# The Ruthenium-Palladium System

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*In this paper, a communication from the Johnson Matthey Research Laboratories, an investigation of the equilibrium diagram of the ruthenium-palladium system by microscopical and X-ray methods is described. It is established that the diagram is of the simple peritectic type. No intermediate phases or eutectoid transformations of the types recently reported by Russian workers have been observed.*

The ruthenium-palladium system had not been investigated until very recently, when Rudnitskii and Polyakova (1) reported that two peritectic reactions occurred. At 1593°C the peritectic reaction between the liquid and the gamma solid solution was found to result in the formation of an intermediate beta phase; a second peritectic reaction in the range 5 to 15 per cent by weight of ruthenium was reported as occurring at 1573°C between the liquid and the beta phase with the formation of an alpha solid solution rich in palladium.

In this laboratory an investigation of the system had been commenced prior to the publication of the Russian work and has been completed since those results became available. No evidence of a double peritectic or of an intermediate phase has been detected in the present investigation, which has shown that the duplex region, below the peritectic line at 1579°C, extends from 15 to 90 per cent of ruthenium.

## Preparation of Alloys

Alloys containing up to 10 per cent of ruthenium were made up by high-frequency melting in alumina crucibles under a carbon monoxide atmosphere. The palladium was melted first, and when all the gas had been given off and the melt was quiet, ruthenium was added and the alloy cast, a carbon monoxide atmosphere being maintained throughout the operation.

Alloys containing more than 10 per cent of ruthenium were melted in an argon-arc furnace. Excessive evaporation losses from the palladium were avoided by increasing the argon pressure in the furnace to approximately three-quarters of atmospheric. Argon-arc ingots were remelted several times to ensure homogeneity. Careful deoxidation before melting was necessary to avoid violent gas evolution. Vacuum sintering at 1400 to 1500°C was reasonably effective in removing gas, but resulted in considerable ruthenium losses due to volatilisation of oxide. In most instances the mixed powders were pressed into a bar and reduced under pure dry hydrogen for one hour at 1100°C, after which hydrogen was removed by vacuum sintering at 1300°C.

Ingots containing up to 25 per cent of ruthenium were hot forged with little difficulty in the temperature range 1200 to 1300°C. After a reduction in area of approximately 50 per cent, cold working became feasible. Although the 50 per cent ruthenium-palladium alloy could be gently worked by hot forging, attempts to work the 70, 80 and 90 per cent ruthenium alloys were all unsuccessful.

All alloys were homogenised by heat treatment in nitrogen at 1500°C before any detailed work on the diagram was undertaken. Worked alloys were quenched after 16 hours at temperature, while the cast specimens were soaked for 70 hours.

## Solidus Determinations

Solidus determinations were carried out by microscopic methods. A vertical quenching furnace wound with a 30 per cent rhodium-platinum resistance wire was made for this work, and determinations were carried out in a nitrogen atmosphere. Specimens were placed on a platinum wire mesh in a cylindrical platinum can which was suspended vertically in the furnace tube. The bare hot junction of a platinum : 13 per cent rhodium-platinum thermocouple was immediately above but not touching the specimens.

Preliminary experiments showed that the thermocouple rapidly lost its calibration due to ruthenium contamination, but this source of error was eliminated by sheathing the specimens in a small gas-tight box of platinum foil. Since only the specimen corners touched the platinum container negligible diffusion occurred. The thermocouple was checked at the palladium point before and after each run and it was rarely found that the calibration had altered by more than 1°C.

