

The Chemical Characterisation of Rhodium-Platinum Surfaces

CHANGES PRODUCED ON CATALYST GAUZES DURING PRETREATMENT AND AMMONIA OXIDATION

By A. R. McCabe

Johnson Matthey Technology Centre

and G. D. W. Smith

Department of Metallurgy and Science of Materials, University of Oxford

During the manufacture of nitric acid, rhodium-platinum gauzes are used to catalyse the oxidation of ammonia, an operation that results in a major reconstruction of the alloy surface. In this study, the effect of pretreatments, similar to those employed to prepare the catalysts for commercial use, have been examined to determine both the chemical and the physical effects on the surface. A successful pretreatment is shown to produce a generally clean, chemically receptive surface containing reactive crystal orientation sites. Additionally, the nature of the surface during catalyst operation has been investigated using a rapid quench facility in a miniature reactor. It has been established that, during catalyst operation, the surface of the catalyst is metallic, and not covered by an oxide layer as previously thought.

The complex surface structural changes that occur on rhodium-platinum alloy catalysts when exposed to ammonia-air gas mixtures have been the subject of a number of papers (1-5). One such study followed in detail the nucleation and growth of the large scale cage-like features which are formed, concluding that a vapour phase mechanism involving the transport of platinum oxide was responsible for the observed physical reconstruction (6). The operation of this process over a limited range of temperature and pressure was also explained.

The chemical characterisation of the catalyst surface is, however, far less complete. In particular, the necessity for the catalyst to undergo an activation pretreatment process prior to insertion in a commercial plant is not well understood, and no conclusive evidence has been presented as to whether the operational catalyst surface is metallic or oxidic in nature. We have looked at these areas using a range of high resolution microscopical and surface

microanalytical techniques, and report on the surface chemical changes occurring on the catalyst.

Activation trials and the exposure of 10 weight per cent rhodium-platinum gauze samples and field ion microscopy (FIM) catalyst needles to a variety of reaction conditions were carried out in a miniature catalytic reactor. The reactor, details of which have been reported previously (6), includes the facility to either air cool or quench the reaction by applying a backpressure of argon gas. Use was also made of a pilot plant at Johnson Matthey, Materials Technology Division, Wembley (7).

The FIM-Atom Probe facilities at Oxford University (8) were used to establish the surface chemical and structural changes taking place during the reaction. Further analysis was carried out by photoelectron spectroscopy (XPS), and by electron probe microanalysis using both energy dispersive (EDX) and wavelength dispersive (WDX) methods. XPS was well

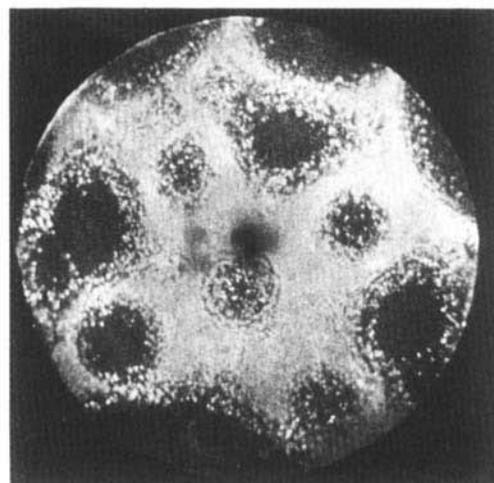
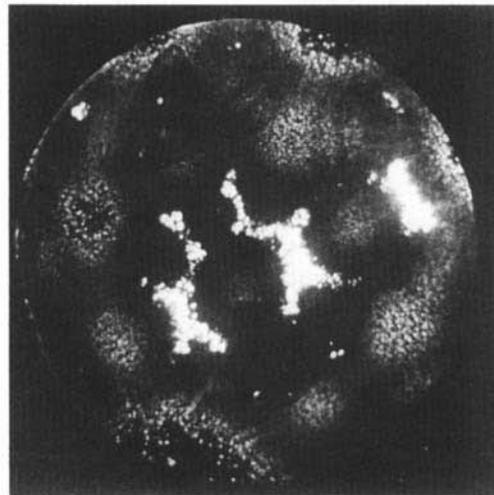
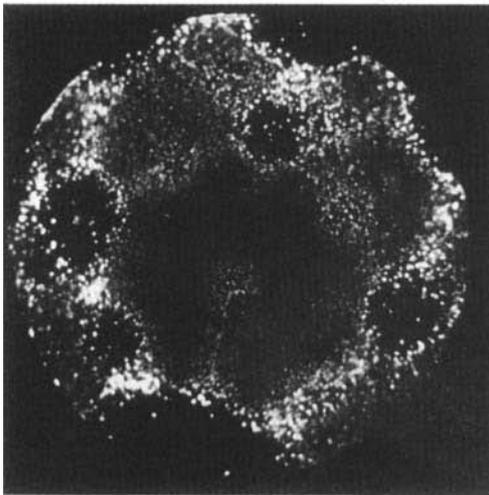
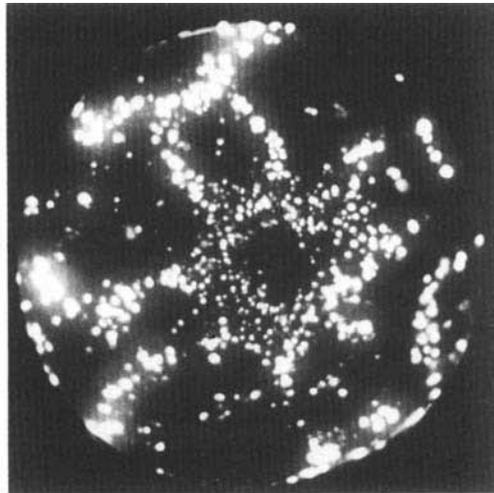


