

# Rhodium-Platinum Alloys

## A CRITICAL REVIEW OF THEIR CONSTITUTION AND PROPERTIES

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Owing to their extensive employment, alloys of rhodium and platinum have an industrial significance greater than that of any other noble metal system.

Rhodium was first isolated in the opening years of the nineteenth century, and shortly after this Russia began to develop her platinum resources in the Urals. Ore from this source frequently contained twelve times as much iridium as rhodium. Platinum-rhodium-iridium alloys, obtained by the direct fusion of crude platinum, were found to be very resistant to corrosion and were frequently employed for coinage and for chemical plant (1, 2).

Interest in the binary rhodium-platinum alloys developed only after Le Chatelier's demonstration in 1887 that reproducible temperature measurements could be obtained with the 10 per cent rhodium-platinum thermocouple (3). Since 1927 the International Temperature Scale, over the range 660° to 1063°C has been defined in terms of the e.m.f. generated by the 10 per cent rhodium-platinum thermoelement, and industrial pyrometry depends very largely upon the thermal stability of this alloy system.

### The Constitutional Diagram

Immediately below the solidus platinum and rhodium form a continuous series of solid solutions. The true equilibrium structure at lower temperatures is still uncertain. The first melting point determinations were made by Wartenberg in 1910 (4). Twenty years later Feussner and Müller used a photoelectric pyrometer for melting point deter-

minations which embraced the entire composition range (5). Only one arrest point was detected, and the authors concluded that solidus and liquidus curves were very close together. Acken's melting point determinations, reported in 1934 (6), were made with a disappearing filament pyrometer. The impurity content of the materials employed was probably less than 0.001 per cent. The pyrometer was focused on the bottom of an axial hole drilled in 75 g ingots which were slowly heated in thoria crucibles in a high frequency furnace. Alloys containing less than 40 per cent of rhodium were melted in air, those of higher rhodium content being vacuum melted. As in the work of Feussner and Müller, only one melting arrest was detected. Acken's results were, in general, approximately 20°C higher than those of the German investigators. Both sets of values, together with the recently determined melting points of platinum and rhodium (7, 8) are plotted on the diagram in Fig. 1. The shape of this curve suggests the existence, immediately beneath it, of a continuous series of solid solutions. X-ray determinations, first reported by Weerts in 1932 (9), repeated by Goldschmidt and Land in 1947 (10), and confirmed by Raub (11), showed that in this region the lattice parameter/atomic composition curve had only a slight positive deviation from linearity. Fig. 2 illustrates Raub's X-ray diffraction data.

Although Acken was unable to detect any phase changes in his alloys, he concluded that slight irregularities in melting points, Brinell hardness, resistivity and thermoelectric force

