

# The Transition Layer in Platinum-Alumina

THE MORPHOLOGY AND PROPERTIES OF THE LAYER IN CRUCIBLES BETWEEN METAL AND CERAMIC

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*Platinum-based composites are potential materials to substitute for platinum in some applications, for example, for containers in which to grow single crystal oxides. Ceramic coated platinum is the best material for crucibles as: first, the cylindrical geometry is suitable for coating with ceramic; second, the ceramic coating carries the basic mechanical loading, with the platinum acting both as the heater and anticorrosive coating; and third, refining this secondary platinum for recycling is neither a complicated nor expensive procedure. Plasma evaporation of alumina onto platinum is a technology that can be successfully applied to manufacturing commercial composite containers. In this paper the problem of cohesive strength between Pt and  $Al_2O_3$ , and the morphology and properties of the transition layer between the metallic matrix and the ceramic will be discussed.*

As a container material for growing single crystals, platinum has to perform three functions:

[a] it must be inert to the scrap materials from crystal making;

[b] as the metallic cylinder it must serve as the heater during induction melting; and

[c] as the container material it must retain its optimal shape (generally cylindrical).

Experience has shown that it is the third function (retaining the optimal shape to determine the mechanical strength of the container) which requires the maximum amount of platinum. The container wall thickness is not important for func-

tions [a] and [b], especially for [a] (1).

This paper describes how the mechanical strength of the containers can be increased – not by increasing the thickness of the platinum – but by using platinum-based composites as the structural material (2, 3). Ceramic-coated platinum is a potential high-temperature material for this use, as it allows crucibles to be manufactured with less platinum, but in similar sizes and with improved properties (4, 5).

The evaporation of ceramic onto metal by plasma methods may be considered an appropriate commercial technology due to its simplicity and

*Fig. 1 Composite Pt- $Al_2O_3$  crucibles; these are manufactured by direct plasma evaporation of the ceramic onto the metallic substrate.*

*The crucibles can have a diameter up to 170 mm with either a flat or spherical base*

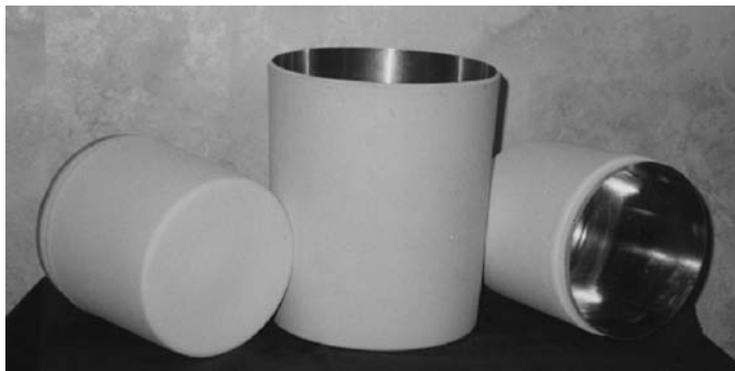


Table I

Vicker's Microhardness of the "Platinum" Side Opposite to the "Transition Layer" Side in the Initial State and after Mechanical Testing of Metallic Samples Cut from Workpieces of Platinum-Alumina Crucibles at Different Stages of Manufacture

Material, state tested	Initial state, MPa	Tension at 20°C, MPa	Creep at 1300°C, $\sigma = 50$ MPa		Creep at 1300°C, $\sigma = 70$ MPa		Creep at 1300°C, $\sigma = 90$ MPa	
			grip, MPa	fracture, MPa	grip, MPa	fracture, MPa	grip, MPa	fracture, MPa
Pt	7.4	8.7	5.6	5.6	5.6	5.6	5.6	5.6
Pt <sub>sanded</sub>	7.4	8.9	5.6	6.6	7.1	5.9	6.9	7.4
Pt+Cer	9.7	9.7	5.9	5.0	5.2	5.5	6.1	7.0
Pt+Cer+An	6.9	8.9	6.1	6.3	6.1	7.4	7.1	7.4

resulting lower costs (6). The composite crucibles, shown in Figure 1, can be produced by a process that includes four steps (7):

- The first step is the manufacture of platinum crucibles that serve as the substrates for the evaporation of ceramic. A crucible is fabricated from rolled platinum (Pt) sheet and can be up to 170 mm in diameter with a flat or spherical base.
- The second step is to process the crucible using alumina particles under pressure or "sanding" (Pt<sub>sanded</sub>). This forms a deep relief on the platinum surface.
- In the third step the ceramic (Cer) (in this case Al<sub>2</sub>O<sub>3</sub>) is applied to the crucible surface by plasma evaporation (Pt+Cer).
- The final step is a stabilising anneal (An) of the alumina coating at 1250°C for 2 hours in air (Pt+Cer+An).

