of creep.

Most of the newly generated dislocations were found at or close to the particle / matrix interface.



## Results

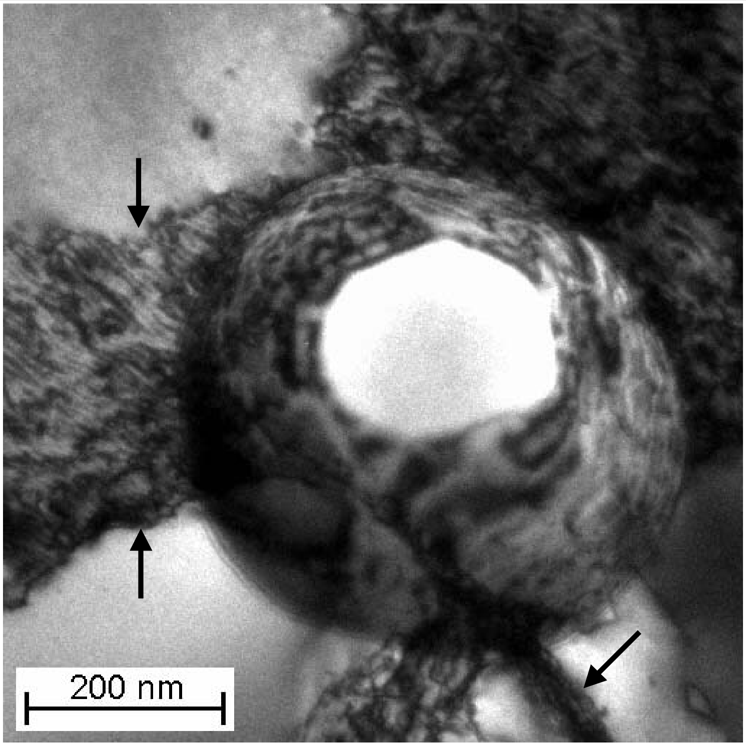
### After 5h creep

- strong increase in dislocation density
- dislocation networks between the particles
- interaction between particles and dislocations

After 5 h creep deformation the dislocation density had increased very greatly and the dislocations had formed clearly defined networks between the oxide particles. This marked increase in dislocation density was surprising because both this and the previous specimen had been exposed to creep deformation in the secondary range where a steady state dislocation density is generally assumed.

The mean chord length of the particles had increased to approximately 500 nm. The authors have no satisfactory explanation for this significant increase in particle size. We do not believe that it is a classical case of Oswald ripening, although this cannot be fully excluded because TEM is not a suitable method for the recognition and full statistical assessment of very small particles – i.e. very small particles may have been overlooked in the material in the initial condition. Another possible explanation is the continued precipitation of oxide during the high temperature creep exposure.

