The Resistance to Fatigue Crack Growth of the Platinum Metals

THEY MAY DISPLAY THE HIGHEST RESISTANCE OF ALL METALLIC MATERIALS

By Professor Markus O. Speidel

Swiss Federal Institute of Technology, Zürich, Switzerland

The effect of the cyclic stress intensity on the growth rates of fatigue cracks in the platinum metals in air can be predicted on the basis of established correlation equations. These suggest an inverse relationship between the growth rate of fatigue cracks in a material and its elastic modulus, and this has been experimentally confirmed for platinum and palladium and for a 30 per cent rhodium-platinum alloy. It may therefore be expected that ruthenium and rhodium have a higher resistance to fatigue crack growth than most other metals. Osmium and iridium may have absolutely the highest resistance to fatigue crack growth of all metallic materials. The effect of an evacuated test environment is also considered.

A quantitative study of the resistance to the growth of fatigue cracks in the elements platinum, palladium, rhodium, iridium, osmium and ruthenium is of interest because the platinum metals include materials with extreme elastic properties as well as materials with extreme corrosion resistance. Both the elastic properties and environmental influences—corrosion—are known to affect the fatigue crack growth rates in many other metals significantly (1, 2, 3, 4, 5, 6). It appears, therefore, that some platinum metals and their alloys have the potential to exhibit higher resistance to fatigue crack growth than any other metallic material. In the present paper the results of fatigue crack growth rate tests are given for platinum, palladium, and a 30 weight per cent rhodium-platinum alloy. The analysis of these test results confirms earlier predictions; it also points to the high interest in a similar study of the fatigue crack growth rates in rhodium, iridium, osmium, ruthenium and rhenium. This could shed light on the mechanism of fatigue crack growth and might have applications where extreme fatigue crack growth resistance is called for.

Fracture Mechanics and Fatigue Crack Growth

Fatigue is the nucleation and slow growth of cracks under cyclic loading conditions. It is well established that the major mechanical influence governing the growth rate of fatigue cracks is the cyclic stress intensity range, ΔK, as defined by fracture mechanics (1, 2, 3, 4, 5, 6).

All measurements of fatigue crack growth presented in this paper have been carried out with massive precracked specimens of the shape, and of the dimensions indicated in Figure 1.

The progress of the fatigue crack length, Δa, was measured on both sides of the specimen, using a calibrated low-power microscope. The corresponding nominal cyclic stress intensity range, ΔK, can be determined according to the K-calibration (7, 8) shown in Equation (i):

$$K_1 = \frac{P \cdot a}{B \cdot H^{3/2}}(3.46 + 2.38\frac{H}{a}) \qquad \text{(i)}$$

The symbols in this equation are defined in Figure 1. To obtain the nominal ΔK from this equation, the load excursion P is measured on the load cell of the hydraulic fatigue machine and inserted into the equation, together with the actual crack length, a, and the specimen dimensions, H and B. The fatigue crack in a precracked specimen does not grow unless the crack faces separate and the precrack opens. For this to occur the externally applied load must first overcome the residual compressive stresses which close the crack and force the crack faces together. Thus, the actual crack tip experiences an effective stress intensity which is the difference between the nominally applied stress intensity and the crack closure stress. In the present work this effective stress intensity has always been measured directly by an accurate determination of the crack opening, deflection δ, at the load line. The effective stress intensity range, ΔK, was evaluated using the K-calibration of Equation (ii) (8, 9):

$$K = \frac{E\,\delta\,H\,[3H\,(a + 0.6H)^2 + H^3]^{1/2}}{4[(a + 0.6H)^3 + H^2 a]} \qquad \text{(ii)}$$

where E is the modulus of elasticity (Young's modulus), δ is the deflection at the load line, and a, H are as defined in Figure 1.

For specimens with a saw-cut instead of a crack, the **nominal** stress intensity, Equation (i), and the **effective** stress intensity, Equation (ii), are identical. However, in cases where high fatigue loads had been applied to produce a fatigue precrack, the effective stress intensity as measured by the deflection δ was up to 30 per cent smaller than the nominal stress intensity. Unless otherwise stated, all cyclic stress intensity ranges, ΔK, in this paper have been measured using deflection δ and Equation (ii).

