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THE EFFECT OF THIN ANODIC OXIDE FILMS ON THE FATIGUE BEHAVIOUR OF AN ALUMINIUM ALLOY

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THE RELATION OF HUMIDITY TO THE FATIGUE ENDURANCE OF AN ALUMINIUM ALLOY

abstract promised
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PHYSICAL METALLURGY DIVISION

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(1) The Effect of Thin Anodic Oxide Films on the Fatigue Behaviour of an Aluminium Alloy

E. G. Eeles

In a recent paper[1] the effect of atmospheric humidity on the fatigue life of a commercial aluminium alloy was studied and it was suggested that variations in the natural surface oxide films were responsible for changes in the endurance. Similar tests have now been carried out in moist and dry environments on samples of the same material suitably anodized to give differing thicknesses of anodic oxide film. It has already been shown[2] that thick anodic films can exert a marked restraining influence on the matrix and, therefore, it was planned to use considerably thinner films to avoid this possibility.

Anodizing was carried out in a 5% aqueous tartaric acid solution, titrated with ammonium hydroxide to a pH of 5·5. This solution is the same as that used by Hunter and Fowle[3,4] to determine the barrier-layer thickness of anodic and natural oxide films on pure aluminium, and it was found, for this material, that the base- or barrier-layer thickness[3] was ~ 14 Å per volt. Similar measurements on the alloy used in the present investigation* showed that the barrier oxide current leakage was greater than that reported for pure aluminium and the thickness/voltage relation is therefore probably less than this figure. Anodizing was carried out at room temperature using maximum applied voltages of 0·5, 2, and 10 V. The applied voltage was raised slowly to limit the current to 4 m.amp/cm^2 of immersed specimen area and the technique is thus similar to that of barrier-layer measurement. Hence, the anodizing voltages quoted probably represent films with barrier-layer thicknesses ranging from a few Ångstroms to ≯ 100–140 Å.

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* Corresponding approximately to B.S.S.-NS4-1/2H (see Ref. 1).