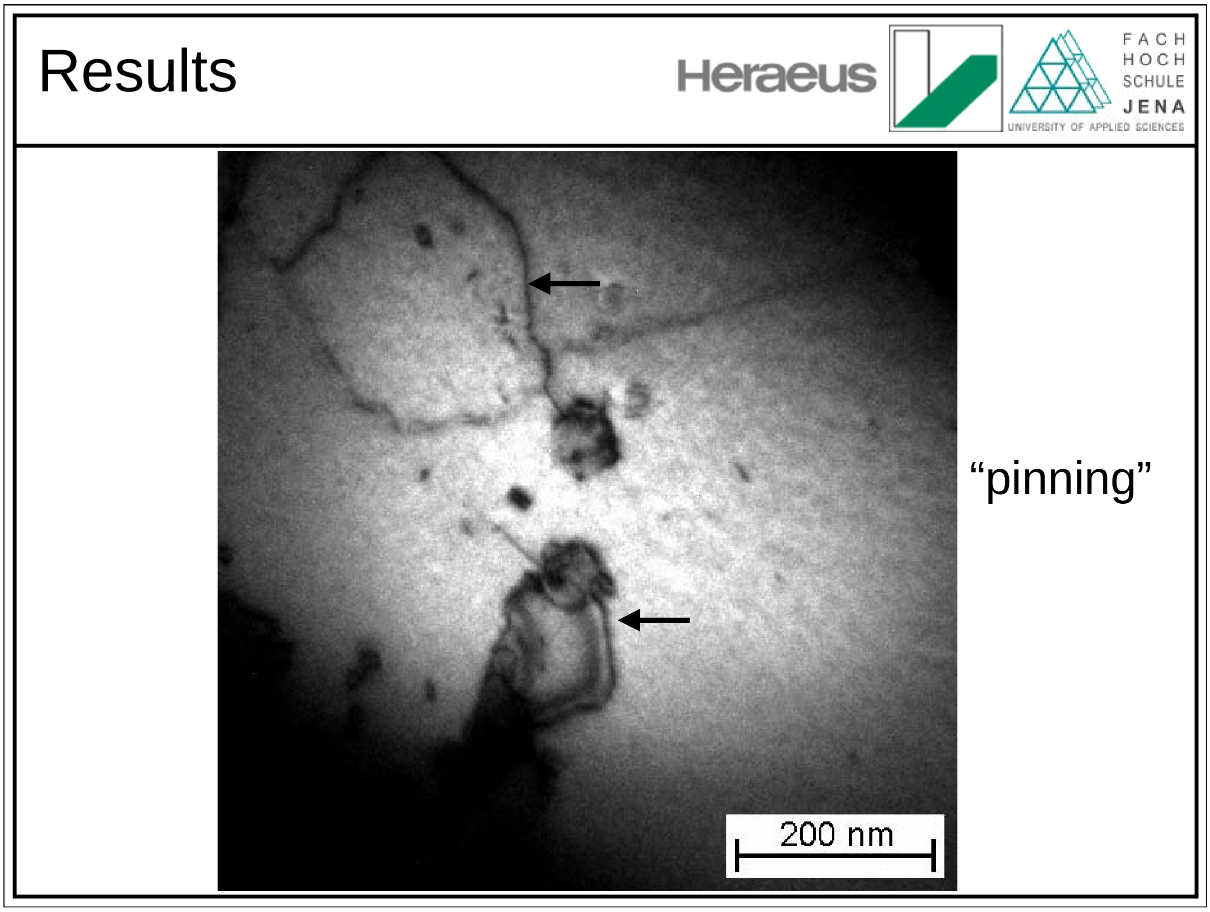
# Results



This micrograph shows a detail from page 14 and demonstrates the very marked interaction between the dislocation networks and a typical particle.

The interface between the particle and the platinum matrix contains a large number of dislocations although these are to be distinguished from the rather broader interference fringes.

The light, dislocation-free area is due to the platinum matrix having been polished away, leaving the oxide particle standing proud of the surface.

