Platinum-Based High Temperature Selective Absorber Coatings

OPTICAL PROPERTIES EXHIBIT REMARKABLE THERMAL STABILITY

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Magnetron sputtering technology enables large substrate areas to be coated, and is therefore applicable to the production of solar energy receivers. Co-deposited platinum-alumina graded cermet coatings have been investigated and their great thermal stability in air makes them highly suitable for medium temperature collectors.

In photothermal energy conversion the absorbed solar flux is converted to heat which is then used directly or is converted to mechanical or electrical energy. Efficient receiver design requires that thermal losses from the absorber surface, which is the hottest element of the system, be minimised. Receivers are, in fact, generally classified according to their operating temperature (1, 2). Thus one has low temperature collectors (T < 200°C), which are used primarily for space and water heating, medium temperature collectors (200 < T < 500°C), which can be used for absorption air conditioners and to heat the working fluid for low temperature heat engines, and high temperature collectors (T > 500°C), which can be used to drive high temperature engines for electric energy conversion. Convection and conduction losses can generally be reduced to acceptable levels by proper mechanical design. Radiation losses are minimised by the use of spectrally selective surfaces (3).

The concept of the spectrally selective surface is based on two facts. The first is that about 98 per cent of the solar flux is in the wavelength range below 2000 nm, while thermal radiation losses are at longer wavelengths (Wien's law), except at temperatures above 700°C. The second is Kirchhoff's law, which states that the total hemispherical spectral absorptance, $\alpha(\lambda)$, is equal to the total hemispherical spectral emittance, $\varepsilon(\lambda)$, at any given wavelength λ. A spectrally selective surface is therefore one that possesses a high spectral absorptance at wavelengths within the solar spectrum—typically 300 to 1500 nm—and a low spectral absorptance, and therefore a low spectral emittance, at longer wavelengths. Such surfaces can have a pronounced effect on the performance of photothermal collectors operating at temperatures below about 700 to 800°C (3).

Bulk materials with highly selective surfaces do not appear to exist. Therefore coatings must be used. An effective coating consists of an optical filter which passes the long wavelength radiation ($\lambda > 1500$ nm) while absorbing the short wavelength radiation, deposited over a low emittance base layer. The requirement is therefore for a multi-layer optical coating, with unusual thermal stability as far as optical coatings are concerned, and with economy of large scale production.

This paper describes a platinum-alumina cermet coating which is believed to be the thermally most stable selective absorber coating developed thus far. The coating was first studied by Professors Sievers and Buhrman and their students at Cornell University in the late

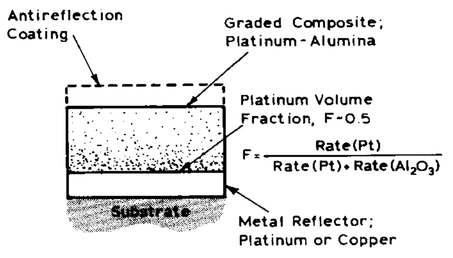

Fig. 1 The configuration of platinum-alumina graded cermet selective absorber coatings is shown. Aluminium oxide antireflection coatings were used in our work, but not in the original coatings deposited at Cornell University

1970s (4, 5). Their coatings were deposited by co-evaporation from platinum and alumina sources using electron-beam sources. We have subsequently explored these coatings in considerable detail (6, 7) using magnetron sputtering methods that are more applicable to large area deposition than are evaporation sources (8). Hemispherical absorptances as high as 0.97 in combination with room temperature emittances in the 0.06 to 0.08 range have been achieved. The hemispherical absorptances and emittances referred to here are weighted averages calculated over the solar and room temperature black body spectra, respectively (3).

Sputtered Platinum-Alumina Cermet Coatings

The basic configuration of the coatings is shown in Figure 1. A platinum layer about 150 nm thick serves as the low emittance base layer. Our substrates were Corning type 7059 borosilicate plates or type 316 stainless steel. When stainless steel substrates were used, a 50 nm thick aluminium oxide diffusion barrier was deposited between the stainless steel and the platinum layer. Cermet thicknesses were typically in the range from 50 to 250 nm. The platinum volume fraction was varied from about 0.4 to 0.7 at the rear surface to zero at the front surface. The graded cermet layer was generally overcoated with a pure aluminium oxide antireflection layer having a thickness in the 20 to 70 nm range.

