Yield Point Effects in Palladium

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A pronounced yield point effect is sometimes encountered when heavily worked palladium is aged between 500° and 800°C. Such strain-ageing phenomena are usually associated with body centred cubic metals such as iron, and it is surprising to find that palladium, a face centred cubic metal, can exhibit analogous behaviour. In this article it is shown that the effect is caused by the presence of silicon, in concentrations as low as a few parts per million, which can be taken up even from a nominally pure alumina crucible in melting under reducing conditions. The precise mechanism involved is not understood, although the effect, when it occurs, complicates fabrication procedures such as wire drawing, contact manufacture and the production of high quality sheet. Working difficulties of this sort can, however, be avoided by adding small quantities of sodium or calcium to the palladium in the course of melting.

Interesting and unusual deformation characteristics have recently been detected in heavily cold worked palladium which had been subsequently annealed at moderately low temperatures. The effect was first observed in a sheet of palladium containing 1 per cent of ruthenium, which developed, after annealing, a remarkable system of strain markings similar to those illustrated in Fig. 1. In addition to these striations the sheet exhibited a number of sharp edged inflexions and responded to the slightest handling by a sudden yielding, with the formation of a sharp-edged bend. Bending was frequently accompanied by a faint cracking noise reminiscent of "tin cry".

This behaviour has since been occasionally observed in nominally pure palladium, in dilute alloys such as iron-palladium, and other materials. Because discontinuous yielding complicates subsequent working procedures the underlying reasons for this deformation behaviour were investigated in some detail.

Specimens of those batches of material which exhibited this effect were subjected to tensile testing and all were found to possess a pronounced yield point. Material that exhibited a yield point had a much higher elastic limit than normal palladium. The yield point was present only in heavily worked specimens that had been freshly annealed, and was destroyed by the slightest working or bending. After destruction it could be restored by annealing at moderately low temperatures, the optimum treatment being ¾ hour at 640°C. Below 500°C the yield point was not restored, while above 820°C it was completely lost. Annealing atmospheres had no effect upon the yield point, which developed just as strongly in vacuum annealed specimens as in those treated in hydrogen.

Effect of Impurities

Although no correlation appears to exist between alloy composition and the incidence of discontinuous yielding, the effect has so far not been detected in palladium containing more than 5 per cent by weight of alloying elements. In view of the similarities between this effect and strain-ageing in body centred metals, attention was first concentrated upon those impurities likely to be present in interstitial solid solution. Vacuum annealing experiments ruled out the possibility of hydro-

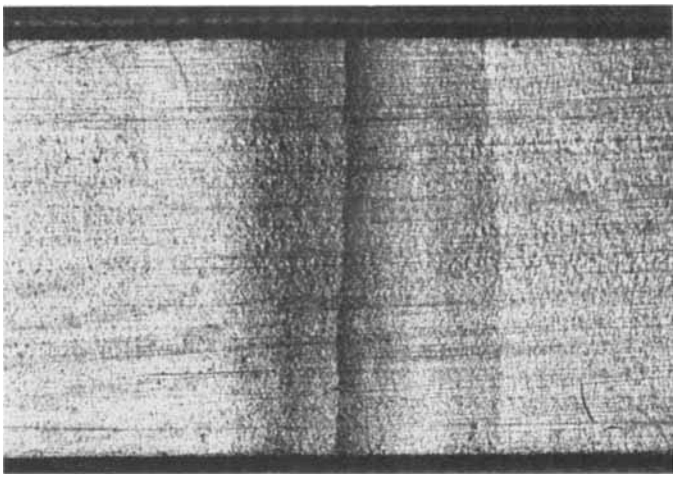

Fig. 1 Strain markings sometimes observed on the surface of palladium containing about 10 p.p.m. of silicon after annealing between 600 and 700°C

gen being responsible and the results showed that sulphur content had no influence upon yield point. Similarly silicon did not appear a likely suspect as the yield point effect was frequently encountered in specimens containing as little as 0.001 per cent of this element.

At an early stage in the investigation strong yield point effects were detected in dilute iron-palladium alloys which also contained significant quantities of carbon. It seemed possible that iron and carbon could react together during low temperature annealing to form Fe_3C and that the reinforcing effect of small particles or layers of cementite might be responsible for the yield points observed. As those alloys which exhibited the strongest yield points contained approximately ten times as much iron as carbon this hypothesis appeared most convincing. Attempts to verify it by testing synthetically produced iron-carbon-palladium alloys were, however, unsuccessful. In one instance, for example, an alloy containing 0.12 per cent of iron was melted in air, thus reducing