Contrary to expectations, the cohesive strength of such a platinum-alumina join is very strong. The coating does not separate from the platinum even, for instance, after using a composite crucible for 7000 hours to grow PbWO<sub>4</sub> single crystals. Also, the appearance of cracks in the ceramic did not lead to separation of the coating from the substrate.

Using plasma technology therefore provides a join of high cohesive strength, but the reason for this high cohesive strength is not yet understood, and the nature of the cohesion mechanism between the Pt and Al<sub>2</sub>O<sub>3</sub> is not clear. In this paper the morphology of the transition layer at the interface between the metallic matrix and the ceramic

coating, and the effects of this layer on the mechanical properties of platinum will be considered.

## Experimental Procedure

It is well known that the adhesion characteristics of plasma coatings depend strongly on the geometry of evaporation (or shape of the metallic substrate) (6). In addition, the stress state of a cylindrical surface is different to that of a layered parallelepiped of comparable width and thickness (8). Hence, data obtained from ceramic coated flat samples would not explain the behaviour of a composite cylindrical container. Therefore, such laboratory samples of Pt-Al<sub>2</sub>O<sub>3</sub> composite were not made for testing. Instead, test samples were cut from the platinum substrate of composite containers (wall thickness 0.5 mm) taken during the four stages of manufacture: Pt, Pt<sub>sanded</sub>, Pt+Cer and Pt+Cer+An. These samples had a standard "double spoon" shape with a working area of 20 × 3 mm<sup>2</sup>. The ceramic layer (3 mm thick) was separated from the metallic matrix prior to cutting the samples, as it was impossible to cut samples from a 'metal-ceramic' crucible. Similar metallic samples were also taken from containers which failed in use. Both the back surfaces of the samples ("platinum" and "transition layer" sides) were studied in detail in their initial states by optical and scanning electron microscopes (SEM). Tensile tests were carried out in a regime of semi-creep when the traverse rate was very slow: 0.1–1 mm h<sup>-1</sup> (applied stresses of 50, 70 and 90 MPa) at 1300°C in air,

while some of the samples were stretched at room temperature (at a traverse rate of  $1 \text{ mm min}^{-1}$ ). After that, their back and fracture surfaces were again studied.

Clearly, the information obtained cannot directly characterise the mechanical behaviour of a Pt- $\text{Al}_2\text{O}_3$  composite container, but it can allow an understanding of the adhesive mechanism between the platinum and the alumina coating.

### Morphology of the Transition Layer between Pt and $\text{Al}_2\text{O}_3$

As the platinum crucible has been pressed out of rolled sheet without intermediate recrystallisation annealing, the platinum substrate is in a deformed state, see Table I. Treating this platinum surface with alumina particles ( $\sim 300 \mu\text{m}$  in size) leads to the appearance of a relief consisting of approximately flat areas oriented to the substrate plane at arbitrary angles. The shapes and sizes of these regions are similar to those of the alumina particles used for sanding the platinum. The depth of the relief ( $\sim 30 \mu\text{m}$ ) also correlates with the particle size, as long as the work-hardening of the platinum, which prevents the alumina particles from penetrating into the metallic matrix, is taken into account. There are two kinds of alumina inclusions in the sanded platinum: large and small. On SEM images, they appear as dark regions, see Figure 2(a). The dimensions of the large inclusions,  $\sim 20\text{--}30 \mu\text{m}$ , correspond to the pyramidal ends of alumina particles used for sanding. Therefore, the large inclusions may be considered to be the sharp tips of particles which have been stuck into the metallic matrix.

The average size of the small inclusions is  $\sim 1 \mu\text{m}$ . Large and small inclusions are uniformly distributed on the surface; their positions are not connected with the distribution of surface defects caused by preliminary processing of the surface. Despite the appearance of the relief, sanding does not influence the microhardness of the “platinum” side of the samples because of the considerable thickness of the crucible walls (Table I).