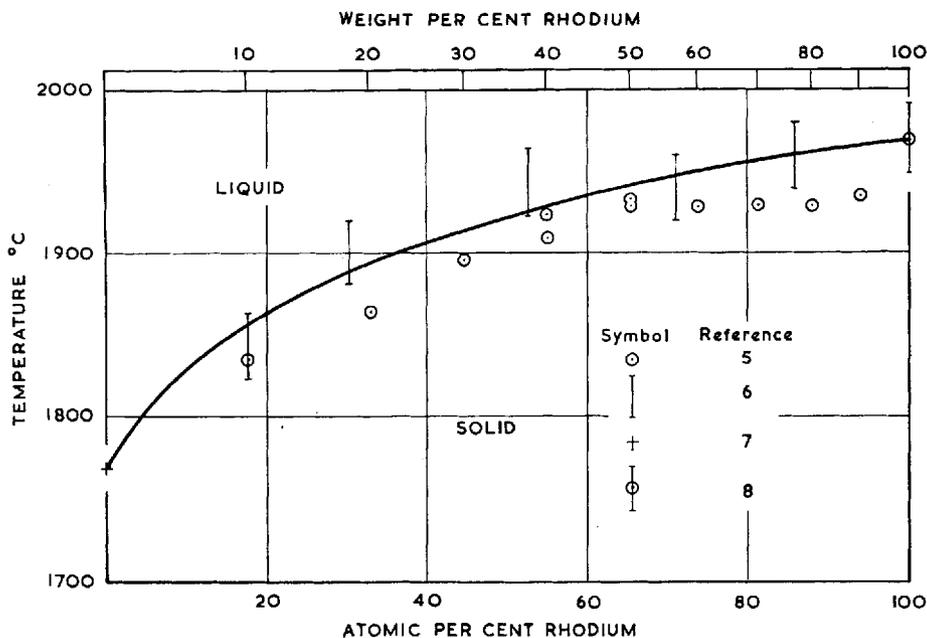


Fig. 1 Constitutional diagram of the rhodium-platinum system

might indicate some departure from complete miscibility. Nemilov and Voronov (12), on the other hand, concluded that the physical and metallurgical characteristics of the system were those of a typical solid solution. A detailed study of the evidence suggests that the system may not be so simple as hitherto supposed. Hildebrandt's magnetic susceptibility measurements (13), when plotted as a

function of composition, exhibit a fairly sharp inflexion over the range 20–25 atomic per cent rhodium. Although originally interpreted as being indicative of an order-disorder reaction, this behaviour could be caused by a simple change in solubility. Wide miscibility gaps are exhibited in the platinum-iridium, palladium-rhodium and palladium-iridium systems, and Raub (11) predicts the occurrence of a similar

gap, having a critical temperature of approximately 780°C in the platinum-rhodium system.

Allotropic modifications in pure rhodium have been reported by several investigators but the evidence is not conclusive. Jaeger and Zanstra (14) concluded that alpha rhodium, stable up to 1200°C, had a simple cubic structure of lattice parameter 9.211Å, while beta rhodium, stable above 1200°C, had a face centred

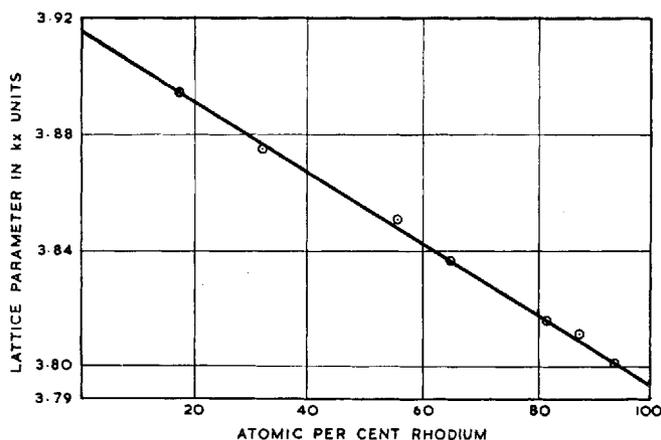


Fig. 2 Lattice parameter curve for rhodium-platinum alloys rapidly cooled from below the solidus (Reference 11)

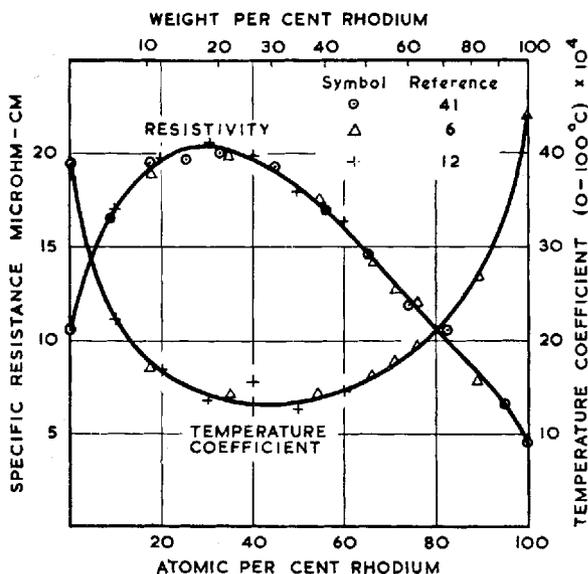


Fig. 3 Resistivity and temperature coefficient of annealed rhodium-platinum alloys