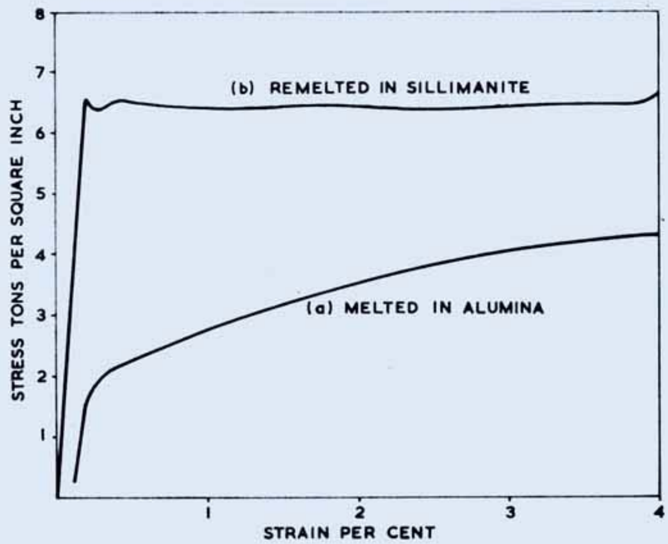

Fig. 2 Stress/strain curves of aged palladium rod made from metal melted under an atmosphere of 10 per cent hydrogen/nitrogen (a) in pure alumina (b) in sillimanite

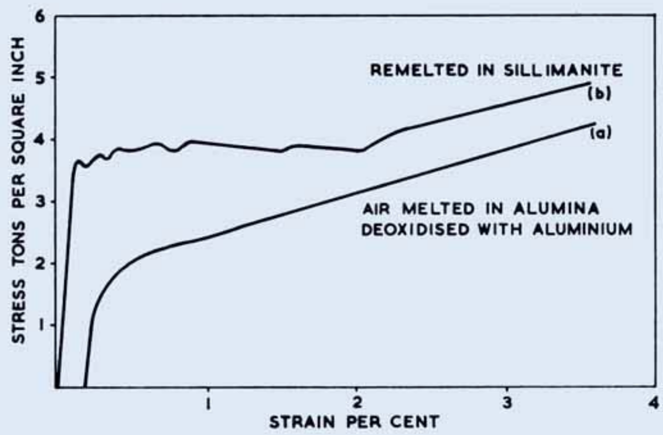

Fig. 3 Stress/strain curves of palladium (a) melted in air in an alumina crucible and then deoxidised with aluminium (b) palladium as in (a) remelted in sillimanite under a 10 per cent hydrogen/nitrogen cover

the carbon content to 0.009 per cent. This alloy, when worked and annealed, exhibited a slight yield point. It was remelted under an atmosphere of 10 per cent hydrogen/nitrogen in an alumina crucible and 0.01 per cent of carbon added. When this ternary alloy was subsequently worked and aged the yield point effect was more difficult to detect than it had been before the carbon was added.

Metal-Crucible Reactions

As most of the experiments had hitherto been made on metals and alloys melted under production conditions, it was decided to ascertain whether laboratory melted palladium exhibited similar effects.

Pure palladium grain was first induction melted under a 10 per cent hydrogen/nitrogen atmosphere in an alumina crucible (Morgan Triangle R). The resultant ingot was cold worked to $\frac{5}{16}$ inch diameter rod and then aged in nitrogen for $\frac{3}{4}$ hour at 640°C. Tensile testing yielded the lower stress-strain curve on Fig. 2, which is typical of that displayed by a pure ductile metal. This batch of metal was then remelted in a sillimanite pot, again under 10 per cent hydrogen/nitrogen, the ingot being worked down to rod which was aged at 640°C. As shown by the upper curve in Fig. 2, this material exhibited a pronounced yield point, the elastic limit being approximately three times higher than that of the original alumina-melted material.

Similar results were obtained when palladium grain was melted in air in an alumina crucible and then deoxidised by the addition of 0.04 per cent of aluminium. The lower curve in Fig. 3 illustrates the extreme ductility of this material after ageing at 640°C for $\frac{3}{4}$ hour. The upper curve shows the effect of remelting in a sillimanite crucible under a 10 per cent hydrogen/nitrogen mixture. Whatever was picked up from the sillimanite has increased the elastic limit and introduced a pronounced yield point.

Some pure palladium sponge was converted to ingot form by argon arc melting on a water cooled copper hearth and then reduced, without annealing, to $\frac{5}{16}$ inch diameter rod which contained less than 50 p.p.m. of impurities. This rod, when aged and tested, provided no evidence of discontinuous yielding. After remelting in alumina under an atmosphere of pure hydrogen, a pronounced yield point developed.

