

Research on Single Crystals of Some Platinum Group Metals

A STUDY OF THEIR PHYSICAL AND CHEMICAL PROPERTIES

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The microstructure and some physical and chemical properties of the platinum group metals iridium, rhodium, ruthenium and osmium, prepared by electron-beam melting, have been investigated and the results are reviewed in this article. The degree of anisotropy of these properties has been evaluated and high plasticity has been demonstrated for single crystals of the refractory platinum group metals.

The control of anisotropy in materials and the orientation of single crystals to obtain the optimum combinations of physical, chemical, technological and service properties is an important trend in metallurgical development.

A metal is a physico-chemical system which changes under the influence of both external conditions and intrinsic properties. The main components of this system are the crystals of the basic metal, grain boundaries, sub-grains and sub-boundaries together with various impurities and defects. Weak areas in such polycrystalline metals may be associated with impurities and defects concentrated at grain boundaries (1).

An analysis of as-refined powders of platinum group metals has shown the presence of considerable amounts of impurities, both metallic, such as magnesium, lead, iron, copper, silver or other platinum group metals, and non-metallic, including silicon, carbon, oxygen and hydrogen, which on melting or high temperature treatment interact with the primary metal and with each other. Investigations carried out on platinum group metals by Auger spectroscopy, low-energy electron-diffraction and mass-spectroscopic analysis of gases liberated from molten or solid samples on vacuum heating have found high contents of oxygen, hydrogen, nitrogen and carbon

dioxide on the surface and in the bulk of the metal. Although under normal conditions the platinum group metals do not form carbides, nitrides or hydrides, and most of their oxides are volatile, nevertheless the purity of starting materials is of particular importance. The readiness with which alloys are formed is explained by the particular thermodynamic relationships between the platinum group metals and other elements. They interact, to a certain extent, with all elements to produce numerous chemical compounds and solid solutions based on platinum and other platinum group metals (2). On melting, the non-metallic impurities contained in the starting material may form solid solutions and low-melting eutectics with the platinum metal, thus producing thin grain boundary layers. They can also form brittle chemical compounds not only with the metal but also with interstitial impurities. During hot working or heat treatment, and when subjected to high temperatures, oxidative and corrosive conditions, any base metal impurities present in the platinum group metal may react with their surroundings. As a result, intercrystalline oxidation of impurities takes place, or some new non-metallic complex phases are formed. These phases may be weakly bound with the matrix, and initiate brittle fracture.

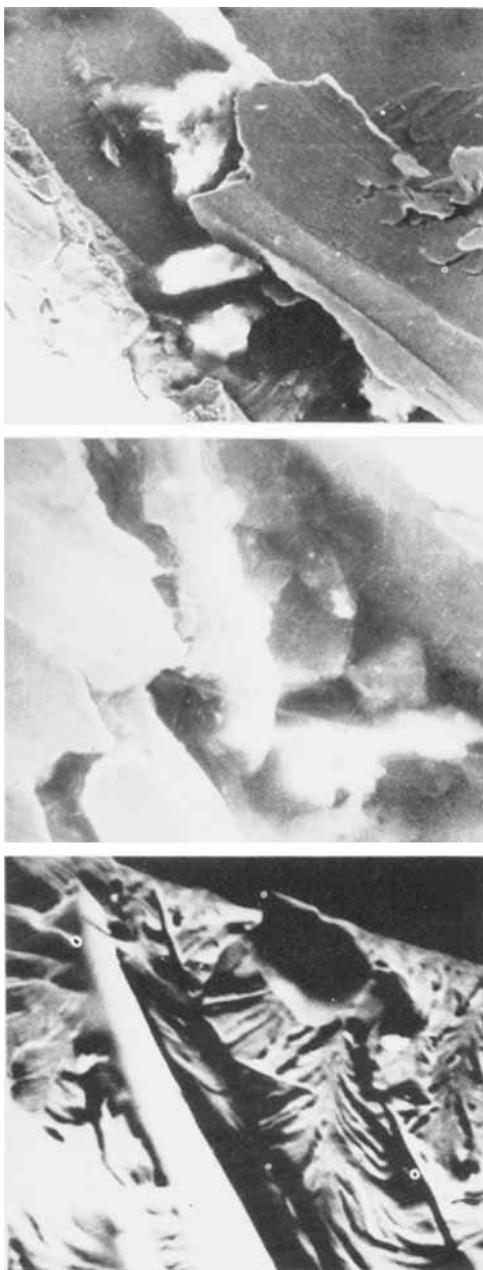


Fig. 1 Glass-like inclusions occur in fractured polycrystalline rhodium and ruthenium.

