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# On the mechanism of internal oxidation in platinum–zirconium alloys A TEM study

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## Abstract

Internal oxidation of platinum–zirconium alloys has been studied using scanning and transmission electron microscopy. Nucleation sites of internal oxides are identified and different oxide particle morphologies are characterised. It is shown that the migration of grain boundaries during the internal oxidation process plays an important role concerning the oxide distribution and morphology. Coalescence of oxides in grain boundaries and inside the grains is described qualitatively. A consistent view of the internal oxidation of platinum–zirconium alloys based on grain boundary migration controlled internal oxidation is presented.

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## 1. Introduction

Internal oxidation of alloys is a long known process that is used advantageously to generate oxide dispersion strengthened (“ODS”) materials. It has been studied in a variety of alloys over the past 60 years [1–6]. Until present the main focus of research is the creation of finely dispersed non-metallic internal precipitates for effective dispersion strengthening [6,7]. A further research field is the prevention of undesirable internal corrosion effects [8,9]. For platinum alloys oxide dispersion strengthening is used to improve the high temperature properties of the material [10]. ODS platinum alloys are used in technical applications, but little is known about microstructure details of the correlation between processing parameters and oxide particle distribution.

The basic model that allows for specifying requirements for internal oxidation was presented by Wagner [11]. He characterised internal oxidation as a special type of oxidation of alloys with a certain amount of noble and less noble constituents. He also defined a correlation between internal oxidation and the formation of external oxide layers depending on concentration,

solubility and diffusion coefficients of the constituents of an alloy. Furthermore he described the movement of the internal oxidation front with parabolic time scaling. The theory was reviewed and expanded by various authors, e.g. Rapp [9] and Böhm and Kahlweit [12].

For producing ODS alloys with high creep strength for high temperature applications, not only the time which is necessary to fully internally oxidize a bulk material is of interest. High temperature creep strength and other mechanical properties of ODS alloys strongly depend on the mean particle size, the particle size distribution, their spatial distribution and the morphology of the internal oxide particles. The formation of an external oxide layer on the surface of the material can impede or prevent internal oxidation, as thick and dense external oxide layers may constrain the access of oxygen into the material.

The results of different internal oxidation experiments with different alloys have been summarized by Douglass [13]. He concludes that the shape of the particles is very much alloy dependent and not uniform from grain to grain within one material. Reasons are stresses resulting from the misfit between the particles and the surrounding matrix and/or anisotropy of the surface energy of the particles. He also emphasises that the spherical shape of the particles as assumed by Wagner is rather uncommon. It can vary between spheres, bands, faceted crystals, dendrite- or fishbone-like structures.

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Many internal oxidation experiments were carried out using single crystal materials. The influence of grain boundaries was thus not considered. However, it is well known that grain boundaries and other crystal defects strongly affect internal oxidation. Additionally the existing particles can influence the diffusion rate of oxygen and of the less noble constituent of the alloy due to the interface between the particles and the matrix [14,15].

Early internal oxidation experiments on platinum alloys were carried out by Reinacher [16] in the early 1970's. He described a preferred oxidation along the grain boundaries of the material. Later Fischer [17] describes a similar effect.

Some manufacturers of ODS platinum alloys claim a far developed process control, yielding spatially homogeneously distributed oxide particles inside the grains (see e.g. [18]). However, in simple annealing experiments with platinum alloys such a particle distribution is not attained. The low solubility of oxygen in the platinum matrix prevents the formation of oxide particles inside the grains while the higher solubility of oxygen inside the grain boundaries results in the formation of oxide layers along the grain boundaries. To achieve spatially homogeneously distributed oxide particles inside the grains, a complex production process of cold working and heat treatment steps is generally applied (see e.g. [18]). In publications on platinum alloys the detailed internal oxidation mechanism is not described [17,18]. The authors of the present work assume that the higher density of lattice defects after cold working increases solubility and diffusivity of oxygen in the platinum matrix and thus allows for the formation of oxide particles inside the grains. However, open questions remain concerning nucleation sites and spatial distribution of the particles.