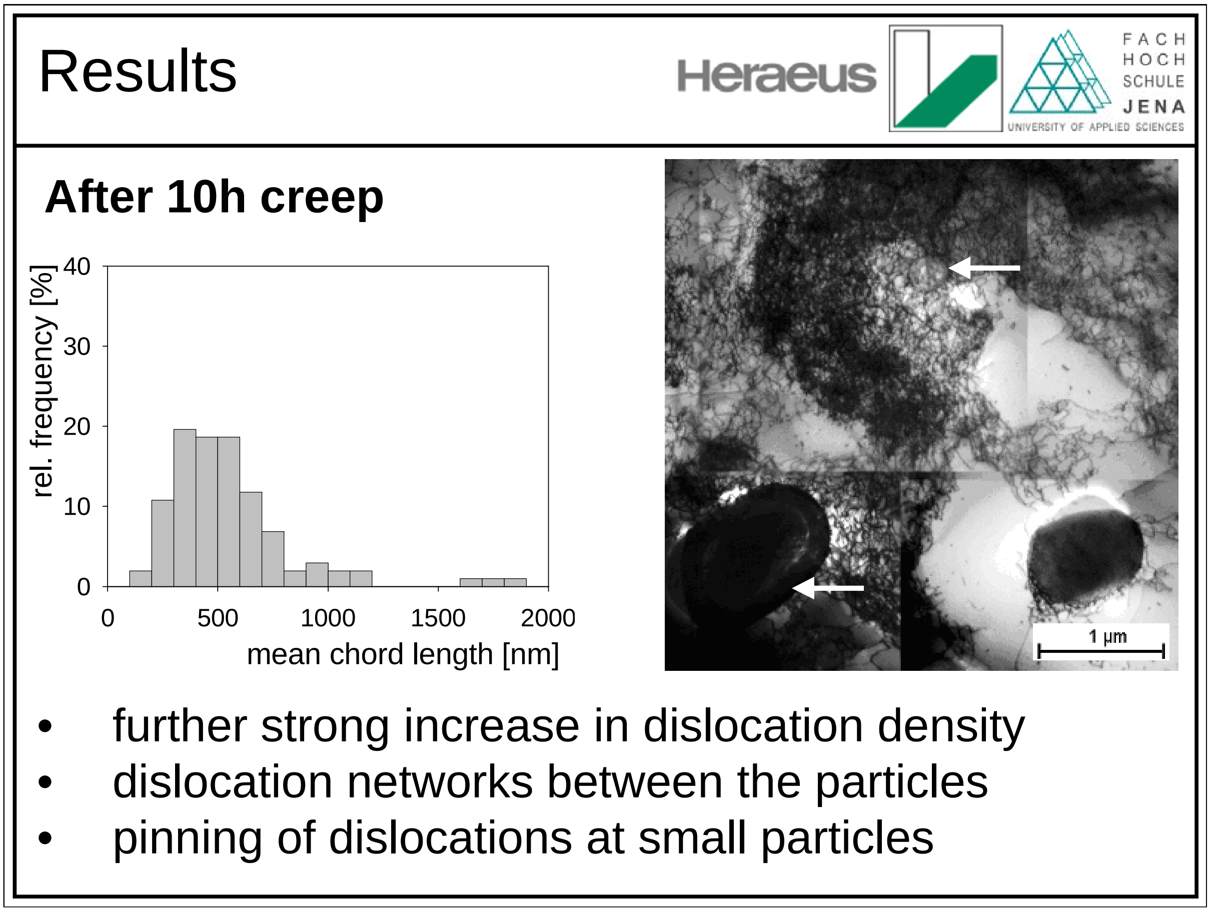


## Results

“pinning”

In addition to the larger particles (> 150 nm) the sample was also found to contain a particle fraction with an average diameter < 100 nm.

Individual dislocations in the same sample were found to be attached to the small particles. This is a clear example of the effect generally described as “pinning” in the literature.