Rhodium, scanning electron micrographs: Top left $\times 650$; middle left $\times 1000$

Ruthenium, bottom micrograph, optical $\times 630$

and ruthenium samples prepared by electron-beam and arc melting, see Figure 1. Besides complex oxide inclusions, small graphite particles have also been detected when the fractured surfaces of refractory platinum group metals have been examined by metallographic techniques, in both the etched and unetched states. The distribution of these depends on the nature and crystalline structure of the metal.

The problems of producing pure and perfect single crystals of platinum group metals are very similar to those of producing single crystals of refractory and rare metals (2). These problems could only be solved after the development of new chemical methods for the production of pure substances, the introduction of vacuum metallurgy and of new powerful heating sources, such as electron beam and plasma heating.

We have successfully used zone melting for the production of single crystals of platinum group metals (4). To evaluate purity and perfection, both physical and chemical methods have been used, such as chemical and electro-chemical etching, back reflection Laue X-ray photography using $\text{CuK}\alpha$ radiation and the Berg-Barrett X-ray diffraction technique. Misorientation of crystal blocks measured by various methods did not exceed 10 to 20 minutes of arc. The purity of crystals was estimated by residual resistivity ratio measurements.

During zone melting, single crystal growth is accompanied by purification resulting from selective evaporation and transportation to the ends of the sample. Table I relates impurity content to the production method.

It has been thought that iridium, osmium,

Metallographic studies by optical and scanning microscopy, in combination with electron probe micro-analysis, have shown that glassy oxide inclusions containing silicon, aluminium and other base metals may be responsible for brittle fracture in rhodium

rhodium and ruthenium are inherently brittle but our investigations proved that this was not so. Single crystals of the refractory platinum group metals—like single crystals of tungsten and molybdenum—demonstrate high plasticity. Rhodium single crystals can be cold deformed to more than 90 per cent without failure, and iridium single crystals can be knotted cold (2). Electron beam melted ruthenium can be deformed in an inert atmosphere at 300 to 400°C lower than arc melted ruthenium (5).

Ruthenium single crystals produced by electron-beam zone melting oxidise on heating in air at a slower rate than arc-melted polycrystalline material, Figure 2 (6). On heating in vacuum much smaller amounts of gases are liberated from single crystals than from polycrystals (7). X-ray and electron spectroscopic studies have revealed oxygen

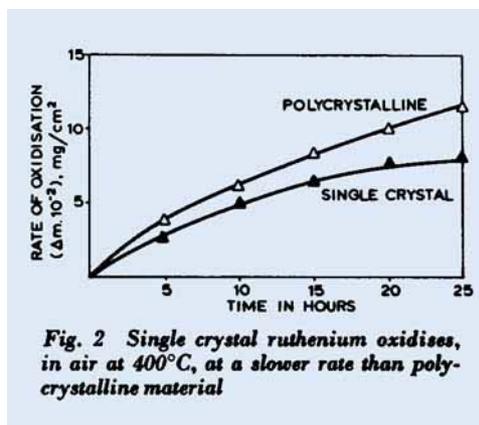


Fig. 2 Single crystal ruthenium oxidises, in air at 400°C, at a slower rate than polycrystalline material

and carbon on the surface of ruthenium single crystals and polycrystals subjected to ionic bombardment for three minutes at room temperature; moreover, the content of these elements is less on the surface of single

