SIMULATION OF THE MICROSTRUCTURE EVOLUTION OF DISPERSION-STRENGTHENED PLATINUM MATERIALS

M. Rettenmayr[1], X. Song[1], M. Oechsle[2], S. Zeuner[2]
[1] Technische Universität Darmstadt, Institut für Materialwissenschaft, Darmstadt
[2] OMG AG, Hanau

Introduction

Platinum materials are by far the most thermochemically stable class of metal and alloy materials. Because of their extraordinarily high oxidation and corrosion resistance, glass melting plants use platinum materials for the components of basins, grooves, and channels as well as for active-flow components, heating and refining units, and feeder systems. In particular, the use of platinum and platinum alloys for manufacturing technical and optical glass makes it possible to produce highly pure and homogenous glass qualities, because corrosion and erosion products are prevented by coating or cladding refractory materials with the noble metal platinum.

The high processing temperatures in glass melts, where temperatures above 1500 °C are not unusual, place extremely high demands on the physical stability of the material. In addition to the composition of the alloy, this stability depends largely on the alloy's microstructure: Only a fine grain structure can guarantee the required characteristics. For long-term stability at the prevailing operating temperatures, it is therefore necessary to prevent coarsening of the grain structure.

Today, computer simulations can reconstruct the grain structure's long-term evolution, even for complex alloys and structures. In the present paper, this is performed for a Pt/Au alloy. In this system, the results obtained from the simulation are in good agreement with experimental results because appropriate etching can make the grain structure clearly visible. However, some further effort is still necessary to transfer the results to other platinum materials. Simulation and experiment are both show that no significant coarsening of the grain structure is to be expected, even after long endurances.

FKS platinum materials

In FKS platinum materials (FKS is the German acronym for "**f**ein**k**orn**s**tabilisiert" = fine-grain stabilized), stabilization of the grain structure is usually accomplished by dispersion strengthening. This is accomplished by introducing finely distributed particles of ZrO_2 (approx. 1 vol.%) with a diameter of only 20–140 nm into the platinum or platinum alloy. The particles greatly restrict the mobility of the grain boundaries. The following FKS alloys manufactured by OMG AG are typical of this type of material: FKS 16Pt, FKS 16PtRh10 and FKS 16PtAu5 (16 stands for a dispersoid content of 0.16wt.%). These materials permit endurances as high as seven years and/or operating temperatures up to 1650 °C (FKS16 PtRh10) to be attained.

OMG produces its FKS platinum materials by means of powder metallurgy. The materials are subject to strong deformations during the compacting and shaping that occurs in the manufacture of semi-finished products. At high temperatures, recrystallization can partially

reduce the deformation energy that this introduces into the material. A completely new grain structure, whose size distribution can differ substantially from that of the source structure, forms during recrystallization. In single-phase (not dispersion-strengthened) metal alloys, the recrystallization generally occurs at temperatures above $0.5T_m$ (T_m = melting temperature in degrees Kelvin), which for platinum materials means about 750 °C, a temperature far below the operating temperature. Because of the dispersoid particles, a much higher recrystallization temperature can be expected for FKS platinum materials. More precise studies about the recrystallization of platinum materials are not currently documented in the literature.

Fine grain stabilization by means of particles

Stabilization of the grain structure in platinum materials is a function of the interaction between the oxide particles and the grain boundaries: The interfacial energy of the system's matrix particles declines as long as a particle is present on a grain surface. This is a basic principle that is independent of the type of particle (cf. [1]). The lower interfacial energy caused by the particle's presence means that it takes a higher flow stress for a moving grain boundary to release itself from the particle. The result is that the grain boundary will "hang tight" between two particles (see Fig.1).

