

The Elastic and Plastic Properties of the Platinum Metals

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Among the papers given at a Conference on New Engineering Materials organised by the Process Engineering Group of the Institution of Mechanical Engineers in Birmingham in October, was a contribution by Dr Darling on "Some Properties and Applications of the Platinum Metals and Rhenium". This surveyed the physical and mechanical properties of the metals, their melting and working, and described certain of their alloys employed in industrial processes. The extract from this paper given here comprises a review of the more fundamental physical properties of the six platinum metals and of their interrelationships.

The platinum metals fall within and comprise an integral part of the second and third long periods of the transition elements. These metals occupy positions in the periodic table where an incomplete group of eight electrons expands systematically into one of eighteen by the gradual acquisition of *d*-band electrons. The resulting tendency towards higher valencies in the later periods reflects itself in the physical and mechanical properties of the metals and it should be emphasised that, with the exception of aluminium and magnesium, all the metals of structural significance fall inside this important area of the periodic table.

From the engineering point of view these rare refractory metals are of importance primarily because of their ability to withstand substantial stresses under oxidising

conditions at temperatures above 1000°C. Melting points and elastic moduli both provide an approximate indication of the cohesive strength or stability of an element, and it is of interest, therefore, to examine the distribution of these parameters within this selected group of metals.

Fig. 1 shows that the peak melting points are exhibited by metals in group VIA. Tungsten has the highest melting point of any element in the periodic table but is closely flanked by rhenium and osmium. Similar dispositions occur in the second long period, where molybdenum with the highest melting point is closely followed by ruthenium.

It is assumed here that one will define the cohesive strength of a metal in terms of the average number of electrons per atom participating in resonating covalent bonding. Pauling (1, 2) suggests that the valency remains constant at 5.78 for metals to the right of group VA. Hume-Rothery (3), however, rejects this hypothesis and assumes a maximum valency of 6 for molybdenum and tungsten which have the highest melting points. Any movement to the right is considered to cause a decrease in valency because the additional electrons enter non-bonding orbitals and couple with electrons which previously contributed to the metallic bonding.

This approach has been generalised by Robins (4), who believes that the properties of the metals in the second and third long periods can be interpreted on the assumption that a tendency exists for the number of bonding electrons per atom to be equal to half the co-ordination number. This tendency can be used to explain why tungsten

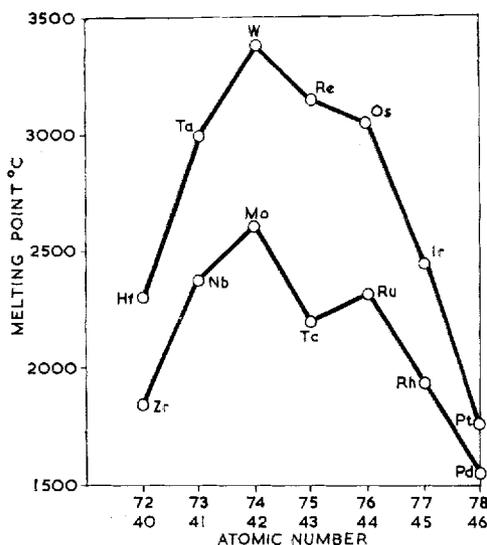


Fig. 1 The melting points of the more refractory transition elements

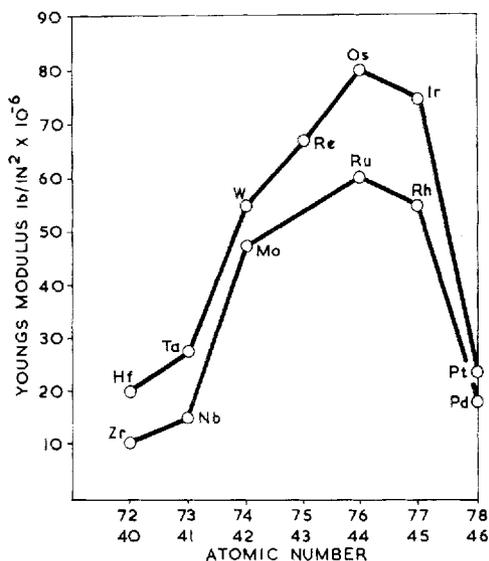


Fig. 2 Elastic moduli of the transition elements

and molybdenum, which are presumed to have six valency electrons and an effective co-ordination number of 12, have the highest melting points in their respective series.