Impurity	Platinum Group Metal								
	Ruthenium			Osmium			Rhodium		
	Refined Powder	Arc Melted	Electron-Beam Melted	Refined Powder	Arc Melted	Electron-Beam Melted	Refined Powder	Arc Melted	Electron-Beam Melted
Platinum	10	10	10	30	7	7	200	150	100
Palladium	10	10	10	1	21	1	1	1	1
Iridium	10	—	10	60	27	10	30	30	10
Rhodium	40	10	10	3	3	3	—	—	—
Copper	10	10	5	5	5	1	10	10	5
Iron	10	10	8	60	18	18	10	10	8
Silicon	30	30	20	50	—	40	10	—	—
Magnesium	30	—	6	3	3	2	—	—	—
Aluminium	20	—	—	56	20	8	—	—	—
Sodium	10	—	—	10	—	—	20	—	—
Lead	10	—	—	—	—	—	20	—	—
Sulphur	—	40	—	—	—	—	—	100	—
Carbon	300 250	200 170	100 50	—	—	—	20	10	10
Oxygen	—	150 200	80 60	—	—	—	—	30	30
Hydrogen	—	9	2	—	—	—	—	1	1

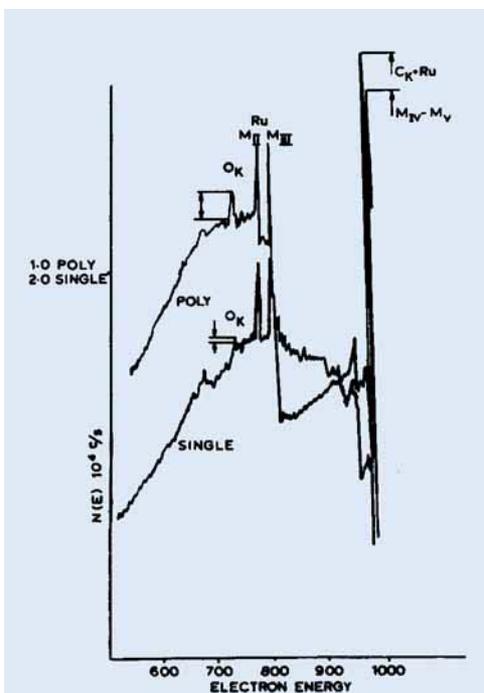


Fig. 3 After refining by ionic bombardment, for 3 minutes at room temperature, oxygen and carbon are present on the surfaces of both single crystal and polycrystalline ruthenium; however there is less on the single crystal material

crystals than on polycrystalline surfaces, the data being given in Figure 3.

The high corrosion resistance of platinum group metals, as well as the lack of standard methods to study their microstructures, give rise to difficulties in metallographic investigations. Electropolishing and electrochemical methods recommended for studying the structure of platinum group metals are given in Table II (2).

Electrochemical etching (8) and ion bombardment (9) were used to study the microstructures of single crystals.

Electrochemical investigations of the structure of the hexagonal metals ruthenium and osmium were carried out on (0001), ($\bar{1}100$), (10 $\bar{1}1$) and (11 $\bar{2}4$) planes, and for the face-centred cubic metals rhodium and iridium on (100), (111) and (101) planes. The effects produced by etching have a form characteristic of these crystallographic planes, and have been observed previously on some low melting point metals and chemical compounds with similar structure. They result from the crystal structure defects decorated with impurities and are shown in Figure 4.

The growth structure of a ruthenium single crystal as revealed by ion bombardment is shown in Figure 5. A comparison of data

Table II
Reagents for Electropolishing and Electro-etching

Metal	Reagent	Conditions	Effect
Ruthenium	10 per cent solution of HClO ₄	$u = 24V$, electrode—stainless steel, alternating current	Polish
	10 per cent solution of oxalic acid	Electrode—stainless steel, ruthenium, alternating current	Etch
Osmium	20 per cent solution of H ₃ PO ₄ few drops of H ₂ O ₂	$u = 24V$, electrode—stainless steel, tantalum, alternating current	Polish
	10 per cent solution of HCl	The same electrode, alternating current	Etch
Iridium	25 to 30 per cent solution of HCl	$u = 10V$, electrode—graphite, alternating current	Etch
Rhodium	1 HCl + 4NaCl, saturated solution	$J = 5A$, $t = 10$ min, alternating current	Etch