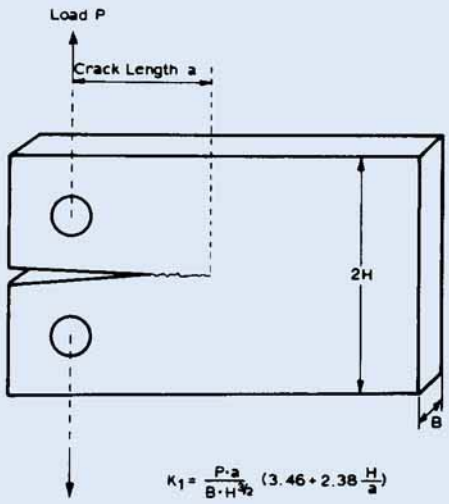

Fig. 1 The massive Double Cantilever Beam (D.C.B.) specimens used in this study to measure the fatigue crack growth rate as a function of the cyclic stress intensity range ΔK measured 10 mm x 60 mm x 100 mm, or more

Fatigue Crack Growth and the Modulus of Elasticity

There are early indications in the literature that the growth rate of fatigue cracks in metals may be a function of their modulus of elasticity (1). Extensive experimental investigations have shown that the fatigue crack growth per load cycle, $\Delta a/\Delta N$, could be normalised for many metals by plotting it versus $\Delta K/E$ where ΔK is the cyclic stress intensity range and E is the modulus of elasticity (3, 4). A striking example is shown in Figures 2 and 3. The fatigue crack growth rates of five different metals with vastly different moduli of elasticity are plotted versus the cyclic stress intensity in Figure 2. Note the extreme difference in fatigue crack growth rates between the different metals. For example, to obtain a growth rate of 10^{-8} m per load cycle, a cyclic stress intensity range of $1\ MN \cdot m^{-3/2}$ is required in the case of lead. To obtain the same growth rate in tungsten, a cyclic stress intensity range of $24\ MN \cdot m^{-3/2}$ would be necessary. Another comparison of growth rates could be made at a constant cyclic intensity range, ΔK, if it were acceptable to extrapolate the fatigue crack growth rate law for tungsten to small ΔK values; Figure 2 would then indicate that at a given ΔK (say, for example, $\Delta K = 3\ MN \cdot m^{-3/2}$), fatigue cracks in lead would propagate 10^5 times faster than in tungsten. In view of these huge differences in crack growth rates in different metals it is remarkable how well $\Delta K/E$

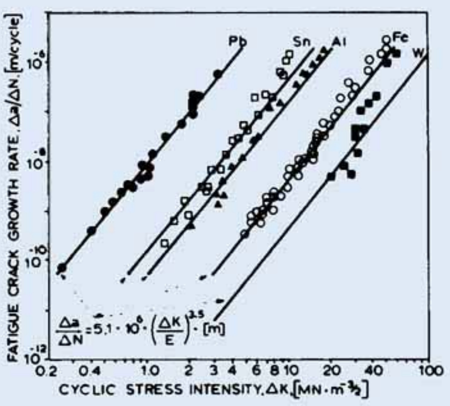

Fig. 2 Effect of the cyclic stress intensity range, ΔK, on the fatigue crack growth rates, in air, in a series of metals with vastly different moduli of elasticity, E.
50 per cent r.h., 2.3 hertz, R = 0, temperature 23°C except for tungsten when it was 420°C
● *lead, dispersion strengthened, E = 16 GN/m²*
□ *tin-base bearing metal, E = 53 GN/m²*
▲ *aluminium 99.9 per cent, E = 72 GN/m²*
○ *iron-0.2 per cent carbon, E = 206 GN/m²*
■ *tungsten, E = 390 GN/m²*

normalises all the crack growth rate data, as shown in Figure 3. It appears that a common fatigue crack growth rate law for the metals and stress intensity ranges shown in Figures 2 and 3 may take the form of Equation (iii) (3, 4, 5):

$$\frac{\Delta a}{\Delta N} = 5.1 \cdot 10^6 \cdot \left(\frac{\Delta K}{E}\right)^{3.5} \qquad \text{(iii)}$$