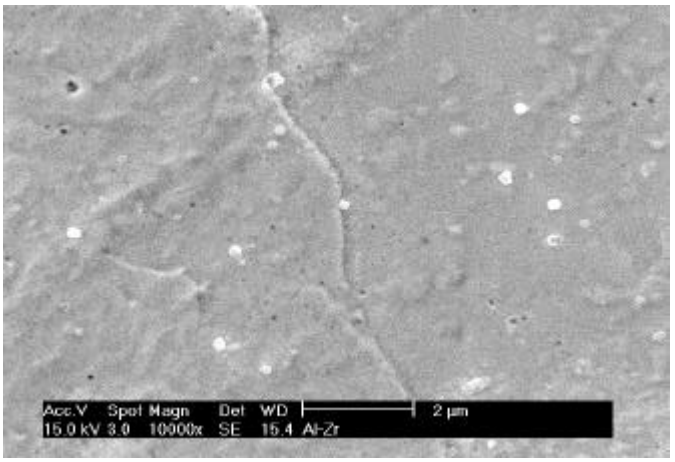


Fig. 1: Grain boundary in FKS 16 Pt; the ZrO_2 particles locally hold the grain boundary tight. Between them, it has advanced.

Changes in the microstructure

There are two different reasons why the grain structure can evolve further in the course of manufacture and application without external physical influences. The first is that the microstructure of dispersion-strengthened platinum materials (Fig. 2) can arise through normal grain growth with the reduction in the energy of the grain boundary serving as the driving force. The other is that it may arise through recrystallization with the reduction of the elastic strain. The dispersoid particles play a major role in microstructure evolution in both cases. For a dispersion-strengthened alloy that doesn't recrystallize, in other words an alloy whose recrystallization temperature is higher than the operational temperature and in which only normal grain growth can consequently change the average grain size, a maximum attainable grain size D_Z can be calculated from the Zener relationship [2]. For an average particle diameter of 50 nm, D_Z has an order of magnitude of 5 µm. Since FKS alloys exhibit average grain sizes of partially over 100µm (see Fig. 2), a higher driving force than just the

reduction in the energy of the grain boundary, in other words a reduction of the elastic strain, must have been present.

a) b) c)

Fig. 2: Micrographs of the 3 alloys FKS 16Pt (a), FKS 16PtRh10 (b), and FKS 10PtAu5 (c).

The following supports this conclusion: In observing a large number of particles that are randomly distributed within a matrix, a retarding force (in units of N/m^2) can be derived as the measure for the retardation of the grain-boundary motion. It is a function of the volume content and average radius of the particles and of the interfacial energy between particles and matrix. For a volume content of dispersoid particles of 1% and average particle diameter of 50 nm, which are specified in FKS Pt materials, the retarding force is approximately $3\times10^5 N/m^2$. The driving force for recrystallization is a function of the deformation and has an order of magnitude of 10^6 to $10^7 N/m^2$, which is thus greater than the retarding force. These considerations show that at least a partial recrystallization of the Pt materials will occur during full annealing.

Stability of the dispersoid particles

The stable grain structure desired for application can be achieved only if the average size of the dispersoid particles also does not vary over time, in other words if there is no coarsening of the particles ("Ostwald ripening"). Pronounced Ostwald ripening would operate as follows: The oxide particles' high proportion of surface area in relation to volume would mean that the fine particles will dissolve and that the dissolved volume will separate from the coarser particles. The average particle diameter will consequently rise and the total number of particles will decline. The retardation of the grain-boundary motion will consequently decline due to the smaller number of coarse particles. There would no longer be any long-term stability of the microstructure.

For dispersoids in general however, coarsening does not occur to any measurable extent, in contrast to other separations in the microstructure. This leads us to suspect that particle coarsening is not relevant to the study of grain growth and that the structures of FKS 16 Pt materials will remain stable when used at high temperatures [3].

Effect of the particles on the nucleation of recrystallization

Another effect that dispersoid particles can exercise on microstructure evolution is to accelerate and facilitate the nucleation of recrystallizing grains (PSN, "particle stimulated nucleation", cf. [4]). This effect can appear if the particles do not also become deformed when the matrix is deformed. This is certainly the case for the hard dispersoid particles in the ductile matrix of Pt materials. A second necessary condition for the appearance of PSN is a minimum particle size of about 1µm. Fig. 3 depicts a measured distribution of particle diameters. The average particle diameter is close to 52 nm and the maximum is 140 nm. It is therefore not necessary to consider the effect of PSN in Pt materials.