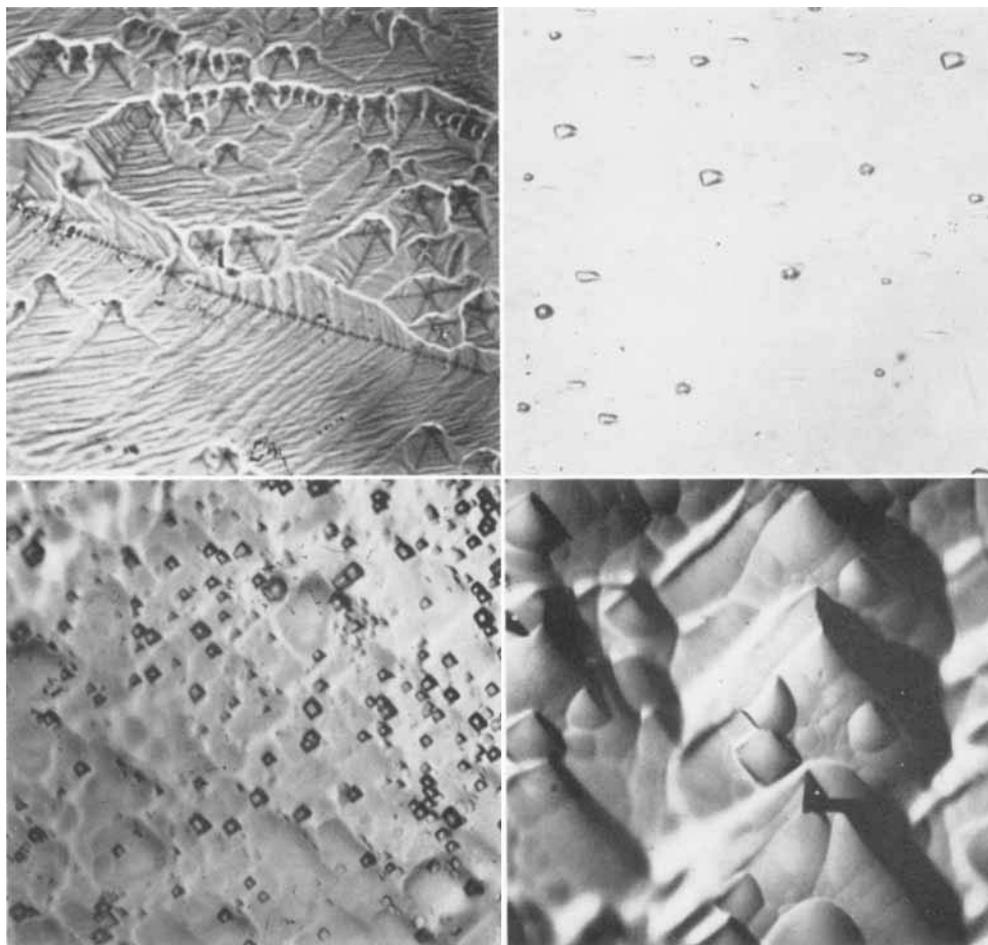


Fig. 4 The microstructure of single crystal ruthenium and rhodium is characteristic of the crystallographic plane examined: Top left, ruthenium (0001) plane $\times 500$. Top right, ruthenium (1011) plane $\times 500$. Bottom left, rhodium (101) plane $\times 500$. Bottom right, rhodium (100) plane $\times 2000$

Fig. 5 The growth structures on the (10 $\bar{1}$ 0) face, left, and the (11 $\bar{2}$ 0) face, right, of single crystal ruthenium revealed by ionic bombardment are probably due to dislocations introduced during crystallisation $\times 1000$