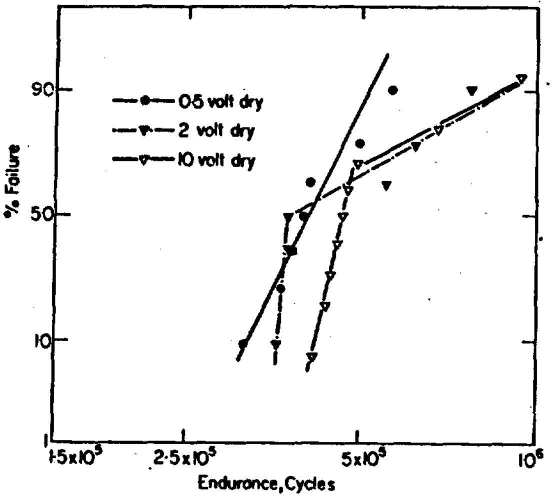

Fig. 1 *Effect of anodizing voltage; dry air;* 32,000 *lb/in*^{2} *max.*

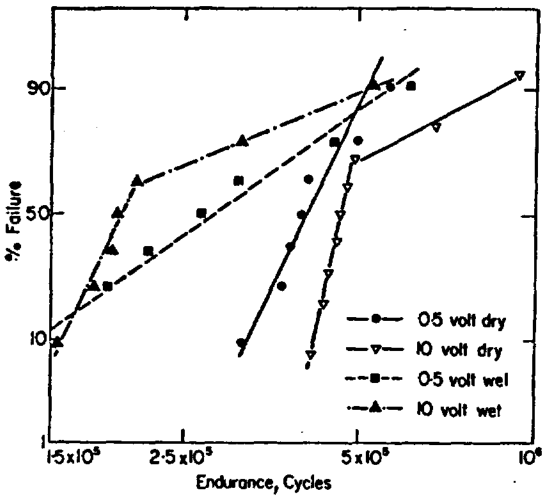

Fig. 2 *Effect of change in environment;* 32,000 *lb/in*^{2} *max.*

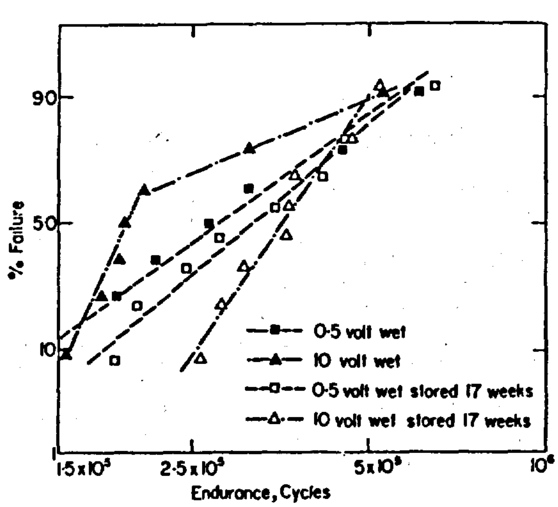

Fig. 3 *Effect of storage;* 32,000 *lb/in*^{2} *max.*

The endurances obtained are shown graphically as logarithmic normal-distribution probability plots, using median-rank[5] estimation of failure position. Fig. 1 illustrates the effect of anodizing voltage on the fatigue endurance in a dry environment. The results for 2 and 10 V exhibit a distinct departure from linearity, indicating a probable bimodal distribution of data.

Fig. 2 gives the test data for samples anodized at 0·5 and at 10 V, tested in dry and moist environments, while Fig. 3 deals with the effect of prolonged storage in a moist environment on samples anodized at these voltages.

Discussion

The graphical method of presentation of the results emphasizes the statistical bimodal distribution encountered with samples anodized at 2 and 10 V. Such distributions have been reported previously [1,6] and it was shown for samples with naturally grown oxide films[1] that they are related to the stability of the sample with respect to the test environment. The changes in the endurance of samples anodized at 10 V and stored for a prolonged period in a moist environment (Fig. 3) are in agreement with these findings. As the film with presumably the thinnest barrier oxide (0·5 V) does not show bimodal distribution and as no appreciable change was found after prolonged moist storage (Fig. 3), some pseudo-stability with respect to moist air is implied. This is of interest, as in dry air (Fig. 1), where previously[1] bimodal behaviour was not found, the 0·5-V series is the one group exhibiting apparently linear behaviour. It is suggested, therefore, that anodizing at 0·5 V produced an oxide layer differing in some unknown way from films grown at higher voltages.

While no quantitative conclusions can be drawn, it is clear that an increase in barrier-layer oxide thickness has materially changed the fatigue properties in dry and moist air (Fig. 2). It should be noted that the relative positions of the probability curves alter with the change in environment. Hunter and Fowle[4] noted, for pure aluminium, that exposure to water vapour decreased the barrier-layer thickness of samples previously heated to higher temperatures. Some degradation or similar process is undoubtedly occurring in the commercial alloy (10-V curves, Fig. 3) and this additional environmental degradation is hence a factor contributing to the reduced fatigue life in moist air.

If the degradation process is as suggested,[4] namely, concurrent hydration and growth of the barrier oxide, then the results for the samples anodized at 10 V and stored in moist air (Fig. 3) show that the barrier layer is associated with the results upon which the primary portion of the distribution curve is based. This conclusion is, however, qualified by the necessary assumption that the curve for the stored 10-V samples is of the same mode, and presumably failure mechanism, as the primary portion of the curve for freshly anodized samples. This assumption seems reasonable since the slopes of the curves are substantially similar.

The hypothesis was advanced earlier[1] that cracking of the surface oxide film may create a strain discontinuity across the coherent interface and thereby act as a dislocation source. As the barrier layer is the base layer of both natural and anodic oxide films, it therefore seems probable that endurance variations are related to environment-induced changes in this part of the oxide, rather than in the outer layers in direct contact with the environment.

