RESEARCH ON LIGHT METALS IN THE METALLURGY DIVISION, NATIONAL BUREAU OF STANDARDS

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THE Metallurgy Division of the National Bureau of Standards has accelerated its research programme on metals in order to meet the increased demand for materials with improved and special properties so essential for continuing the technological advances of the space age. Much of the work is designed to furnish basic information on metals and alloys in terms of their structures. Studies are being conducted on problems related to creep, fatigue, corrosion, metal physics, preparation of extremely pure metals and other related fields. Some of the emphasis of the programme is being placed on evaluating specific properties of aluminium, titanium, magnesium, and their alloys as indicated by the following.

Deformation of metals

Titanium: Titanium and its alloys, because of their high strengh-to-density ratios and high resistance to corrosion, are promising materials for many cryogenic applications and for certain aircraft and missile components. The Division has made a study of the mechanical properties of this comparatively new metal as a part of a comprehensive research programme on the deformation of metals.

The study, recently completed,[1, 2, 3] was designed to evaluate the effects of notch geometry on the flow, fracture and ductility in tension of commercially pure titanium (99+% Ti) and a titanium alloy (4% Al, 4% Mn) at low temperature. Notch geometry is significant because brittle failures in service at low temperatures are often associated with the presence of a notch either as a design feature or a defect. Tension tests were made on initially annealed cylindrical specimens (Fig. 1) with notch depths ranging from 5 to 87 per cent, root radii ranging from 0·005 to 2·0 or 10 inches, at temperatures ranging from 100 to –196°C; V-notch of 60° angle and a constant minimum diameter of 0·350 inch at the root of the notch were used.

The effect of varying the notch depth on the flow characteristics at 25°C of titanium specimens with a root radius of 0·05 inch is illustrated by a comparison of the true stress-true strain curves* of Fig. 2. The flow stresses increased materially with increase in triaxiality induced by increase in notch depth. This increase in flow stress is significant even with a shallow notch of 5 per cent. The true strain at maximum load (M) did not vary appreciably with the notch depth whereas the strain at fracture (F) decreased greatly with increase in notch depth.

An example of the influence of root radius on the tensile behaviour is given in Fig. 3 for titanium specimens with 50 per cent notch depth fractured at 25°C. Again, the flow stress increased significantly with increase in triaxiality induced by decreasing the root radius down to 0·025 inch. With root radius less than 0·025 inch, the stress concentration factor

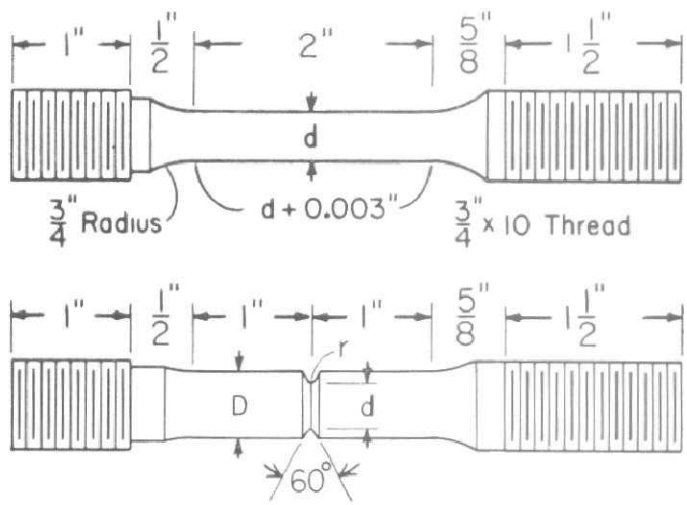

Fig. 1.

Unnotched and notched specimens used in the tension tests on titanium and titanium alloy.

* The true stress was determined by dividing the load by the concurrent minimum cross-sectional area of the specimen. The true strain was determined as the natural logarithm of the ratio of the original minimum cross-sectional area of the specimen Ao, to the current minimum cross-sectional area, A.