## Results

### After 10h creep

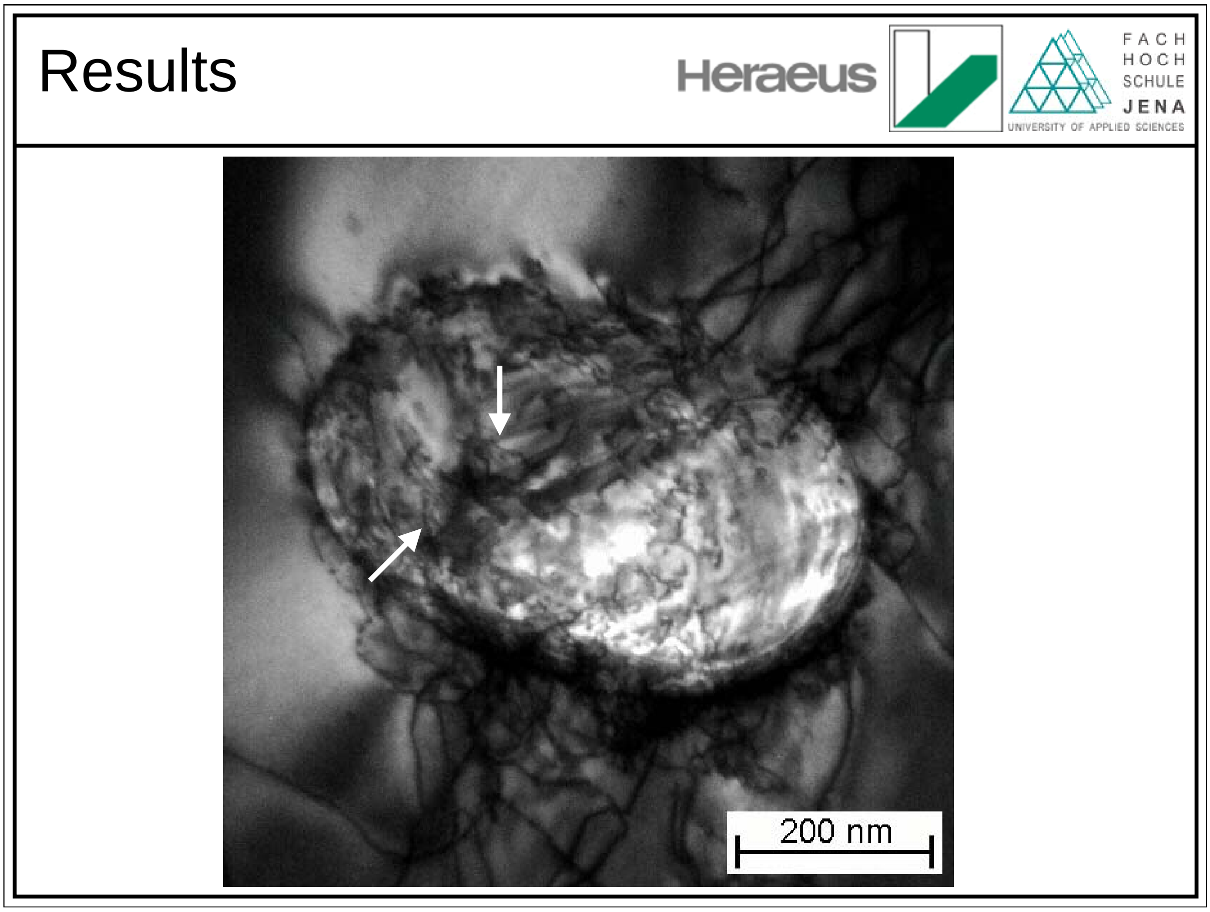
- further strong increase in dislocation density
- dislocation networks between the particles
- pinning of dislocations at small particles

The micrograph from the specimen exposed for 10 h to creep deformation shows a further strong increase in dislocation density, although this specimen was also still in the secondary creep range.

The mean chord length of the oxide particles has again increased slightly to approximately 550 nm.

The dislocation networks between the particles have become very apparent, but there is no indication that a true subgrain structure is developing.

Once again two distinctive size fractions of particles could be distinguished in the material.

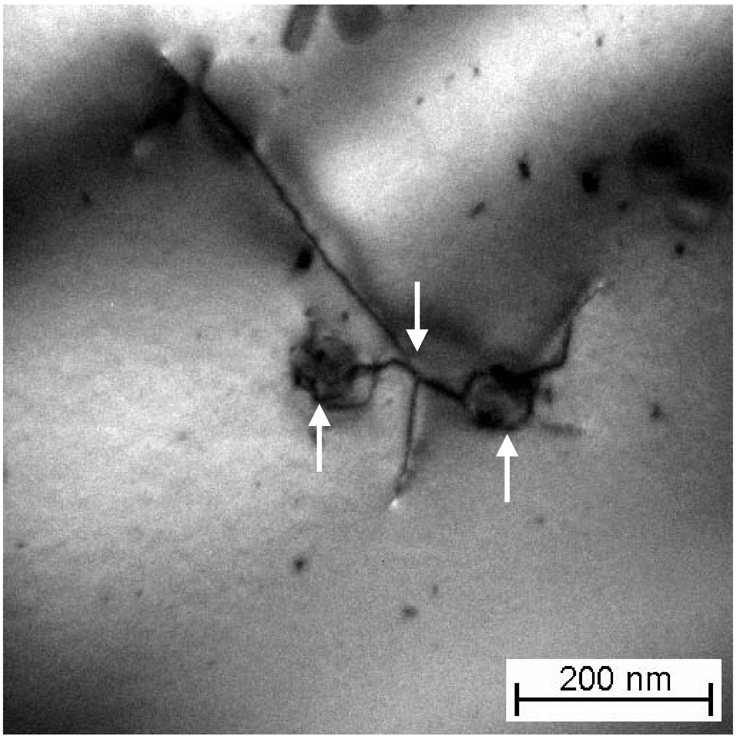


## Results

This micrograph shows a detail from the micrograph on page 17.