The goal of the present investigation is to contribute to the understanding of the process of internal oxidation of platinum–zirconium alloys. The formation of internal oxide particles is studied in the TEM. Nucleation and growth of the internal oxide particles are characterised as an initial point for understanding size and spatial distribution of the particles generated by internal oxidation.

## 2. Experimental

For the investigation a Pt–10%Rh–0.16%Zr alloy was used (all concentrations in weight %). This alloy composition is used in a wide range of applications in the glass and chemical industries. The sample form was foils with a thickness of about 100  $\mu\text{m}$ . The internal oxidation processing step was a heat treatment under air atmosphere. Discs with a diameter of 3 mm were punched out of the foil and placed into a horizontally positioned  $\text{ZrO}_2$  tube. The  $\text{ZrO}_2$  tube protects the specimen from excessive contamination from the furnace. Both ends of the  $\text{ZrO}_2$  tube were open, so that there was no restriction concerning the contact of the specimen with the atmosphere. The  $\text{ZrO}_2$  tube was placed into a preheated muffle furnace. Following earlier investigations on internal oxidation of platinum alloys by Reinacher [16], two different heat treatment temperatures were chosen, particularly 1400 and 900  $^\circ\text{C}$ . The foils were oxidized between 10 and 80 h. The samples were first studied by SEM in order to determine if and to what extent external oxidation had occurred. After removing the surface of the foils by mechanical and electrochemical polishing, the samples were again studied by SEM to verify where and to what extent internal oxidation had occurred. Afterwards the foils were prepared for TEM studies by dimple grinding using the "Gatan Dimple Grinder 656" and electrochemical etching using the "Struers Tenupol-3" with KCN as etchant at a voltage of 30 V and a current of approxi-

mately 1 A, depending on the quality of the etchant. To identify zirconium oxide particles above 10 nm diameter EDX analysis was used. For smaller particles with a diameter of less than 10 nm diameter EDX does not yield unambiguous results, the composition of the particles as zirconium oxide was confirmed qualitatively using the Z-Contrast.

## 3. Results

SEM analysis of the surface of the specimen after the heat treatment showed that external oxidation occurred at both of the annealing temperatures. However, the morphology and the chemical composition of the external oxides were different after the different heat treatment temperatures. On the surface of the specimens which were exposed to 900  $^\circ\text{C}$ , rhodium oxide had formed (Fig. 1a). Rhodium oxide is known to become unstable and evaporate above  $\sim 1140^\circ\text{C}$  [19,20]. Zirconium oxide could not be found on the sample surface.

On the surface of the specimens which were exposed to 1400  $^\circ\text{C}$  the grain structure is visible due to thermal etching. Instead of rhodium oxide there were spheres with a maximum diameter of less than 2  $\mu\text{m}$  which were identified as zirconium oxide (Fig. 1b).

The spheres in the grain boundaries are much larger than those on the grain surface and the spheres in the grain boundaries are approximately equidistant. Both the rhodium oxide and the zirconium oxide did not form a dense protective external oxide layer.

To get insight into the formation of internal oxide particles a surface layer of approximately 20  $\mu\text{m}$  thickness was polished off mechanically and electrochemically. It could be shown that oxidation took place inside all specimens irrespective of the heat treatment temperature (Fig. 2). Inside the foils the oxides mainly cover the grain boundaries. The thickness of the oxide layers in the grain boundaries and the grain size of the matrix material depend on the heat treatment temperature. After the heat treatment at 900  $^\circ\text{C}$  the grain boundary zirconium oxide layer has a thickness of about 1  $\mu\text{m}$  (Fig. 2a), and after the heat treatment at 1400  $^\circ\text{C}$  of about 10  $\mu\text{m}$  (Fig. 2b). Oxide particles inside the grains could not be detected by SEM, independently of the heat treatment. The different grains sizes of approximately 10  $\mu\text{m}$  after the heat treatment at 900  $^\circ\text{C}$  and of approximately 100  $\mu\text{m}$