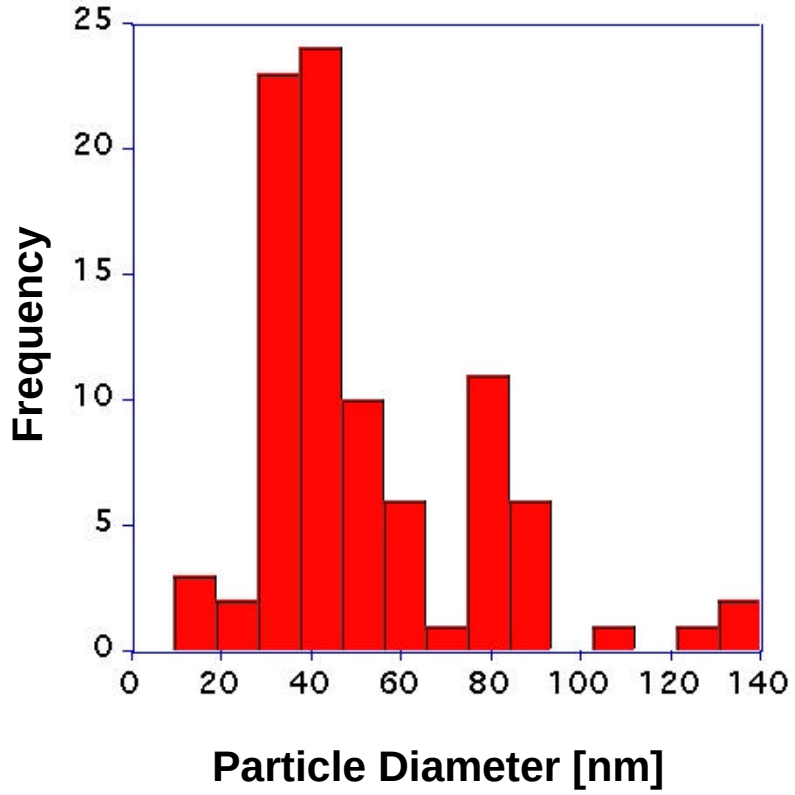


Fig. 3: Particle size distribution of ZrO_2 particles in FKS 16 Pt.

In addition to their size distribution, the arrangement of particles in the alloy is also critically important to their effect. A random distribution, which retards grain growth in all directions uniformly, is the most favorable. But a homogenous particle distribution can only be achieved at the cost of a high investment in process engineering. Production steps in which molten phases or physical deformation occur will result in a rearrangement of particles that will generally not be homogenous. Both linear arrays and higher particle densities can appear at the grain boundaries.

The following conclusions for simulation of the microstructure evolution can be derived from the above theoretical consideration and from the experimentally observed results:

- It is necessary to simulate both recrystallization and grain growth.
- The motion of the grain boundaries is determined by the particles.

- It is safe to assume that the particle size distribution doesn't vary with time.
- Of the possible effects of particle solidification, only the retarding force on the grain boundaries needs to be considered.
- The particle arrangement isn't random.

Simulation calculations

Numerous simulation methods that describe microstructure evolution during recrystallization and grain growth are listed in the literature. Monte Carlo methods have proven their worth for complex systems [5]. The algorithm that has already been used for particle-reinforced aluminum alloys and which has now been modified for Pt materials is documented in the references [6-8]. The principle of the Monte Carlo calculations is based on determining the system's change in energy when a region containing one grain (with a typical diameter of several µm) transfers to a neighboring grain. If this reduces the total energy of the system, then there is a high probability that the transition will occur. It has been shown that such calculations must be performed in three dimensions when particles are present; otherwise they will not correctly reproduce the kinetics of grain growth [9]. Fig. 4 is a schematic illustration of the model used in the paper presented here.