Dislocations can be clearly identified in the networks which are anchored to the larger oxide particles.

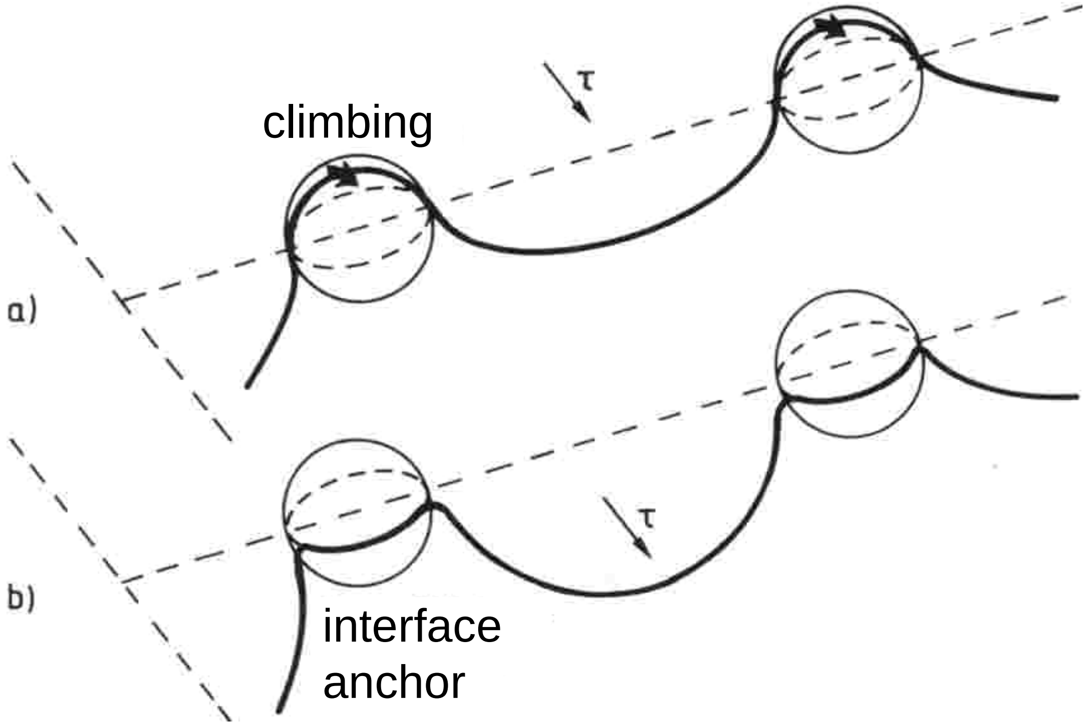
# Results



The finer particle fraction in the sample shown on page 17 again shows clear indications of the pinning of individual dislocations.