Acknowledgement

The author wishes to thank Mr. D. Sutherland for carrying out most of the experimental work and Mr. R. C. A. Thurston for many fruitful discussions.

References

1. E. G. Eeles and R. C. A. Thurston, *J. Inst. Metals*, 1967, **95**, 111.
2. T. H. Alden and W. A. Backofen, *Acta Met.*, 1961, **9**, 352.
3. M. S. Hunter and P. Fowle, *J. Electrochem. Soc.*, 1954, **101**, 481.
4. M. S. Hunter and P. Fowle, *ibid.*, 1956, **103**, 482.
5. L. G. Johnson, *Indust. Mathematics*, 1951, **2**, 1.
6. S. R. Swanson, *Canad. Aeronaut. J.*, 1960, **6**, 221.

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The Relation of Humidity to the Fatigue Endurance of an Aluminium Alloy

E. G. Eeles and R. C. A. Thurston***

Fatigue tests on a commercial aluminium–magnesium–chromium alloy have shown that considerable changes in endurance are found with changes in the test environment and the environmental history of the test-pieces. It is suggested that variations in the surface oxide film are responsible.

The effect of atmospheric environment on the fatigue behaviour of many metals and alloys has been recognized for some time. The early work of Gough and Sopwith[1,2] established certain quantitative data and led to the conclusion that the principal atmospheric constituents affecting fatigue endurance were water vapour and oxygen. More recently, Broom and Nicholson[3] showed that, for an age-hardened aluminium alloy, water vapour was the only significant constituent and they surmised that water reacts at a free surface created by slip and that the hydrogen so formed diffuses into the lattice.

Although water vapour has been found to be the controlling influence for aluminium alloys,[1,2,4] oxygen alone appears to be the dominant factor for copper[5] and lead.[6] For an aluminium alloy, Liu and Corten[4] noted that the application of a surface coating of petroleum jelly virtually eliminated environmental variations, but the effective mean endurance was comparable to that of uncoated test-pieces in an environment of intermediate humidity.

Holshouser and Bennett[7] reported that some gas was evolved from certain metal surfaces during fatigue stressing. The evolved gas was hydrogen and the phenomenon was most pronounced in a variety of aluminium alloys, thus demonstrating in part the existence of a reaction already postulated.[3]

Bennett[8] has shown that the method of studying this effect by application of pressure-sensitive tape to the surface before testing results in endurances comparable to those in a dry environment and he suggested that the tape retarded access of moisture to the surface. He concluded that gas evolution was due to a high rate of reaction of some moisture which diffused through the tape, and that this reaction only occurred after cracks had formed in the surface oxide film. As there is some evidence of hydration of oxide films on aluminium,[9] it is possible that gas evolution could be produced from moisture in the film rather than from that diffusing through the tape.

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In the present study, five series of tests were carried out. Series 1 consisted of preliminary tests on an aluminium alloy to check the statistical distribution of endurance values at one stress level under controlled humidity conditions. In Series 2 tests, the *S/N* curves for the alloy in high- and low-humidity environments were established. A series of tests (Series 3) was then carried out to determine the effect of an initial oxide film. Finally, Series 4 and 5 were made to study the effects of environmental history and of a controlled period of oxide film growth, respectively.

Experimental Details

Although quantitative data have already been published for age-hardened aluminium alloys, there is some evidence[10] of structural changes occurring during fatigue stressing of alloys of this type. For this reason a work-hardened alloy was chosen for the present investigation. A low-alloy-content material with good corrosion-resistance was considered desirable, so that the oxide film formed would not be expected to differ substantially from that of pure aluminium, for which oxidation data are available.