Specimens were heated rapidly to about 50°C below their estimated melting point, held at this temperature for approximately one hour and then heated at 20°C an hour to the desired temperature, which was maintained for 15 to 30 minutes before quenching. The temperature of quenching was increased by increments of approximately 4°C until signs of fusion were observed in polished and etched microsections. Etching was performed in a dilute solution of aqua regia in glycerol. Signs of fusion were easy to detect in these alloys, and typical examples of the microstructure of a single phase alloy just

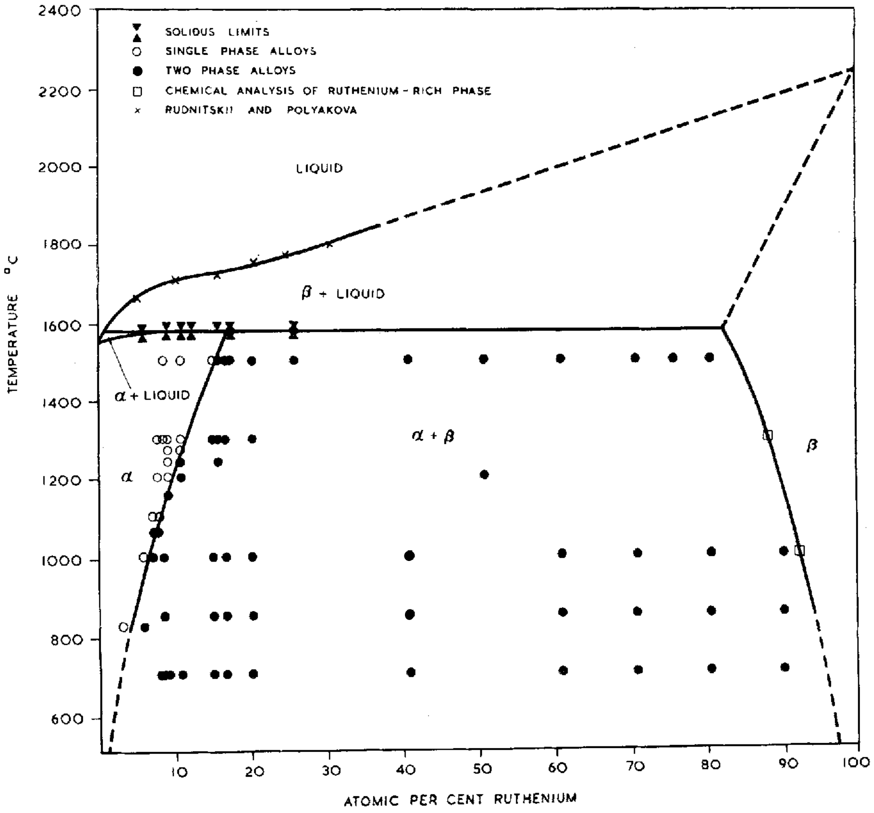


*Fig. 1 Equilibrium diagram of the ruthenium-palladium system*

*Fig. 2 Microstructure of 5.94 at.% Ru-Pd, quenched from 1571°C, × 215*

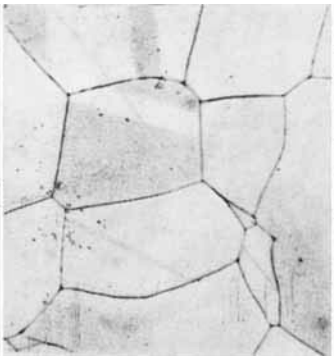


*Fig. 3 Microstructure of 5.94 at.% Ru-Pd, quenched from 1575°C, showing incipient fusion, × 215*

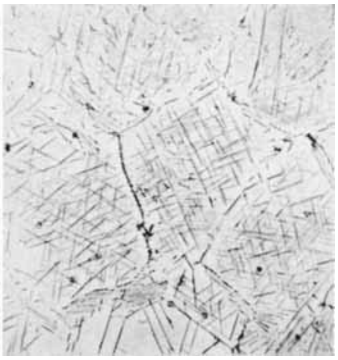


*Fig. 4 Widmanstätten structure of 15.07 at.% Ru-Pd, quenched from 1500°C, reheated and quenched after 64 hours at 1300°C, × 215*

below and just above the solidus are shown in Figs. 2 and 3.

