

# Microstructure and Properties of Some Dispersion Strengthened Platinum Alloys

## THE INFLUENCE OF YTTRIUM AND ZIRCONIUM ADDITIONS

By Qiaoxin Zhang, Dongming Zhang and Shichong Jia

Advanced Materials Institute, Wuhan University of Technology, Wuhan, China

and Wulin Shong

Department of Materials Engineering, Huazhong University of Science and Technology, Wuhan, China

*The effect of adding very small amounts of yttrium and zirconium to platinum alloys has been investigated. The results indicate that a platinum alloy which contains both elements has a higher recrystallisation temperature and superior mechanical properties than a platinum alloy containing only zirconium. In addition, the platinum alloy which contains both yttrium and zirconium has a stable structure in which regular second phases have been found both in the grains and on the grain boundaries.*

Platinum has excellent properties when used at high temperatures in oxidative atmospheres, although its industrial application is restricted by its relatively low strength. In order to improve its strength, rhodium was initially used as a strengthening element at contents less than 20 to 25 per cent (1). Since the 1970s, ZGS platinum (2) and ODS platinum have been developed; these being strengthened by well dispersed additions of zirconium oxide,  $ZrO_2$ , and yttrium oxide,  $Y_2O_3$ , respectively. The ZGS platinum and ODS platinum alloys have much improved properties, but their processing technologies have to some extent limited their possible applications.

For this reason, we have studied the effects that two alloying elements, yttrium and zirconium, have on the properties of platinum. The alloys were made by the metallurgical method described below and the results were encouraging.

### Alloy Preparation and Experimental Methods

A mixture of platinum with yttrium and zirconium, having purities of 99.95, 99.9 and 99.9 per cent, respectively, were electron-beam melted in vacuum. The total weight fraction of zirco-

nium, or of yttrium and zirconium, was less than 0.7 weight per cent.

The ingot sized platinum-zirconium and platinum-yttrium-zirconium alloys were cold forged and rolled into sheets suitable for microstructural examination and also drawn into wires for mechanical testing. No annealing was done during these forming processes. However, to facilitate rolling it may be better to include an anneal.

The alloys were then annealed at various temperatures and later etched in a mixture of hot hydrochloric and nitric acids for measurement of the grain diameters.

### Microstructure and Stability of the Materials

The properties of these materials are determined by their microstructures. As shown in Figure 1, which is typical of many metals, the hardness of the platinum, platinum-zirconium and platinum-yttrium-zirconium alloys varied with the annealing temperature (annealing lasted for 0.5 hours) and decreased rapidly over the temperature range in which recrystallisation took place.

The hardness and also the recrystallisation temperature of the platinum-yttrium-zirconium

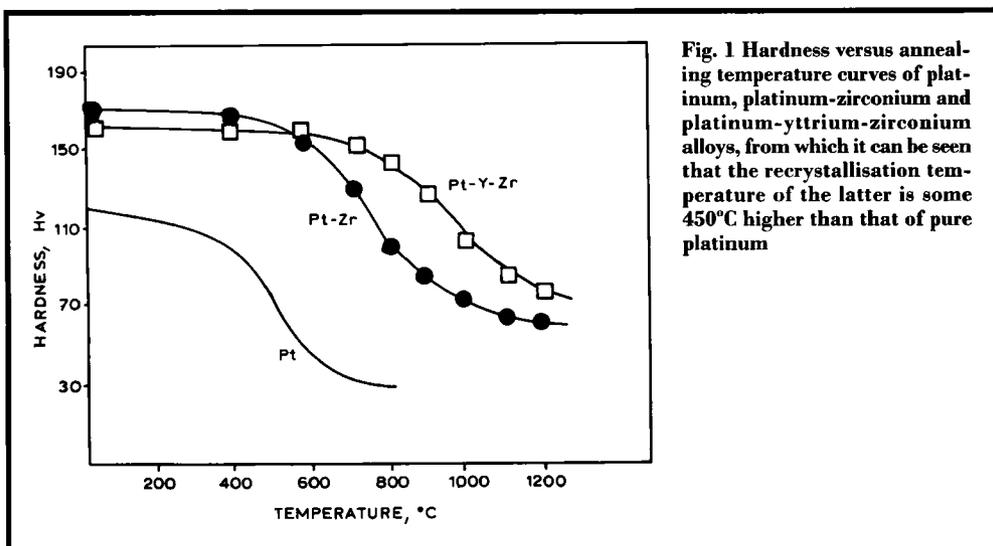


Fig. 1 Hardness versus annealing temperature curves of platinum, platinum-zirconium and platinum-yttrium-zirconium alloys, from which it can be seen that the recrystallisation temperature of the latter is some 450°C higher than that of pure platinum

alloy have higher values than those of platinum-zirconium. The hardness, Hv, of the platinum-yttrium-zirconium alloy annealed at over 1200°C is 72, and its recrystallisation temperature is approximately 450°C higher than that of pure platinum.