A commercial 0·050-in.-thick sheet alloy, Alcan 57S, was used in the nominally half-hard condition. The manufacturer's limits of composition for the alloy are: 2·2–2·8% Mg, 0·15–0·35% Cr, 0·10% max. each Cu, Mn, and Zn, 0·45% max. Fe + Si. This alloy corresponds approximately to B.S.S.-NS4-1/2H.

Test-pieces were machined with a single-point tool to an 11-in.-radius toroidal test section of 0·500 in. minimum width. The machining procedure was found to affect slightly the endurance of the test-pieces and, therefore, direct comparison has been made only between groups of samples with an identical machining history.

The finishing operation for all test-pieces consisted of solvent degreasing, followed by light polishing of all surfaces of the test section with dry 400-grit silicon-carbide paper in a longitudinal direction. Particular care was taken to break the edges adequately and consistently. Dry polishing was used as this was the only certain way of producing uncontaminated surface films, since an oil-based surface preparation has apparently some undefined effect on endurance.[4]

The samples were all tested in pulsating tension in a Sonntag SF-1-U fatigue machine, which operates at 1800 c/m. For all tests the ratio of minimum to maximum stress was 0·05. Static and dynamic calibrations were carried out in advance of the investigation.

The required environment was maintained around the test-piece by means of a thin polyethylene bag, sealed to the grips of the machine. The grips themselves each contained a single-bore tube for ingress or egress of controlled-humidity air. The water content of the air was regulated by a dew-point technique. Compressed air was passed successively through three water-filled dispersion-type bubbler units, maintained at room temperature (75–80° F, 25–30° C). This resulted in a humidity > 95% relative. Low humidity was obtained by drying the air with silica gel and cooling to −50° F (−45° C) before warming to ambient temperature; the low humidity was detectable but not measurable on an electric-resistance hygrometer.

After passage through the test chamber, the air was monitored for humidity and then vented to the atmosphere under a head of ~ ¼ in. of light oil, to maintain slight positive pressure in the system.

Results

Series 1 Tests

The results of fatigue tests on aluminium alloys have usually shown more statistical scatter than those for the majority of other metals and alloys, and the necessity of testing a large number of samples has now been accepted by most workers in this field. Swanson[11] has shown that, over a portion of the *S/N* curve for an age-hardened aluminium alloy, the results should be interpreted on a bi-distributional basis, with each test statistic belonging either to one group or the other, and each group characteristic of separate *S/N* functions. Preliminary tests on the alloy in the present investigation showed that considerable scatter of results was occurring, particularly at the lower stresses. To examine this feature 21 samples were tested at 34,000 lb/in^2 maximum stress in a high-humidity environment. The results are shown in Fig. 1 as a median-rank[12] probability diagram, which assumes, in this case, a log/normal data distribution. Clearly, these tests should be interpreted as belonging to two, slightly overlapping, statistical distributions. Mean endurance values for each distribution can be assigned with reasonable accuracy.

Series 2 Tests

Tests were then carried out to establish stress/endurance (*S/N*) curves for environments of high and low humidity. The test-pieces differed slightly in edge-machining procedure from those used for the results shown in Fig. 1. The test-sections of all samples were finished immediately before placing them in the test chamber, and testing began after a period of 30 min for environment stabilization. The number of tests under one set of conditions was varied, depending on whether or not the presence of bimodal distribution was suspected. Where required, probability diagrams were used to group the test data. Bimodal distribution was positively identified only in data for tests in high humidity.

The results are shown as mean-value *S/N* curves in Figs. 2 and 3. The number against each graphical point is the number of test results associated with it, and, for the highest stress, ± one standard deviation is also shown. The outline curves from Figs. 2 and 3 are combined in Fig. 4.