Table I gives the solidus limits over the range 5.95 to 25.86 atomic per cent of ruthenium. The solidus rises gently from the melting point of palladium, until at a ruthenium content of 9.24 per cent it arrives at a constant value of approximately 1579°C. The solidus points obtained are plotted on the equilibrium diagram in Fig. 1.

## Microstructure of the Alloys

Alloys containing from 3 to 90 per cent of ruthenium, homogenised as described, were heated at various temperatures for times ranging from 16 hours at 1500°C to 216 hours at 700°C. The structures observed in the quenched alloys are denoted in Fig. 1, which shows that the solubility of ruthenium in palladium decreases rapidly below the solidus. Alloys containing up to 15.07 per cent of ruthenium are all single phased at 1500°C. The change in microstructure at 1500°C over the composition range 10.97 to 71 per cent of ruthenium is illustrated in Figs. 5 to 10, which show that there is no single phase area corresponding to the beta phase reported by Rudnitskii and Polyakova. The ruthenium-rich phase first appears at 1500°C between 15.07 and 15.83 atomic per cent of ruthenium, and increases proportionally with the ruthenium content across the entire width of the duplex region.

The two phases, it was found, could be conveniently separated by chemical methods. The palladium-rich phase can be dissolved away in a dilute solution of aqua regia, leaving the more noble ruthenium-based phase intact. By facilitating the separate chemical analysis of the two constituents, this simple technique permitted the phase boundary position to be fairly accurately defined. Table II shows the results of such analyses carried out on samples quenched after heat treatment for 64 hours at 1300°C and 72 hours at 1000°C.

These values confirm the microscopical phase boundary determinations with respect

**Table I**
**Solidus Determinations**

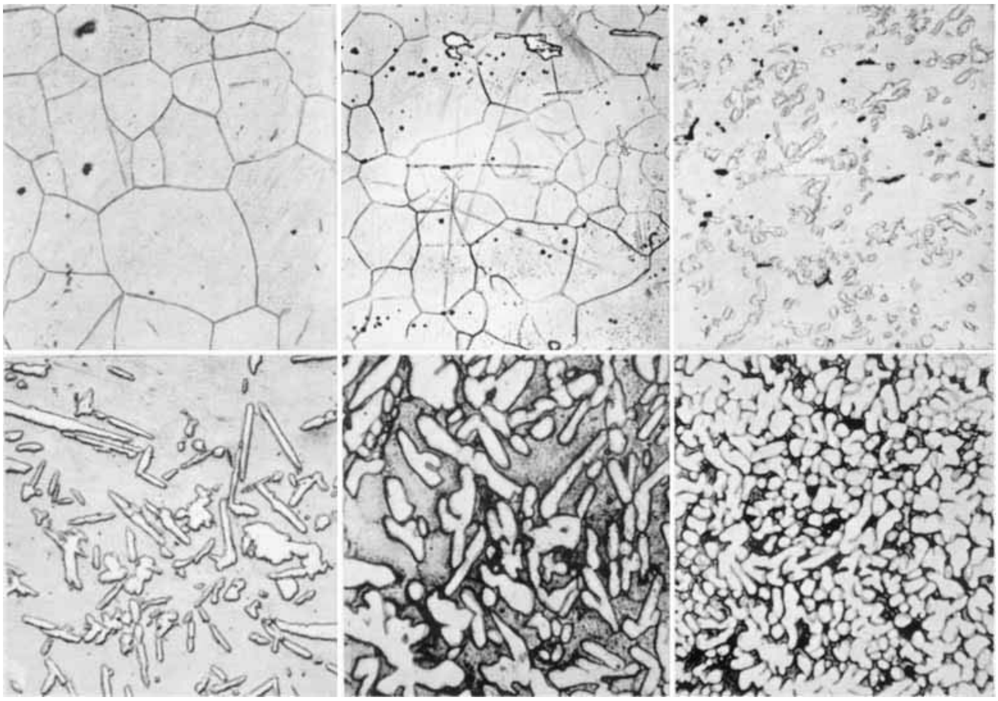
| Ruthenium content | | Solidus limits °C |
|---|---|---|
| Weight % | Atomic % | |
| 5.70 | 5.95 | 1571–1573 |
| 8.85 | 9.24 | 1578–1582 |
| 10.50 | 10.98 | 1577–1582 |
| 11.90 | 12.42 | 1574–1580 |
| 15.22 | 15.83 | <1581 |
| 16.70 | 17.41 | 1577–1582 |
| 25.00 | 25.86 | 1577–1582 |

