Mechanical stability of Pt/Pd thermocouples

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Numerous investigations of Pt/Pd thermocouples are mainly addressed to the characterisation of their thermoelectric properties. Burns, Ripple and Battuello [1] published data for the construction of the reference function for Pt/Pd thermocouples, Hill [2] and Bentley [3] presented advanced investigations concerning thermoelectric stability and homogeneity of Pt/Pd thermocouples. Investigations on highest level and practical experiences have shown the advantages of Pt/Pd thermocouples compared to Pt/Rh alloyed thermocouples (types S, R, B) by lower measuring uncertainties due to the higher thermoelectric stability and homogeneity of the pure thermoelements. Pt/Pd thermocouples can be used at temperatures from 0 °C to about 1500 °C. Therefore they could replace the so far predominantly used type S and R thermocouples in this important temperature range.

In spite of the advantage of Pt/Pd thermocouples problems in their practical application have to be considered. It is known, that the oxidation of palladium in the temperature range between about 550 °C and 800 °C cause a reversible change in the Seebeck coefficient, which restrain the accessible measuring uncertainty to about 0,1 K [2]. But there are no information published about irreversible changes of the palladium thermoelement which even can cause complete failures of the Pt/Pd thermocouples.

Routinely used Pt/Pd thermocouples of PTB showed a noticeable embrittlement of the Pd thermoelement already after some hours exposure at temperatures above about 1000 °C. After failure of two thermocouples by breakage of the Pd wire near the measuring junction selective investigations were performed to verify the reasons of the breakage and to allow the application of preventive measures to avoid further failures.

Several specimens of the Pd wire from the two failed thermocouples (15/02 and 14/98) were investigated by metallographic slices, by scanning electron microscopy (SEM) as well as by energy dispersive X-ray analysis (EDS) for the detection of impurities. These investigations were performed in the "Forschungsinstitut für Metallchemie und Edelmetalle" (fem), Schwäbisch-Gmünd, Germany. The Pt/Pd thermocouple 15/02 was used in a temperature range between 1090 °C and 1200 °C over a period of about 80 hours. The other Pt/Pd thermocouple 14/98 was used as a standard thermocouple for calibrations in the temperature range between 0 °C and 1100 °C. Both thermocouples failed at measurements at the freezing point of copper (1084.62 °C). An overheating can be definitely excluded.

In addition to the samples of Pd wire of the used thermocouples well directed heat treated Pt/Pd samples exposed to specific conditions were also analysed to emphasise the results of the investigations mentioned above. Due to the fact that the breakage of the Pd wires occur within about a 8 mm distance from the measuring junction of the thermocouples also different welding methods for preparing the measuring junctions were compared to verify its influence on the mechanical stability of the Pd thermoelement. Finally two samples of an as-delivered Pd wire before and after the typical wire annealing process (1300 °C, 10 h) were investigated.

In Table 1 the investigated Pd samples of the thermocouple Pt/Pd 15/02 are summarised.

Table 1: Pd samples investigated at fem

notation	part of the sample	impurities	remarks
Pd1 (Pt/Pd 15/02) (measuring junction consisting of about 8 mm Pt and Pd wires)	fractured surface, brink	Pt	
	fractured surface, core	Al, O	precipitation at grain boundaries
	surface	Pt, Si, Al, O	near fractured surface
Pd2 (Pt/Pd 15/02) (Pd wire of about 25 mm with fractured surface and "clean" end)	brink near fractured surface	Si, O	measurements at longitudinal sections
	core near fractured surface	-	
	brink near "clean" end	-	
Pd3 (Pt/Pd 15/02) (Pd wire from the reference junction)	precipitation at grain boundaries	Al, O	measurements at longitudinal sections

In the SEM-micrograph (Figure 1) free frozen surfaces are cognisable at the brink of the fractured surface of sample Pd1 which implicate molten palladium during breakage. In the region of the core an inter-crystalline structure with relative large grains is visible (Figure 2). At the grain boundaries sporadically precipitation (aluminium, oxygen) could be identified by EDX analysis. Furthermore the elements palladium and platinum were found in the small-grained brink, whereas only palladium was found in the core region of this sample. Figure 3 shows a SEM-micrograph of the surface of the Pd-wire together with the welded joint. By a further EDX analysis the elements palladium and platinum were detected again as well as the elements silicon, aluminium and oxygen near the fracture surface.