The deposition apparatus is shown schematically in Figure 2. The graded cermet layers were deposited by continuously rotating the substrates at speeds of 0.5 to 10 r.p.m. while simultaneously sputtering from a r.f. driven planar magnetron source having an alumina target and a DC driven planar magnetron having a platinum target. The alumina target was fabricated from Coors AD-995 alumina of 99.5 per cent purity. The platinum target was fabricated from 99.99 per cent pure platinum sheet, 0.76 mm thick. The current to the platinum source was adjusted, while sputtering the alumina component at a constant rate, so as to provide a platinum composition that varied near-linearly from the back to the front surface. A stationary array of eight quartz heating lamps located within the substrate mounting drum assembly were used to maintain substrate temperatures at various values in the range from about 150 to 500°C.

Coatings with absorptances in the range from 0.93 to 0.95 were consistently obtained.

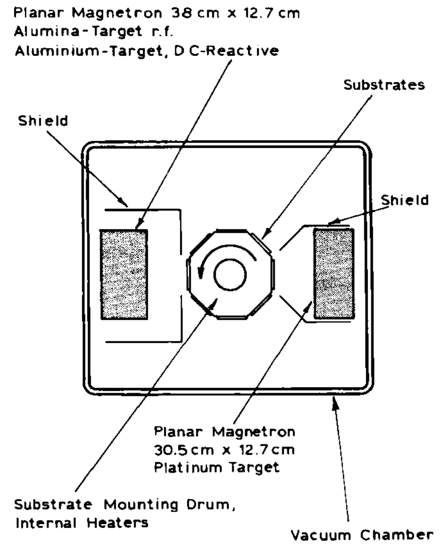

Fig. 2 This schematic illustration shows the multisource deposition apparatus that was used to deposit platinum-alumina coatings. The assembly is mounted on wheels which allow it to be rolled into the vacuum chamber

Optimisation of the antireflection layer thickness yielded hemispherical absorptances as high as 0.97. Figure 3 shows spectral reflectance and composition data for an identical pair of coatings deposited at 350°C. The low emittance platinum base layer, the linear grading within the cermet layer, and the aluminium oxide antireflection layer are clearly discernible. The exact cermet thickness, as well as the platinum content and grading profile, do not appear to be critical. This is an important advantage for coating substrates of complex shape. However, we did observe a slight decrease in absorptance for coatings deposited at high rotational speeds (7). The coatings deposited at temperatures of about 350°C or above exhibited the greatest thermal stability.

A few thin coatings (25 nm thick) of uniform composition (with the volume fraction of the metal component (F) ~ 0.33) were deposited onto carbon grids at various temperatures and examined by transmission electron microscopy (7). The aluminium oxide layers were amorphous, independent of the substrate temperature. The platinum was present in the form of a discernible second phase consisting of particles that appeared to range in size from about 1 to 3 nm for the coatings deposited at 150°C, to about 3 to 10 nm for coatings deposited at about 300°C.

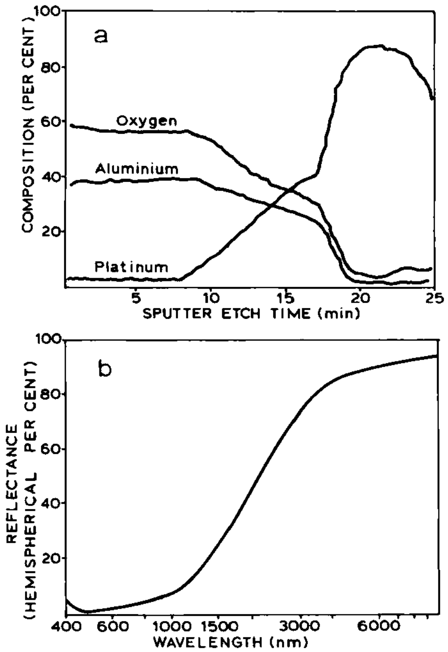

Fig. 3 Auger depth profile composition (a) and spectral reflectance (b) data for an identical pair of graded cermet coatings which were deposited at elevated temperature (≈350°C) upon glass substrates. The emittance data for various temperatures, which are given in (b), were calculated from the reflectance data using the Planck function. An identical coating showed no change in optical properties after being heated for 700 hours in air at 600°C. After Reference 7