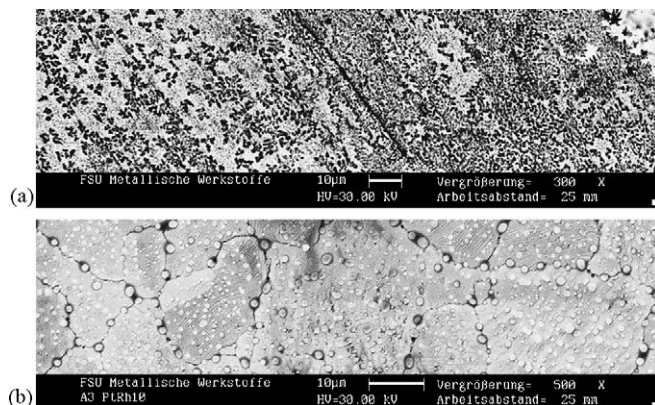


Fig. 1. Surface oxides (a) external rhodium oxide after heat treatment at 900  $^\circ\text{C}$  and (b) external zirconium oxide after heat treatment at 1400  $^\circ\text{C}$ .

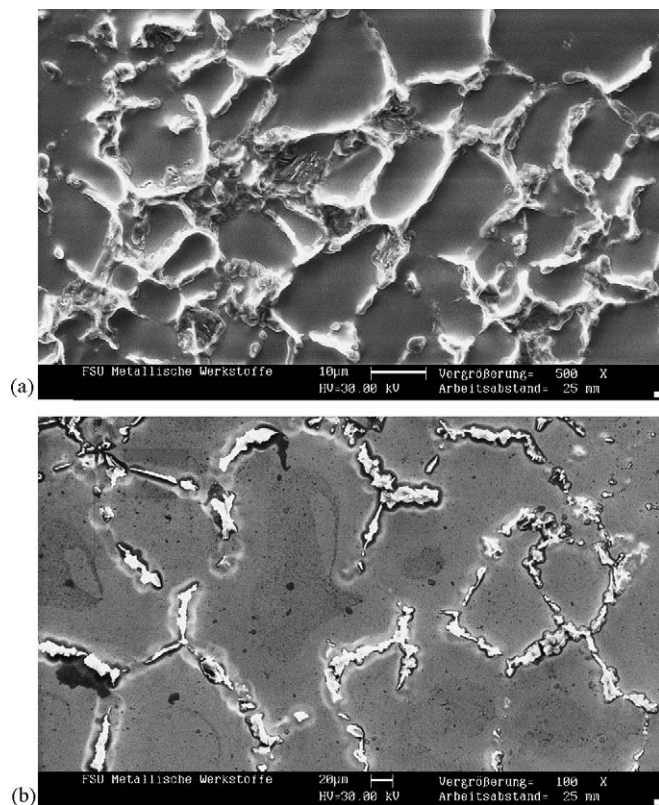


Fig. 2. Zirconium oxide layers (white) at the grain boundaries; (a) after heat treatment at 900 °C, SEM in BSE-mode and (b) after heat treatment at 1400 °C, SEM in BSE-mode.

after the heat treatment at 1400 °C are caused by recrystallisation and subsequent grain coarsening (normal grain growth) of the material during the heat treatment.

Because SEM does not show any particles inside the grains independent from the heat treatment temperature, TEM analyses were carried out to obtain images with higher resolution and magnification.

After the heat treatment at 1400 °C oxide particles inside the grains were not found by TEM. During the heat treatment at 1400 °C zirconium oxide exclusively formed in the grain boundaries. In the samples that were heat treated at 900 °C oxide particles were found in the grain boundaries and inside the grains (“internal oxide particles”). The bulk particles are all located close to grain boundaries (maximum distance approximately 2 µm). It is interesting to note that they were only found on one side of the grain boundary. The internal oxide particles vary strongly with respect to their morphology. Some are in the form of bands parallel to the grain boundaries, some have a spherical shape and others display facets. In some instances complex branched structures were found. The smallest internal oxide particles with diameters well below 10 nm were found in the grain boundaries. An overview over different types of particle shapes, particle sizes and particle locations is given in Fig. 3.