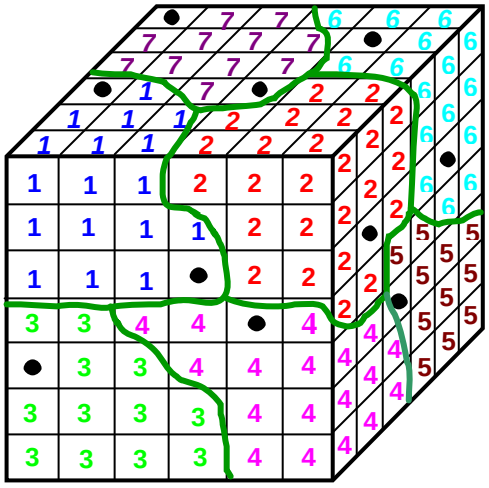
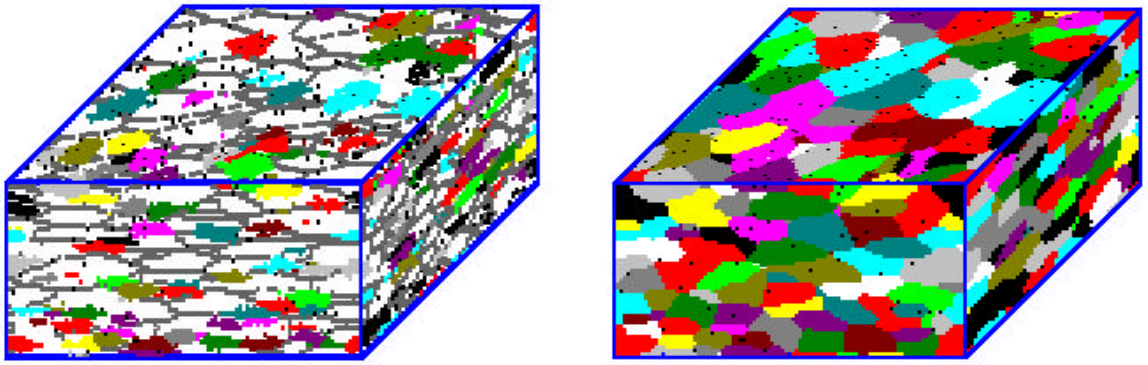


Fig. 4: Schematic representation of the microstructure in the Monte Carlo simulation (prior to deformation); every cubic unit is assigned a number that describes the orientation of the grain; units with the same number belong to the same grain; units containing particles contain a point; lines indicate grain boundaries.

The calculations begin by first generating a source microstructure with globular grains (Fig. 4). The deformation introduced by the manufacturing process is simulated by expanding the source microstructure in the direction of deformation in a purely geometrical manner, generating elongated grains. The microstructure is then redivided into cubic units as shown in Fig. 4. The proper elastic strain and an orientation index are then assigned to each of the units. (In the present paper, it is assumed that the deformation is homogenously distributed over the volume). Germs of recrystallizing grains are then distributed randomly within the lattice.

For each cubic unit, the Monte Carlo algorithm checks whether an energy gain is associated with its reorientation. This will always be the case if a region that hasn't recrystallized reorients to the reorientation index of a neighboring recrystallizing grain. But a partial energy

gain can also occur during reorientation if a neighboring unit has not recrystallized either. If reorientation is undertaken, this corresponds to grain growth in the source microstructure. When the entire microstructure has recrystallized, reorientation processes will continue to take place with the reduction of the interfacial energy constituting the driving force. In this case, we are talking about normal grain growth in recrystallized material. Temperature effects make themselves apparent in a different nucleation rate and a different probability of reorientation. This description makes it clear that the Monte Carlo model describes the basic processes that are relevant to microstructure formation in Pt materials.



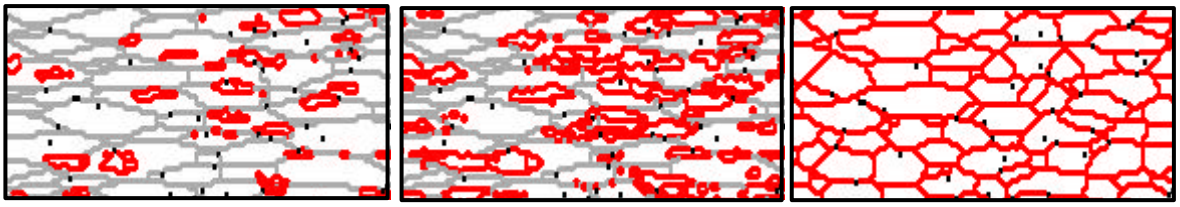
a) b)

Fig. 5: Simulated microstructure with recrystallized volume contents of 35% (Fig. 5a) and 100% (Fig. 5b); the grain boundaries of the source microstructure are illustrated by lines, the recrystallizing grains by regions of different gray levels.