The fatigue crack growth rate law of Equation (iii) has a much wider range of validity than might be deduced from Figures 2 and 3 alone; it describes, within certain limits of stress intensity, also the fatigue crack growth in many other metals, such as magnesium, titanium and cobalt, and nickel-base alloys (4), including nickel base superalloys (3), as well as stainless steels (4, 6) and gold (5). Thus, it would be of interest to see whether it does or does not work for the platinum metals too. Equation (iii) is an experimental correlation which normalises the fatigue crack growth in many metals and alloys when these are tested in air. In many, but not in all cases, fatigue crack growth rates are slower by a factor of about three when the metals are tested in vacuum (3, 4, 5), and then the fatigue crack growth rate may be correlated using Equation (iv) (3, 4, 5):

$$\frac{\Delta a}{\Delta N} = 1.7 \cdot 10^6 \cdot \left(\frac{\Delta K}{E}\right)^{3.5} \qquad \text{(iv)}$$

In the absence of experimental information, Equations (iii) and (iv) may be used to predict the fatigue crack growth behaviour of metals and alloys with known moduli of elasticity. It is, however, important to keep in mind that at very low ΔK a threshold stress intensity for fatigue crack growth may be approached and at high ΔK values the fracture toughness of the material under test may be approached, where bursts of brittle crack extension may accelerate the crack growth beyond the values indicated by Equations (iii) and (iv). Thus it appears that the fatigue crack growth rate laws (iii) and (iv) are best applicable in the intermediate ΔK

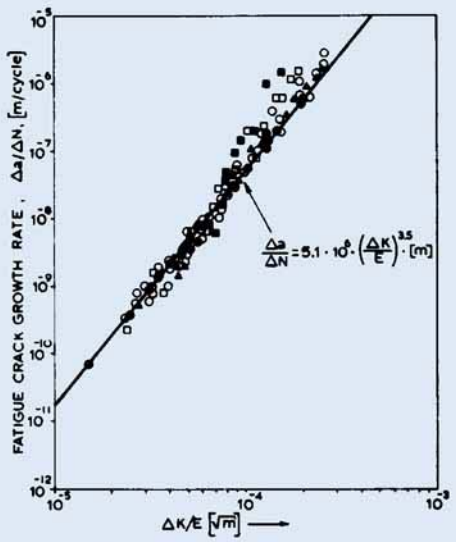

Fig. 3 The fatigue crack growth rates of Figure 2 are plotted here against ΔK/E. Note how well ΔK/E normalises the fatigue crack growth rates in different metals

ranges where fatigue crack growth is due to alternating slip and shear (4).

The modulus of elasticity is indicated in Figure 4 for the elements of the fourth, fifth, and sixth periods of the Periodic Table. It is obvious that the four platinum metals rhodium, iridium, osmium and ruthenium have some of the highest moduli of elasticity available in metals. Note also that the elements included in Figures 2 and 3, from lead to tungsten, already include the largest difference in modulus available in non-noble metals of technical usage and easy availability.

Fatigue Crack Growth in Platinum, Palladium and Rhodium-Platinum

Equations (iii) and (iv), together with the data for the elastic moduli shown in Figure 4 allow a prediction of the fatigue crack growth behaviour of the platinum metals. It is the aim of this section to compare the prediction with the experimental data on such platinum metals and alloys of which massive fatigue specimens could be obtained. The three Double Cantilever Beam (D.C.B.) fatigue test specimens, with dimensions of 10 mm × 60 mm × 100 mm, were kindly provided by the Métaux Précieux S.A. Company, Neuchâtel, Switzerland. The experimental results, along with the predictions, are presented in Figures 5, 6, and 7. The elastic moduli indicated on the figures were measured with the method described in (14); they agree well with published data (10, 13, 15).