Fig. 3a and b show the nucleation stage of oxide particles within the grain boundary. The use of Z-Contrast is useful, because small oxide particles are hardly visible in BF-mode

(Fig. 3a), but can clearly be identified by the mass contrast (Fig. 3b). In Fig. 3c–f different sizes and morphologies of internal oxide particles are shown. Fig. 3c shows oxide particles with facets of equal orientation. This morphology could only be found for some of the internal oxide particles with less than 40 nm diameter. All internal oxide particles with diameters above 40 nm show smooth rounded edges (Fig. 3d and e). Some of the internal oxide particles have coalesced as can be seen in Fig. 3d and e. Fig. 3d also shows that coalescence between the internal oxide particles proceeds along the grain boundary and in the side grain close to the grain boundary. In Fig. 3e it is obvious that the coalescence between the internal oxide particles (white circles) follows preferred directions (black lines in Fig. 3e).

#### 4. Discussion

The formation of external oxide layers during the heat treatment under air atmosphere is shown in Fig. 1a and b. Since the external oxide layers are not closed they do not have a marked influence on the internal oxidation behaviour of the bulk material. However, the temperature dependent diffusion rate of zirconium in platinum leads to faster diffusion of zirconium to the surface of the specimens during the heat treatment at 1400 °C (Fig. 1b) and results in excessive external oxidation to zirconium oxide. Consequently the volume fraction of internal zirconium oxide particles decreases. The influence of the grain boundaries on external oxidation of the material can clearly be seen in Fig. 1b. Due to the higher diffusion rate of zirconium in the grain boundaries than in the bulk the external oxides in the grain boundaries grow larger than the external oxides on the grain surface within the same time.

The oxide layers in Fig. 2 show clearly that internal oxidation of platinum–(rhodium)–zirconium alloys yielding a spatially statistical particle distribution is by no means trivial. The formation of zirconium oxide layers in the grain boundaries as a result of the heat treatment occurred at both applied temperatures. However, the thickness of the grain boundary oxide layers and the grain size are 10 times smaller for the lower than for the higher heat treatment temperature. The different grain sizes show that recrystallisation and normal grain growth occur and proceed until the grain boundaries get pinned by the formation of the zirconium oxide. The assumed direct influence of lattice defect density on the internal oxidation process cannot be confirmed. Apparently recrystallisation reduces the lattice defect density before the grain boundaries get pinned by oxide particles. Recrystallisation and grain growth only affect the grain size and the amount of internal interfaces, i.e. the grain boundary area inside the material.

In Fig. 3a and b the nucleation sites of oxide particles are identified. Nucleation of oxide particles occurs exclusively in the grain boundaries. Particles with less than 5 nm diameter were not found inside the grains. The diffusion rate of oxygen in platinum is high [19], but due to the “markedly low solubility of oxygen in platinum” as indicated by Fromm and Gebhardt [19], internal oxidation of platinum–(rhodium)–zirconium alloys is not possible applying the same processing route as, for e.g.