cubic structure with  $a = 3.7957\text{\AA}$ . Similar findings were reported by E. T. Dixon (15) and Jaeger and Rosenbohm (16). Rudnitsky, Polyakova and Tyurin (17) studied the thermoelectric behaviour of rhodium by a refined thermoelectric technique and concluded in 1956 that the alpha-beta transformation occurred at  $1030 \pm 5^\circ\text{C}$ . Although constitutional studies in the palladium-rhodium system (18) appeared to confirm this temperature, more recent work by Raub, Beeskow and Menzel (19) did not show any change of crystal structure in rhodium up to  $1500^\circ\text{C}$ . The high temperature lattice parameter data of Raub and his co-workers disagree with those of Bale (20), and the subject could be profitably investigated in greater detail.

### Electrical Properties

Fig. 3, based on the work of several investigators, indicates that the highest resistivity of the series, approximately 30 microhm-cm, is developed by alloys containing approximately 30 atomic per cent of rhodium. The 45 atomic per cent alloy has the lowest temperature coefficient. An interesting feature of the

resistivity curve is the slight negative inflexion over the range 70 to 80 per cent rhodium which has been confirmed by several workers.

Although no systematic experiments on the effect of heat treatment have been reported, the resistivities of quenched and slowly cooled alloys are not appreciably different.

Resistance variations at high temperatures are presented in Fig. 4, which illustrates the negative curvature of the pure rhodium line first observed by Holborn and Wien in 1895 (21).

### Thermoelectric Properties

The thermoelectric properties of rhodium-platinum alloys have been the subject of fundamental and industrial concern since the pioneer work of Le Chatelier in 1886 (22). Holborn and Wien (21, 23) demonstrated the stability of rhodium-platinum thermoelements over the period 1892-1899, and concluded that the 10 per cent rhodium or Le Chatelier couple com-

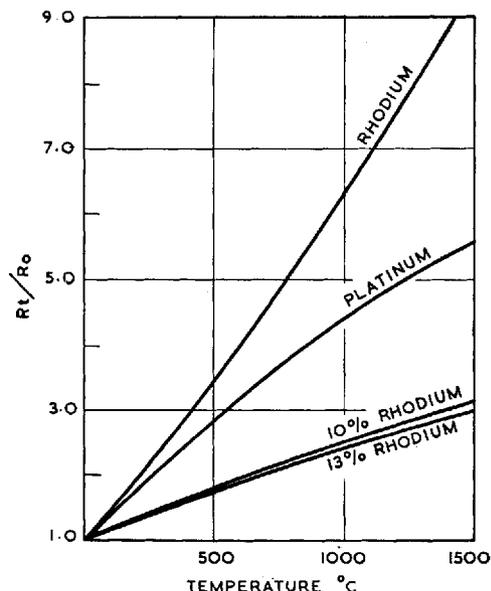


Fig. 4 High-temperature resistance variations of rhodium, platinum and two alloys (Reference 41)

pared favourably with the platinum resistance thermometer for accurate temperature measurement. Commenting upon the extremely rapid growth of industrial pyrometry, Henning and Moser (24) remarked that at the Physikalische Technische Reichanstalt alone 9915 rhodium-platinum thermocouples were calibrated between 1900 and 1930.

Fig. 5, taken largely from Caldwell's data (25), illustrates the thermoelectric force in millivolts generated between rhodium-platinum alloys and pure platinum at various temperatures. An important feature of these curves is the reasonably flat plateau displayed at lower temperatures by alloys containing 20 to 50 atomic per cent of rhodium. No evidence of a phase change within the dotted area has yet been advanced.