Robins' interpretation presupposes that the cohesive strength of an element is best indicated by its melting point and the heat of sublimation. These characteristics involve a change of state, however, and Pauling (2) considers that the most reliable index is provided by the atomic distance and by the bulk modulus of elasticity.

The fundamental elastic constants of the metals under consideration are illustrated in Fig. 2, where the peak values are those of osmium and ruthenium rather than of tungsten and molybdenum with the highest melting points. This displacement of maximum properties towards the elements of higher atomic number is reconcilable with Robins' hypothesis if the possibility of bonding mechanisms additional to those of resonance are allowed for.

Osmium and iridium have the highest elastic moduli of any of the elements in the periodic table. They are less compressible and deform elastically less than other metals when subjected to shear and tension. Fig 3 presents evidence (5, 6) which provides

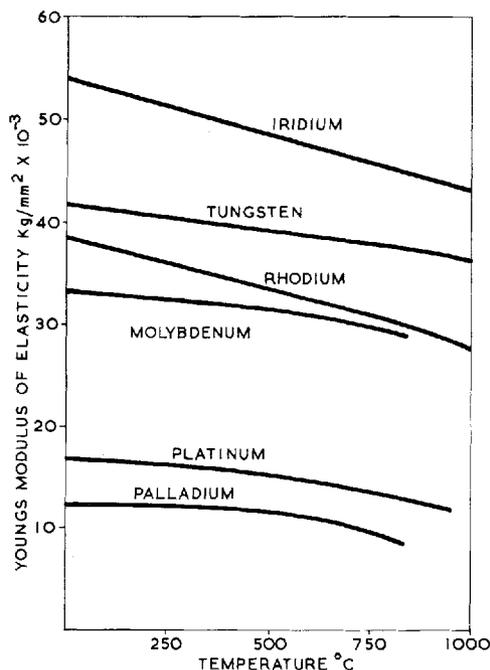


Fig. 3 Variation of elastic modulus with temperature

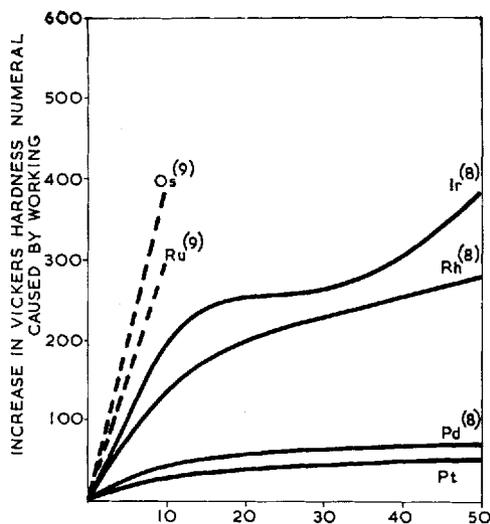


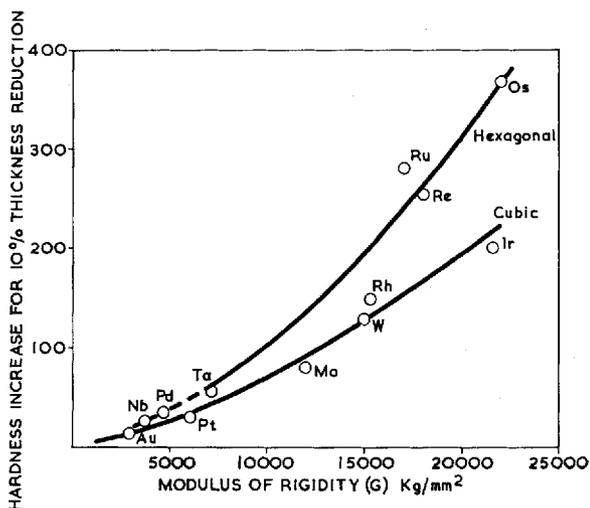
Fig. 4 Increase of hardness caused by working