Effect of Silicon Content

The preceding experimental results confirmed that yield point effects were caused by impurities picked up from the refractories when melting under reducing conditions. Further experiments, which were confined

Effect of Atmospheric Conditions upon the Silicon and Aluminium Contents of Palladium Melted in an Alumina Crucible			
Material	Si Wt.%	Al Wt.%	Yield Point
1 Palladium grain	0.0001–0.0002	not detected	
2 Melted under carbon monoxide	0.0005	0.003	No
3 Melted under pure hydrogen	0.003	0.003	Yes
4 (2) Remelted with silicon addition	0.002	0.003	Yes
5 Vacuum melted after hydrogen reduction	0.001		Yes

largely to high purity alumina refractories, showed that yield point effects were due entirely to the presence of silicon. The results of these tests are summarised in the table.

These figures show that silicon contents as low as 0.001 per cent can induce discontinuous yielding effects in palladium. As there is little free silica in Triangle R alumina the affinity of molten palladium for silicon must be considerable. Where the silicious content of the refractory is high, as in zircon and sillimanite, high reduction potentials are not required for silicon transfer. Palladium melted in these refractories under protective covers of carbon monoxide or a 10 per cent hydrogen/nitrogen mixture frequently exhibited well defined yield points.

Melting Additions

Although yield point effects were rarely detected in palladium melted under carbon monoxide in a pure alumina refractory, some method of protection against inadvertent silicon contamination was obviously desirable. The effect of alloying additions that would react strongly with silicon to form stable compounds was therefore investigated.

Calcium additions were found to be very beneficial (1) and Fig. 4 illustrates some of the effects obtained with this metal. These curves relate to a 600 g charge of palladium grain melted originally in an alumina crucible under a carbon monoxide atmosphere. Curve 1 illustrates the stress strain behaviour of this material after ageing at 640°C. When remelted under pure hydrogen in the same crucible, it exhibited, after ageing, a pronounced yield point as shown by Curve 2. A calcium addition of 0.5 per cent added to the melt under a protective cover of carbon monoxide almost completely eliminated the yield effect as shown by Curve 3, although in this instance the elastic limit was still above that of the silicon-free material. The analytical results of these tests showed that calcium reduced the silicon content from 0.005 to 0.002 per cent and that approximately 0.04 per cent of calcium remained in the palladium.

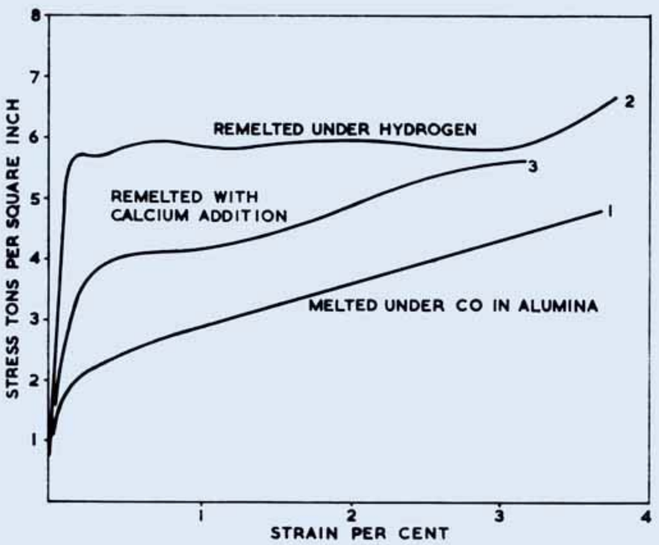

Fig. 4 Effect of calcium addition on the stress/strain curve of palladium containing a small quantity of silicon

Subsequent work on larger production melts

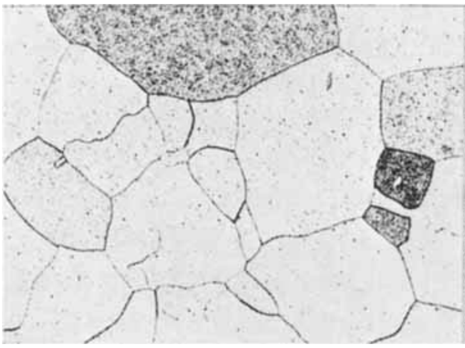

Fig. 5 Microstructure of fully annealed palladium reduced 20 per cent in area by cold swaging and then aged at 640°C (×100)

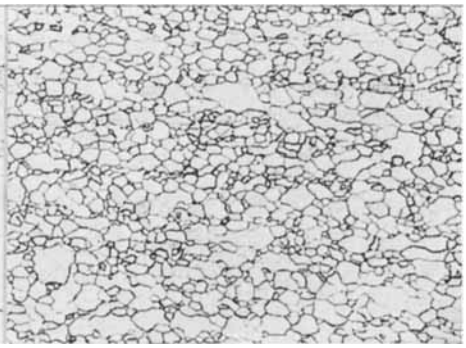

Fig. 6 Microstructure of fully annealed palladium reduced 75 per cent in area by drawing and then aged at 640°C (×100)

has shown that additions of 0.05 per cent of calcium are quite adequate to ensure freedom from silicious contaminations. Because little excess calcium remains behind in alloyed form the resultant palladium is no harder than that of untreated material. Sodium additions are found to be as effective as calcium, although the high volatility of sodium makes it difficult to add to the melt. Aluminium, potassium and magnesium additions have no effect on the yield point behaviour, nor upon the elastic limit of palladium containing silicon.