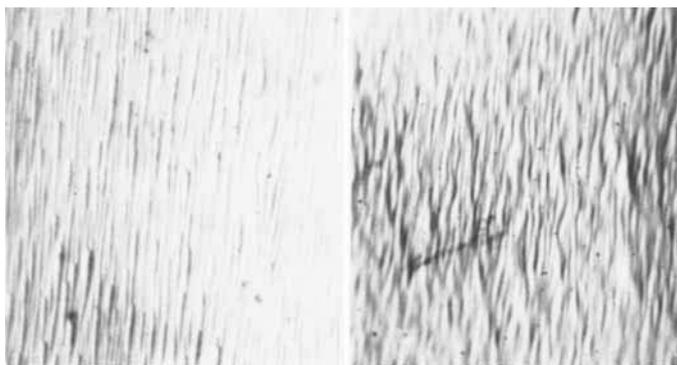


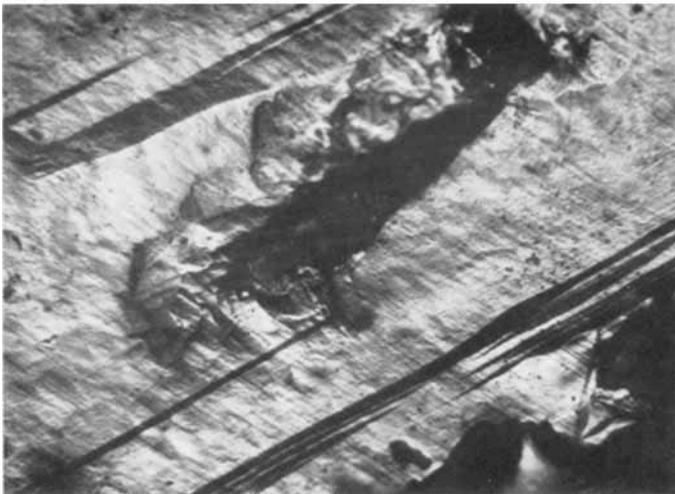
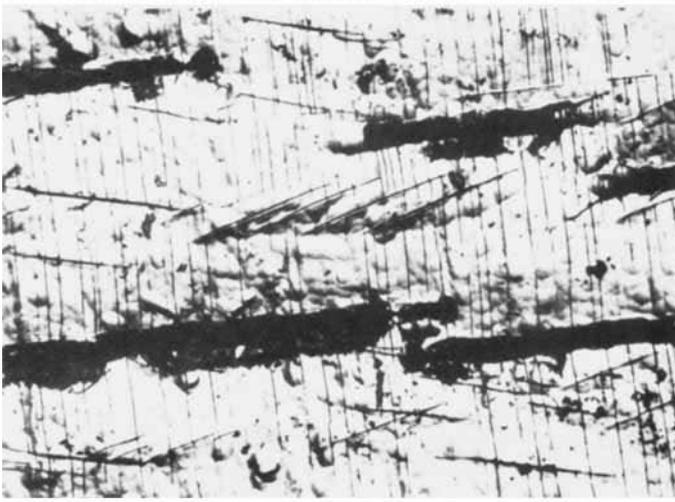


Fig. 6 Deposits of graphite on the surfaces of single crystal ruthenium-carbon alloys:

Top, 0.08 atomic per cent carbon, (0001) face $\times 800$

Middle, 1 atomic per cent carbon, (11 $\bar{2}$ 0) face showing three slip systems $\times 340$

Bottom, 1 atomic per cent carbon, (0001) face with slip again evident $\times 340$



suggests that this is due to dislocations introduced during crystallisation.

Single crystals of ruthenium containing 0.08 and 1 atomic per cent carbon were prepared and the carbon distribution studied (10). In single crystals with 0.08 atomic per cent (0.01 weight per cent) of introduced carbon a concentration of etch figures, that is carbon-pinned dislocations, has been observed on the basal plane (Figure 6). A study of the crystal structure with 1 atomic per cent carbon showed that graphite is deposited parallel to the basal planes in the form of flakes of irregular form and different size. In the crystal cross-section on the plane (1120), these graphite flakes appear as lines of different length (Figure 6). Graphite in this form has a considerable effect on plastic deformation of single crystals. As a result of cold rolling by 7 to 10 per cent along the C-axis of a single crystal with 1 atomic per cent carbon, damage on the basal plane takes place. Three slip systems revealed on the (1120) plane due to deformation perpendicular to the C-axis are shown in Figure 6.