some support for the view that the bonding processes of the refractory platinum metals differ somewhat from those of tungsten and molybdenum. Although initially lower, the direct elastic moduli of tungsten and molybdenum decrease with temperature less rapidly than those of iridium, rhodium and rhenium (7). Between room temperature and 1000°C the modulus of iridium decreases 20 per cent while that of tungsten falls by only 14 per cent. Rhodium has a modulus which decreases 28 per cent over the same range, while that of molybdenum decreases by only 18 per cent.

The rapid fall in high temperature modulus exhibited by platinum and palladium is probably attributable to recrystallisation which occurs in these pure metals at temperatures approaching 600°C.

The platinum group metals embrace a wide range of ductility; within each sub-group the rate

Fig. 5 Rate of work-hardening plotted as a function of modulus of rigidity



of work-hardening varies systematically with increasing atomic number. These work-hardening relationships are illustrated graphically in Fig. 4 which confirms the systems of vertical similarity previously mentioned.

Ruthenium is the least malleable metal of the lighter group, and osmium, its heavier counterpart, has never been effectively worked either hot or cold. Rhenium and iridium, which flank osmium in the periodic table, resemble each other in ductility. Iridium resembles rhodium in that both can be worked readily when hot but deform with difficulty at room temperature. Palladium and platinum are characterised by extremely high room temperature ductility and are comparable to nickel in this respect.

Although the hexagonal metals tend to work-harden rather more rapidly than those with cubic symmetry there is no fundamental reason why they should be inherently brittle. The low axial ratios of osmium and ruthenium are certainly unfavourable to easy plastic deformation but the glass-like fragility of osmium cannot be ascribed completely to this effect. Serious attempts to improve the ductility of ruthenium by very careful zone refining have been at best only marginally successful and there is no evidence to suggest that highly refined osmium shatters any less readily than the untreated grade of metal.

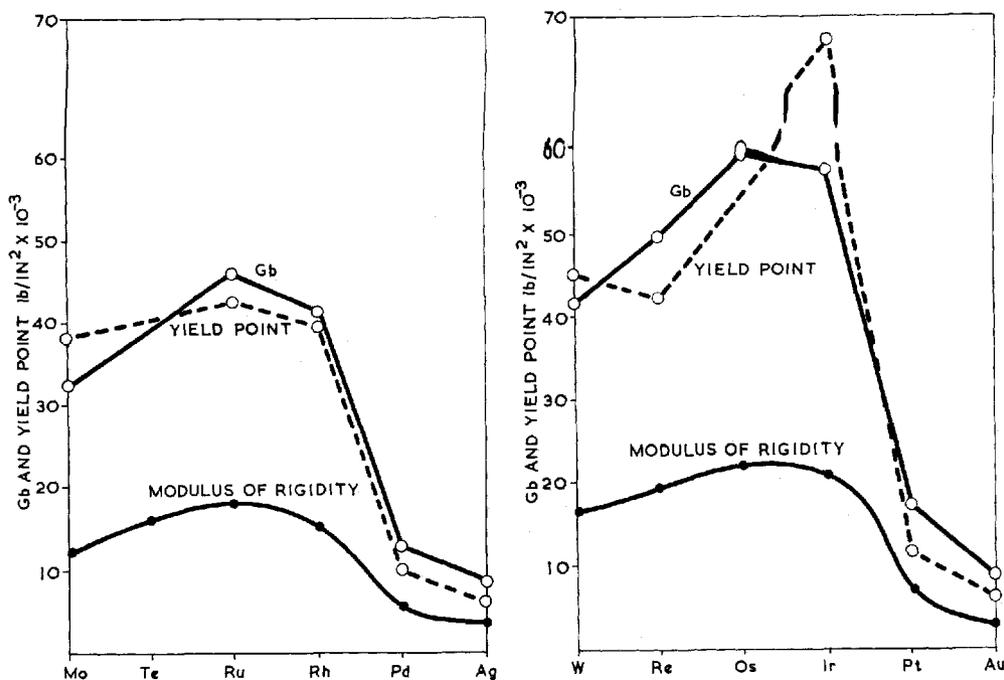


Fig. 6 The product of modulus of rigidity, G , and Burgers' vector, b , plotted on the same co-ordinates as yield point and modulus of rigidity