Microstructure

Microscopic examination showed that the discontinuous yielding in palladium was not completely analogous to strain ageing in body centred cubic metals because it always involved recrystallisation.

In one series of experiments a work-hardened bar of palladium containing 0.1 per cent of iron was selected because this material, when aged, exhibited a very strong yield point. Vacuum annealing for $\frac{1}{2}$ hour at 1000°C completely destroyed the yield point, even though ageing at 640°C was carried out for periods up to 16 hours in nitrogen. The cross-section of this test piece was then reduced in a swage by 20 per cent after which ageing failed to restore the yield point. The same test piece was then drawn to $\frac{1}{8}$ inch diameter wire, a reduction in area of 75 per cent being involved. Subsequent ageing completely restored the yield point.

These results suggested that the cold work imposed must be great enough to ensure complete recrystallisation of the metal during annealing, and microscopic examination seemed to bear out this hypothesis.

Fig. 7 Cellular structure of aged section of palladium exhibiting a strong yield point. Silicon content 0.002 per cent (×100,000)

Fig. 8 Structure of palladium remelted with 0.08 per cent of calcium, thus destroying yield point. (×200,000)

Fig. 5, for example, shows the structure of the vacuum annealed material which, after being reduced in area by 20 per cent and subsequently aged, did not develop a yield point. The metal aged after a 75 per cent reduction in area had recrystallised completely as shown in Fig. 6.

Under high power optical examination, the grain boundaries of material which exhibited a pronounced yield point were indistinguishable from those of normal ductile palladium and no evidence of precipitation on ageing was ever detected with the optical microscope. The structure as revealed by high power transmission electron microscopy is shown in Fig. 7. No constituent that might be responsible for the strong yield point exhibited by the material from which this specimen was taken can be observed in this diffuse cellular structure. Calcium, when added to destroy the yield point, appears to clarify the microstructure to some extent. The globular dispersion shown in Fig. 8 probably represents the residue of the calcium silicide or silicate phase which did not separate from the palladium and adhere to the refractory during melting.

Acknowledgements

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Reference

1 R. G. Hollister, British Patent Appln. 43404/63

The Palladium-Hydrogen System

The Palladium-Hydrogen System, by F. A. Lewis, Pp. xii and 178. Academic Press, London and New York. 45*s*. ($9.00)

The ability of palladium to dissolve very large volumes of hydrogen without losing its ductile metallic character continues to fascinate many gifted investigators and few problems in physical chemistry have received such detailed attention as this remarkable binary system. Dr Lewis has been active in this field of study for many years and he provides in this book a concise and accurate summary of the present state of knowledge.

Until quite recently the palladium-hydrogen system was of theoretical rather than of practical importance and it was generally believed that a fuller understanding of the constitutional relationships of its non-stoichiometric phases would help to resolve some basic thermodynamic anomalies. The chapter dealing with thermodynamic factors can, in fact, be regarded as a monograph complete in itself.

The chapter dealing with the effect of hydrogen on the shape and properties of palladium is of direct practical importance, and provides what is probably the first complete and systematic survey of this problem. Alloy characteristics are interpreted in metallographic terms and much of the information provided should be of direct value to engineers using semi-permeable membranes of palladium for chemical separation processes and fuel cell development.

Palladium cathodes can be readily charged with hydrogen, and the electrochemical techniques which have been employed for quantitative studies of the hydrogen content and dissociation pressures of palladium-hydrogen solid solutions are comprehensively treated in this book. Industrial considerations are not neglected, however, and considerable attention is given to the rates at which hydrogen diffuses through palladium and its alloys and to the technical problems involved. Pure palladium is unsuitable for use as an industrial diffusion membrane because of the distortion and cracking which occurs when it is cooled in the presence of hydrogen. The characteristics of silver-palladium alloys, some of which are free from this defect, are well described and alternative materials such as platinum, gold and boron palladium alloys are mentioned.

The references provided supplement and bring up to date the bibliography of D. P. Smith, and the book can be confidently recommended to those chemists, engineers and metallurgists involved in the rapidly increasing industrial applications of palladium and its alloys.

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