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THE OFFICE OF NAVAL RESEARCH

Contract NONR - 222 (67), Project NR 036-041

FINAL SUMMARY REPORT

of

RESEARCH INVESTIGATIONS CONDUCTED UNDER THE PROVISIONS

of

Contract NONR - 222 (67), Project NR 036-031

by

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FINAL SUMMARY REPORT OF INVESTIGATIONS

The investigations performed under the terms of Contract NONR - 222 (67), Project NR 036 041, began June 15, 1958, and terminated September 30, 1962.

All of the investigations have been repor+~d in detail in technical reports and publications to the Office of Naval Research under the following titles and dates:

Technical Report	Title	Date
1	"The Observation of Fatigue Processes in MgO Single Crystals"	June 1960
2	"A Study of Fatigue Deformation by Reflection Electron Microscopy"	1961
3	"The Effect of Surface Treatment on the Bending Characteristics of MgO Single Crystals"	May 1961
4	"Effect of Reynolds Number on Corrosion of Copper by Sulfuric Acid"	October 1961
5	"The Analytical Prediction of Corrosion of Pipe Walls by Fluids in Laminar Flow"	1962
6	"A Study of Corrosion Fatigue in High Purity Aluminum Single Crystals"	Dec., 1962
7	"A Temperature Dependent Process in the Corrosion Fatigue of Aluminum"	Dec., 1962

The substance of each of these reports has been published or submitted for publication as shown in the following bibliography:

APPENDIX

THE OBSERVATION OF FATIGUE PROCESSES IN MgO SINGLE CRYSTALS

Fatigue of ionic crystals has been studied primarily in magnesium oxide. Under cyclic stress dislocations move irreversibly; they multiply; slip bands form and grow; cracks nucleate and propagate, and failure occurs. The use of ionic crystals such as MgO is advantageous in such investigations because they are optically transparent. Individual dislocation intersections with (100) surfaces may be observed with a standard microscope, using etchpit techniques. Slip, deformation, crack formation, and fracture in MgO crystals under cyclic stress are compared with corresponding processes in metals.

A STUDY OF FATIGUE DEFORMATION BY REFLECTION ELECTRON MICROSCOPY

Coarse-grained polycrystalline specimens of super-high purity (99.996%) aluminum were electropolished and fatigued to failure at a stress of 8000 lb/in^2 in plane bending. Specimens were photomicrographed under oblique light. Sections were then cut from the fatigued specimen and mounted in an electron microscope set at a tilted illumination of 7° with the specimen inclined at 10°-15° to the electron beam. Examination in the electron microscope under these conditions showed, through fluorescence, that the whole surface of the specimen was covered with an oxide layer. The edges of one extrusion micrographed were about 1000 A^o thick, and the base of this extrusion was so thin that it was barely opaque to the electron beam. It was deduced that the shape of this extrusion was lenticular. It was concluded that reflection electron microscopy could give much information about extrusions which might be barely detectable in the light microscope.

THE EFFECT OF SURFACE TREATMENT ON THE BENDING CHARACTERISTICS OF MgO SINGLE CRYSTALS

As-cleaved specimens of magnesium oxide which were chemically polished in phosphoric acid, acetic acid, ammonium acetate, and distilled water exhibited on bending in air a sudden load drop phenomenon. This effect was believed to be associated with the removal of mobile surface dislocation half-loops by the environment. The load drop in bending was attributed to sudden nucleation of slip bands on the bottom and top surfaces of the specimen. Growth of the first slip bands may have caused stress concentrations that had helped to nucleate new slip bands.

Specimens of MgO which were fatigue strained and then polished in phosphoric acid did not exhibit the load drop effect. Fatigue straining before polishing introduced many mobile dislocations which were not removed by polishing.

Specimens of MgO which were alternately deflected 0.02 inch in bending and polished in phosphoric acid exhibited greater deflection than as-cleaved specimens.