TABLE I

Endurance (cycles) of Thermally Aged Samples Tested at 34,000 lb/in^2 max. in a Moist Environment

As Aged	Lightly Refinished
× 10^5	× 10^5
0·235	0·399
0·276	0·579
0·285	0·805
0·348	0·822

TABLE II

Comparative Log$_{10}$ Mean Endurances

Figures in parentheses are standard deviations

Group A	B	C	D	E
5·7209 (0·346)	5·3874 (0·109)	5·5803 (0·209)	5·7105 (0·174)	5·7703 (0·249) 6·2774 (0·075)

Series 3 Tests

The effect of a variation in initial oxide film thickness was examined by preparing 8 test-pieces as outlined previously and ageing in air at 93° C for 7 days. Four samples were tested, as aged, in a high-humidity environment, at 34,000 lb/in^2, and four were similarly tested after very light dry refinishing of the test section with 400-grit silicon-carbide paper to remove the surface oxide. The endurances are given in Table I.

Series 4 Tests

Four groups of nine tests were then carried out at 34,000 lb/in^2 stress in a high-humidity environment. The samples were prepared by the same machining practice as for the data shown in Fig. 1.

One group (A) was prepared and stored in the room atmosphere (~ 15% relative humidity) for a minimum of 18 days before testing. The second group (B) was prepared and stored in a high-humidity atmosphere for between 11 and 18 days. Group C was prepared and stored in high humidity for 10 days, and then held in the laboratory atmosphere for between 9 and 21 days. Group D was the inverse of Group C, the periods being 10 days in the laboratory and between 22 and 29 days in high humidity before testing.

Probability distribution diagrams were drawn for each group, and these showed that the results from Groups B, C, and D definitely each belonged to a single distribution. The results from Group A were unevenly distributed and did not lie readily on a single straight line, nor did they logically divide into more than one group. It seems unlikely therefore, but not proved, that a simple bimodal distribution exists for this group. Table II gives the logarithmic mean of each group, together with the two distributional means identified from the earlier group (Fig. 1), denoted Group E.

Series 5 Tests

The previous results (Series 4) suggest that variations in environmental history influence the endurance, and tests

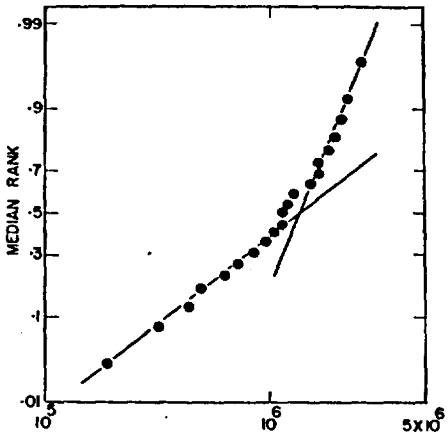

Fig. 1 Median-rank probability curve.