After the evaporation of alumina and the separation of ceramic from the substrate, particles of  $\text{Al}_2\text{O}_3$  are observed on the platinum surface. The

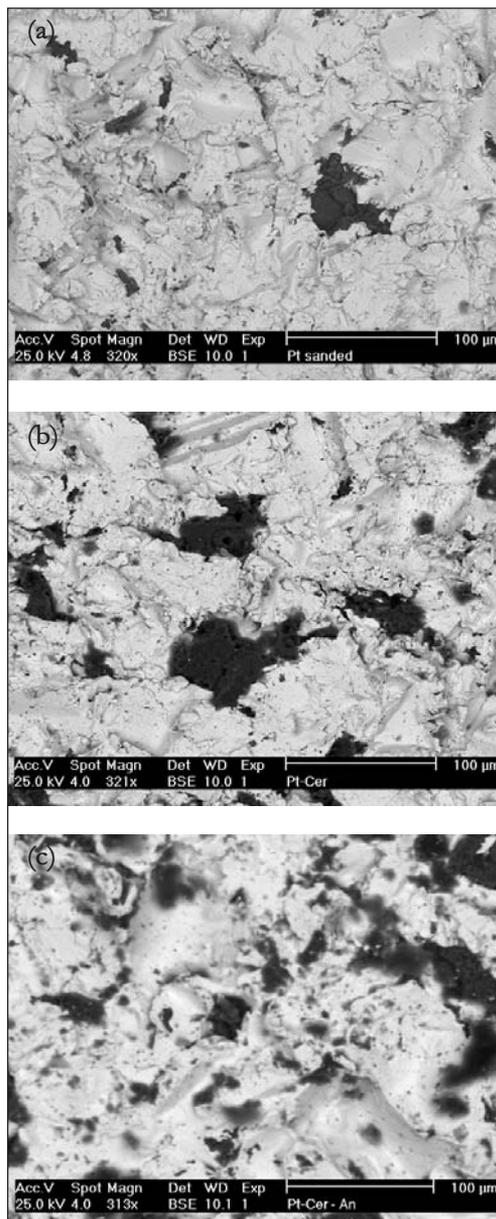


Fig. 2 Surface of the transition layer between Pt and  $\text{Al}_2\text{O}_3$  at different stages in the manufacture of composite containers:

- (a) *Pt<sub>sanded</sub> sample*
- (b) *Pt + Cer sample*
- (c) *Pt+Cer+An sample*

Black areas are  $\text{Al}_2\text{O}_3$  particles inserted into platinum

average size of the large inclusions has increased to  $\sim 50 \mu\text{m}$ , see Figure 2(b), although their quantity per unit area of surface remains the same. By contrast, the dimensions and concentration of the

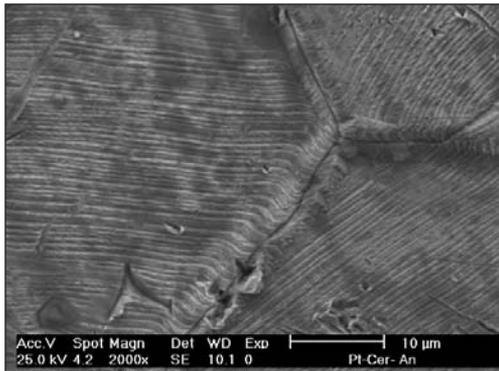


Fig. 3 The coarse grained structure of the platinum surface in a composite crucible after a stabilising anneal (1250°C for 2 hours, in air) at the Pt-Cer-An stage

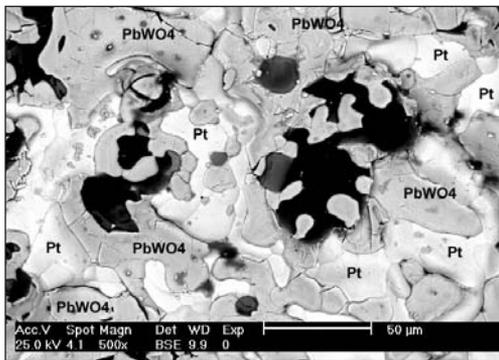


Fig. 4 Scrap ( $PbWO_4$ ) areas in the transition layer between Pt and  $Al_2O_3$  of a damaged composite crucible

small inclusions have not changed. The microhardness of the “platinum” side in the Pt+Cer samples has considerably increased, see Table I.