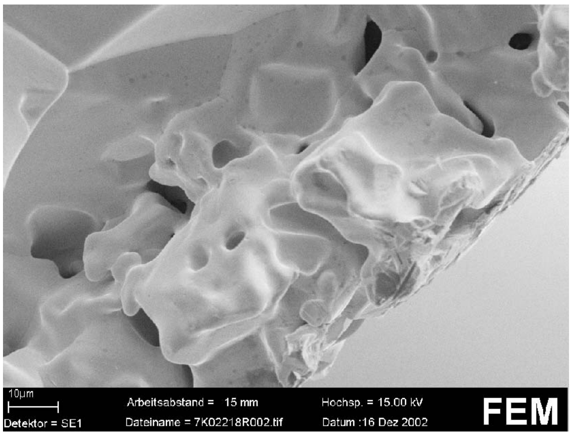

Figure 1: Fracture surface of the brink region (Pd1)

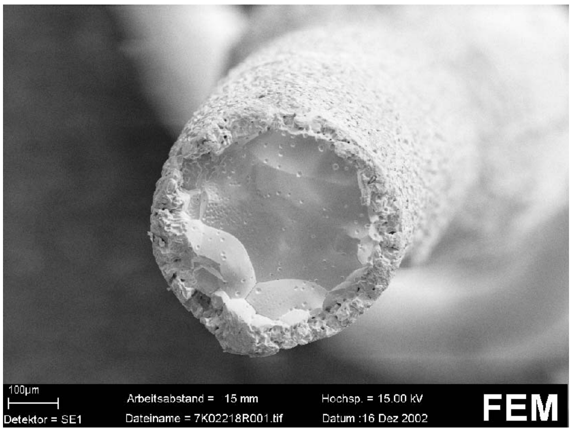

Figure 2: Fracture surface (overview) (Pd1)

A LM-micrograph by optical microscope of a longitudinal section (Pd2) is shown in figure 4. Solely in brink region near the fracture surface hollow spaces (lucanas) were found, which are partly filled with transparent phases consisting of silicon and oxygen. Again platinum was analysed, but only near the fracture surface in the brink region.

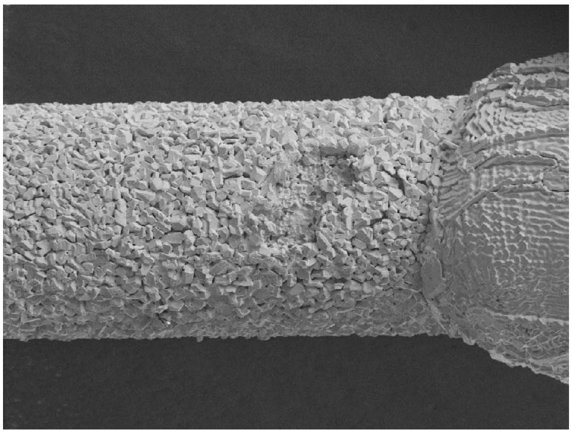

Figure 3: Pd wire with welded junction (Pd1)

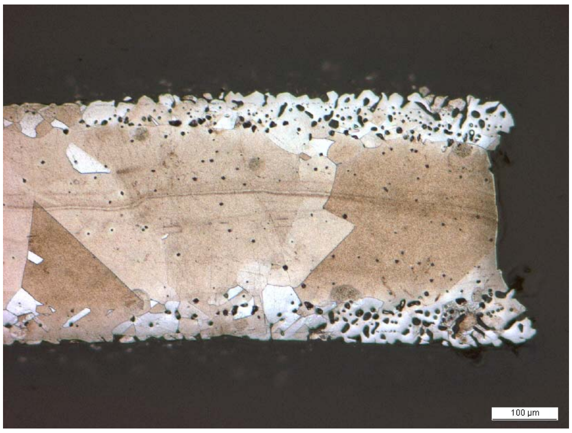

Figure 4: Longitudinal section of Pd-wire (Pd2)

Further investigations of sample Pd3 from the reference junction of the Pd wire show a similar structure as presented in Figure 4: in the brink region a small-grain structure and in the core region a coarse-grained structure. At the grain boundaries in the brink region also precipitation of aluminium and oxygen were detected like in sample Pd2, however hollow spaces were not found there.

Additional investigations of a sample of the Pd thermoelement of Pd/Pt 14/98 resulted in similar outcomes. Therefore it is assumed that a significant change of the mechanical properties of the Pd wire occurs at the fracture surface by diffusion of silica along the grain boundaries. Palladium and silicon form an eutectic system with a eutectic melting temperature of about 816 °C. Additional silica can cause a local melting point depression which results in a breakage of the palladium along the grain boundaries. This would explain the appearance of the fracture surface in Figure 1.

