vanadium. As mentioned previously, k_0 is related to the diffusion coefficient and may be expected to be the same for each sample.

In order to calculate k_0, Q_0 and α from the available data, we begin with the plots of Fig. 1. Since there are more data points at 14 at. %, we use a least square fit on this curve to obtain k_0. The average value of $Q(X)$ for each curve is then calculated. Fig. 2, a plot of $Q(X)$ versus X, shows a linear relation between $Q(X)$ and X. A least square fit to this curve gives Q_0 and α. The values of k_0, Q_0 and α are found to be 45.6 cm^2 sec^{-1}, 87.3 kcal mol^{-1} and $-$ 1.666 kcal mol^{-1} respectively. The negative value for α is to be expected since, at low concentrations, diffusion occurs less rapidly.

Equation 5 now becomes

$$t_1 = 2.2 \times 10^{-10} \exp (87\,300 - 1666X)/RT\,. \quad (6)$$

As a check on the accuracy with which this formula reproduces the original data, we have tabulated the quoted times, times calculated from Equation 6 and the percentage deviation in Table I.

In most instances the agreement between experiment and calculation is within 10 to 20%. This is remarkable when one considers that (1) the range of times encountered covers five decades and (2) the sensitivity of Equation 6 to small changes in Q_0, α and T. For example, a 1% decrease in α gives almost perfect fit for the 14 at. % data.

It is interesting to compare the directly measured values of Q_0 with the present value. Most direct measurements of Q_0 are taken at higher temperatures, 900 to 1833°C, where Q_0 is not completely temperature independent but varies from 74 to 99 kcal mol^{-1} [8]. The present value, 87.3 kcal mol^{-1}, is thus reasonable.

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SEM characterization of fatigue crack tip deformation in stainless steel using a positive replica technique

Three measurable parameters have been correlated extensively in attempting to understand fatigue crack growth: (1) macroscopic growth rate ($\mathrm{d}a/\mathrm{d}N$); (2) striation spacing; (3) plastic zone size. However, certain factors crucial to the linking of these quantities, including crack tip opening displacement (CTOD), crack tip configuration, and the mechanism of incremental crack growth, often have been lacking. This note describes a technique for obtaining this information through the replication of loaded fatigue crack tips, and crack tip yielding in 304 stainless steel is discussed.

Recently Wu *et al.* [1], reported the development of a technique for obtaining positive metal replicas of non-conducting materials such as polymers, for observation in the SEM. The writers have been using the same technique, but with the above problem in mind. Single-edge-notched specimens containing fatigue cracks are cycled under load control; at various stress intensity levels, cycling is suspended. Using Bioden methyl acetate replicating material, negative replicas are obtained of the crack tip region in both the loaded and unloaded condition. (COD measurements obtained using a clip-on displacement gauge provide an estimate of the accuracy of the replicated features. A series of experiments during which COD was monitored both under cyclic loading, and also as a

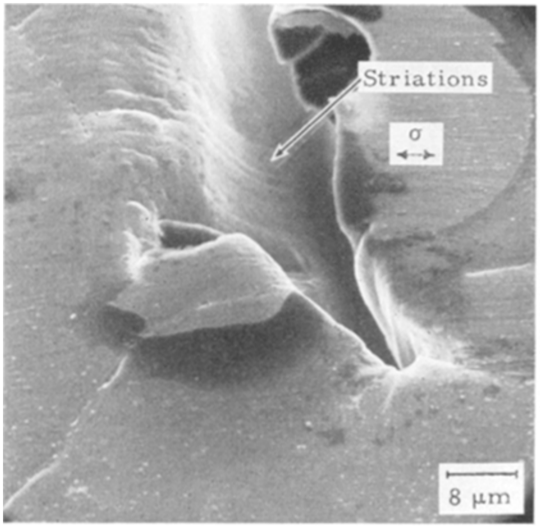

Figure 1 Front view of crack tip blunting and shear under load (ΔK = 26 MN m$^{-3/2}$).

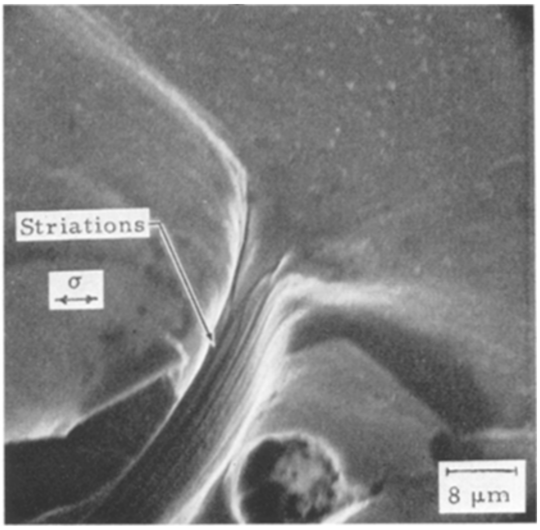

Figure 2 Rear view of crack tip, showing striation configuration under load (ΔK = 26 MN m$^{-3/2}$).

