The High Temperature Stress-Rupture Properties of Platinum and Palladium

THE EFFECT OF ENVIRONMENT AND COMPOSITION ON SERVICE PERFORMANCE

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The industrial applications of platinum and palladium in wrought form derive, in large measure, from the unique ability of these metals to maintain their mechanical properties over long periods in oxidising environments at high temperatures. Published data on the strengths of these metals and their alloys is, however, somewhat confusing and often contradictory. A critical appraisal of the data, including some results from experimental work carried out recently in this laboratory, is presented so that the creep-rupture strengths of high purity platinum and palladium can be specified and discussed in terms of environmental sensitivity and of the role played by impurities.

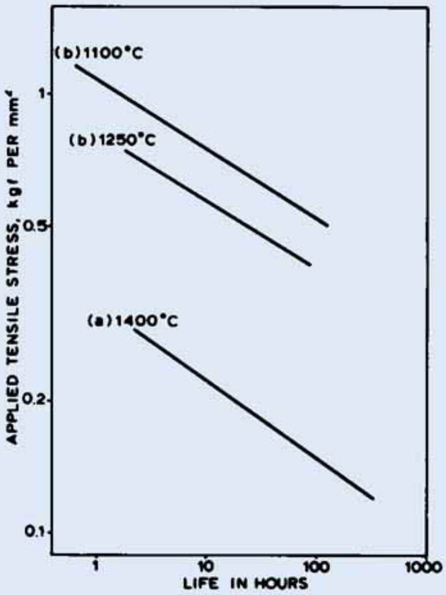
Stress-rupture curves are often used to specify the high temperature performance of structural materials. These curves give the load dependence of the times to failure for a specified testing environment and they generally display a discontinuity if the material being tested is environmentally sensitive. A discontinuity corresponding to a transition to longer rupture times as the applied load is decreased is commonly referred to as a strengthening effect. Conversely, weakening corresponds to a transition to shorter rupture times.

Environmental sensitivity may arise as a result of interactions between either the metal or its impurities and the testing environment. Interactions between the metal itself and the environment are referred to as generic effects because they are an inherent property of the pure metal and as such they may place fundamental limitations on its practical application. While stress-rupture testing, which manifests the combined effects of creep deformation and crack growth, cannot be employed to characterise environmental effects—generic or otherwise—directly, it can be a sensitive indicator of their occurrence. The embrittlement and intergranular fracture that arise as a result of exposing nickel and its alloys to air at high temperatures (1) appears to be a characteristic feature of environmental degradation in these materials at high temperatures, and is accompanied by an air-strengthening effect (2) clearly discernable in the stress-rupture curves. It is therefore reasonable to use stress-rupture data to monitor the effects of environment on a particular metal or alloy.

Platinum

While early work (3–6) with platinum indicated that air weakening took place at various temperatures, other and largely more recent work (Fig. 1) particularly in the temperature regime above 1200°C, has shown that neither air-weakening nor strengthening is observed on testing both sheet and wire

Fig. 1 These high temperature stress-rupture curves for high purity platinum wires show neither air weakening nor strengthening
(a) Selman et al., 99.9 wt.%, 1 mm diameter
(b) Reinacher, 2 mm diameter



specimens (7–12). The air weakening effects that were recorded can probably be attributed (7, 13) to the presence of oxidisable impurities. Several mechanisms have been suggested, most of which, according to a recent review (14), involve either the intrusion of environmental atoms which interact with impurities or the loss of impurities. Thus, the appropriate control of impurity levels gives reproducible high temperature strengths for platinum and its alloys, and rupture curves of the type presented in Figure 1 can be used with confidence to predict the performance of these materials.

Palladium

Stress-rupture data reported by several sets of workers and obtained using palladium wire specimens tested in air at temperatures above 1000°C are summarised in Figure 2. Material which was 99.9 weight per cent pure displayed an air-strengthening effect at 1100 and 1250°C (15). Material of a higher purity, 99.95 weight per cent, while being stronger than the 99.9 weight per cent material (as is usually the case if the impurity level is decreased) nonetheless showed an air-weakening effect at 1150°C (16). Moreover, it can be inferred that this relatively pure material was no stronger than 99.9 weight per cent material tested at 1200°C (17). On the basis of these results there would appear to be a complex relationship between the impurity content and the stress-rupture behaviour of palladium.

In order to separate these impurity effects from a possible generic effect it is necessary to examine material of even higher purity than that tested elsewhere. Accordingly, high purity palladium sponge was argon arc melted, swaged and cold drawn without intermediate annealing to 1 mm diameter wire. Lengths of the wire were annealed in air at 1200°C for fifteen minutes before being stress-rupture tested, four at a time, by hanging them under dead-weight loading conditions in stagnant air contained within a vertical tube furnace held at 1200°C. Spectrographic analyses of the wire before testing gave the following average impurity levels in ppm by weight:

Pt, 200; Rh, 50; Al, 2; Ca, 1; Cu, 5; Fe, 5; Mg, 1; Ni, 10; Si, 3; Ag, 2.