Fig. 1 The sequence of FIM images on the left shows the progressive removal of the surface film from a sample exposed in the miniature reactor for 10 minutes to a 10 per cent ammonia-air mixture. The sample is faceted, and a rhodium-rich layer has formed

suiting to provide additional information on the chemical states of the first few atom layers of the specimen surface.

The electron probe microanalysis results, reported more fully elsewhere (9, 10), show a clear distinction between air oxidised and ammonia oxidised gauzes exposed for similar times and temperatures in their respective environments. Air oxidation resulted in a surface oxide strongly enriched with rhodium (the presence of oxide being confirmed by cathodoluminescence), while ammonia oxidation gave rise to a thinner, more metallic surface layer whose composition approached that of the bulk material. Some variations in rhodium:platinum ratio were observed through the depth of a gauze pack.

Of necessity, FIM samples are in the form of delicate needles, and so any exposure in the miniature reactor can only be for short periods of time. After exposure in the reactor, the surface film can be progressively stripped off in the field ion microscope, using a series of voltage pulses, so working down through the surface film to the bulk substrate material. In the basic FIM this is recorded visually, while in the FIM-Atom Probe an aperture is inserted, and the material removed from the selected area is analysed in a time-of-flight mass spectrometer; thus building up a composition depth profile through the surface film to the substrate.

A FIM image sequence showing the progressive removal of the surface film of a sample exposed to a 10 per cent ammonia-air gas mixture in the miniature reactor for 10 minutes behind a gauze pack is shown in Figure 1. The sample is faceted, and a rhodium-rich oxide layer has been formed, indicating that the sample had merely oxidised. However, a sequence for a sample exposed for 30 minutes under similar conditions (Figure 2) shows no such oxide film. The surface has a disordered structure and is metallic in nature. Thus it is inferred that

the sample had lit-off and started acting as a catalyst. FIM-Atom Probe analysis of this sample showed the disordered metal layer to be about a nanometer thick, and the composition approximately that of the bulk rhodium-platinum with a large amount of adsorbed gas species, hydrogen and nitrogen. However the gas levels fell sharply to zero on entering the ordered bulk material.

“Ladder Diagrams” of the number of rhodium ions detected versus the number of platinum ions, and of oxide species versus metallic species, are shown in Figure 3. A sample which had been reacted as a catalyst and then air cooled was covered with a thin surface oxide film approximately 4 to 5 atomic layers thick, while the sample argon-quenched from reaction had only a monolayer of surface oxide, possibly arising from storage prior to examination. The sudden change in rhodium:platinum ratio between the surface oxide and the substrate reinforces these figures.