The stabilising anneal of the ceramic has no influence on the size of both kinds of alumina inclusions or their distribution on the surface, but “jogs” on the surface becomes round or fused, see Figure 2(c). However, the microhardness of the “platinum” side has decreased in comparison with the Pt and Pt<sub>sanded</sub> samples (Table I). A coarse grained structure, in which all the crystallites are in the deformed state, appears on the “platinum” side, see Figure 3, while features of recrystallisation, such as grain boundaries or a new kind of relief, do not appear on the rough “transition layer” side. After evaporation of the ceramic and its stabilising anneal, the character of the distribution of the alumina inclusions on the surface remains the same.

The results obtained are important for understanding the cohesion mechanism between platinum and alumina in composite crucibles manufactured by plasma technology. The main feature is the “point”, “fragmentary” or “discontinuous” contact of the  $Al_2O_3$  with the transition layer (9). Because of such a join, both the environment and the melted scrap could percolate between the metal wall and the ceramic coating, see Figure 4. However, this circumstance does not affect the usefulness of the containers. Indeed, the scrap never chemically reacts with the walls of the crucible, and the level of mechanical stress due to scrap percolation between wall and coating is not sufficient to break the cohesion of the join. Moreover, experience has shown that separating the ceramic from the platinum in used crucibles requires as much effort as in new ones, and the number and size of the large alumina inclusions in the platinum is the same in both cases. It should be particularly noted that small inclusions of alumina are absent on the samples.

The alumina particles either do not chemically react with platinum, or, if reactions do occur then the region where it happens is so thin that it cannot be detected by conventional SEM or X-ray techniques. Therefore, the join between the platinum and alumina may be considered as

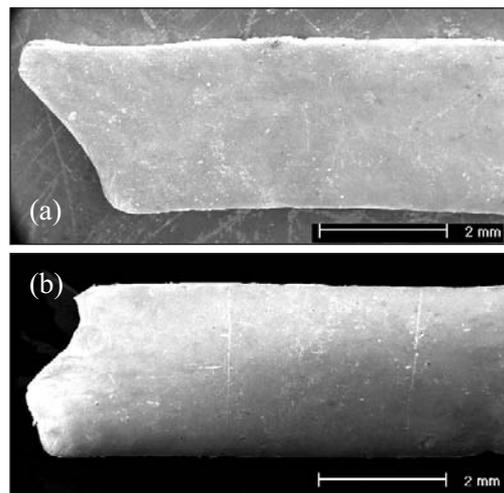


Fig. 5 The back surfaces (“platinum” side) of samples after tension at 20°C: no necking is observed: (a) Pt sample; (b) Pt+Cer+An sample

“mechanical” when the sharp ends of the ceramic particles penetrate into and remain in the metallic matrix. The large inclusions serve as anchors for the ceramic coating which “glues” to them during plasma evaporation. No joining of alumina to platinum is revealed in other places, although the ceramic replicates in detail the surface of the transition layer. The increase in size of the large inclusions, the preservation of their numbers and character of distribution on the surface after evaporation of the ceramic agree with this supposition. On the other hand, small inclusions can play the role of second phase particles which increase the yield stress of the metallic matrix by blocking dislocation motion as it takes place in dispersion strengthened metals.

### Mechanical Properties of Platinum with a Transition Layer on the Surface

Identical mechanical behaviour is inherent in all the materials: Pt, Pt<sub>sanded</sub>, Pt+Cer, Pt+Cer+An at room temperature (10). Samples fail after ~ 3–5% elongation, and no necking is observed on their back surfaces, see Figure 5. Localisation of plastic deformation takes place near fracture surfaces, but happens in a very narrow region, see Figure 6. This is very unusual behaviour for a pure f.c.c. metal, which should have high plasticity (11). On the other hand, analysis of fracture surfaces (where necking to a line occurs even in the most strength-

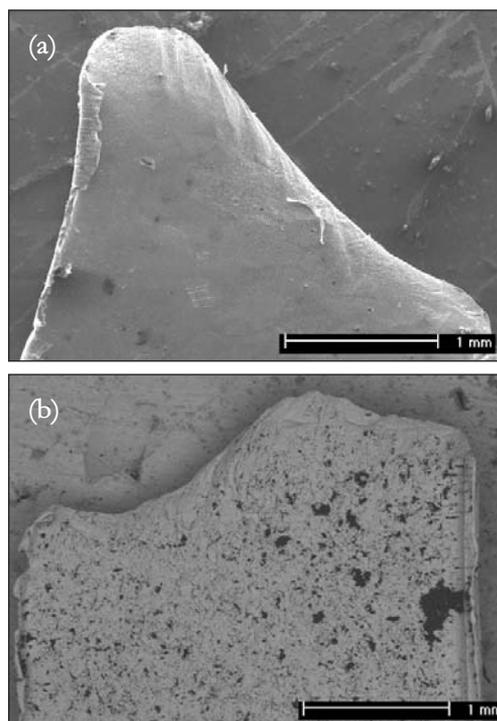


Fig. 6 Back surfaces near the fracture place of the samples after tension at 20°C: (a) Pt sample; (b) Pt+Cer+An sample (“transition layer” side)