Fig. 5 is a three-dimensional view of two stages in the simulated microstructure evolution. The lines represent grain boundaries in the non-recrystallized microstructure. Recrystallized regions are colored in different gray levels, depending on the orientation of the grain in question. Fig. 5a shows an early stage with approximately 35% recrystallized volume content. Fig. 5b shows the stage in which a completely recrystallized state has been attained. When the morphology of the grains and relative grain size obtained from the simulation are compared with experimental results for FKS platinum materials, very good qualitative agreement can be found.

Quantitatively, the microstructures in Fig. 5 cannot be compared to experimentally produced microstructures directly. The latter are always observed in a metallographic section (transverse, longitudinal, or surface micrograph) that represents a two-dimensional section through the three-dimensional structure. To perform a better comparison, the Monte Carlo simulation was programmed to also calculate two-dimensional sections at various points in time. These are shown in Fig. 6. The starting structure (gray lines) and recrystallized grains (black lines) can be recognized. A micrograph of the alloy FKS 16 PtAu5 is shown in Fig. 7 for comparison. The microstructures show good quantitative agreement with respect to average grains size, grain size distribution, and degree of grain elongation.

If the calculation is extrapolated over very long times, it is possible to estimate to what extent the recrystallized grain structure will continue to change when this material is used. However, the simulation calculations showed no change in the average grain size after recrystallization ended. Local reorientation processes cause the average grain size to still fluctuate slightly (Fig. 8). However, no trend toward larger values could be detected even after very long computing times.



a) b) c)

Fig. 6.: Two-dimensional sections through the microstructure computed in three dimensions at different times with recrystallized volume contents of 10% (a), 35% (b) and 100% (c); the gray lines represent the grain boundaries of the source microstructure, the black lines that of the recrystallized microstructure.