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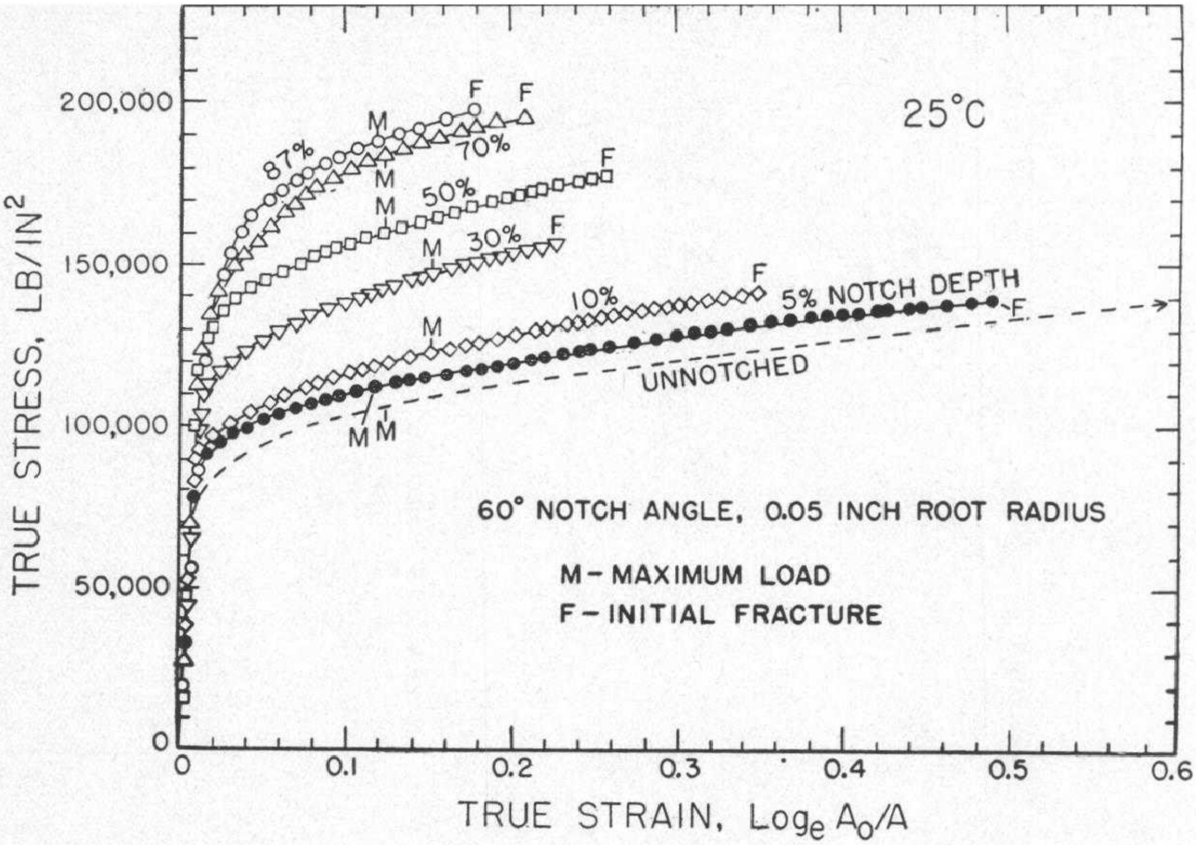

Fig. 2.
True stress-true strain relations obtained in tension tests at 25°C on titanium specimens of 0·05 in. root radius and selected notch depths.

increased markedly with increase in sharpness of the notch and this was the predominating factor in causing the fracture to occur before reaching a true maximum load; the triaxiality did not vary appreciably with change in root radius below 0·025 inch. Obviously the ductility as measured by the true strain at fracture (F) decreased greatly with a decrease in radius; the strain at maximum load (M) was not significantly affected by the sharpness of the notch.

The influence of temperature on the strength and ductility of the titanium is illustrated for unnotched specimens in the results given in Fig. 4; the effects were even more marked for the notch specimens and also for the alloy. The strength increased and the ductility decreased as the temperature was lowered from 25 to –196°C.

Analysis of the data obtained in this investigation on titanium and a titanium alloy show that the strength indices (resistance to flow, notch strength, true stress at maximum load and fracture stress) are generally increased and the ductility is decreased by increasing the notch depth or sharpness and by lowering the temperature. The decrease in ductility with increase in depth and sharpness of the notch is attributed to stress concentration at the root of the notch and the triaxial stress system induced by the notch. In general, the embrittling effect associated with the stress concentration was greater than that caused by triaxiality. The results emphasize the importance of taking special care to eliminate notches in the use of these relatively notch-sensitive materials, particularly at low temperatures. If they are unavoidable, their embrittling effect should be minimized by designing notches with the largest possible root radius.