Three Pt/Pd samples consisting of palladium and platinum wires (diameter 0.5 mm) welded to each other and one single Pd wire of the same diameter were prepared in different ways to investigate the influence of SiO_2 on the mechanical stability of palladium and to verify the results of the investigations at fem described above. At first the four samples (length: 2-3 cm) were cleaned separately in an ultrasonic bath each for two minutes in ethanol and in distilled water. Then each of them was prepared in a different way (Table 2) and was put into a separate tube of alumina (Al_2O_3, purity 99.7%) with a length of 40 mm and a inner diameter of 4 mm which were annealed before at a temperature of 1200 °C for 2 hours. The four alumina tubes with the sample were adjusted radially in an annealed ceramic protection tube of 15.5 mm inner diameter to ensure the same annealing temperature for the four samples. The samples were annealed two times at a temperature of 1100 °C for 20 h and 15 h. To avoid the oxidation of the Pd wires the whole assembly was removed from the furnace rapidly at a temperature of about 1050 °C. Before and after the first and second run the samples were investigated by a light-optical microscope (and after the second annealing additionally in fem by SEM and EDS as mentioned above. Es liegen noch keine Ergebnisse vor)

Table 2: Preparation of samples PTB-1 - PTB-4

notation	material	preparation
PTB-1	platinum/palladium welded	additional cleaning in an ultrasonic bath (ethanol, distilled water)
PTB-2	platinum/palladium welded	direct contact with sweat
PTB-3	palladium	direct contact with SiO_2 powder in the ceramic tube
PTB-4	platinum/palladium welded	direct contact with SiO_2 powder in the ceramic tube

At the microscopic analysis of the samples before the annealing no anomalies were detected on the metallic bright surfaces. The Pd wires exhibit narrow (2 mm) rings of black colour at a distance of about 5 mm from the welded joint. These rings are the result of the oxidation of palladium which occurs between about 550 °C and 800 °C. Therefore these parts of the Pd-wires were exposed to this critical temperature range during the welding. At temperatures above about 850 °C the palladium oxide is decomposed and therefore after the first annealing step no oxide was visible any longer.

After the annealing at 1100 °C the surfaces of the Pd-wires of the samples PTB-1, PTB-2 and PTB-4 showed a substantial roughness which was most advanced at PTB-4. At this sample clear grain boundaries occur which partially degrade in groovings. Furthermore single outgrowing grains were visible near the welded junctions of the three samples and at those parts of the Pd-wire (of sample PTB-2) where the Pd was in direct contact with the Pt-wire during the annealing. Solely the Pd-wire of sample PTB-3 showed a lightly metallic-bright surface but also single grains were observable by different reflection. The Pt-wires of all samples were nearly unchanged and exhibited the typical metallic-bright surfaces.

Notable is the disordered surface of the Pd-wire at sample PTB-1 in spite of the careful preparation and the avoidance of SiO_2. Possibly platinum or oxides of platinum (PTB-1, PTB-2 and PTB-4) could act as catalysts for changes of the surface structure in palladium. Platinum and palladium form a solid solution because of their chemical affinity. Both metals are completely miscible at each composition at temperatures above about 770 °C. At lower temperatures there exists a gap of complete miscibility in a wide range and therefore during cooling both elements can crystallise separately in clusters side by side. Platinum or platinum oxide can be transported via gas phase to the Pd-wire and particularly adsorb at grain boundaries causing the rough surface of the Pd-wires. After the second annealing step no further significant changes of the surfaces were observable by optical analysis.

The investigations of different welding methods for preparing the measuring junctions were performed at electrotherm GmbH with the aim to verify reasons for the mechanical instability of the Pd wire near the measuring junction. It is known that the absorption of hydrogen by solid palladium results in an increasing brittleness by the expansion of the lattice of the metal. Therefore the conventional method by using a hydrogen-oxygen flame and a laser welding method to prepare the junctions were compared. Two measuring junctions, ET1 and ET2 were welded by a hydrogen-oxygen flame, ET1 by a normal, pure flame, ET2 by a impure flame with reduced pressure. The third junction ET3 was prepared by a Neodym-YAG laser. This method differs from the first ones by a fine allotted energy supply which reduces the thermal stress of the wires. After the preparation the three samples were annealed two times (135 h and 75 h) at a temperature of about 1075 °C, quenched to room temperature and investigated by optical analysis.

After the first annealing the Pd wire of all samples showed a marked-off zone starting at the welded junction characterised by a coarse surface with a 1-2 mm wide changeover to the typical metallic-bright surfaces. The length of these crystalline zones were about 5-6 mm at ET1 and ET2 and about 3 mm at ET3 respectively. After the second annealing the marked-off zone disappeared and the range of the coarse surface was extended by about 15 mm. Notable is the formation of crystalline structures especially on the near side of the Pd wire to the Pt wire. This observation corresponds to the cognition received above with the specially treated Pt/Pd samples PTB1 - PTB4.