**Table II**

**Compositions of Palladium and Ruthenium-rich Solid Solutions after Treatment at 1300 and 1000°C**

| Temperature, °C | Total Ru content of alloy | | Ru content of Pd-rich phase | | Ru content of Ru-rich phase | |
|---|---|---|---|---|---|---|
| | Weight % | Atomic % | Weight % | Atomic % | Weight % | Atomic % |
| 1300 | 16.29 | 16.92 | 10.20 | 10.66 | 88.15 | 88.75 |
| | 19.63 | 20.34 | 11.12 | 11.60 | 87.33 | 88.00 |
| 1000 | 14.50 | 15.07 | 5.41 | 5.64 | 92.89 | 93.26 |
| | 16.29 | 16.93 | 4.43 | 4.62 | 91.95 | 92.36 |
| | 19.63 | 20.35 | | | 92.60 | 92.96 |

to the palladium-rich solid solutions, and show that no intermediate phase exists between limits of 5 and 92 per cent of ruthenium at temperatures above 1000°C. Beautiful Widmanstätten structures resulted when alloys, originally single phased, were taken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8 9 10

*Microstructures of ruthenium-palladium alloys after quenching from 1500°C*
*Fig. 5 10.97 at.% Ru, × 120; Fig. 6 15.83 at.% Ru, × 120; Fig. 7 20.35 at.% Ru × 120; Fig. 8 25.86 at.% Ru, × 120; Fig. 9 61.20 at.% Ru, × 215; Fig. 10 71.09 at.% Ru, × 215*

below the ruthenium solubility curve at temperatures around 1300°C. Fig. 4 shows the microstructure of the 15.07 atomic per cent alloy, originally homogenised and quenched from 1500°C, which had been reheated and quenched after 64 hours at 1300°C.

## X-Ray Analysis

A systematic X-ray diffraction study of the system was carried out in parallel with the microscopic work. Lattice parameter measurements were determined with a 19 cm Debye camera using Cu K$\alpha$ radiation. Back reflection photographs were also taken from polished and etched microsections.

Much of the preliminary work was carried out on wires 0.015 inch in diameter. These, it was found, gave satisfactory diffraction patterns for the palladium-rich solid solution alloys. Due to some masking effect, however, the diffraction patterns of the ruthenium-rich phase did not show up on alloys containing less than 25 per cent of ruthenium, and in order to study conveniently the crystal structure of this phase it was separated chemically from its matrix as described in the previous