Aluminium: The deformation in tension of a polycrystaline metal is affected greatly by the size and orientation of the grains and the presence of their boundaries, and these factors further complicate an analysis of the kinetics and mechanism of the process. Thus, the present study of the effects of notches in single crystals of high-purity aluminium (99·99+% Al) appears promising for furnishing fundamental information of the mechanism of deformation under multistress system and low temperature. Accordingly, pairs of single crystals of the same orientation are being grown in the form of tensile specimens (Fig. 5); one is grown

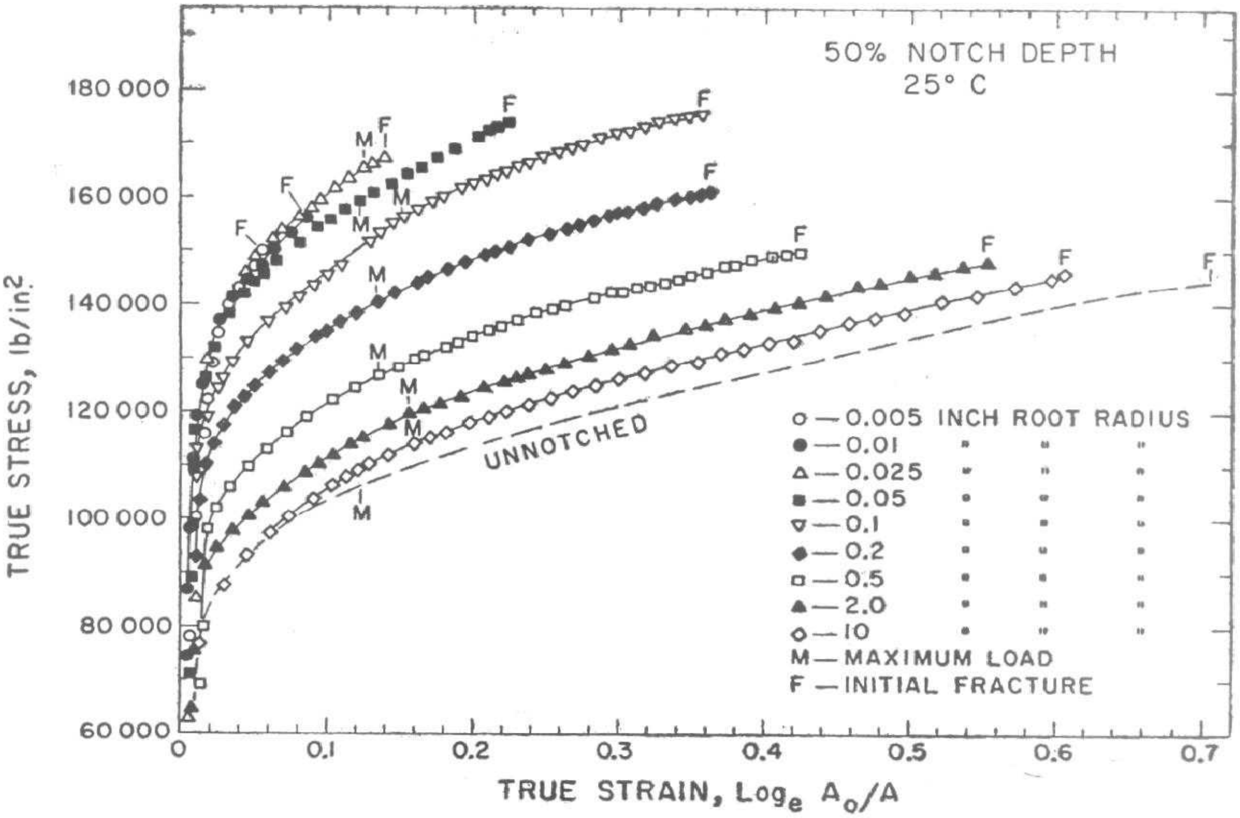

Fig. 3.

True stress-true strain relations obtained in tension tests at 25°C on titanium specimens of 50 per cent notch depth and selected root radii.

without a notch, the other with a notch of selected geometry. The initial specimens, grown by the Bridgman method in the form of a rectangular cross section of $\frac{1}{4}$ in. $\times \frac{3}{8}$ in. with a length of 5 inches, are annealed, and electropolished prior to testing in tension at 25°C. Studies are being made of the slip lines and other deformation markings developed on their surfaces as affected by (1) orientation, (2) notch geometry, (3) stress, (4) strain and (5) temperature.