Microscopical analysis indicates that after annealing at 800°C for 0.5 hours recrystallisation of the platinum-zirconium alloy occurs, with a very small grain size but with the elongate structure resulting from rolling still visible in some areas; the platinum-yttrium-zirconium alloy does not show any recrystallisation. After annealing at 1000°C for 0.5 hours, the

grain size in the platinum-zirconium has grown significantly, and the platinum-yttrium-zirconium alloy has begun to recrystallise, but its grain size is still relatively small, see Figure 2.

When annealed at 1200°C for longer periods, the grain size of the platinum-zirconium changes substantially while the platinum-yttrium-zirconium grain size is little changed, as shown in Figure 3.

Therefore, it can be deduced that alloying platinum with both yttrium and zirconium gives superior structural stability compared with alloying platinum with zirconium alone. This is very important for materials employed at high

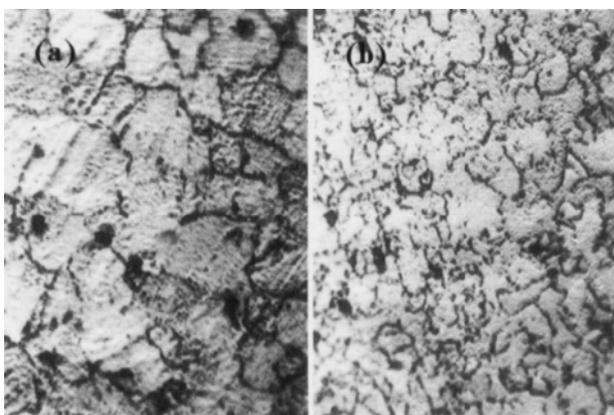
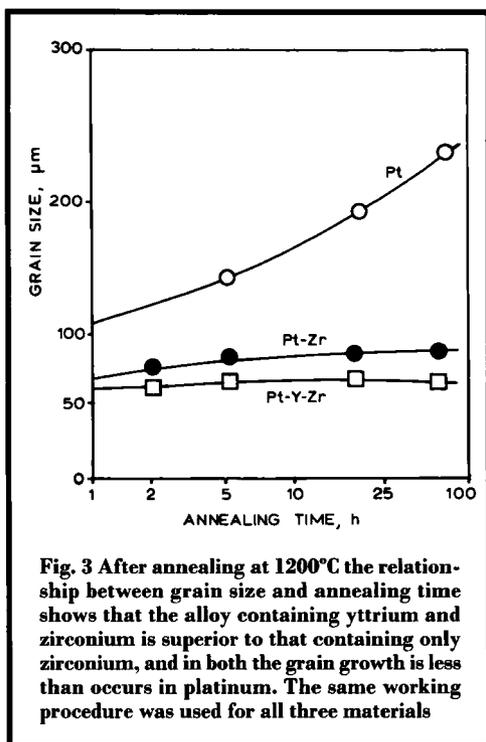


Fig. 2 Photomicrographs for platinum-zirconium and platinum-yttrium-zirconium after annealing at 1000°C for 0.5 hours. The grains of the latter are smaller:  
 (a) platinum-zirconium  
 (b) platinum-yttrium-zirconium  
 Magnification of (a) and (b) × 450



temperature. Additionally, it is considered that platinum-yttrium-zirconium is more stable than platinum-zirconium; the initial tendency to change is apparent in platinum-zirconium, but not in platinum-yttrium-zirconium.

The distribution of a second phase in platinum-zirconium and platinum-yttrium-zirconium alloys annealed at 1200°C is illustrated in Figure 4. The second phase in the platinum-zirconium, which exists mainly on the grain boundaries, was analysed using an Energy Analysing Electron Microscope and found to be a zirconium compound. The main compounds in the platinum-zirconium alloy system are PtZr, Pt<sub>2</sub>Zr and Pt<sub>3</sub>Zr, and these are formed when the platinum alloy contains more than 3 per cent zirconium (4).