Thermal Stability and Cost

The coatings exhibited remarkable thermal stability in air. Graded platinum-alumina cermet coatings of the type shown in Figure 1 that were deposited onto borosilicate glass substrates at elevated temperatures in the range 300 to 500°C exhibited no change in optical properties (<1 per cent) after being maintained in air at 600°C for 700 hours. A similar performance was found for coatings on type 316 stainless steel substrates, provided that an alumina diffusion barrier was used between the stainless steel and the platinum base layer. Thus one such coating on a type 316 stainless steel substrate exhibited no change in absorptance after about 2000 hours at 600°C in air. A similar coating was tested by the University of Houston group under Professor Ignatiev and found to show no change in optical properties after being exposed to an intensity of 2800 suns for 2 hours (10).

Coatings deposited onto glass or stainless steel at 150°C were stable in air at 400°C in tests ranging in length from 1400 to 1700 hours but degraded slightly at higher exposure temperatures, probably due to inferior quality in the aluminium oxide layer.

The great thermal stability of these coatings in air is undoubtedly attributable to the resistance of platinum against oxidation over the temperature range of interest. Similar coatings with chromium, nickel, and molybdenum metal phases were stable only to about 500 to 550°C (9). Coating costs based on a platinum cost of $500 per troy ounce were estimated to be about $4 to $5 a square foot when deposited over large areas. This cost is dominated by the cost of the platinum in the low emittance base layer, $3 a square foot, but this is not unreasonable for high performance receivers. Alternative base layer materials such as carbon, nickel, molybdenum and zirconium boride were tested and found to yield inferior performances compared to the platinum (9).

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Catalytic Retexturing of Platinum Surfaces

The occurrence of surface restructuring in platinum based catalysts is well known, perhaps the best example being that produced in platinum-rhodium gauzes during the oxidation of ammonia. Many previous investigations into the nature of this surface change have used very low pressures and clean platinum surfaces, such as single crystal faces. A study of the heterogeneous oxidation of carbon monoxide on platinum wire, carried out at atmospheric pressure and temperatures up to 600K, has been reported (A. K. Galwey, P. Gray, J. F. Griffiths and S.M.Hasko, *Nature*, 1985,**313**,(6004),668.

Kinetic measurements were made using the catalyst, in the form of a coil, as its own resistance thermometer. The difference in power supplied to maintain a constant mean wire temperature in first an inert and then a reactive gas mixture was related to the heat of reaction at that temperature. Under oxygen-rich conditions, kinetic and diffusion controlled regimes were identified, with hysteresis between the two causing a region of instability.

The surface of wires, after several hours at 500K, developed a structure similar to that produced by the oxidation of ammonia on platinum. X-ray energy dispersive and wave dispersive analyses indicated the presence of a surface layer of PtO in both textured and unchanged areas of used catalyst wires and also at the surface of pristine wires.

To explain their observations, the authors suggested that recrystallisation occurs only on the surface of suitably oriented grains, textural discontinuities being caused by grain boundaries. It is proposed that at temperatures well below the melting point of platinum (2045K), surface atoms have considerable mobility and that PtO actively promotes or controls the reaction. These considerations are consistent with two alternative representations of the oxidation process. In the first, surface oxide is reduced by chemisorbed carbon monoxide, with carbon dioxide formation occurring at the metal-metal oxide interface. In the second, platinum in a mobile chemisorbed phase bonds with carbon dioxide and/or carbon monoxide by transitory compound formation to produce two-dimensional intermediates. It appears that surface concentrations of active constituents are sensitive to prevailing conditions and previous catalyst treatment.

Much remains to be learnt regarding the chemistry of surface species on platinum catalysts if the mechanism of reactions such as these are to be better understood. E.P.W.