EFFECT OF REYNOLDS NUMBER ON CORROSION OF COPPER BY SULFURIC ACID

Corrosion of electrolytic tough-pitch copper pipe was determined in aerated 2.1N sulfuric acid at 30°C. A closed loop circulating system was used, with 1 in., 3/4 in., and 1/2 in. diameter test sections. There was a gradual increase of corrosion rate with increasing Reynolds number in the laminar flow regime, $Re < 2100$; a rapid increase in corrosion rate with increasing Reynolds number in the low turbulent flow regime, Re 2100 to 10^4; and a relatively constant corrosion rate due to polarization at Reynolds number $> 10^4$. Reynolds number as a corrosion parameter permitted useful generalizations and comparisons with published heat and mass transfer correlations.

THE ANALYTICAL PREDICTION OF CORROSION OF PIPE WALLS BY FLUIDS IN LAMINAR FLOW

A corrosive fluid in laminar flow may corrode pipe walls at a rate dependent on fluid mechanical parameters, in some systems. Modified Graetz and Lévêque solutions are used here to predict analytically the corrosion rates to be expected.

Comparison of theoretical analysis with experimental data indicates reasonable agreement.

A STUDY OF CORROSION FATIGUE IN HIGH PURITY ALUMINUM SINGLE CRYSTALS

High purity aluminum single crystals of fixed orientation have been prepared as Krouse flat sheet fatigue specimens. These specimens have then been subjected to cyclic strain at 1625 rpm, at 25°C, with a zero mean strain. Specimens have been fatigued in air or in 4% NaCl aqueous solutions for a period of time, reroved, examined in a metallograph, electropolished and cleaned, reexamined in a metallograph, and then subjected to further cyclic strain. Development of persistent slip lines, microcracks, and large cracks have been followed on photomicrographs at fixed coordinates.

Fatigue and corrosion fatigue curves are presented. In air the fatigue life of the single crystal high purity aluminum ranges from 6×10^5 cycles at a strain of 6.6×10^{-4} to 10^7 cycles at a strain of 3.5×10^{-4}, and there is an endurance limit below strains of 3.2×10^{-4} at which more than 3×10^8 cycles will not break the specimen. In the aqueous 4% sodium chloride solution corrosion fatigue occurs. At a strain of 6.6×10^{-4} the number of cycles to failure is reduced 50% as compared to air fatigue. At a strain of 3.5×10^{-4} the specimen breaks in 1.4×10^6 cycles, less than 15% of the number of cycles sustained in air. Even at a strain of 1.5×10^{-4}, which corresponds to a stress below the yield point, failure occurs in about 1.4×10^7 cycles. There is no fatigue limit discernible in the corrosive environment. The data are reasonably self-consistent.

Slip in these aluminum single crystal specimens is primarily on the close packed 111 plane in the $\bar{1}01$ direction, with conjugate slip on the $\bar{1}11$ plane in the 101 direction. The orientation is such that the resolved shear stress is greater on one slip plane than on the conjugate slip plane. Therefore slip lines form initially almost entirely in one direction. The intersecting conjugate slip system is activated early. Thereafter persistent slip patterns and microcracks tend to concentrate along these intersecting slip systems the microcracks being more numerous along the initial slip system.

Slip is more frequent and more intense; microcracks are more numerous, wider, deeper and longer in the corrosion fatigue environment. Cracks grow and failure occurs early in the salt solution, at a number of cycles where the air fatigue specimen is relatively undamaged.

Pits are not particularly characteristic of the corrosion fatigue cracking of these aluminum specimens. The salt solution environment acts mainly to propagate cracks, late in the life of the specimen rather than early. Initial stages of slip and microcrack formation are not visibly affected by the corrosive environment.

The growth of some of the cracks appears to indicate that cyclic strain induces a high state of stress, which causes cracks to form and propagate, and the stress then becomes inversely proportional to the time the crack grows. Major cracks grow by joining of minor cracks which have been growing simultaneously, and cracks cross over from one slip plane to another parallel slip plane some distance away.

In this study failure was not perpendicular to the applied cyclic tensile stress, but was determined by crystal orientation. Slip formed initially on a preferred plane; an intersecting slip system on a conjugate plane was then activated. The intersections resulted in dislocation pile-ups and stress concentrations, nucleating cracks principally on the initial slip system which had the higher resolved shear stress. It is postulated that in the aqueous 4% sodium chloride solution, chemical attack on the aluminum could occur preferentially at dislocation pile-ups and tangles. Also the chemical attack could advance on crystal planes which were not necessarily high in resolved shear stress, permitting a crack to cross over from one slip system to another parallel system some distance away, independent of the orientation of the tensile stress relative to the crystal orientation.