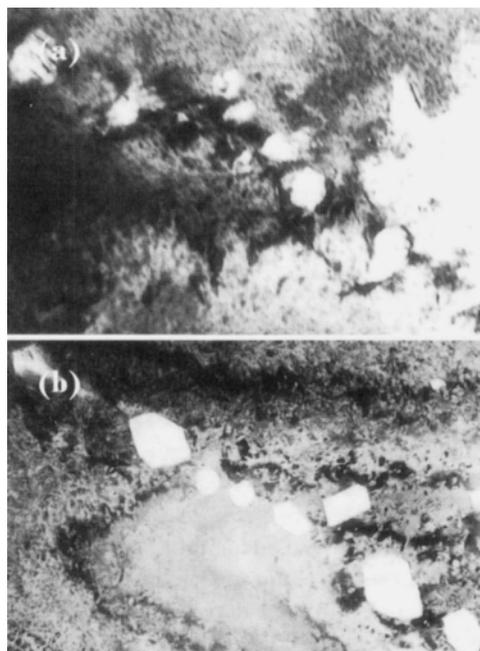
However, as the amount of zirconium in the platinum-zirconium alloy which we were investigating was less than 0.7 per cent, the compound was not likely to be any of these three platinum-zirconium compounds. It may be reasonable to deduce that the zirconium compound

in our platinum-zirconium alloy is zirconium oxide formed during processing. In addition to this zirconium oxide on the grain boundaries, the platinum-yttrium-zirconium alloy also has some regular shaped particles of an yttrium and zirconium compound distributed within the grain.

These particles, which are only tens of nanometres in size, have not yet been studied, but are likely to improve creep resistance and high temperature stability. This is to be the next step of our work.

### Physical Properties of the Materials

The resistivities of platinum-yttrium-zirconium and platinum-zirconium alloys are a little higher than that of pure platinum, while their elongations are slightly less. However, their hardnesses and strengths are greatly improved compared to platinum, especially the high temperature strength and the creep resistance of the platinum-yttrium-zirconium alloy, see the Table.



**Fig. 4** Distributions of the second phase in platinum-zirconium and platinum-yttrium-zirconium alloys after annealing at 1200°C:

- (a) platinum-zirconium alloy × 60,000  
 (b) platinum-yttrium-zirconium alloy × 72,000

<b>Properties of Platinum, Platinum-Zirconium, Platinum-Yttrium-Zirconium and Platinum-10 per cent Rhodium Alloys (3, 5)</b>				
	Pure Pt	Pt-Zr	Pt-Y-Zr	Pt-10%Rh
Resistance at 20°C, $\mu\text{cm}$	10.6 (3)	12.46	12.42	18.4 (3)
TCR*/°C; mean 1~100°C	0.0039 (3)	0.0017	0.0011	0.0017 (3)
Tensile strength, UTS, MPa (annealed)	124 (3)	278	283	330 (3)
Elongation, per cent, (annealed)	40 (3)	36	35	35 (3)
Hardness, Hv (annealed)	40 (3)	65	72	75 (3)
UTS at 1200°C, MPa	35.2 (5)	40.0	44.6	58.8 (5)
Rupture time, at 1200°C, 25 MPa, h	11.5 (5) (at 4.9 MPa)	3	7.6	307 (5) (at 4.9 MPa)

\* TCR: Temperature coefficient of resistance

The values for hardness given in the Table were measured on sheet; all the other values in the Table were determined using wire samples. The strength of the alloys increases with increases in the total volume fraction of yttrium and zirconium, but the elongation decreases.

The stress-rupture life for platinum-yttrium-zirconium at 1200°C and 25 MPa is similar to that of platinum-10 per cent rhodium alloy at 1000°C. Further work on stress rupture and creep data is presently being undertaken.

The following three factors are believed to result in the properties of the platinum-yttrium-zirconium alloy being superior to those of platinum-zirconium.

#### [a] Solution Strengthening

The difference in the atomic radii between platinum (1.38Å) and zirconium (1.579Å) is less than that between platinum and yttrium (1.797Å), so the platinum-yttrium-zirconium lattice is more distorted than the platinum-zirconium lattice, which results in increased hardness.

The difference in electronegativity between platinum (2.2) and zirconium (1.4) is less than that between platinum and yttrium (1.2), so the bond forces and the polarisation effect in platinum-yttrium-zirconium are greater; this improves the high temperature strength (6). This is a special effect that occurs in alloys containing very small additions of alloying elements.

The interaction between zirconium and rare

earth yttrium dissolved in platinum increases the alloy strength more than yttrium alone in the platinum-yttrium alloy.

#### [b] Dispersion Strengthening

The second phase in platinum-yttrium-zirconium, distributed on the grain boundaries and also in the grains, improves the high temperature strength and the creep resistance.