ened material, such as Pt+Cer, see Figure 7) shows that all the samples are in a ductile state. The results for the Pt samples (Table II) confirm metallographic observations and measurements of

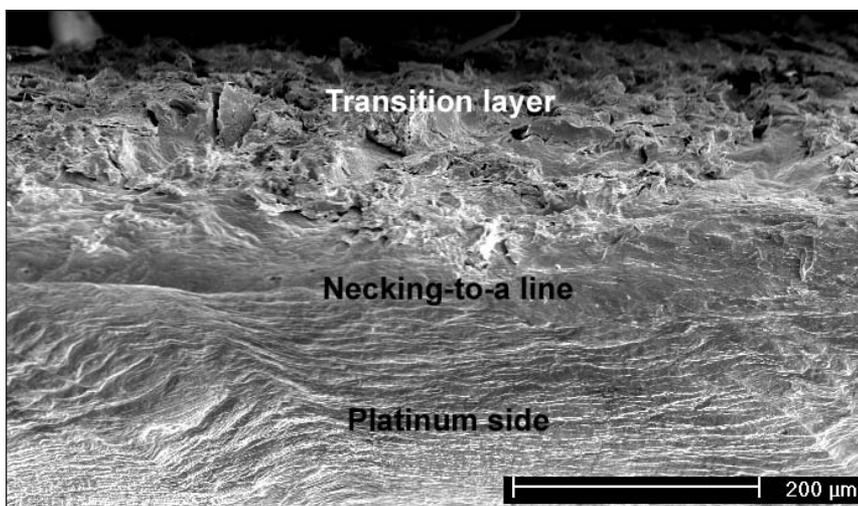


Fig. 7 Fracture surface of a Pt+Cer sample after tension at 20°C. This sample shows the material is in a ductile state – as analysis of all the fracture surfaces has shown

Table II Mechanical Properties of the Platinum Matrix at Different Stages of Preparation of "Pt-Al <sub>2</sub> O <sub>3</sub> " Composite					
Material	Yield stress ( $\sigma_{0.2}$ ) at 20°C, MPa	Strength ( $\sigma_B$ ) at 20°C, MPa	Creep-rupture life at 1300°C, $\sigma = 50$ MPa, hours	Creep-rupture life at 1300°C, $\sigma = 70$ MPa, hours	Creep-rupture life at 1300°C, $\sigma = 90$ MPa, hours
Pt	55	155	18	4	1.5
Pt <sub>sanded</sub>	100	170	18	4	2
Pt+Cer	130	235	10	1.5	1
Pt+Cer+An	65	160	13	3	1.5

microhardness, indicating that the metallic matrix had been hardened before test: yield stress is 55 MPa.

Sanding the platinum increases the yield stress by a factor of two (100 MPa), but has practically no effect on the strength and microhardness of the Pt<sub>sanded</sub> samples (170 MPa and 8.9 MPa, Table II and Table I, respectively) in comparison with Pt samples. This is normal behaviour for f.c.c. metals, as the volume of a sample generally determines its strength, while the surface makes a significant contribution to the yield stress of a metallic sample. In practice, the sanded surface does not change its morphology up to the fracture area, and the alumina inclusions disappear only in the vicinity of the fracture surface because of local plastic flow of the material, see Figure 6(b). Evaporation of ceramic

causes a big rise in the microhardness (9.7 MPa, Table I) and yield stress (130 MPa, Table II) in the Pt+Cer samples, and in doing so the strength of the material increases by  $\sim 100$  MPa, as in the Pt samples and the Pt<sub>sanded</sub> samples, while the microhardness of their "platinum side" after mechanical test remains the same (9.7 MPa, Table I). A stabilising anneal decreases the initial microhardness and yield stress for Pt+Cer+An samples (6.9 MPa and 65 MPa, respectively). After tensile testing, this parameter becomes 8.9 MPa and the strength reaches 160 MPa, respectively. Despite differences in some mechanical properties ( $\sigma_{0.2}$ ,  $\sigma_B$  and  $H_V$ ), the morphology of the fracture and back surfaces of the Pt+Cer and Pt+Cer+An samples does not change.