Figure 5 and 6 show LM-micrographs of a longitudinal section of an as-delivered Pd-wire before and after the wire annealing process at 1300 °C (10 h) respectively. It is clearly seen that the large grain structure of the core is a result only of the heat treatment. The maintained small-grained brink regions can be caused by the fact, that any surface act as a disruption of the structure of an ideal crystal. Therefore most of the impurities and dislocations will be concentrated in this region and avoid the growth of larger grains.

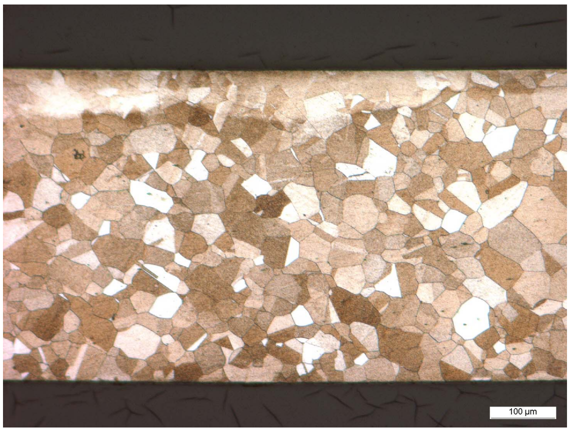

Figure 5: Longitudinal section of a Pd-wire before annealing

Figure 6: Longitudinal section of Pd-wire after annealing (1300 °C, 10 h)

The investigations described above can be summarised as follows:

- The assumed reason of the breakage of the Pd-wires near the measuring junction was a local enrichment of silica which form an eutectic system with palladium. Thus the melting temperature of palladium was decreased at parts of the brink of the wire which causes in a failure of the Pt/Pd thermocouples. The found transparent phases of silicon and oxygen in the lucanas of the brink region near the fractured surface confirm this assumption. To avoid a breakage of the Pd wire it is important to avoid any elements which can decrease the melting temperature of palladium. One source of silica could be the ceramic insulation of furnaces. Therefore it is recommended to use Pt/Pd thermocouples always with closed protection tubes without any component which contains silicon.
- The irreversible changes of the surface of the Pd wire which appear as a coarse crystalline structure probably are caused by platinum or oxide of platinum which are adsorbed mainly at grain boundaries which degenerate in crenated grooves. This effect is mostly pronounced near the measuring junction but can be found also at parts along the Pd wire which are exposed to high temperatures. The degree of the disordered surface depends on the working time and the distance from the measuring junction, respectively from the platinum source. Therefore it can be assumed, that the platinum or platinum oxide is transported to the Pd wire mainly via gas phase but also by diffusion along the Pd wire. This process causes an increasing brittleness with decreasing mechanical stability of the palladium wire which results in a reduced life time of a Pt/Pd thermocouple. Nevertheless it must be concluded that the presence of platinum can not be avoided but an extra insulation of the Pt-wire outside the two hole capillary tube can reduce the active surface of the platinum and therefore prolongate the effect of increasing brittleness.
- Precipitation of aluminium and oxygen was found at grain boundaries over the length of the Pd wires exposed to high temperatures independent of the appearance of a coarse crystalline surface (for instance at PTB-3 and at parts of the Pd wires which are located in a greater distance from the measuring junction). Therefore these elements can not be responsible for the degradation of the mechanical properties of the Pd wire.
- The inter-crystalline structure of the core of the Pd wire with large grains (Figure 4, 6) after a 10 hour annealing at a temperature of about 1300 °C favoured a breakage of the wire because of the easier movability of single grains along the grain boundaries. The mechanical stability of the Pd wire can be

maintained only by avoiding an excessive grain growth of the palladium. This could be done by a well directed contamination of the Pd wire by a suitable thermoelectric inert material.

[1] G.W. Burns, D.C. Ripple, M. Battuello; *Platinum versus palladium thermocouple: an emf-temperature reference function for the range 0 °C to 1500 °C*; Metrologia, 1998, 35, 761-780
[2] K.D. Hill; *An investigation of palladium oxidationin the platinum/palladium thermocouple system*; Metrologia, 2002, 39, 51-58
[3] R.E. Bentley; *A thermoelectric scanning facility for the study of elemental thermocouples*; Meas. Sci. Technol. 11, (2000), 538-546