The Le Chatelier thermocouple was in general use until 1922, when tests carried out by the U.S. Bureau of Standards showed that 10 per cent couples of British manufacture were less stable than their American counterparts (26). Chemical analysis indicated the presence of up to 0.34 per cent of iron in the British alloy. Improved refining methods eliminated the iron, with the result that 13 per cent of rhodium was required to develop an e.m.f. comparable to that of the American 10 per cent couple. The 13 per cent couple was found to be very stable and is generally preferred in this country to the 10 per cent couple, which gives a lower e.m.f. British Standard 1826, 1952, defines the e.m.f.s generated by the two couples at temperatures up to the melting point of platinum. The values specified are based largely upon determinations carried out by C. R. Barber (7) at the National Physical Laboratory and represent average values maintained by manufacturers for many years before 1950.

Since 1927 the 10 per cent rhodium-platinum : platinum thermocouple has been used to define the International Temperature Scale

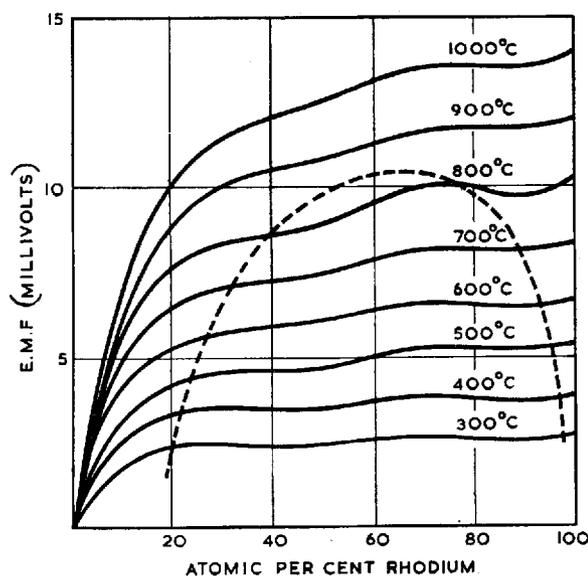


Fig. 5 Thermoelectric force in millivolts generated between rhodium-platinum alloys and pure platinum at various temperatures (Reference 25)

over the interval from 660°C to the melting point of gold.

The high temperature stability of rhodium-platinum thermocouples is adversely affected by contamination, by slight preferential volatilisation of rhodium, and by gradual diffusion of rhodium into the pure platinum limb. Although ultimate failure is usually due to attack by metallic or other vapours, prolonged heating at temperatures in the region of 1500°C may lead to appreciable change in calibration. Lead and zinc vapours, and sulphur-bearing gases frequently cause brittleness and hot shortness (27), and thermocouples should be protected by impermeable sheaths against such contaminants. Rhodium-platinum alloys have a great affinity for silicon. At temperatures above 1000°C reducing conditions tend to break down silicious refractories, thus liberating silicon which attacks the noble metal. Intimate contact between metal and refractory is not essential, as the reaction can proceed through the silicon monoxide vapour phase. The melting point of a thermocouple contaminated by silicon in such a way may be as low as 1200°C. Complete avoidance of silicon is difficult as even

the purest oxide refractories are not completely free from this element. Experience has shown that the incidence of attack depends largely on the reduction potential of the atmosphere rather than on the silicon content of the refractory.

Silicon attack can, however, occur even when conditions do not appear to be reducing. Research on this problem was stimulated by the frequent thermocouple failures encountered soon after the general introduction of the quick-immersion technique for liquid steel temperature measurement. Land (28) and Reeve (29) confirmed that contamination did not occur in the absence of traces of oil. The complete mechanism of silicon transfer was finally established by Chaston (30), who showed that embrittlement was caused by the sulphur present in traces of oil left in the thermocouple. This sulphur, in the presence of carbon monoxide, reacts with the refractory to produce volatile silicon sulphide, which dissociates on the surface of the couple wires to form brittle silicides. The rhodium-platinum limb is usually the more seriously embrittled. The silicide forming in the rhodium alloy is a hard constituent with a bluish tint, while that in the platinum member is softer and grey in appearance (31). A further crystal boundary constituent is frequently found in the rhodium alloy. These three silicides have been studied microscopically and by X-ray diffraction techniques. A contraction of lattice parameter indicates a slight solubility of silicon in platinum but the exact composition of the silicide phases has not been precisely determined (10). This type of attack can, in practice, be avoided by baking out the steel protection tubes at dull red heat in the presence of a current of air.