The fatigue crack growth rate data for palladium are shown in Figure 5. Note that the bulk of the data generated in air is in excellent agreement with the prediction of Equation (iii). The R value is defined as the ratio of minimum to maximum stress intensity during the fatigue load cycle. R = 0 thus indicates zero-to-tension cycling. The fatigue data for R = 0 in Figure 5 drop off from the prediction at very low stress

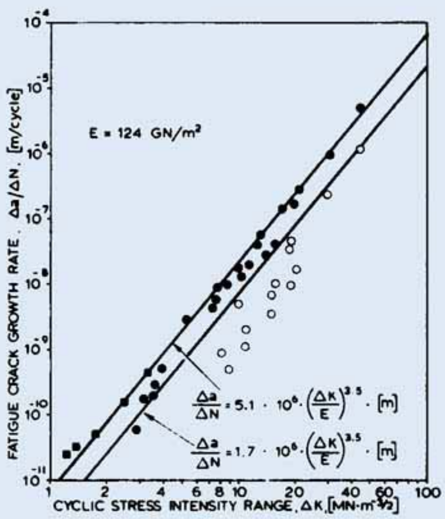

Fig. 5 The effect of stress intensity and environment on the growth rate of fatigue cracks in cold rolled pure palladium. Sinusoidal wave load at 23°C. The lines represent the predictions of Equations (iii) and (iv)

● tests in air, 2.3 hertz, R = 0

■ tests in air, 60 hertz, R = 0.7

○ tests in vacuum, 2.3 hertz, R = 0

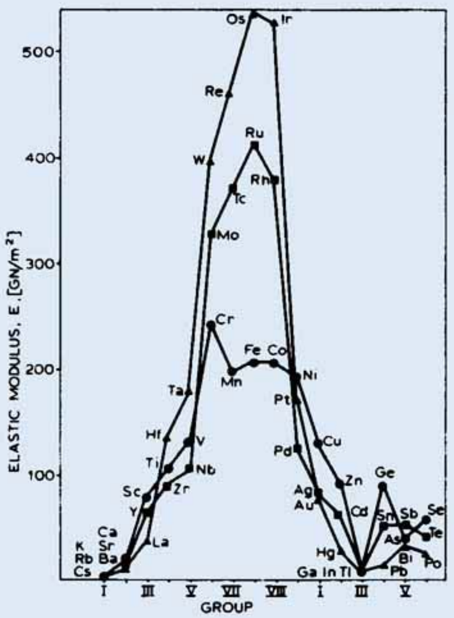

Fig. 4 The elastic modulus—Young's modulus—of the elements of the fourth, fifth and sixth periods of the Periodic Table. This is based upon data in (10, 11, 12 and 13) and own measurements made using the method described in (14)

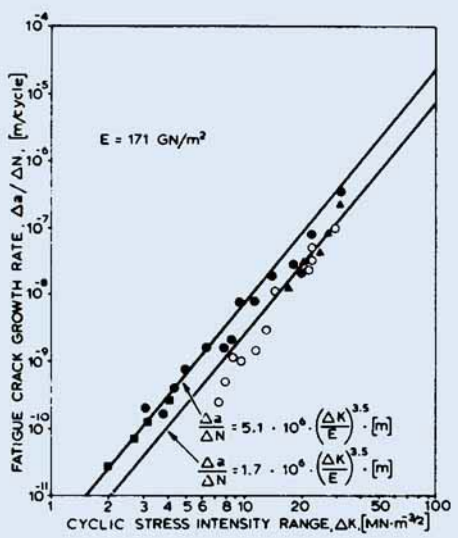

Fig. 6 The effect of stress intensity and environment on the growth rate of fatigue cracks in cold rolled pure platinum. The lines represent the predictions of Equations (iii) and (iv)

● ***tests in air, 2.3 hertz, R = 0***

■ ***tests in air, 60 hertz, R = 0.7***

○ ***tests in vacuum, 2.3 hertz, R = 0***

▲ ***tests in 5M NaCl solution, 2.3 hertz, R = 0***

intensities (low ΔK's). This effect has been noted previously for other metals (3, 4, 5) and it may be an indication that a stress intensity threshold for fatigue crack growth is approached. With higher mean loads (R = 0.7), the fatigue crack growth data follow the prediction down to much lower ΔK's.