The production of vacuum-melted refractory platinum group metals and the development of procedures for growing perfect single crystals have enabled various physical and chemical parameters to be measured which show the anisotropic characteristic of the crystals. The hardnesses on different single crystal faces are 100 and 250 kg/mm² for ruthenium, and 350 and 600 kg/mm² for osmium. The hardness of polycrystalline ruthenium is 200 to 350 kg/mm², and that of osmium, 350 to 670 kg/mm² (4).

The melting point of platinum group metals of single crystal purity was measured by a black body radiation method (12). The melting point of rhodium is 2237 ± 5K, and the latent heat of fusion 27352 ± 783 J/mol. The melting point of ruthenium is 2607K, the enthalpy and heat capacity of liquid ruthenium, in the range 2613 to 2757K, are $H_{\text{T}} - H_{298,15} = -4080 \pm 1239$ cal/g.at. and 12.4 cal/g.at. (11-12).

A study of the thermal diffusivity of

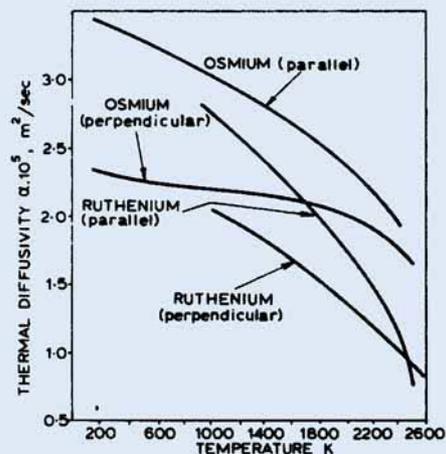


Fig. 7 The temperature dependence of the thermal diffusivity of single crystal ruthenium and osmium perpendicular and parallel to the C-axis. For each metal the anisotropy decreases with increasing temperature

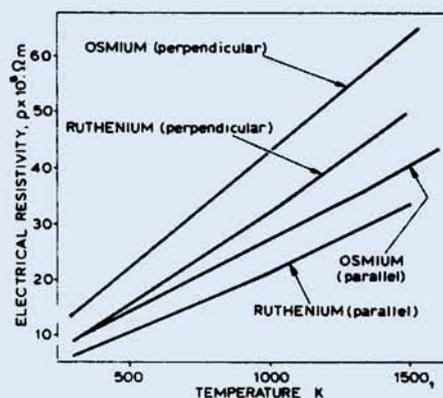


Fig. 8 The temperature dependence of the electrical resistivity of ruthenium and osmium, on samples cut perpendicular to, and parallel with, the C-axis

ruthenium and of osmium, in the range 1000 to 2600K and 900 to 3300K respectively, and of the heat capacity of ruthenium at 1000 to 2000K was made on poly- and single crystals (13). The anisotropy in thermal properties was found to decrease continuously with increasing temperature, even though the

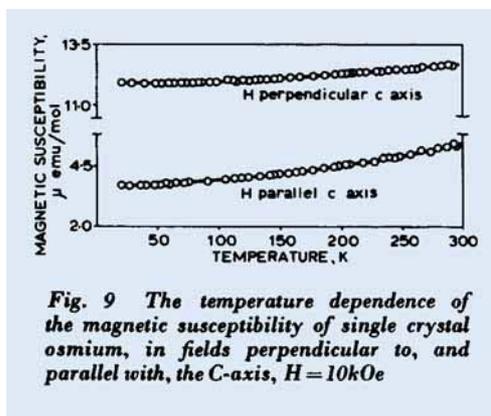


Fig. 9 The temperature dependence of the magnetic susceptibility of single crystal osmium, in fields perpendicular to, and parallel with, the C-axis, $H = 10\text{kOe}$

ruthenium and the osmium crystal lattices remain hexagonal up to the melting temperature. The data are presented in Figure 7.

To measure the electrical resistivity of ruthenium and osmium at temperatures of 290 to 1600K, samples cut parallel and perpendicular to the C-axis were used, Figure 8. The temperature dependence of ρ_1/ρ_{11} for single crystals of ruthenium and osmium is large with values of 1.45 for ruthenium at 900K and 1.6 for osmium at 1000K (13).