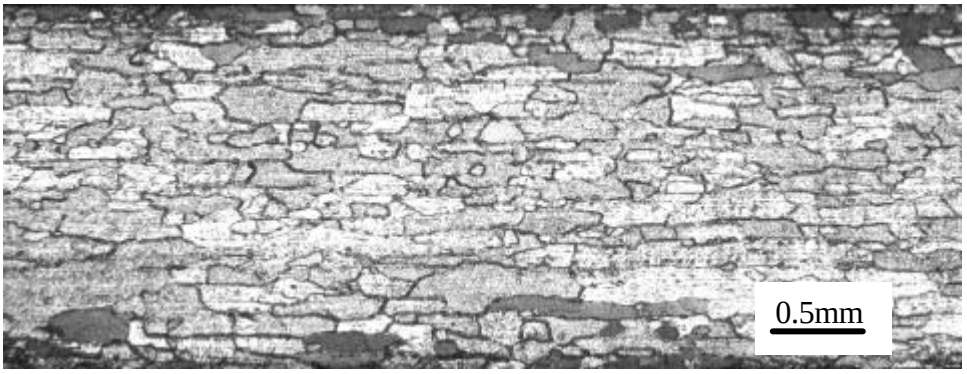


Fig. 7: Recrystallized microstructure in FKS 16 PtAu5

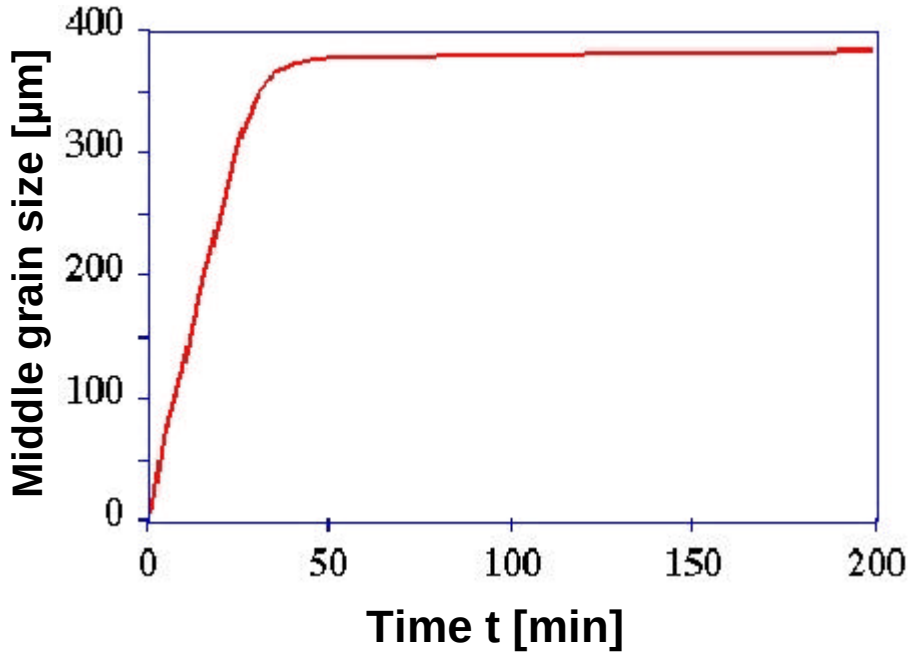


Fig. 8.: Evolution of the average grain size over time.

One of the difficulties in simulation calculations using the Monte Carlo method is the fact that the calculations are performed in relative units. Experimental initial and final grain sizes are then used to assign real spatial dimensions to the simulated microstructure. The dimension for the average grain size in Fig. 8 could be easily defined through a comparison with the grain sized in Figs. 6 and 7. The temporal dimension is somewhat more difficult. In the simulation calculations presented here, which concentrate on the question of the stability of the final state, the assumption of a linear relationship between real time and the time computed in the simulation ("Monte Carlo steps") is certainly justified. The correlation of experiment and calculation shows that one Monte Carlo step corresponds to approximately one minute. Fig. 8 depicts the average grain size during recrystallization and several hours thereafter. Further calculations were carried out to 10^6 Monte Carlo steps (corresponding to approximately 2 years) without resulting in a perceptible increase in the average grain diameter. Long-term stability in high-temperature applications has therefore been proven quantitatively through observations from actual applications and quantitatively through simulation calculations.

Conclusion

The evolution of grain structure in dispersion-strengthened platinum materials was studied in simulation calculations and experiments. The mechanisms and driving forces that can contribute to the formation of grain structure have been pointed and discussed. The conditions pertaining to platinum materials were incorporated into a Monte Carlo model as initial and boundary conditions. The two types of study displayed agreement. A coarsening of the grain structure of FKS platinum materials is not to be expected, even after very long operational times. It can be assumed that the properties of the material do not vary over time.

References

1 J.W. Martin, R.D. Doherty, *Stability of Microstructures*, Cambridge University Press, Cambridge 1976
2 Zener, personal communication to C.S. Smith, Trans. Met. Soc. AIME **175** (1949) 15
3 W. Bergmann, *Werkstofftechnik*, Teil 2, Anwendung, Hanser Verlag, Munich, 1991
4 R.D. Doherty, D.A. Hughes, F.J. Humphreys, J.J. Jonas, D.J. Jensen, M.E. Kassner, W.E. King, T.R. McNelley, H.J. McQueen, A.D. Rollett, Mater. Sci. Eng. **A238** (1997) 219
5 D. Raabe, Acta mater. **48** (2000) 1617
6 X. Song, M. Rettenmayr, submitted to Acta materialia
7 X. Song, M. Rettenmayr, C. Müller, H.E. Exner, Metall. Mater. Trans. **32A** (2001) 2199
8 X. Song, M. Rettenmayr, in print, Mat. Sci. Eng. A
9 X. Song, G. Liu, N. Gu, Mater. Sci. Eng. **A270** (1999) 178