Such assumptions lead to consideration of the possibility of alternative reasons for the poor working characteristics of these two rare metals. It is perhaps significant that the rate of work-hardening of pure metals increases with increasing elastic modulus in a remarkably regular manner. This behaviour is illustrated in Fig. 5, where the rate of hardening caused by a 10 per cent reduction in thickness at room temperature is plotted against the rigidity modulus of a number of transition metals (10). Although the hexagonal metals work-harden more rapidly than those with cubic symmetry both curves are smooth and appear to represent a systematic trend.

Empirical relationships between plastic and elastic properties of metals were first discussed by Pugh in 1954 (11). This analysis was based on earlier work by Frank and Read (12) who showed that the theoretical flow stress of a pure metal depended upon the force required to push an edge dislocation through the lattice. This force varies as Gb , the product of the modulus of rigidity and of the Burgers' vector, or inter-

atomic distance in the direction of slip. This vector, b , is equal to $\frac{a}{\sqrt{2}}$ in face centred cubic crystals and to a in the close-packed hexagonal metals. Values of b , in Ångstroms, for the platinum metals are as follows:

Pt	Ir	Os	Pd	Rh	Ru
2.774	2.714	2.734	2.751	2.689	2.706

The generalisation is unfortunately impossible to verify completely, as grain boundaries, lattice defects, and traces of impurities can increase the flow stress many times without any corresponding change of elastic modulus. The relationship can, however, be illustrated in a qualitative manner by plotting yield points, modulus of rigidity, and the product Gb on the same system of co-ordinates, as in Fig. 6. The modulus of rigidity, being structure and purity insensitive, is known to a high degree of accuracy. The shape of both these graphs leaves little doubt that a fairly direct relationship exists between the rigidity modulus and the initial resistance to plastic deformation.

The ductility or malleability of a metal depends upon the difference between the stress required to cause fracture and that which first causes plastic flow. Brittle fracture occurs when the stress required to cause flow is higher than that needed to break the metal and form fresh surfaces. Ductile metals, however, require very high stresses to initiate fracture, although plastic flow commences when a low shear stress is applied. Such materials neck down to a point or knife edge before breaking in tension.

The stress required to cause ultimate fracture is related to the energies of freshly-created surfaces. It was shown by Elliot (13) in 1947 that fracture surface energies can be directly related to the bulk modulus of the deformed metals.

Arguments of this type suggest that the ratio of bulk to rigidity modulus should form a satisfactory index of metal ductility. Although this was attempted by Pugh, more precise values for the elastic constants have since become available, and the table below shows how accurately this generalisation holds good.

The metals having a low ratio of bulk to shear modulus are in fact all brittle and diffi-

cult to work. Ruthenium is a typical example having a K/G ratio of only 1.71. Tantalum, on the other hand, which is very ductile, has a K/G ratio of 3.02. The different ductilities of platinum and iridium are easily understood when their modulus ratios are considered, and the last column of the table provides a useful qualitative index of the relative ductilities of the various metals involved.

Poisson's ratio is a constant easily related to K/G , and it appears that all metals with low values of N are likely to be of limited workability.