The results of the stress-rupture testing are plotted in Figure 2. It can be seen that the rupture properties of our high purity material at 1200°C were similar to those of the impure

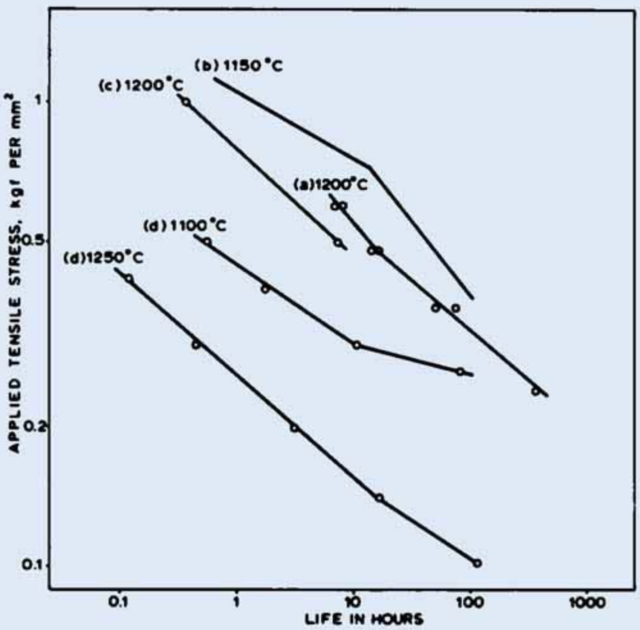


Fig. 2 High temperature stress-rupture curves for palladium wires having different impurity levels
(a) This study, 99.98 wt.%, 1.0 mm diameter
(b) Darling, 99.95 wt.%, probably ≈ 1 mm diameter
(c) Rytvin et al., 99.80 wt.%, 0.8 mm diameter
(d) Reinacher, 99.9 wt.%, 2.0 mm diameter

material. Moreover, the rupture curve for the high purity palladium displayed no significant discontinuity or at the very most a weak air-strengthening effect. A pronounced air-weakening effect similar to that observed (16) for 99.95 weight per cent material tested at 1150°C was not detected. The results of the present study therefore indicate that pure palladium, like platinum but unlike nickel, is essentially insensitive to air exposure at high temperatures. Moreover, previously reported data showing both air-strengthening and air-weakening effects can probably be attributed to the presence of oxidisable impurities.

Discussion

It has been argued (1) that the high temperature embrittlement of nickel is caused by the pinning of grain boundaries following exposure to oxygen. This pinning prevents the movement of grain boundaries to remove the build up of dislocation debris which takes place when grain boundary sliding during creep is accommodated by slip. An inherent or generic effect arises if oxygen which is segregated at grain boundaries is able to pin the boundaries. This effect may be reinforced by additional pinning brought about by the segregation and oxidation of impurities at the boundaries. Alternatively, the effect can apparently be suppressed if boron is allowed to segregate to the boundaries (18). Nickel oxide is stable throughout the temperature range within which embrittlement occurs. It is therefore reasonable to suppose that the segregation of oxygen modifies the structure and properties of nickel grain boundaries to give a generic embrittlement effect.

Palladium and platinum oxides on the other hand are unstable at high temperatures so it is less likely that any oxygen which is segregated at grain boundaries can restrict the movement of these boundaries. The conclusion is that pure platinum and palladium and their alloys, unlike nickel, do not suffer from a generic form of high temperature embrittlement or weakening on exposure to environments containing oxygen. Furthermore, by carefully controlling impurity levels it is possible to ensure that these two platinum group metals will provide consistent and reliable performance, when employed as structural components in high temperature process equipment.

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Platinum Catalysts in Oil Refining

STUDIES OF REACTION MECHANISMS

One of the most important processes in petroleum refining is the catalytic reforming of naphtha feeds, using platinum on alumina catalysts, to yield the high-octane gasoline required in automobiles. Since this process was first introduced by Universal Oil Products in 1949 there have been many attempts to elucidate the mechanisms of the catalytic reactions, and a recent article by S. R. Tennison of the BP Research Centre at Sunbury, Middlesex reviews the current position (*Chem. Br.*, 1981, **17**, (11), 536–540). This interesting paper describes the use of advanced surface examination techniques to increase our understanding of the physics and chemistry of the catalyst surfaces, but as the author admits, a number of questions remain unanswered.

Naphtha feeds are distillate fractions consisting of alkanes, cycloalkanes and aromatics, boiling at 70 to 190°C and with research octane numbers (RON) in the range 20 to 50. Catalytic reforming raises the octane number to between 85 and 95, and the addition of alkyl lead compounds further increases the RON to the 93 to 100 for sale at the pump. The principal upgrading reactions serve to increase the concentrations of *iso*-alkanes and aromatics, using temperatures of 500 to 525°C and 25 bar pressure. A typical catalyst for this reaction is 0.3 weight per cent platinum supported on alumina and promoted by about 1 weight per cent chlorine, although more recently 0.3 weight per cent of a second metal may also be incorporated. Under such conditions, hydrogen to hydrocarbon ratios of 6:1 are used with a liquid hourly space velocity of 2.

The reactions are thought to proceed sequentially over metallic and acidic sites. The skeletal rearrangements take place on the acidic alumina sites, and the hydrogenation/dehydrogenation reactions on the metallic platinum. Two side reactions that take place on both kinds of site need to be minimised; these are cracking, which reduces the liquid yield, and coke formation which reduces the catalyst life.

Reports of platinum-support interactions to give platinum-oxygen-aluminium species are reviewed. The two most important defects of reforming catalysts are sintering and coke formation, and methods for rejuvenation and decoking are described. The use of oxygen or air to reactivate the catalysts could involve conversion back to the $[(Al\text{-}O)_xPtCl_2]$ complex that has been observed in the fresh catalysts.

Multimetallic Platinum Catalysts

Although monometallic catalysts are not yet fully understood, they have been superseded by bimetallic catalysts such as platinum-rhenium, platinum-gallium, platinum-germanium and platinum-tin, and tri- and tetra-metallic systems are now being studied. Bimetallics tend to produce less coke and are more stable, this permits higher severity operation giving improved liquid yields and RONs. The continued use of advanced surface analysis techniques is increasing our understanding of interactions between the two metals and the support. This knowledge will aid the design of improved catalyst systems to give the increased aromatisation activity and liquid yields necessary to reduce oil utilisation and to increase the RON as the allowable levels of lead in gasoline are reduced.

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