The magnetic susceptibility of osmium single crystals measured in the temperature range 4.2 to 273K on the plane perpendicular to the C-axis does not depend on the magnetic field direction. In the plane parallel to the C-axis one can observe 180° anisotropy of the magnetic susceptibility depending on the crystallographic direction. The temperature dependence of magnetic susceptibility reveals

	Polycrystal	Single Crystal	
Iridium	5.4	(110) 4.85	(100) 5.50
Ruthenium	4.68	(0001) 5.40	(10 $\bar{1}$ 0) (11 $\bar{2}$ 4) 5.14 4.52

noticeable anisotropy, that is the temperature susceptibility ratio is higher if the field is parallel to the C-axis, see Figure 9 (14).

Thermionic emission is one of the most sensitive anisotropic features of crystals. Experimental data for the work function of electrons in eV for iridium and ruthenium are given in Table III (15, 16).

The data were obtained under a vacuum of 10^{-9} mm Hg by the Richardson straight line method (15, 16).

Adsorptive and electrochemical properties of ruthenium and osmium were studied on the surface of single and polycrystal samples, and estimated by oxygen and hydrogen adsorption and desorption on electrode-samples in 1N sulphuric acid (17). The curves for hydrogen adsorption on ruthenium (0001) and (11 $\bar{2}$ 0) faces, in contrast to those on the (0001) and (11 $\bar{2}$ 4) osmium faces, show the maximum which is responsible for the presence of hydrogen in the bound form on a ruthenium surface. Note that for the (0001) face this maximum is more evident. Hydrogen and oxygen adsorption and hydrogen desorption on osmium reveal higher anisotropy than on ruthenium. Hydrogen adsorption on osmium (0001) and (11 $\bar{2}$ 4) faces differs by 3 times, and oxygen by 10 times (Figure 10). Oxygen desorption from osmium

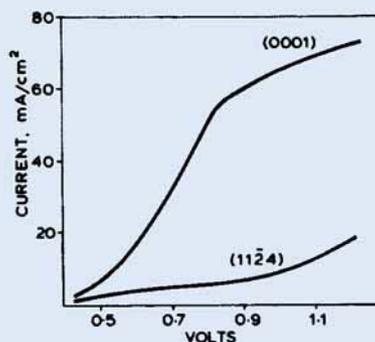


Fig. 10 Potentiodynamic adsorption curves for oxygen on the (0001) and (11 $\bar{2}$ 4) faces of single crystal osmium

(0001) and $(1\bar{1}24)$ faces differs by 7 to 8 times, and from ruthenium faces (0001) and $(1\bar{1}20)$, by 3 to 4 times. The process of oxygen desorption from an osmium surface is slower than from a ruthenium surface.

The investigations carried out on the purification and production of platinum group metal single crystals, the analysis of their

structure at macro- and microscopic levels, and their interactions with metallic and non-metallic impurity inclusions have provided a physico-chemical basis for the brittleness of refractory platinum group metals, and allowed us to determine some fundamental physical and chemical properties and to evaluate their anisotropy.

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Energy Storage System Uses Palladium Catalyst

The difficulty of providing sufficient electricity where and when it is required, and the wish to conserve the power that is available at times when it is not needed, has motivated many attempts to find additional methods of storing energy.

A new method of hydrogen storage proposed by Richard Williams, Richard S. Crandall and Allen Bloom of the R.C.A. Laboratories, Princeton, New Jersey, has recently been reported (*Appl. Phys. Lett.*, 1978, **33**, (5), 381-383). They describe a series of reactions which starts with the use

of surplus electricity for the electrochemical reduction of carbon dioxide in water to form formic acid in aqueous solution. This is easily stored and transported and may be used as a fuel, either by combustion or in a fuel cell. Alternatively when energy is required the formic acid may be catalytically decomposed using a standard palladium on carbon hydrogenation catalyst to give carbon dioxide and hydrogen.

While the process is clearly at an early stage of development the authors are encouraged by the efficiency they are obtaining.