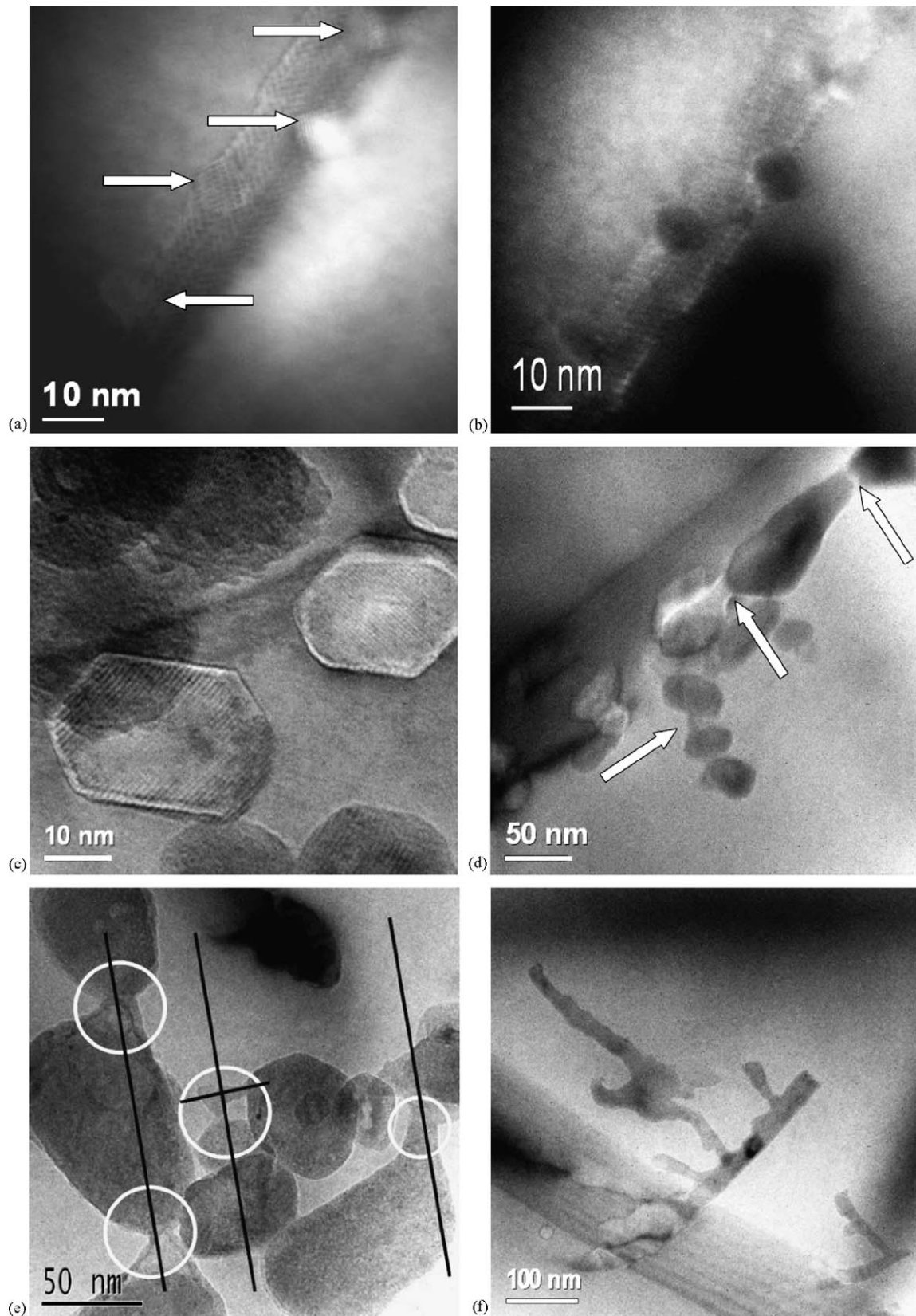


Fig. 3. Overview of the TEM images (a) BF-image of small internal oxide particles (arrows) inside grain boundary; (b) Z-Contrast-image of the same location as (a), small internal oxide particles clearly identified by mass contrast; (c) BF-image of internal oxide particles with parallel facets; (d) BF-image of spherical internal oxide particles close to grain boundary showing coalescence (white arrows); (e) BF-image of spherical internal oxide particles showing coalescence (white circles) in preferred directions (black lines); (f) BF-image of complex branched internal oxides close to grain boundary.

silver–cadmium alloys. Due to the higher solubility of oxygen in the grain boundaries of the material, the conditions for nucleation of internal oxidation are fulfilled only there. At this early stage of the oxidation process the grains are free of internal oxide particles. At later stages all of the internal oxide particles which were found inside the grains were larger than 15 nm in diameter.