Observation of the behaviour of the samples at 1300°C in air has shown that they are typical of

f.c.c. metals at high temperatures: the applied stress and roughness of the back surface determine the creep-rupture life ( $\tau_{life}$ ) of the sample under load (11). In practice, at high stress (90 MPa), the  $\tau_{life}$  and the morphology of the back surface near the fracture zone do not depend on the type of material

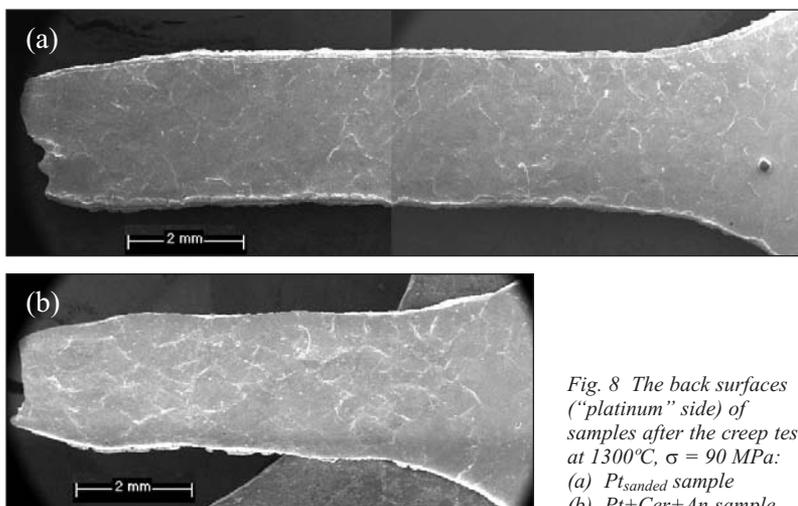


Fig. 8 The back surfaces ("platinum" side) of samples after the creep test at 1300°C,  $\sigma = 90$  MPa: (a) Pt<sub>sanded</sub> sample (b) Pt+Cer+An sample

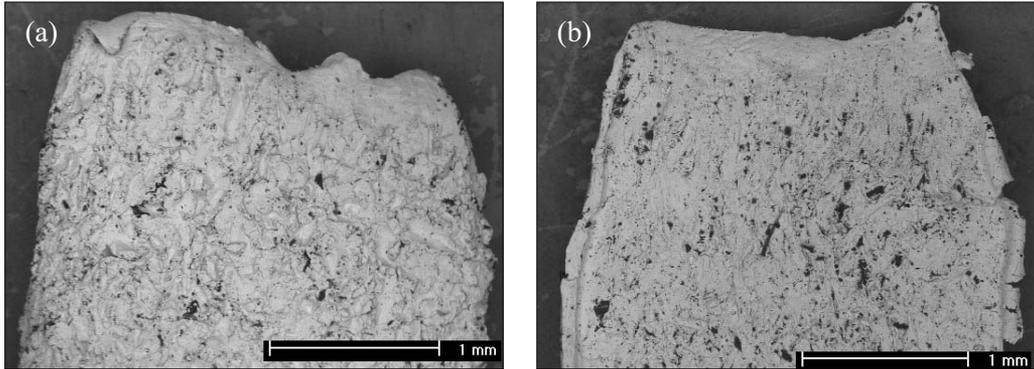


Fig. 9 The back surfaces near the fracture place after creep tests at 1300°C,  $\sigma = 90$  MPa: (a)  $Pt_{sanded}$  sample (b)  $Pt+Cer+An$  sample

(Table II, and Figures 8 and 9). Lowering the applied stress increases the sensitivity of  $\tau_{life}$  to the state of the surface layer (Figures 10 and 11). For

example, the size and number of neck regions in the samples start to grow at middle and low applied stresses. This causes an increase in the area