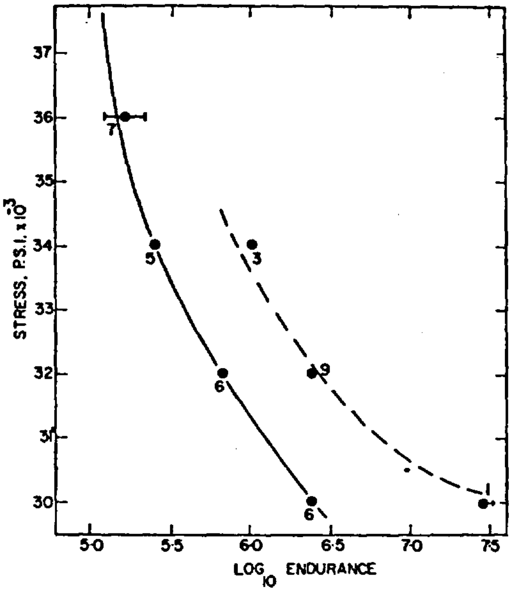

Fig. 2 Mean-value S/N *curves for high humidity.*

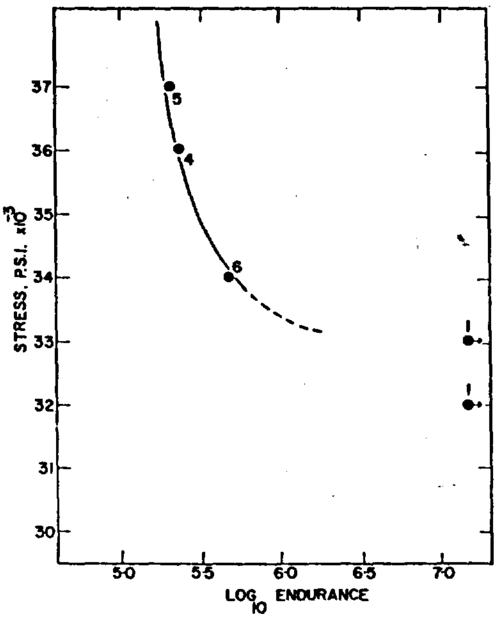

Fig. 3 Mean-value S/N *curve for low humidity.*

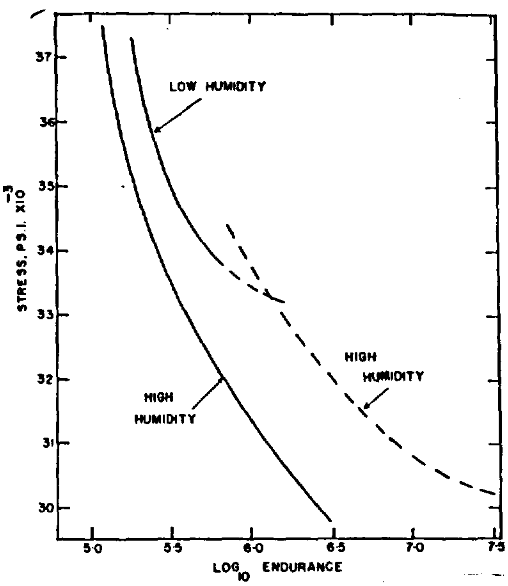

Fig. 4 Composite mean-value S/N *curves.*

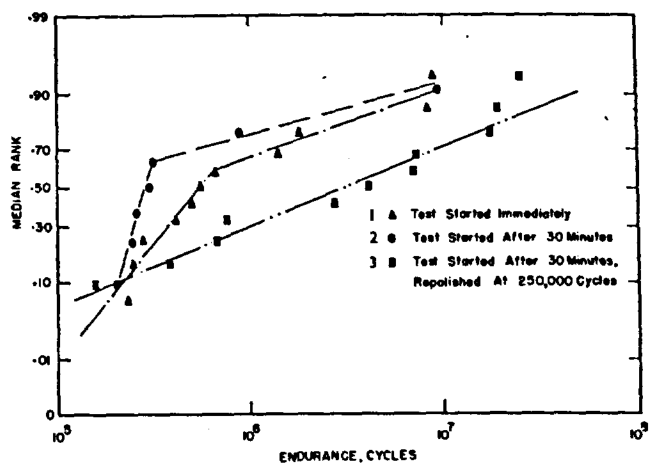

Fig. 5 Median-rank probability curves (see text).

were therefore undertaken to investigate time periods and conditions differing from those for the data in Table II. Tests were carried out on a different machine of the same type, at a stress of 34,000 lb/in^2 max. in a moist environment.

The specimens were prepared as before, except that an additional final light abrasion with dry 400-grit silicon-carbide paper was given after the test-piece had been mounted in the machine and immediately before sealing the polyethylene bag to the grips. In the case of Curve 1 (Fig. 5) the test was started immediately after this final operation, whereas for Curve 2 there was a further interval of 30 min before testing began.

Curve 3 shows the results for a further group of samples prepared as for Curve 2, but after 250,000 cycles the test was stopped and the surface lightly refinished with dry 400-grit silicon-carbide paper. One failure occurred before the refinishing operation.