Prolonged heating in air in the complete absence of sulphur can frequently induce appreciable change of thermoelectric force even though mechanical failure need not occur. The pure platinum limb of the couple is generally most affected by this type of deterioration. Chaussain (32) reported that whereas at 1300°C silica and alumina affected

the thermoelectric characteristics of pure platinum considerably more than those of the rhodium-platinum alloy, thoria appeared to be inert to both couple legs. Tests by Ehringer (33) led to similar conclusions. At 1400°C in air the resistance to attack by pure alumina, mullite or silica increased with rhodium contents up to 30 per cent, which was the richest alloy studied. Although reducing conditions accelerated the rate of attack, rhodium alloys in contact with pure alumina was not appreciably contaminated. Lapp and Maksimova (34) confirmed the high stability of rhodium alloys heated in contact with alumina for long periods at 1500°C.

Additional tests with alumina, beryllia, magnesia and thoria showed that all these refractories were equally stable towards rhodium-platinum, and that the most stable alloy contained 30 per cent of rhodium. Experiments by Bennett (35) had results which suggested that couple deterioration of this type may be primarily induced by impurities in the refractory rather than by the refractory itself.

Rhodium and platinum both volatilise from

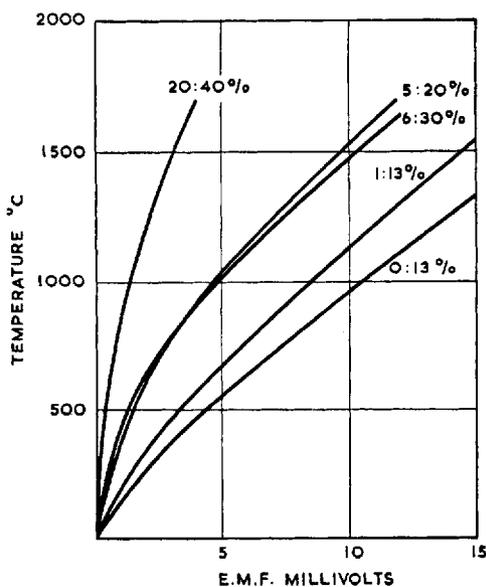


Fig. 6 Calibration curves of 1:13, 5:20, 6:30 and 20:40 per cent rhodium-platinum thermocouples compared with that of the standard 13 per cent rhodium-platinum couple

the surface of heated noble metal thermocouples, although the effect of such evaporation on the calibration is frequently exaggerated. Bennett (35), for example, has heated a complete platinum : 13 per cent rhodium-platinum thermocouple between terminals in free air at 1500°C for 30 hours. Although a total loss in weight of 16.5 per cent occurred, the e.m.f. generated at the gold point had decreased by only 3°C. Data on the relative evaporation rates of rhodium and platinum from couple wires are rather contradictory. Mrs. McQuillan (36), as a result of tests carried out at 1600°C, concluded that platinum evaporated slightly more than rhodium. Jewell and Knowles (37) reported a slight preferential evaporation of rhodium. The more recent results of Raub and Plate (38) indicate that rhodium evaporates from the alloy less readily than platinum.

A gradual diffusion of rhodium into the pure platinum limb is probably the most important factor contributing to the deterioration of thermocouples heated for long periods above 1400°C. Very slight contamination of the pure platinum limb by rhodium results in a pronounced decrease in the e.m.f.

generated by the couple. Rhodium is transferred from the alloy limb of the couple by diffusion through the hot junction and by evaporation, the latter effect being predominant. Volatilisation of rhodium from adjacent furnace windings often contributes to the deterioration of the pure platinum couple limb.