Corrosion of metals

Aluminium: Most of the research on corrosion carried out in the United States has been empirical and the basic mechanisms by which metals corrode are not clearly understood. The Division is now engaged in a study of the fundamental nature of the corrosion process and its relation to crystal structure as affected by deformation in tension.

Single crystals of high-purity aluminium[4] are grown by the Bridgman method in the form of flat tensile specimens approximately 0·025 in. thick by $\frac{1}{4}$ in. wide in the reduced section by 1 in. long with $\frac{3}{8}$ in. gauge length (Fig. 6). Several crystals with identical surface orientation but with different orientations (at their edges) in the direction at which the tension is to be applied are used for each test. The crystals are electropolished and then extended in tension a predetermined amount in a special fixture attached to an X-ray diffraction unit. A transmission Laue' pattern is obtained through the gauge section of the unstressed specimen and after each of six extensions of 0·010 in. (0·060 in. total extension). The deformed specimen is then immersed in a corrodent (aqua regia + 5% HF) for a period sufficient to develop etch pits. An attempt is made to determine the corrosion characteristic of the undeformed and deformed crystals by observation of the etch pits. Preliminary results indicate that the deformed crystal corrodes (etches) differently from the undeformed crystals but, as yet, no definite correlation has been obtained between the amount of deformation, direction of slip and degree of corrosion. A noteworthy observation is the general absence of etch pits in the slip bands of the deformed crystals.

Magnesium: Stress corrosion cracking due to the combined effects of stress and corrosion is a damaging type of failure that is characteristic of certain classes of alloys. In some alloys, the corrosion cracking occurs along the grain boundaries whereas in others the cracks proceed across the grains.

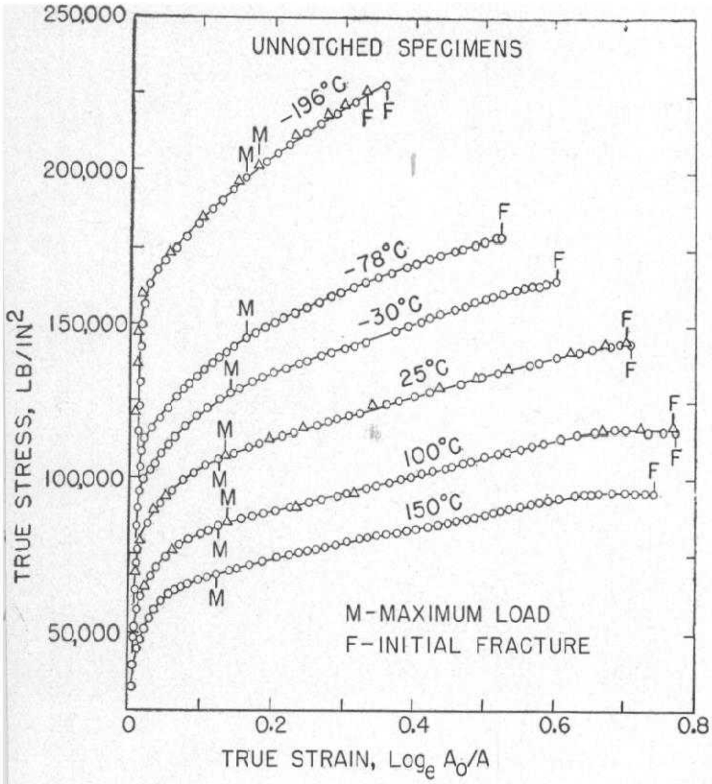

Fig. 4.

True stress-true strain relations obtained in tension tests at selected temperatures on unnotched titanium specimens.