function of time at load for several ΔK values, showed that the replicated CTOD exceeds the actual, maximum CTOD under cyclic conditions by no more than 5%. Moreover, during the period in which the replica is setting up on the specimen, the tip has time to creep no more than 1%, accommodated by exceedingly localized flow within the crack tip shear zones.) A positive replica of each negative may then be secured by vapour-depositing a thin film of palladium onto the plastic. Wu *et al.* [1], used gold-palladium; we have found that pure gold gives very poor quality detail. Finally, the positive replica is plated with nickel to provide a strong, tough backing. The plastic may be stripped away with tweezers or dissolved in acetone, and the replica is ready for SEM observation. If very high magnifications are required, it also is possible to replicate the positive replica and coat with carbon and palladium for TEM observation.

As an example of the information which can be obtained, Fig. 1 shows a loaded crack tip in 304 stainless steel, at a stress intensity factor of 26 MN m$^{-3/2}$. From this front view of the approaching crack, blunting is clearly evident, and the tip appears to be shearing in two slip zones oriented approximately 90° relative to one another. Looking down along the walls of the crack, fatigue striations can be seen. A clearer view of the striations is gained by rotating the replica by 180° and then tilting it to reveal the tip and the most recently formed striations (Fig. 2). It is interesting to note that they are extremely sharp and clean, in contrast to the older striations further back from the tip (Fig. 1). The latter apparently have lost some of their detail, indicating the effect of crack closure.

At this point the crack growth rate was approximately 0.05 μm per cycle, in agreement with the results of others [2, 3] (Table I). Bathias and Pelloux [3] also measured striation spacings on fracture surfaces, and for ΔK = 26 MN m$^{-3/2}$, found a spacing of about 0.5 μm. From Fig. 2, the observed spacing measures approximately 0.7 μm, again in general agreement. It has been assumed [4, 5] for some time that da/dN should be related rather directly to CTOD, the relation derived by Rice [6] generally being accepted as a good approximation for CTOD, namely,

$$\frac{\mathrm{d}a}{\mathrm{d}N} = \frac{\mathrm{CTOD}}{2} = \frac{0.25(\Delta K)^2}{2\sigma_\mathrm{y} E}$$

where σ_y is the 0.2% cyclic yield strength and E is the elastic modulus. According to this

TABLE I

	Measured	Calculated	Bathias and Pelloux [3]
da/dN (μm per cycle)	0.05	2.4	0.04
Striation spacing (μm)	0.7	—	0.5
CTOD (μm)	6.5	4.8	—

relationship, we should expect to find da/dN = 2.4 μm, and CTOD = 4.8 μm. (The CTOD was calculated on the basis of a correction to account for the crack tip plastic zone size r_p = 0.1 $(\Delta K/\sigma_y)^2$ [3], which was added to the measured crack length.)

There is good agreement between the observed and calculated CTOD, but the calculated da/dN is much larger than the macroscopic growth rate, and significantly greater than the average striation spacing. While it is often possible to correlate da/dN or striation spacing changes with changes in CTOD [5], in the present instance there is certainly no one-to-one quantitative relationship between any of the three parameters. On the other hand, there must exist some physical correlation, based on the actual dynamic opening and closing of the crack front and the associated development of micro-instabilities at the blunted tip during the unloading portion of the load cycle. We are presently looking into the details of this process, for 304 stainless steel and for 6061-T6 aluminium, by loading and unloading crack tips in increments and replicating at each increment. In this way, the sequential development of features such as those shown in Fig. 2 are observed. Key questions involve whether striations are actually formed on the loading or unloading half-cycle, whether multiple striations can form on a given half-cycle, and why there exists a correlating relationship between CTOD and da/dN changes even though they may differ in absolute magnitude by a factor of 100. Results of this work in progress will be reported in detail in a subsequent paper.

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Short Notices

Fast Ion Transport in Solids: Solid State Batteries and Devices

Edited by *W. van Gool*

North-Holland, Amsterdam, 1973. 728 pp. Dutch florins 100, approx. US $35

This large and very impressive volume contains the proceedings of an international "study institute" held in Italy in September 1972. The field covered by the many participants has recently expanded very rapidly, partly under the impetus of the sodium-sulphur battery in which two molten reactants are separated by a "super-ionic conductor", solid β-alumina. Super-ionic conductors are crystals with little or no electronic conductivity in which some of the constituent ions occupy a minority of a particular type of site, and by easy hopping to adjacent vacancies contribute a large ionic conductivity. The papers in this collection deal predominantly with the theory of this fast diffusion; existing methodologies for treating normal diffusion are distinctly creaky when applied to this new complex problem. Experimental methods, contributions of interfaces, a number of particular established solid electrolytes, and a number of promising newcomers are all reviewed, and a pithy envoi by R. A. Huggins summarizes the achievements to date and the road-blocks which must next be tackled. A stimulating, difficult book.

R.W.C.