### Table III

### Lattice Parameter Measurements

| Ruthenium content Weight % | Atomic % | Time of treatment, hours | Quenching temperature °C | Type of specimen | Phases present F.c.c. a | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C.p.h. a | c | c/a |
| 8.85 | 9.24 | 1 | 1300 | Wire | 3.8784 | | | |
| 8.85 | 9.24 | 117 | 700 | | 3.8792 | | | |
| 14.50 | 15.07 | 72 | 1000 | Powder | F.c.c. | 2,7013 | 4.2784 | 1.5835 |
| 16.29 | 16.93 | 72 | 1000 | | F.c.c. | 2.7018 | 4.2788 | 1.5837 |
| 19.63 | 20.35 | 72 | 1000 | | F.c.c. | 2.7017 | 4.2788 | 1.5837 |
| 14.50 | 15.07 | 64 | 1300 | Powder | F.c.c. | 2.7019 | 4.2821 | 1.5848 |
| 16.29 | 16.92 | 64 | 1300 | | F.c.c. | 2.7020 | 4.2813 | 1.5844 |
| 19.63 | 20.35 | 64 | 1300 | | F.c.c. | 2.7025 | 4.2813 | 1.5841 |
| 8.20 | 8.57 | 16 | 1500 | Back reflection | 3.87892 | | | |
| 14.50 | 15.07 | 16 | 1500 | | 3.87468 | | | |
| 16.29 | 16.93 | 64 | 1500 | | 3.87507 | 2.7030 | 4.2845 | 1.5851 |
| 19,63 | 20.35 | 64 | 1500 | | 3.87635 | 2.7031 | 4.2836 | 1.5847 |
| 70.00 | 71.09 | 64 | 1500 | Powder | | 2.7030 | 4.2851 | 1.5853 |
| 80.00 | 80.88 | 64 | 1500 | | | 2.7026 | 4.2851 | 1.5855 |
| 90.00 | 90.50 | 64 | 1500 | | | 2.7024 | 4.2845 | 1.5854 |
| 14.50 | 15.07 | 168 | 850 | Powder | F.c.c. | 2.7024 | 4.2786 | 1.5833 |
| 14.50 | 15.07 | 216 | 750 | | F.c.c. | 2.7023 | 4.2785 | 1.5833 |

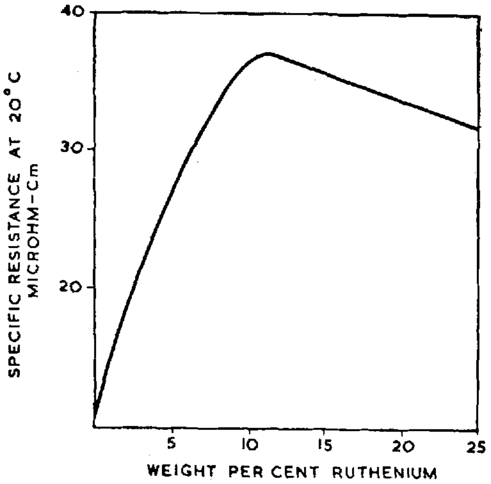

*Fig. 11 Resistivity of palladium-rich alloys after quenching from 1340°C*

section. Drillings were taken from heat treated specimens and disintegrated in a 25 per cent aqua regia solution, the insoluble phase being carefully washed and mounted in the powder camera. It had in all instances a close-packed hexagonal structure similar to that of pure ruthenium. Table III summarises the results of the lattice parameter determinations. The absolute values of the figures quoted are estimated to be accurate to within one part in 8,000.

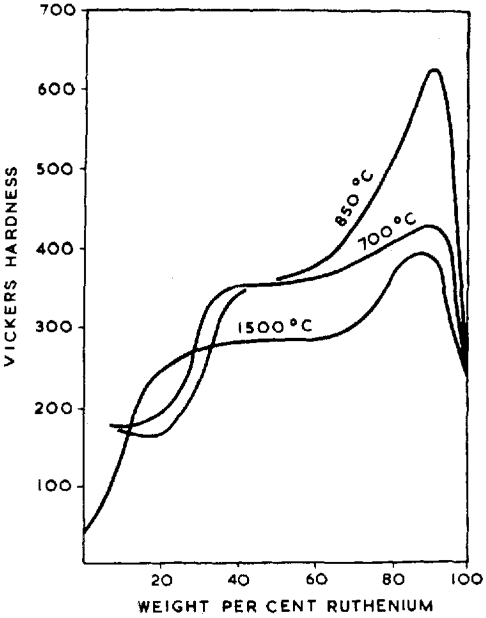

*Fig. 12 Hardness of ruthenium-palladium alloys quenched after 16 to 24 hours at 1500°C, 168 hours at 850°C, and 216 hours at 700°C*

The X-ray results show clearly that only two phases exist below the solidus in this system. The second phase which begins to appear at 1500°C when the ruthenium content exceeds 15.07 atomic per cent is identical with that in the ruthenium-rich alloys. The parameter data were plotted to obtain the boundaries of the two-phase region which are given in Table IV. Some lattice parameter data by Hellawell and Hume-Rothery (2) were observed to be in good agreement with our own determinations. Due to its low rate of change with ruthenium content, however, the lattice parameter of the ruthenium-rich solid solutions does not afford a sensitive index of composition.