The temperature at which a gauze starts to react, the so-called light-off temperature, gives a clear indication of its activity, and hence can

| Sample treatment | Light-off temperature |
|--------------------------------------|-----------------------|
| Hydrogen flamed | 255–275°C |
| Aqua regia etched | 250–270°C |
| Recrystallised at 1200°C under argon | 305–370°C |
| As received gauze | Failed to light-off |

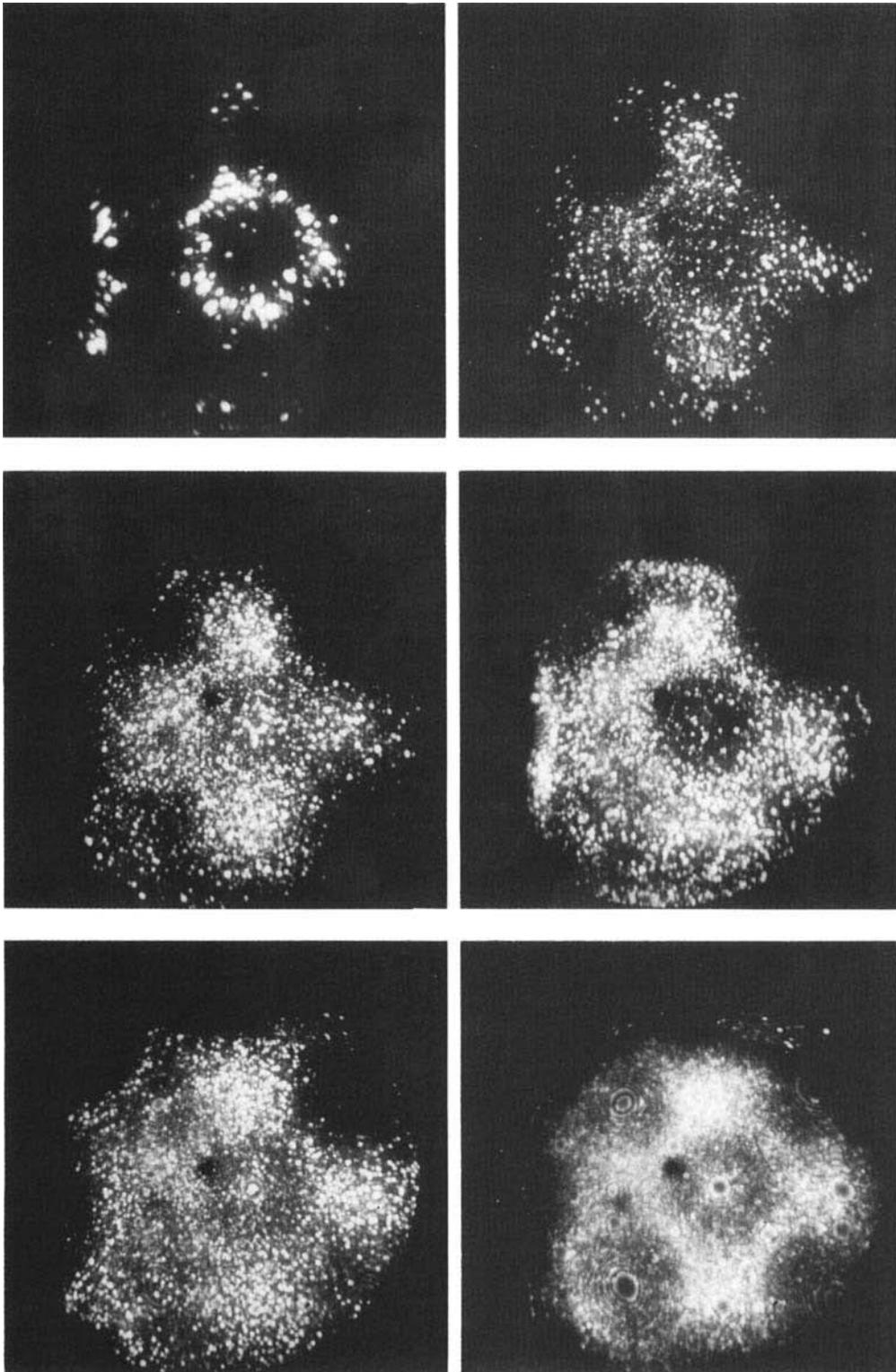


Fig. 2 The progressive removal of the surface film from a sample exposed to a 10 per cent ammonia-air mixture for 30 minutes in the miniature reactor is shown in this sequence of FIM images. The structure of the surface is disordered and metallic in nature, and the underlying substrate is soon revealed. It is inferred that the sample had lit-off, and started acting as a catalyst