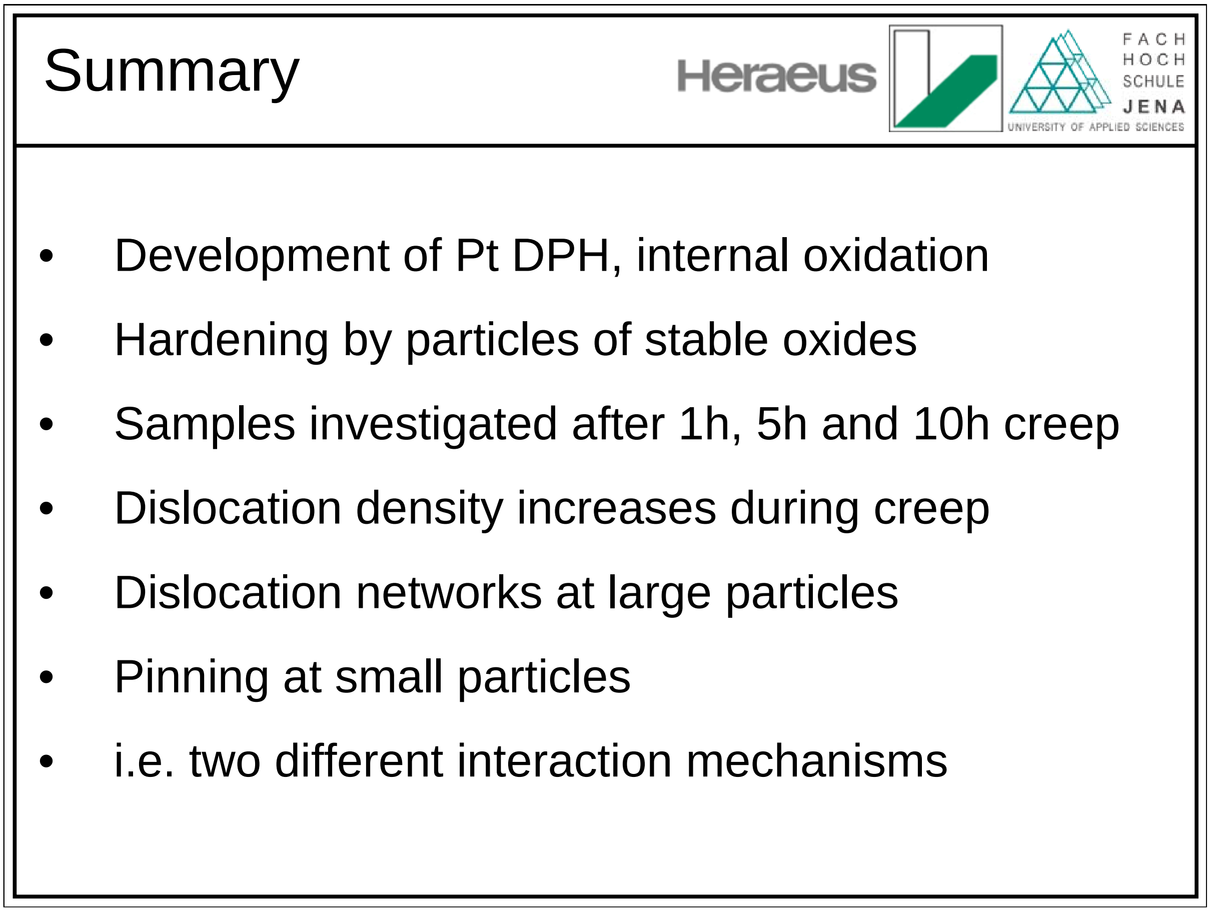
It is interesting to compare this micrograph with a schematic diagram of the Rösler-Arzt model as shown on the next page.

## Pinning



The Rösler-Arzt model is based on the climb of dislocations around the second-phase particles, the anchoring of the dislocations at the particles and the bowing out of the dislocations between the particles under the influence of applied stress.

We regard the micrograph on page 19 as a particularly clear demonstration of the model.



## Summary

- Development of Pt DPH, internal oxidation
- Hardening by particles of stable oxides
- Samples investigated after 1h, 5h and 10h creep
- Dislocation density increases during creep
- Dislocation networks at large particles
- Pinning at small particles
- i.e. two different interaction mechanisms

In summary, the development of the Pt DPH materials with the generation of an oxide dispersion by means of internal oxidation has been described.

The TEM investigations demonstrated that the hardening is achieved by interactions between dislocations and particles of stable oxides.

Samples investigated in TEM after creep deformation for 1 h, 5 h and 10 h – i.e. all in the secondary creep range – showed that the dislocation density increased substantially during creep deformation with strains of 0.36 %, 1.08 % and 2.10 %.

Two different mechanisms of interactions between the dislocations and the oxide particles could be identified. Larger particles (> 150 nm) serve as anchoring points for dislocation networks, whereas small particles (< 100 nm) pin individual dislocations in correspondence with the Rösler-Arzt model.

Although the TEM investigation of the Pt DPH material does not permit a truly quantitative comparison between the two mechanisms of dislocation / particle interactions, the authors believe that the dislocation networks play the major role in achieving the high temperature strength. This is probably the reason for the greatly improved ductility and formability of the Pt DPH materials compared with other oxide dispersion strengthened materials.