Small additions of rhodium are frequently made to the pure platinum limb to minimise the effects of rhodium diffusion. Although such additions lower the couple e.m.f., its thermal stability is greatly improved. The 1 per cent rhodium-platinum : 13 per cent rhodium-platinum thermocouple is sometimes used in this country (39), while the 0.5 per cent rhodium-platinum : 13 per cent rhodium-platinum thermocouple is used to a limited

extent in America (35). Such rhodium additions minimise the susceptibility to attack by refractories and increase the high temperature mechanical properties. Considerations of this type suggest that the rhodium content of the negative couple limb might be considerably increased. The alloy combination selected should be one in which the e.m.f. generated is as high as possible and the melting point of the limb poorer in rhodium

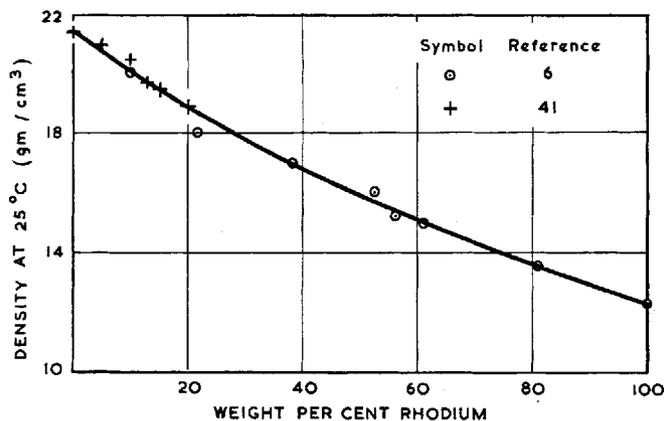


Fig. 7 Density of rhodium-platinum alloys

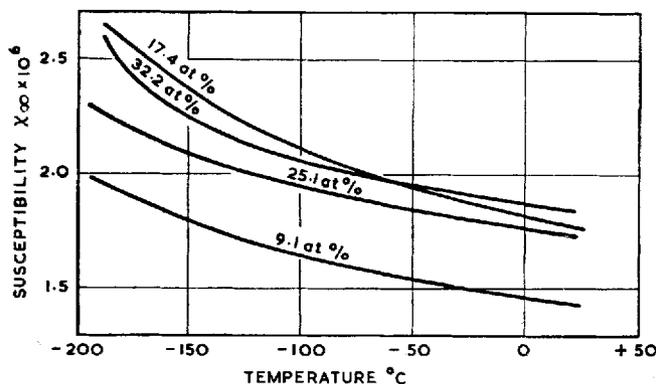


Fig. 8 Variation of mass-susceptibility with temperature for various rhodium-platinum alloys (Reference 13)

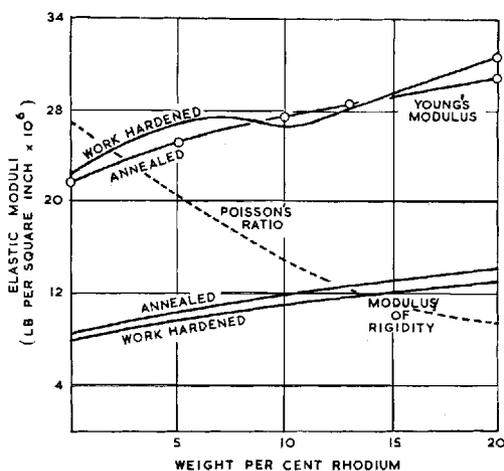


Fig. 9 Young's modulus, modulus of rigidity, and Poisson's ratio of alloys containing up to 20 per cent by weight of rhodium (Reference 41)

is also as high as possible, and three rhodium-platinum thermocouples of this type are now in general use. British practice favours the 5 per cent rhodium-platinum : 20 per cent rhodium-platinum couple as having the best general properties, while the 6 per cent rhodium-platinum : 30 per cent rhodium-platinum thermocouple is used in Germany (33).