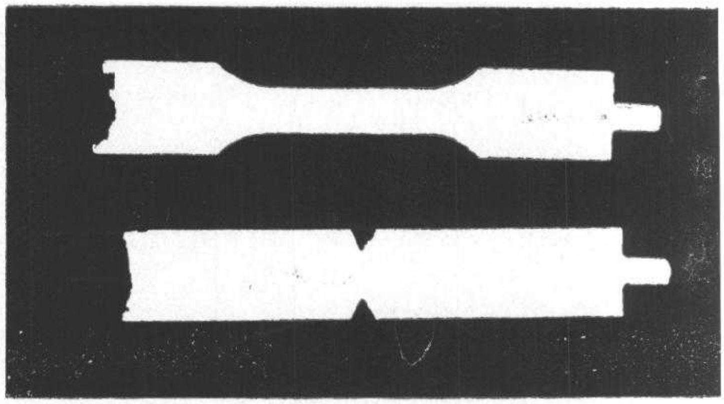

Fig. 5.

Single crystals of high-purity aluminium as grown in the shape of unnotched and notched tensile specimens. The specimens are 0·250 in. thick. ×1

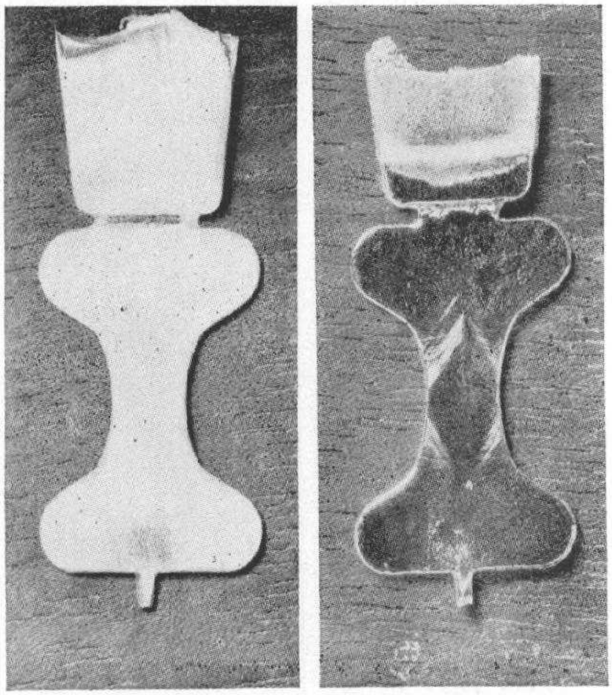

Fig. 6.

Single crystals of high purity aluminium as grown in the shape of flat tensile specimens. The specimens are approximately 0·025 in. thick. Left as grown; right, electropolished (1 part conc. HNO_3 –2 parts methyl alcohol) and then extended about 0·060 inch in tension. ×2

The Division has been making a study of the nature and mechanism of the stress corrosion of metals[5]. A magnesium alloy (AZ31, 3% Al, 1% Zn, 0·3% Mn) is now being used because it is especially suited for this type of study. Failures can be made to occur in specimens of this alloy in less than five minutes and the initiation and growth of the cracks to failure can be readily followed by means of extension-time and electrochemical solution potential-time curves. The extension-time curves for specimens stressed at about 98 per cent of the yield strength in a corrodent (35 g/1 NaCl, 20 g/1 K_2CrO_4) are typical of ordinary creep curves for metals (Fig. 7), that is, an initial extension upon application of the load, followed by a decrease in rate of extension, a period of nearly constant extension and then an increase rate leading to fracture. The electrochemical solution potential becomes more negative with the application of the load. This change is attributed to a rupture of the initial protective film on the specimen. The change in potential immediately after loading is attributed to a repair of the film on the surfaces of favourably oriented grains and the repair continues until the potential attains a maximum and cracking is initiated. Once cracking is started, the bare metal at the tip of the crack tends to make the potential more electronegative and this process predominates until complete fracture occurs.

Light Metals in Soils: A study of the behaviour of commercially pure titanium, high purity aluminium, aluminium clad (Alclad 6061) and aluminium alloys (3003, 5005, 5052, 5086 and 6061) in soil environment is currently a part of the Division's broad programme on corrosion[6].