The identification of the grain boundaries as the only nucleation sites, the fact that internal oxide particles inside the grains were only found close to and on one side of the grain boundaries and the different grain sizes depending on the heat treatment temperature show that grain boundary migration due to grain coarsening (as shown in Fig. 2) plays a significant role for internal oxidation of platinum alloys. Grain boundary migration leads to the detachment of migrating grain boundaries from small nucleated oxide particles, leaving the particles on the back side of the boundaries and inside the growing grains. For this step it is important that the conditions for the detachment of the grain boundaries are fulfilled. Necessary is a small size of the particles which is assumed to be around 5 nm and a sufficient small volume fraction of particles inside the matrix [21,22].

The fact that only after the heat treatment at 900 °C internal oxide particles can be found inside the grains is an evidence for the complex correlation between the internal oxidation process and the heat treatment temperature. During the grain coarsening at 900 °C the combination of nucleation rate of the oxide particles and the migration rate of the grain boundaries allow nucleation of oxide particles in the grain boundaries and following detachment. At both heat treatment temperatures pinning of the grain boundaries by oxide particles occurs, resulting in the formation of zirconium oxide layers along the grain boundaries until the zirconium is completely oxidized.

The extended zirconium oxide layers in the grain boundaries indicate a coarsening or coalescence mechanisms of the oxide particles during the heat treatment. Zirconium oxide is very stable and unlikely to decay to atoms or ions it is thus unlikely that coalescence is based on a diffusional coarsening mechanism. Examples for the coalescence mechanism can be seen in Fig. 3d and e. These figures show the formation of connections with identical crystallographic growth directions between the zirconium oxide particles. As can be seen in Fig. 3d coalescence between the internal oxide particles occurs in both the matrix and in the grain boundaries. The reasons for coalescence are likely to be the stresses which arise around the growing zirconium oxide particles in the platinum matrix. These stresses lead to compression of the particles and to local strain in the matrix lattice raising the solubility of oxygen in the vicinity of the particles. The higher solubility of oxygen because of the tensile stresses and the high diffusion rate of oxygen in platinum enable the further growth of the internal oxide particles inside the grains. If the zirconium oxide particles are close enough to each other their strain fields superimpose, yielding growth toward each other along preferred directions. The different and complex morphologies of the zirconium oxide particles as shown in Fig. 3f are a result of the coalescence mechanism. Former small globular or faceted zirconium oxide particles can grow to long

bands or even more complex structures (dendrite- or fishbone-like, Fig. 3d–f). Especially Fig. 3f shows a complex shape of a zirconium oxide particle with side arms parallel to the grain boundary. According to the presented hypothesis this implies that during the migration of this grain boundary, nucleation of zirconium oxide particles happened in the grain boundary in several stages, followed by a coalescence period of the zirconium oxide particles.

The presented mechanism of grain boundary migration controlled internal oxidation explains the internal oxidation behaviour of platinum alloys but it might also explain the internal oxidation behaviour of other polycrystalline alloys with low oxygen solubility. Even the creation of new ODS alloys with low oxygen solubility, which could not be internally oxidized until present, can be possible applying the grain boundary migration controlled internal oxidation mechanism.

## 5. Summary

In the present study internal oxidation of platinum–zirconium alloys after two different heat treatments was investigated by SEM and TEM. It is shown that nucleation of internal oxide particles occurs in the grain boundaries exclusively. If an adequate heat treatment temperature is chosen, the grain boundaries detach from the nucleating oxide particles due to grain coarsening. The previously assumed direct influence of lattice defect density on the internal oxidation behaviour of the material could not be confirmed.

The presented mechanism of grain boundary migration controlled internal oxidation gives a consistent explanation for the internal oxidation behaviour of platinum alloys. It may also provide a possibility for the production of other internally oxidized materials with low oxygen solubility in the bulk. The described mechanism of coalescence between the internal oxide particles in the grains and the grain boundaries is assumed to be a consequence of the stresses in the platinum matrix, caused by the internal oxide particles growth. Depending on the coalescence mechanism many different particle morphologies can be found.

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