be used to compare various gauze pretreatments. As previously reported (6), degreasing and hydrogen flaming a gauze result in a clean recrystallised surface which gives reasonably consistent light-off temperatures, as is shown in Table 1. On the basis that the change from the texture produced by drawing to a recrystallised grain structure may help to explain activation, some samples were recrystallised under argon at 1200°C. These lit-off at a higher temperature, indicating that they were less active. However, gauzes exposing a large number of different orientation crystal planes, formed by etching severely in aqua regia, lit-off at least as well as hydrogen flamed

gauzes. "As-received" gauze failed to light-off at all, despite degreasing. Further trials showed that moisture in air inhibited light-off, and studies on re-lighting previously run gauzes indicated samples quenched in argon from reaction re-lit more easily than those cooled in air.

Photoelectron spectroscopy (XPS) was used to investigate the chemical states of the surface species on the three types of pretreated gauzes studied above, as well as on two gauzes which had operated for 4 hours in the miniature reactor – one cooled in air, the other argon quenched from reaction. The information on the species present in the surface films, along with data on their relative compositions, oxidation

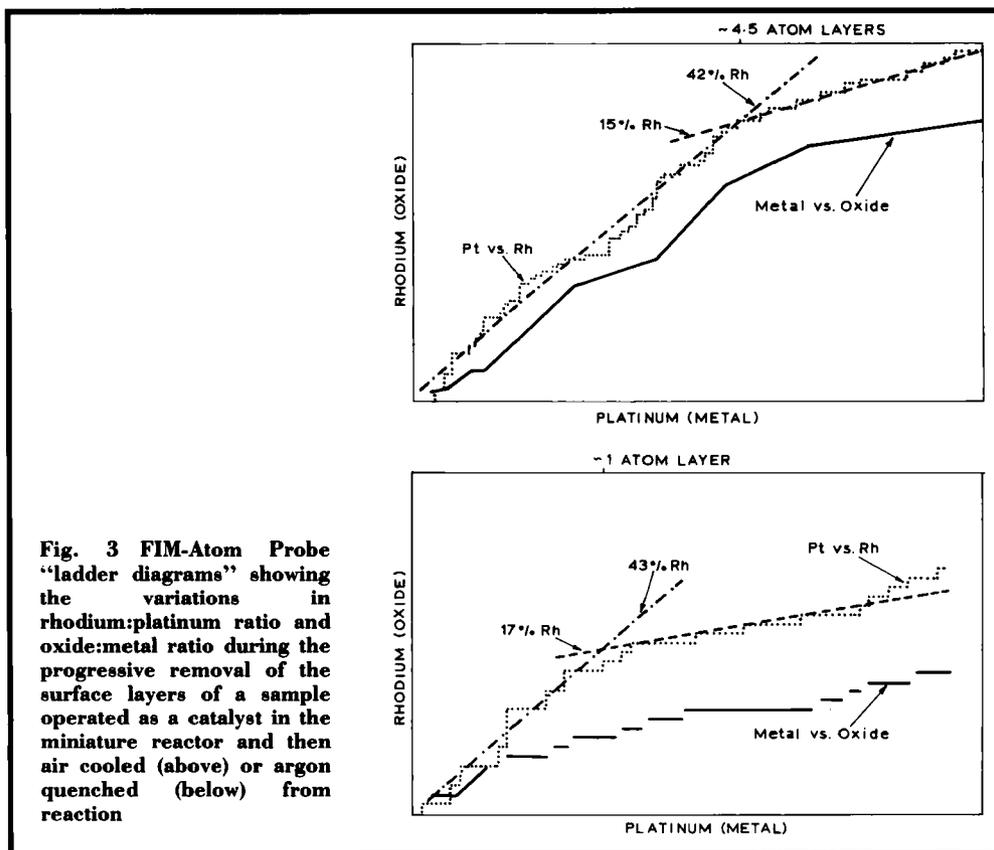


Fig. 3 FIM-Atom Probe "ladder diagrams" showing the variations in rhodium:platinum ratio and oxide:metal ratio during the progressive removal of the surface layers of a sample operated as a catalyst in the miniature reactor and then air cooled (above) or argon quenched (below) from reaction