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Elastic Constants of Some of the Transition Metals						
Metal	Crystal structure	Young's modulus, E , kg/mm ²	Modulus of rigidity, G , kg/mm ²	Bulk modulus, K , kg/mm ²	Poisson's ratio, N	$\frac{K}{G}$
Zirconium ..	C.p.h.	9 750	3 680	9 150	0.33	2.48
Niobium ..	B.c.c.	10 600	3 730	17 670	0.38	4.73
Molybdenum ..	B.c.c.	34 700	12 200	28 000	0.30	2.30
Technetium ..	C.p.h.	40 000	16 000	28 600	0.26	1.78
Ruthenium ..	C.p.h.	43 000	17 200	29 200	0.25	1.71
Rhodium ..	F.c.c.	38 640	15 300	28 010	0.26	1.83
Palladium ..	F.c.c.	12 830	4 610	19 090	0.39	4.13
Silver ..	F.c.c.	8 050	2 940	10 180	0.38	3.46
Hafnium ..	C.p.h.	14 100	5 400	11 150	0.30	2.07
Tantalum ..	B.c.c.	18 820	7 000	21 050	0.35	3.02
Tungsten ..	B.c.c.	39 600	15 140	31 860	0.29	2.11
Rhenium ..	C.p.h.	47 200	18 000	34 000	0.26	1.89
Osmium ..	C.p.h.	56 000	22 000	38 000	0.25	1.73
Iridium ..	F.c.c.	53 830	21 400	37 800	0.26	1.76
Platinum ..	F.c.c.	17 400	6 220	28 090	0.39	4.52
Gold ..	F.c.c.	8 020	2 820	17 460	0.42	6.18

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Oxygen for Space Vehicles

ELECTROLYSIS OF WATER WITH PLATINUM AND PALLADIUM ALLOY ELECTRODES

The electrolysis of water provides one of the most convenient means of generating oxygen for consumption by astronauts in space vehicles. Hydrogen is a valuable by-product of this process, and may be used in several catalytic reactions that are carried out in space capsules. Members of the Battelle Institute, Columbus, Ohio, have reported the results of research carried out during recent years and aimed at providing a water electrolysis system that can operate with high efficiency under the conditions of weightlessness that are encountered in space (1)

Conventional electrolysis cells in which both the oxygen and hydrogen are liberated in a free electrolyte would rapidly decline in operational efficiency under conditions of weightlessness due to progressive blocking of the electrode surfaces by the bubbles of gas liberated there. Systems employing conventional nickel anodes, steel cathodes and asbestos diaphragms and providing an artificial gravity by rotating the cell have, therefore, been investigated; they were found to be too large, heavy and cumbersome to operate.

It was found that the need for an artificial gravity could be avoided by employing a matrix to immobilise the electrolyte which is retained by capillary forces that are effective in the absence of gravity. Initial experiments were carried out using a Teflon matrix containing hydrated phosphorus pentoxide as electrolyte. This separated the two screen electrodes, and water for the continuous electrolysis process was provided by absorption from the air that was circulated through the anode compartment. The oxygen liberated during electrolysis at the anode was passed straight into the circulating air stream.

When an electrolyte matrix separated a

platinum screen anode and a 25 per cent silver-palladium alloy foil cathode, almost all the hydrogen liberated during electrolysis diffused through the cathode into a collection space behind it. The best matrix was found to consist of Teflon fibres holding insoluble calcium hydroxide impregnated with 66 per cent NaOH solution. A carbon-dioxide free water vapour feed was fed to the anode compartment which surrounded the $\frac{1}{4}$ inch diameter 0.005 inch wall palladium alloy tubular cathodes. Such cells, operating at 145°C and 2 volts, with current densities of 75 amp/ft², gave hydrogen transmissions of 97 to 100 per cent during twenty four-hour runs. The water vapour fed to the matrix during this period of operation from a generator at 100°C amounted to more than six times the weight of water originally contained in the matrix, and indicated that steady-state conditions had been achieved.

Based on these preliminary results, a design has been suggested for an electrolysis cell to produce 6 lb per day of oxygen - enough for three men. Such a cell would require 5.1 ft² of silver-palladium alloy surface, in the form of 70 tubes $\frac{1}{4}$ inch diameter, 0.005 inch wall thickness. It would be cylindrical in shape, with a length of 17 inches and an outside diameter of 5 inches; the palladium alloy tubes would each be surrounded by an annular matrix and a platinum screen anode, and the whole tube bundle arranged between manifolds similar to the design on which many tubular heat exchangers are based.

H. C.

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