The growth rates of fatigue cracks in palladium exposed to vacuum are also shown in Figure 5. These crack growth rates follow the prediction of Equation (iv) only for stress intensity ranges between 20 and 45 MN·m$^{-3/2}$. At lower ΔK's the observed fatigue crack growth rates in vacuum are up to ten times slower than predicted. At the same time, vacuum was observed to increase the size of the plastic zone near the fatigue crack tip on the specimen surface; moreover the fatigue crack tip in vacuum was finely divided into several microscopic branches while in air the fatigue crack was single and straight. This effect of vacuum and air on the plasticity and fracture of palladium could be due to partial rewelding of the freshly created crack faces. This crack retardation in vacuum merits further detailed studies, in particular because the inverse is observed with nickel-base superalloys; there, crack growth in **vacuum** follows the prediction of equation (iv), and it is the **air** which retards crack growth by microbranching (16, 17).

For platinum the growth rate data of fatigue cracks are presented in Figure 6. Note again how well the prediction of equation (iii) is fulfilled for the tests in air. The vacuum data in Figure 6 are below the line of Equation (iv), but not as much as with palladium; again fine crack branching was observed in vacuum, and it appears that this is the reason for the slow fatigue crack growth.

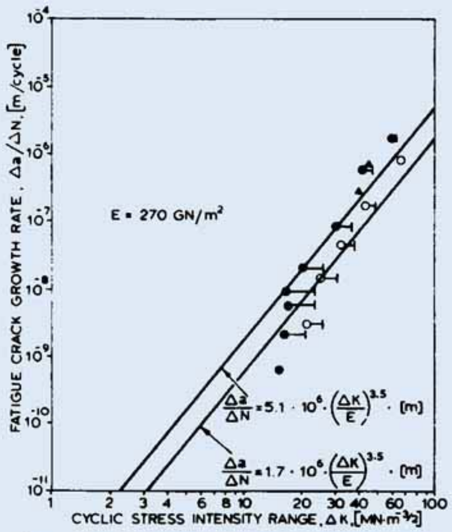

Fig. 7 The effect of stress intensity and environment on the growth rate of fatigue cracks in a cold rolled 30 per cent rhodium-platinum alloy. The lines represent the predictions of Equations (iii) and (iv)

● ***tests in air, 30 hertz, R = 0, 23°C***

○ ***tests in vacuum, 30 hertz, R = 0***

▲ ***tests in 22 per cent NaCl solution, 2.3 hertz, R = 0, 95°C***

● ○ ▲ ***effective stress intensity from deflection measurements***

●—┤ ***nominal stress intensity from***
○—┤ ***load measurements***

Fatigue crack growth in the 30 per cent rhodium-platinum alloy is illustrated in Figure 7. This is the platinum metals alloy with the highest elastic modulus tested so far. Here too, the predictions for crack growth rates in air and the observed facts agree reasonably well. Two deviations, however, are worth mentioning because they occur with many other metals as well. First, the data in air at low stress intensities fall below the predicted line and this may point towards a relatively high threshold stress intensity for fatigue crack growth. Second, at the highest stress intensity ranges, the observed crack growth rates are somewhat higher than predicted, and this may be due to additional crack growth by bursts of brittle fracture on a microscopic scale. This effect is predominantly observed with metals of low ductility, see also Figure 2, and it will be further discussed below. Figure 7 contains also information on the difference between the **nominal** stress intensity, Equation (i) and **effective** stress intensity, Equation (ii). The effective stress intensities are up to 30 per cent smaller than the nominal stress intensities, because of the crack closure effects.