#### [c] Boundary Strengthening

Compared with zirconium, yttrium is more inclined to deposit on the grain boundary, causing impaired boundary diffusion and migration (7). Therefore, it is more effective for platinum to be alloyed with small amounts of zirconium and the rare earth yttrium, than it is to be alloyed with the same amount of zirconium alone.

### Conclusions

The addition of very small amounts of yttrium and zirconium to platinum makes the platinum alloy structure more stable and greatly improves the recrystallisation temperature. The second phase distributed on the grain boundaries and within the grains improves the high temperature strength and creep resistance.

These additions of yttrium and zirconium improve the properties of platinum at both room and elevated temperatures, and alloying with the two elements is more effective than alloying only with zirconium.

## References

- 1 A. S. Darling, G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1968, 12, (1), 7
- 2 G. L. Selman, J. G. Day and A. A. Bourne, *Platinum Metals Rev.*, 1974, 18, (2), 46
- 3 G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1976, 20, (3), 86
- 4 Chunxiao He and Guangchen Ma, "Equilibrium Diagram for Precious Metal Alloys", Metallurgical Industry Press, Peking, China, 1983
- 5 Y. Ning, *Precious Met. (China)*, 1984, 5, (2), 42
- 6 T. T. Kou, Wenhui Shu and Shouyu Dai, *Acta Sci. Nat. Univ. Jilinensis*, 1962, (1), 177
- 7 Kunyu Zhao and Dingxin Li, *Precious Met. (China)*, 1993, 14, (2), 9

# Modelling Techniques for Catalyst Development

## Computer-Aided Design of Catalysts

EDITED BY E. ROBERT BECKER AND CAMO J. PEREIRA, Marcel Dekker Inc., New York, 1993, 640 pages, ISBN 0-8247-9003-0, U.S.\$195.00

This book is the 51st in an occasionally excellent series on the chemical industries, and while it has its limitations it is nevertheless a valuable addition to the collection. The series consists of assembled chapters on a theme contributed by distinguished professionals. As such the volumes often lack coherence and stand or fall on the excellence of the contributions and the timeliness of the theme. This book is certainly timely as the use of computing methods in catalysis is growing rapidly. Computer aided design can mean different things; here the editors define it as "the process of selecting catalyst properties that ..... optimise the reactor performance". The emphasis on choosing catalyst properties means that there is very little on the design of new catalysts in this book. Rather the chapters deal with the methods for the measurement and modelling of catalyst parameters and the application of these methods in various industrial processes. Also missing is any attempt to discuss the modelling and economics of entire processes and plants; the emphasis is firmly on the performance of the reactor section.

The early chapters deal with modelling methods, such as: selectivity patterns in methane partial oxidation; modelling complex mixtures in catalytic cracking using carbon centre methods; Monte Carlo simulations for complex hydro-treating mixtures; pore diffusion models; catalyst pellet impregnation profiles and catalyst wetting effects on multiphase reactions. Later chapters concentrate on particular applications, such as Fischer-Tropsch catalysts, automobile catalysts including transient behaviour in monolith reactors; polymerisation catalysts; membrane reactors and petroleum refining. Platinum group metals feature here most directly, particularly platinum, palladium and ruthenium.

The chapter on the design of Fischer-Tropsch catalysts by E. Iglesia, S. C. Reyes and S. L.

Soled, compares cobalt and ruthenium catalysts in the context of models which combine transport processes and elementary kinetics, and concludes that selectivity is dominated by the transport processes rather than by the nature of the active sites.

Chapters on modelling for automotive emission control by S. H. Oh, and design of monolithic catalysts for improved transient reactor performance by K. Zygourakis, use platinum catalysts as the basis for a discussion of modelling in car exhaust systems. Oh reviews his outstanding work and shows that even with many simplifying assumptions useful predictions as to catalyst loadings and performance may be obtained. The application of this approach to heated catalysts was discussed at the recent North American Catalysis Society meeting. The importance of 2-dimensional modelling for problems such as flow maldistribution and other transient effects is dealt with at greater length by Zygourakis.

Palladium features most extensively in a chapter on catalytic membrane reactors by T. T. Tsotsis, R. G. Minet, A. M. Champagnie and P. K. T. Liu. This topic has a long history and remains popular due to the inherent elegance of controlling reactant addition or product removal by a selective membrane. However large scale applications await the development of membranes that are thin enough and robust enough for the demanding conditions of most petrochemical processes.

This book is a useful contribution to bridging the gap between chemical engineers and chemists in the field of catalyst and reactor design. While individual chapters may disappoint specialists on any given topic, together they provide a valuable introduction to the area and can be read profitably by non specialists; the book will be of use in advanced education. J.C.F.