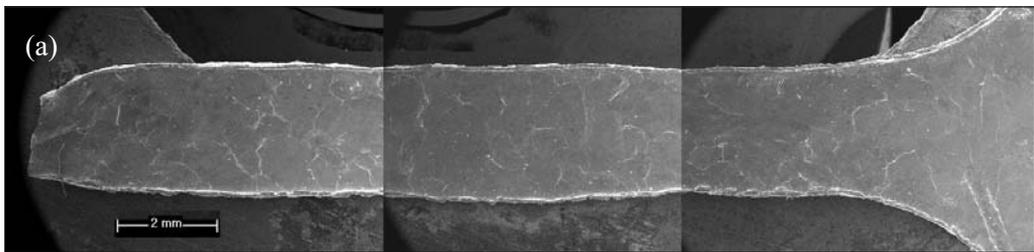


Fig. 10 The back surfaces ("platinum" side) of Pt samples with transition layer after the creep test at 1300°C,  $\sigma = 70$  MPa: (a)  $Pt_{sanded}$  sample (b)  $Pt+Cer+An$  sample

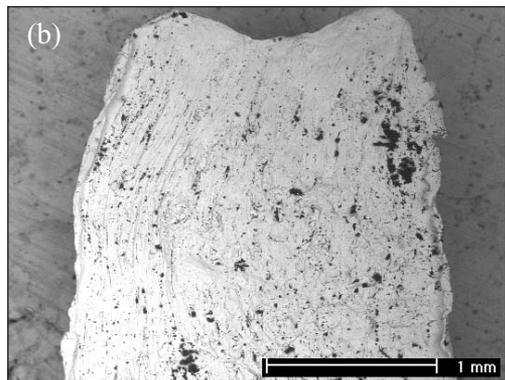
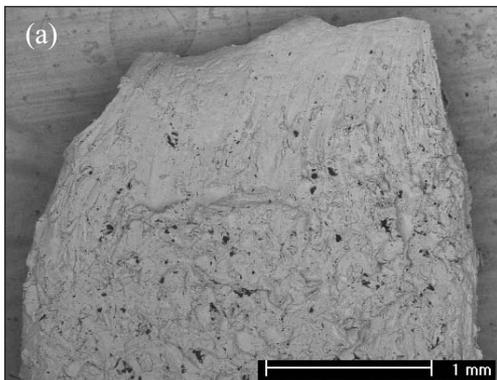
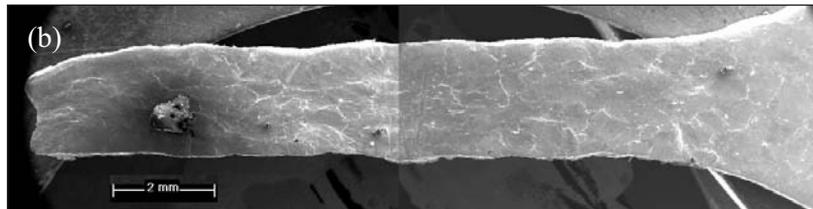
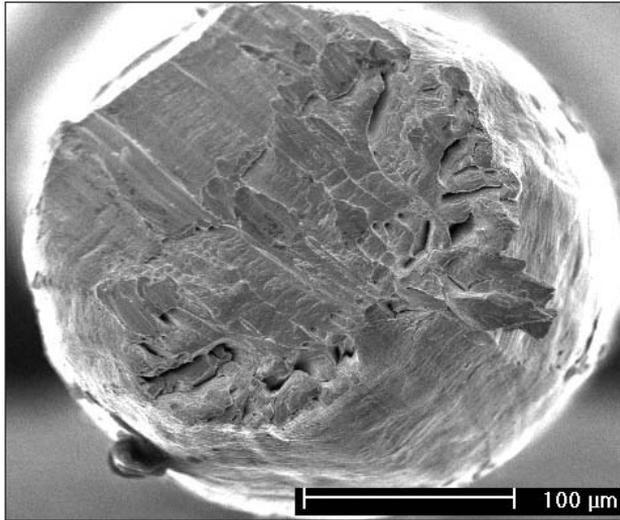


Fig. 11 The back surfaces near the fracture place after creep test at 1300°C,  $\sigma = 70$  MPa: (a)  $Pt_{sanded}$  sample; (b)  $Pt+Cer+An$  sample



*Fig. 12 The fracture surface of dispersion strengthened platinum-alumina wire (creep test in air at 1300°C).*

*At this elevated temperature dispersion strengthened platinum shows necking on the back surface but transcrystalline cleavage on the fracture surface. (The black mark, lower left on the specimen is detritus)*

near the fracture zones where alumina inclusions are absent. The  $\tau_{life}$  for Pt at 70 MPa and 50 MPa (4 and 18 MPa, respectively) are more than 1.5–2 times greater than for Pt+Cer and Pt+Cer+An samples though are the same as the Pt<sub>sanded</sub> samples which also have rough surfaces with implanted alumina particles.