Discussion

In view of the pronounced effect of bimodal distribution on the shape and position of the *S/N* curve, this feature will be considered before discussing the environmental effect. The probability diagram (Fig. 1) clearly establishes that two groups of test results can exist and, therefore, despite the reduced number of test-pieces involved, the assumptions made in establishing two S/N curves for high humidity (Fig. 2) are justified.

Whereas Swanson[11] found essentially two intersecting portions of the S/N curve, the present data show that, under the test conditions involved, there are two approximately parallel portions of the S/N curve at high humidity. It appears, then, that the bimodal distribution reported here is a function of environment. It should be noted that the secondary, longer-endurance curve (Fig. 2) does not replace the primary curve at lower stresses; in fact, the single test result attributable to this group at the lowest test stress suggests that this group may disappear at still lower stresses.

The low-humidity S/N curve is approximately parallel, over a portion of the range, to the primary curve for high humidity. Although general inferences can be made, there is no logical explanation, based on existing theories, for variation in either the position or the slope of the S/N curves with changes in environmental water content. As this factor was the primary variable in the testing procedure and, also, as the procedure additionally resulted in a variable bimodal distribution of results, the interaction of moisture with the sample appears to be complex and not necessarily linear in its magnitude. Since the base metal, in which the eventual fatigue crack initiates, is covered with a so-called protective oxide film, the interaction, if any, of water vapour with this oxide is a factor to be considered, since only when the film is cracked can direct, unrestricted reaction occur between the base metal and the environment.

Alden and Backofen[13] found that, for single crystals of pure aluminium, a thick, unbroken anodic oxide film prevented formation of fatigue cracks in the crystal. However, any crack in the film became a source of failure. Brief electropolishing to remove cracks in the film resulted in a substantial increase in fatigue life. The films studied were considerably thicker than naturally formed oxide films and a direct extension of this phenomenon to thin naturally formed films is not justified. However, some interrelation of oxide film cracking and fatigue failure has been established.

The tests in Series 3, involving thermally aged samples (Table I), indicate that variations in the oxide film—in this case, either in its thickness or its properties—have a marked effect on endurance. The increase in endurance of the refinished test-pieces can only be attributed to the difference in the oxide film, as there was no alteration in the surface finish and as removal of the film could not have resulted in sufficient surface cold work to produce a change in endurance of the magnitude noted.

The kinetics of natural oxide film formation for this alloy is not known; however, the kinetics for pure aluminium has been studied,[9] and it was found that the time taken to form a stable film in moist air is considerably longer than in dry air. The thickness of an oxide film formed in dry oxygen[14] is less than that of one formed in normal air[15] and it may be concluded, therefore, that variations occur in oxide films produced in environments of different humidity.

The results from the tests in Series 4 are given in Table II and, in addition to demonstrating the effect of environmental history on the endurance, they present two significant features. The first is that, when the test-pieces have a stable oxide film (i.e., one already established and characteristic of the test environment), the scatter is significantly reduced (Group B and to a lesser extent Group D). Secondly, bimodal distribution of data is not evident in groups held in a constant environment before testing; the conclusion is, therefore, that such a distribution results from testing immediately after specimen preparation and may be due, in some way, to growth of the oxide film on the test-piece during the actual test.

The data from Series 5 tests, plotted in Fig. 5, show specifically that changes in the oxide film, produced by the 30-min delay period, have a slight but detectable effect on the fatigue behaviour. The removal of the oxide film and regrowth of a thinner film on samples already cyclically strain-hardened gave results with no bimodal tendency. These results indicate that the film exerts no detectable effect during the latter stages of the fatigue process. The absence of primary-mode behaviour for this group also suggests that the primary distribution mode alone is associated in some way with the oxide film.