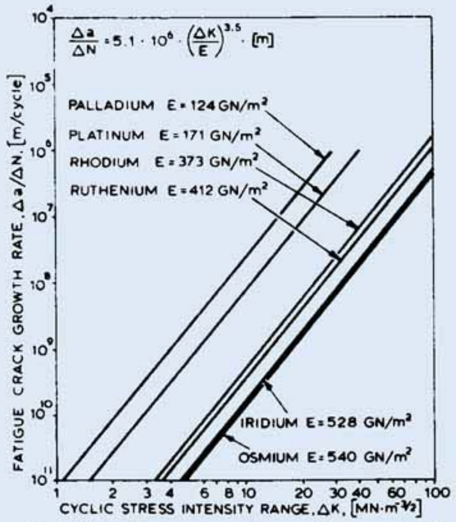

Fig. 8 The fatigue crack growth rates of all the platinum metals, predicted solely on the basis of the modulus correlation, Equation (iii). So far only the two highest lines have been confirmed experimentally, see Figures 5 and 6

The elastic modulus has a very strong effect on the growth rate of fatigue cracks in metals, as indicated by the modulus correlation in Equation (iii) and illustrated in Figures 2, 3 and 5, 6, 7. There is at present no detailed theory available which could quantitatively explain this correlation between elastic modulus and fatigue crack growth rate. However, it is plausible that the fatigue cracks grow by alternating slip and shear, at least at intermediate ΔK ranges where the modulus correlation holds (4). The crack growth per load cycle due to alternating slip will directly depend on the crack tip opening displacement (C.T.O.D.), and C.T.O.D. in turn is a function of $\Delta K/E$. Thus, $\Delta a/\Delta N$ is a function of $\Delta K/E$ (4). The plausibility argument is as follows: the higher the modulus, the less the crack will open under a given load (14), and since the crack growth depends on the crack opening, a higher modulus will result in a smaller crack extension.

Fatigue Crack Growth Prediction and Fracture Toughness of the Platinum Metals

The fatigue crack growth rates of all platinum metals in air could be predicted using Equation (iii) and the modulus data shown in Figure 4 if it could be assumed that Equation (iii) holds for rhodium, iridium, osmium and ruthenium as well as it does for platinum, palladium and 30 per cent rhodium-platinum. This assumption is by no means confirmed, but nevertheless the prediction is illustrated in Figure 8. We hasten to indicate some of its limits. First, the prediction is based on Equation (iii) and thus is appropriate only for tests in air. Second, there may be deviations to **lower** crack growth rates at **low** stress intensity ranges where a threshold stress intensity may be approached. Third, there may be deviations to **higher** crack growth rates at **high** stress intensities, particularly in materials with low ductility. This is illustrated in Figure 9 with a 12 per cent chromium stainless steel; this steel is embrittled by certain heat treatments as

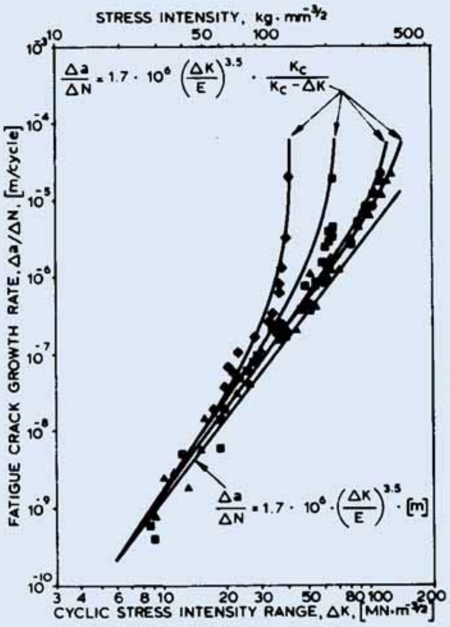

***Fig. 9** The effect of stress intensity on the fatigue crack growth rates in a 12 per cent chromium-0.2 carbon stainless steel exposed to vacuum. Certain heat treatments embrittle the steel, and in such cases the correction factor $\frac{K_C}{K_C - \Delta K}$ describes the acceleration of fatigue cracks as the cyclic stress intensity range, ΔK, approaches the fracture toughness K_C. Conditions: 10^{-5} torr, 2.3 hertz, $R = 0$*