Table II
The Dominant Oxidation States of Platinum-Rhodium Gauzes
Subjected to Various Treatments, Before and After the Removal
of a 2nm Film by Argon Etching

| Sample treatment | At the surface | | After removal of 2nm | |
|---|----------------|--------------------|----------------------|-------|
| | Pt | Rh | Pt | Rh |
| Hydrogen flamed | Pt(O) | Rh(III) + Rh(O) | Pt(O) | Rh(O) |
| Aqua regia etched | Pt(O) | Rh(O) | Pt(O) | Rh(O) |
| Recrystallised under argon | Pt(O) | Rh(III) | Pt(O) | Rh(O) |
| Oxidation in ammonia for 4 hours and argon quenched | Pt(O) | Rh(O) | Pt(O) | Rh(O) |
| Oxidation in ammonia for 4 hours and air cooled | Pt(O) | Rh(III) | Pt(O) | Rh(O) |

states and depth of oxidation (established by removal of the surface layers by argon etching) was very interesting. The dominant oxidation states for each sample, before and after removing a 2 nm layer, are given in Table II, while the corresponding element ratios for rhodium:platinum are presented in Table III. The rhodium:platinum intensity ratios were calculated after applying sensitivity factors to standardise the values measured for the Pt $4f_{(7/2+5/2)}$ and Rh $3d_{5/2}$ peaks.

The main features of the analysis for each sample can be highlighted as follows:

The hydrogen-flamed gauze showed superficial oxidation. Although the platinum was only present as the metal, Pt(O), the rhodium was detected in two oxidation states, Rh(O) metal and Rh(III) oxide. Removal of a 2 nm layer by argon etching removed the Rh(III) peak, and also a shoulder on the oxygen O 1s peak, indicating that Rh₂O₃ had been present on the surface before etching. Prior to etching the

Table III
Platinum:Rhodium Element Ratios from XPS Analysis

| Sample treatment | Platinum:rhodium ratio | |
|---|------------------------|--------------------|
| | At the surface | At a depth of 2 nm |
| Hydrogen flamed | 5.01:1 | 7.91:1 |
| Aqua regia etched | 6.23:1 | 8.09:1 |
| Argon recrystallised | 7.76:1 | 8.36:1 |
| Oxidation in ammonia for 4 hours and argon quenched | 7.00:1 | 7.84:1 |
| Oxidation in ammonia for 4 hours and air cooled | 3.96:1 | 5.03:1 |

surface layer had been slightly rhodium rich.

On the aqua regia-etched sample, platinum and rhodium were present as the metal, Pt(0) and Rh(0), before and after argon etching. Before etching sulphur was detected in oxidation state VI, presumably as sulphate. Argon etching removed this, but revealed traces of iron as Fe(III). During etching, the rhodium:platinum ratio decreased to that of the bulk composition.

Recrystallisation in argon at 1200°C resulted in slight oxidation. Rhodium was present as Rh(III) indicating some surface oxidation had taken place, despite the protective atmosphere. Subsequent argon etching showed only the presence of the metal. The rhodium:platinum ratio decreased only marginally.

The difference in the results of the analyses of the two gauzes operated in the miniature reactor reinforced the results obtained by the FIM-Atom Probe. In the case of the gauze argon-quenched from reaction, no oxides were detected. Platinum and rhodium were both present only as metal, before and after etching. During etching the rhodium:platinum ratio decreased slightly. By comparison, the sample cooled in air from reaction showed a relatively heavily oxidised rhodium-rich surface, rhodium being in the Rh(III) oxidation state. After a 2 nm depth of surface had been removed by argon etching, the bulk metal was again reached.