Thus, the geometrical characteristics of the surface relief and the distribution of alumina inclusions are the same in all three cases. This effect is connected with the structure of the surface layer in the samples, where the deep relief and the second phase inclusions (here, Al<sub>2</sub>O<sub>3</sub> particles) induce the fracture process, including the localised plastic deformation in the platinum matrix. The difference between Pt+Cer, Pt+Cer+An and Pt<sub>sanded</sub> samples may be explained by the fact that in the first two materials (Pt+Cer and Pt+Cer+An) the transition layer is dispersion strengthened platinum, which displays high strength and semi-brittle fracture mode at high temperatures, see Figure 12, whereas in the Pt<sub>sanded</sub> material the surface layer only contains mechanically penetrated alumina particles. Indeed, the regime of heating the platinum substrate during evaporation of alumina is similar to that of the temperature treatment of platinum strengthened by oxide particles. Despite this, the fracture surfaces of all the samples investigated at high temperature have the same morphology attested earlier as necking to a line.

## Discussion

These experiments have shown that the transition layer between the platinum and the alumina coating (30  $\mu\text{m}$  in depth) is formed in stages by sanding and plasma evaporation of ceramics. The transition layer contains small ( $\sim 1 \mu\text{m}$ ) and large ( $\sim 20\text{--}50 \mu\text{m}$ ) alumina inclusions and possesses a rough surface on the ceramic side. The Al<sub>2</sub>O<sub>3</sub> particles have penetrated into the platinum matrix during the sanding stage, but this treatment has not changed the mechanical behaviour of the platinum either at room or elevated temperatures.

Differences begin to show only after the evaporation of alumina, when the sanded surface has been heated to a temperature close to the alumina melting point then cooled very quickly to 300–400°C. Performing a stabilising anneal is important for the mechanical properties of the alumina coating. However, its influence on the morphology and properties of the transition layer is negligible. In performing a stabilising anneal it should be noted that the surface layer, enriched by oxide particles, causes plastic deformation in the recrystallised grains of platinum.

## Dispersion Strengthened Platinum

An assumption that the transition layer is a thin film of dispersion strengthened platinum can explain the results. Indeed, the properties of dispersion strengthened metals do not depend on

annealing after oxide particles have been formed (2, 3), and the inclusions are permanent sources of thermomechanical stress, which induce plastic deformation in the metallic matrix. The thermal stability and high strength of the dispersion strengthened surface layer also become apparent under middle and low tensile stresses at high temperature. Due to these, the lifetimes of the Pt+Cer and Pt+Cer+An samples decrease compared to the sanded platinum.

The thin film of dispersion strengthened platinum, between the metallic matrix and the ceramic coating, with its rough surface containing large Al<sub>2</sub>O<sub>3</sub> inclusions, can explain the high cohesive strength of the join between the platinum and alumina. The evaporated ceramic layer “glues” to these inclusions, while in other places it only covers the metal (without adhesion).

When the crucible is cooled, after a crystal-forming procedure has been completed, gaps appear in places between the ceramic and the metallic matrix; this is due to the difference in thermal expansivity for these materials: as the thermal expansivity for dispersion strengthened platinum is less than that for the pure metal. However, these gaps close during heating, when the container is being used, and the relief on the transition layer should facilitate the lowering of the cleaving stresses at the boundary between metal and ceramic (8).

As a result, the thermomechanical stresses are effectively suppressed due to the morphology of the transition layer, which forms simultaneously with plasma evaporation of the ceramic. Using these Pt-Al<sub>2</sub>O<sub>3</sub> composite containers has shown that such a metal-ceramic join is very resistant to the action of thermomechanical stress. However, it should be noted that growing single crystals is a process where the level of fatigue stress is minimal. Perhaps, this is a third reason for high cohesive strength in this join. An alumina coating would not be considered as suitable corrosion protection for a metallic substrate. However, this does not affect the service characteristics of these composite containers, as platinum, due to its high chemical inertness, does not need protection from either molten scrap or air.

## Acknowledgements

We would like to thank Vladimir Cheremnykh and Alexander Mazaletskii for their help in this work. The Russian Foundation for Basic Research supported part of this project.

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