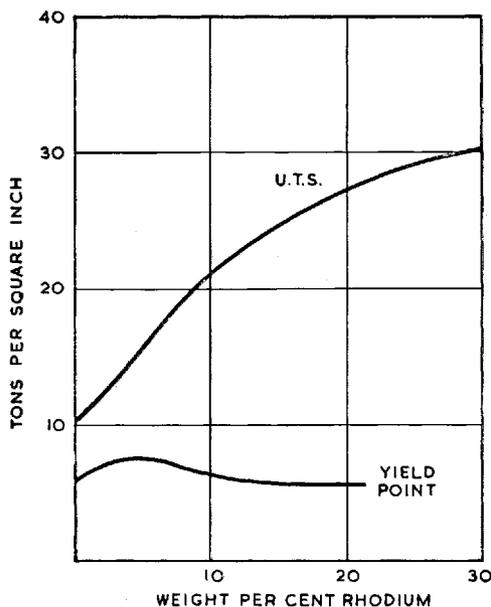


Fig. 10 Yield point and ultimate tensile strength of annealed rhodium-platinum alloys (Reference 41)

The 20 per cent rhodium-platinum : 40 per cent rhodium-platinum thermocouple is suitable for use up to 1900°C and has been used for measuring the temperature of oxygen-blown stainless steels (40). Fig. 6 contrasts the calibration curves of these couples with those of the standard 13 per cent rhodium-platinum couple. Because these special couples generate very low e.m.f.s at room temperature cold junctions and compensating leads are not generally required.

### Physical and Mechanical Properties

As illustrated in Fig. 7, the density of the annealed alloys varies with rhodium content in a continuous manner over the entire com-

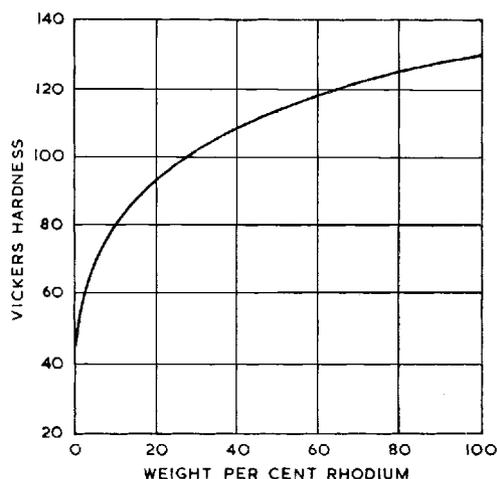


Fig. 11 Diamond pyramid hardness of annealed rhodium-platinum alloys (Reference 41)

position range. Magnetic susceptibility determinations display discontinuities which were at one time interpreted by Hildebrandt (13) as being indicative of an ordering reaction based on the 25 atomic per cent rhodium composition. Fig. 8 shows the variations of mass susceptibility with temperatures for alloys containing respectively 9.1, 17.4, 25.1, and 32.2 atomic per cent of rhodium.

Annealed alloys have a Young's modulus which increases uniformly with rhodium content until a value of  $31 \times 10^6$  lb per sq. in. is reached at 20 per cent by weight of rhodium

(41). Work hardened material has a direct modulus which is lower than that of the annealed alloys over the range 9 to 14 per cent of rhodium. The modulus of rigidity of annealed alloys is approximately 8 per cent higher than that of hard drawn material over the complete composition range. Poisson's ratio, calculated from the data of Fig. 9, decreases from a value of 0.27 for pure platinum to 0.094 for the 20 per cent rhodium alloy.

The ultimate tensile strength of annealed alloys increases from 10.5 tons per sq. in. for pure platinum to 30 tons per sq. in. for a rhodium content of 30 per cent. As illustrated in Fig. 10, however, the yield point remains roughly constant at about 6 tons per sq. in. up to a rhodium content of at least 20 per cent. The curve relating hardness with composition displays no inflexions, although small additions of rhodium rapidly harden the alloy. Fig. 11 illustrates the hardness of annealed specimens of alloys up to 100 per cent by weight of rhodium (41).

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The concluding part of Dr. Darling's article will be published in the July issue of "Platinum Metals Review".

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