**Table IV**

**Phase Boundary Determinations from X-ray Measurements**

| Temperature, °C | Pd-rich solid solution (Atomic % Ru) | Ru-rich solid solution (Atomic % Ru) |
|---|---|---|
| 1000 | | 94 |
| 1200 | 10.8 | |
| 1300 | | 87.5 |
| 1500 | 14.5 | |

The X-ray results can only be interpreted on the assumption that the diagram is of the simple peritectic type, and no evidence in favour of a eutectoidal transformation can be advanced.

## Electrical Resistivity

Specific resistivity determinations were carried out at 20°C on wire specimens of alloys containing up to 25.86 atomic per cent of ruthenium. All the wires, 0.020 inch in diameter, were quenched from 1340°C. Fig. 11 illustrates the results. The resistivity in the single phase region rises rapidly to a value of 37 microhm-cm for a ruthenium content of approximately 12 per cent, further ruthenium additions reducing the resistivity of the duplex alloys in a perfectly linear manner. The position of maximum resistivity confirms the position of the phase boundary shown in Fig. 1.

## Hardness Values

The hardest alloys of this series are those containing approximately 90 per cent of ruthenium. Fig. 12 illustrates the hardness values of alloys quenched from 700, 850 and 1500°C. Characteristic features common to all these curves are the hardness peak reaching a maximum at 90 per cent ruthenium and the curious plateau extending over much of the duplex region. The high hardness of alloys containing 80 to 90 per cent of ruthenium aged at 850°C for seven days might be attributed to the slow decomposition of the supersaturated ruthenium-rich solid solution.

## Discussion

The results of this investigation have been plotted to give the diagram shown in Fig. 1. The liquidus data of Rudnitskii and Polyakova are in fairly good agreement with the general shape of the diagram, but some accurate melting point determinations towards the ruthenium-rich end of the diagram are obviously required. The recent determination of Baird (3) for the melting point of ruthenium, 2250°C, has been accepted in drawing the liquidus.

Detailed study of the ruthenium-rich solid solutions is desirable in view of the possibility of allotropic modifications in this element at temperatures above 1500°C.

## Acknowledgements

Acknowledgements are due to Mr H. W. Webb who carried out the chemical analysis required and to Mr L. A. Ford who carried out the X-ray determinations.

### References

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|---|---|---|
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# Powerforming in the Esso Refinery at Cologne

The new £18 million oil refinery recently put on stream by Esso A.G., Cologne, represents a major addition to German oil refining capacity. Situated near the Ruhr where the principal consumers of fuel oils are concentrated, a range of fuel oils will form over 50 per cent of the plant's annual capacity of 3.5 million metric tons. Diesel fuels will constitute about 25 per cent of output, the remainder being high-octane petrol and raw materials for a variety of petrochemical processes.

Production within the refinery is based on an Aramco feed stock having a research octane number from 25 to 45 and a boiling range from 160 to 400°F. To achieve a substantial up-grading and to yield fuel of research octane numbers exceeding 100, a Powerforming plant of 9000 B/SD capacity is installed.

Powerforming, developed in 1954 by the Esso Research and Engineering Co., New York, is a fixed-bed catalytic reforming process employing a platinum catalyst.

The principal reactions within the Powerformer are the dehydrogenation and dehydroisomerisation of feed stock naphthenes, together with dehydrocyclisation of paraffins. Undesirable hydrocracking is kept to a minimum. Four reactors in series with intermediate reheat furnaces are in operation, together with a swing reactor which enables each catalyst charge to be regenerated without loss of production.