Discussion

A clear distinction has been shown between air oxidation and ammonia oxidation of 10 weight per cent rhodium-platinum. Air oxidation results in the formation of thick, stable, rhodium-enriched oxide films, whereas ammonia oxidation results in a virtually oxide free, disordered metallic surface. The results obtained from all the techniques used led to this same conclusion. Any oxide present on the catalyst surface is formed while cooling down in the reactor after the reaction, or in storage; this being clearly illustrated by the difference in the samples when operated under identical conditions, but with one being argon quenched from

reaction, and the other being air cooled. This evidence points to the oxide build-up on commercial ammonia oxidation gauzes occurring as a result of a gradual deactivation process, not as part of the catalytic reaction. The catalytic ammonia oxidation reaction should also be distinguished from the vapour transport in the surface reconstruction process, and from material loss by volatilisation, as PtO₂.

Other surface observations were associated mainly with deviations from the bulk composition of the uppermost atom layers, normally as rhodium enrichment. The precise rhodium:platinum ratio can be varied throughout all the stages of the ammonia oxidation process, from pretreatment and reactor warm-up, through catalytic operation, to the final close down of the reactor.

FIM-Atom Probe analysis of reactor-exposed specimens had recorded strongly bound hydrogen and nitrogen species in the surface layers. The observation of these ammonia decomposition products on a sample temporarily exposed to air between the reactor and the chemical analysis indicates reacting gas species becoming very strongly bound to the catalyst surface.

Surface pretreatments are normally required to activate a gauze before use in a commercial plant. Flaming with a hydrogen torch is a common method of achieving this. Hydrogen flaming has previously been shown to cause recrystallisation of a gauze (6). XPS revealed that it also cleans the surface, then leaves a very thin oxide layer – probably as a result of the gauze cooling in air after flame removal. Although this does not appear to inhibit light-off, thicker oxide layers, such as those formed on recrystallisation even under an argon atmosphere, are detrimental. Possibly, recrystallisation under a reducing atmosphere could remove any oxygen already present on the surface. The use of aqua regia also cleaned the gauze surface, and produced crystal sites suitable for gas adsorption, which are required to initiate the reaction. Gauze activation therefore seems to require a combination of degreasing – including the removal of any

contaminants from wire drawing and weaving processes, exposure of reactive crystal orientation sites and a chemically receptive surface.

Conclusions

This study has shown that, in the ammonia oxidation process, the surface of an operational catalyst is metallic in nature, not oxide-covered as previously thought. The catalytic process is distinct from oxide build-up as the result of a gradual deactivation process and from material loss by volatilisation, as PtO_2 .

Further, the effects of various catalyst pretreatments have been studied. A successful pretreatment has been shown to produce a generally clean, chemically receptive surface, with the exposure of reactive crystal orientation sites.

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Platinum Modified Aluminide Coatings

The widespread use of gas turbine engines for industrial, marine and aero applications has resulted from many developments which, over a period of some forty years, have improved engine performance and service life. This evolution is continuing and several previous articles in this journal have considered how the turbine blades can be further improved, particularly by using protective coatings (1, 2, 3).

The addition of platinum to aluminide coatings has been found to be beneficial, improving the resistance of nickel-base superalloys to oxidation and hot corrosion. However, the protective mechanism is not fully understood and the available data is somewhat limited.

A recent contribution to the literature reports on an investigation carried out at the Naval Postgraduate School, Monterey, California (4). Platinum modified and unmodified aluminide coatings on substrates of IN-738, a commercial nickel-base superalloy, have been subjected to cyclic oxidation conditions at a temperature of 1100°C for up to 250 hours, and the effects on microstructure and surface topology studied.

With both types of diffusion coating, surface upheavals were observed, this rumpling being

greater on the platinum modified coatings. Factors considered to influence the amount of rumpling included thermal expansion mismatch, thermal gradient across the coated specimens and the mechanical properties of the coating. While the thickness of the coating did have an effect, it was pointed out that for coatings formed by diffusion, different thicknesses of coating also have different compositions. Thus it was concluded that the rumpling is not due to subcoating melting, but to a complex combination and interaction of variables.

While the unmodified aluminide coatings exhibited spalling of the oxide, all the platinum modified coatings exhibited excellent adherence of the oxide, regardless of coating structure and composition.

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