Having established an apparent relation between natural oxide films and fatigue endurance, it is pertinent to examine possible mechanisms by which the oxide could influence the fatigue behaviour. As fatigue is a process involving dislocation generation and movement, the influence of the oxide must be interpreted on this basis. It is not considered possible for a thin, naturally formed, oxide film to exert a restraining influence on the base metal, as was found for thicker anodized films.[13] However, as the oxide/metal interface is assumed to be coherent, the presence of a crack in the oxide will create a strain discontinuity across the interface and could conceivably thus act as a dislocation source in suitably oriented grains in the base metal. This hypothesis is consistent with the results in Fig. 5, in that no effect would be expected during later stages of the test.

An oxide-cracking mechanism can also form the basis for an explanation of the variations in endurance in differing environments. With films of differing properties, either completely or partially formed in differing environments, it would be expected that variations in oxide-cracking behaviour would occur.

It is not suggested that the oxide-crack mechanism described is the sole mechanism by which endurance is influenced. Bennett[8] has proposed that the environmental effect is due to rupturing of the surface oxide film with variations in crack-initiation potential in the metal depending upon the supply of moisture. The results obtained here suggest that the effect is due to variations in oxide film properties in differing environments. Hydrogen evolution[7] indicates that reactions of the type proposed by Broom and Nicholson[3] are definitely taking place, but, as such reactions can occur with the speed noted only after cracking of the oxide film, this mechanism for environmental effect appears to be secondary to the effect of variations due to oxide film property differences. It is, therefore, suggested that changes in fatigue endurance are primarily caused by differences in the ability of cracks to form in the surface oxide due to variations in these films in environments of differing humidity. Depending upon the ability of a crack in the oxide to generate dislocations in the base metal, this mechanism may dominate ancillary reactions occurring after oxide film cracks appear. As Holshouser and Bennett have noted,[7] gas evolution occurs only at a later stage of fatigue tests (at endurances comparable to those studied here) and the proportion of total life at which it starts increases as the total endurance increases. This indicates that, as hydrogen evolution occurs once the surface film has ruptured, the variations in endurance are largely due to variations in the rupture potential of the oxide film and not to other reactive mechanisms.

Conclusions

It is suggested that variations in fatigue endurance caused by testing in environments of differing humidities are attributable to variations in the surface oxide films formed in these environments. These variations would result in differences in cracking of the oxide and, by a mechanism not defined, such cracks could effect subsequent crack initiation in the base metal.

References

1. H. J. Gough and D. G. Sopwith, *J. Inst. Metals*, 1932, **49**, 93.
2. H. J. Gough and D. G. Sopwith, *ibid.*, 1935, **56**, 55.
3. T. Broom and A. Nicholson, *ibid.*, 1960–61, **89**, 183.
4. H. W. Liu and H. T. Corten, *U.S. Nat. Aeronaut. Space Admin. Rep.* (TND-647), 1960.
5. N. J. Wadsworth and J. Hutchings, *Phil. Mag.*, 1958, **3**, 1154.
6. K. U. Snowden, *ibid.*, p. 1411.
7. W. L. Holshouser and J. A. Bennett, *Proc. Amer. Soc. Test. Mat.*, 1962, **62**, 683.
8. J. A. Bennett, *J. Research Nat. Bur. Stand.*, 1964, [C], **68**, 91.
9. M. S. Hunter and P. Fowle, *J. Electrochem. Soc.*, 1956, **103**, 482.
10. A. J. McEvily, J. B. Clark, E. C. Utley, and W. H. Herrnstein, *Trans. Met. Soc. A.I.M.E.*, 1963, **227**, 1093.
11. S. R. Swanson, *Canad. Aeronaut. J.*, 1960, **6**, 221.
12. L. G. Johnson, *Indust. Mathematics*, 1951, **2**, 1.
13. T. H. Alden and W. A. Backofen, *Acta Met.*, 1961, **9**, 352.
14. F. Keller and J. D. Edwards, *Metal Progress*, 1948, **54**, 35.
15. N. Cabrera and J. Hamon, *Compt. Rend.*, 1947, **225**, 59.