Data obtained may be expressed in terms of σ, the stress in psi and N, the number of cycles to failure. In air $\sigma = 221{,}810\ N^{-0.2403}$; in 4% aqueous NaCl solution, $\sigma = 1{,}117{,}200\ N^{-0.3834}$. Alternatively the data may be fitted as follows: In air, $N = 3.089 \times 10^{4}\ e^{27{,}534/\sigma}$; in 4% aqueous NaCl solution, $N = 5.425 \times 10^{4}\ e^{16{,}012/\sigma}$ for the short lived portion, and $N = 3.863 \times 10^{5}\ e^{7{,}438/\sigma}$ for $N > 2 \times 10^{6}$ cycles, where e is the Naperian base.

A TEMPERATURE DEPENDENT PROCESS IN THE CORROSION FATIGUE OF ALUMINUM

Fatigue and corrosion fatigue data were obtained on high purity aluminum single crystal specimens, at temperatures between 3°C and 125°C, in order to indicate processes or mechanisms which might be temperature dependent.

High purity aluminum single crystals of fixed orientation were grown as Krouse flat sheet fatigue specimens. These specimens were cycled at 1625 rpm, at a fixed stress of 6000 psi.

Since the Krouse fatigue machine is adjusted for constant strain, the strain was varied slightly with temperature to correct for the change in modulus of elasticity of aluminum with temperature.

Experiments were run with the specimens insulated electrically from the components of the fatigue machine. Specimens were totally immersed in baths of liquid in a stainless steel tank, with provisions made for heating or for cooling the bath, and for stirring the thermostated liquid. Many tests involved aqueous 4% sodium chloride solution; here the liquid level and the concentration were maintained relatively constant. Experiments with aqueous 4% sodium chloride solution, and with distilled water, were run with the baths open to air, and also with the baths covered with a plastic sheet and purged with flowing nitrogen gas to keep air out.

In the range of temperature investigated for the aqueous solutions, about 3°C to 90°C, there was no change in the number of cycles to failure as a function of temperature, regardless of whether the baths had free access to air or were purged with nitrogen. Several attempts to apply cathodic protection, and other attempts to apply anodic protection, to aluminum specimens being fatigued in the salt solution at about 23°C, proved fruitless. Data scattered badly, which possibly indicated that some of the cathodic protection and some of the anodic protection currents and voltages may have been excessive.

Meanwhile three fatigue tests have been run in a white mineral oil bath open to air. These data fitted an equation $N = 5.103 \times 10^4 e^{-1892/RT}$, where N = number of cycle at constant strain to failure, e is the Naperian base, R is the gas constant, and T is the Kelvin temperature. Data were for 294, 323, and 373°K. The white mineral oil smoked at higher temperatures, and became an opalescent white with condensed moisture at lower temperatures, so that the temperature range was limited.

Further fatigue tests were performed in a siliconized oil at 298, 323, 348, 373, and 398°K. At the highest temperature the data scattered. For the other temperatures, 298 to 373°K, the data fitted an equation $N = 1.266 \times 10^5 e^{-1771/RT}$.

It appears possible therefore that, in both the white oil and in the siliconized oil, fatigue of high purity aluminum single crystal specimens of fixed orientation occurs with a temperature dependent process which has an energy of activation of 1771 to 1892 calories per mole. Such a low energy of activation is encountered in certain dislocation processes; it is also typical of the energy of activation for diffusion of gas in a liquid. It is considered probable that the temperature effect on fatigue of aluminum observed in both the white mineral oil and in the siliconized oil was due to the energy of activation for diffusion of oxygen.

Unfortunately the work described here was halted, first by a major reconstruction of the laboratory building where the work was done, and then by termination of the project support. While the work is unfinished, it is reported at this time because of its potential interest and importance in stimulating further investigation.