Tempering temperature

■ 23°C ◆ 475°C

● 300°C ▲ 720°C

indicated in Figure 9. In the embrittled condition, the fracture toughness, K_C (and, under plane strain conditions K_{IC}) is low. Naturally, a fatigue load cannot exceed the fracture load and thus the cyclic stress intensity range in zero-to-tension cycling cannot exceed the stress intensity K_C which is sufficient to fracture the specimen. As the fracture toughness K_C is reached, the fatigue crack growth rate increases by several orders of magnitude and overload failure sets in. Thus, Equation (iii) needs a correction factor for materials of low ductility (small fracture toughness K_C) when ΔK approaches K_C. This is illustrated in Figure 9. At ΔK's low with respect to K_C, Equations (iii) and (iv) are applicable, but as ΔK approaches K_C, Equation (v) should be used for tests in air.

$$\frac{\Delta a}{\Delta N} = 5.1 \cdot 10^6 \left(\frac{\Delta K}{E}\right)^{3.5} \frac{K_C}{K_C - \Delta K} \qquad \text{(v)}$$

The corresponding equation for tests in vacuum is indicated in Figure 9.

For a proper prediction of the fatigue crack growth rates of the platinum metals of low ductility, based on Equation (v), the fracture toughness of the materials should be known, at least when higher ΔK values are considered. Such fracture toughness data are not yet available. The fatigue crack growth rate of those platinum metals with low fracture toughness is expected to follow Equation (v) at high ΔK values. At low ΔK's or in tough materials Equation (v) and Equation (iii) become equivalent.

Effect of Environments on Fatigue Crack Growth in Platinum Metals

We have shown above that some platinum metals can be expected to have lower fatigue crack growth rates than any other metals, purely based on the modulus correlation, Equations (iii) and (iv). In vacuum, crack growth rates even lower than those predicted by the modulus correlation, Equation (iv) may occur in rhodium, iridium, osmium and ruthenium. This is because of the effect of crack branching or possibly rewelding which is evident in Figures 5 and 6 where it reduces the fatigue crack growth rates below the values expected from the modulus correlation, Equation (iv).

A chloride solution does not accelerate fatigue crack growth rates in platinum, as shown in Figure 6, but the effect of aqueous solutions may strongly depend on the electrode potential (5), and this aspect of corrosion fatigue has not yet been studied with platinum metals.

Conclusions

The fatigue crack growth rates in platinum, palladium and a 30 per cent rhodium-platinum alloy have been studied using massive test specimens and fracture mechanics test techniques. The fatigue crack growth data measured in air follow well the prediction made earlier, based on the modulus correlation for fatigue crack growth rates as a function of the cyclic stress intensity range and the elastic modulus. From this it may be expected that some platinum metals may have the highest resistance to fatigue crack growth of all metals. Vacuum as a test environment may result in crack growth rates even lower than predicted by the modulus correlation. This may be due to partial rewelding of the fatigue cracks and to crack branching on a micro scale, as observed already with platinum and palladium.

A corresponding study of the metals rhodium, iridium, osmium, ruthenium and rhenium would be highly interesting. In some of these metals, the fracture toughness would have to be taken into consideration.

Acknowledgements

Mr Wolfgang Meixner has skillfully helped with the fatigue crack growth experiments. The BBC Brown Boveri Company, Baden, Switzerland, has permitted the tests to be run with the excellent facilities in its Research Centre. The Métaux Précieux S.A. Company of Neuchâtel, Switzerland, has lent the massive noble metal specimens necessary for this study.

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New United Kingdom Refinery for the Platinum Metals

A new multi-million pound plant for the refining of the platinum metals is to be built for Matthey Rustenburg Refiners (U.K.) Limited, the refining company owned jointly by Rustenburg Platinum Mines (Pty) Limited of South Africa, and Johnson Matthey.

Instead of employing selective precipitation for the separation and purification of the individual platinum metals the new plant will employ a novel process incorporating solvent extraction. This has been researched and developed at the Johnson Matthey Group Research Centre and in the Development Department of Matthey Rustenburg Refiners, at Royston, where pilot plant trials have generated the design data for the new plant.

The process reduces both the number of refining stages and the time required, while it also yields higher purity products than the conventional process. In addition, the fundamental change from selective precipitation to solvent extraction will enable increased automation to be utilised in the refinery.

It is anticipated that construction work will be completed in late 1982, and that the plant will be operating early in 1983.