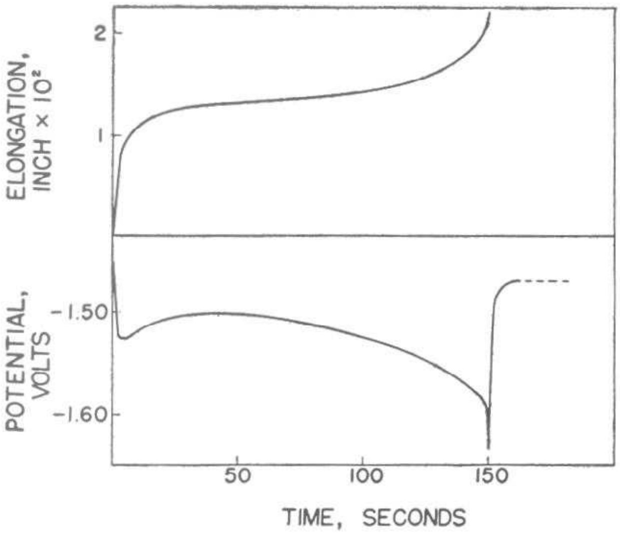

Fig. 7.
Idealised extension-time and potential-time curves for a magnesium alloy (AZ31) that failed in about 150 seconds. The applied tensile stress was about 98 per cent of the yield strength on specimens immersed in a corrodent (35 g/l NaCl+ 20 g/l K_2CrO_4). Potentials were measured against a calomel electrode of saturated KCl type.

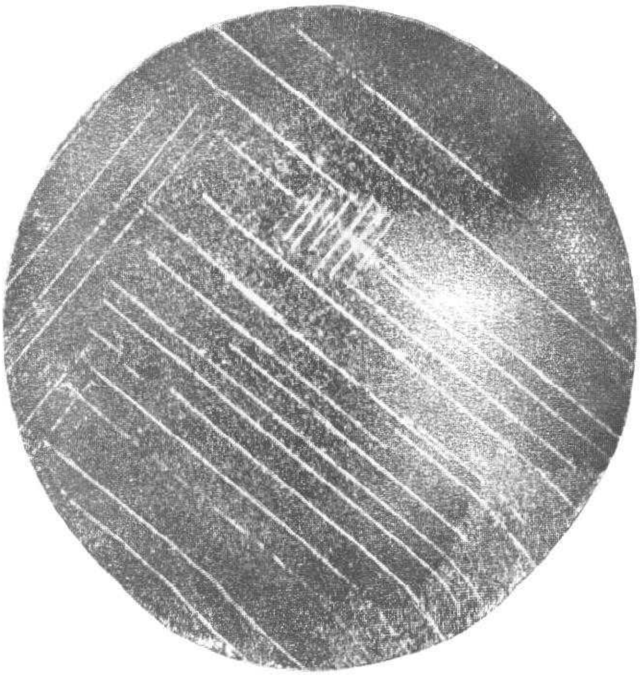

Fig. 8.
Surface of an aluminium alloy specimen subjected to reversed torsional loads. The direction of the slip bands (white lines) is different in each grain, even in the small grain near the centre which is completely surrounded by a grain of a different orientation. Keller's etch ; ×25.

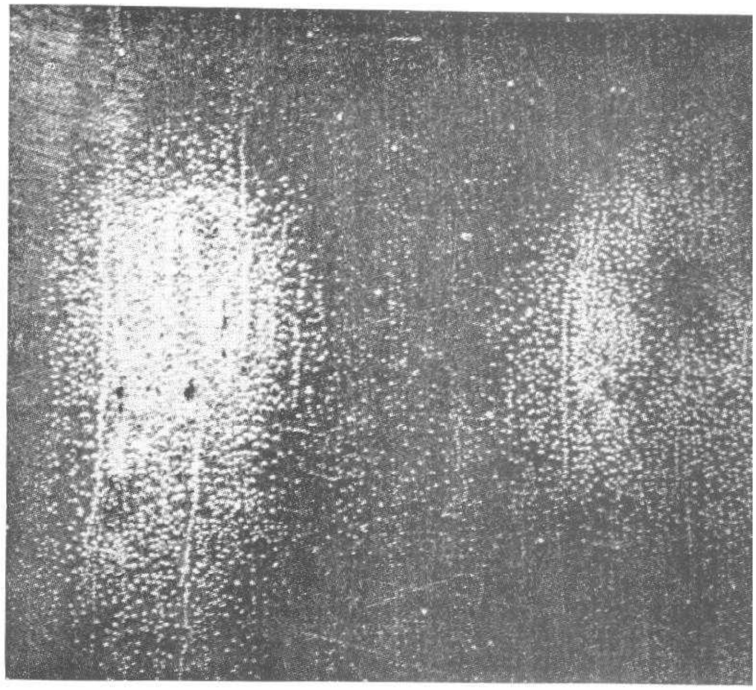

Fig. 9.
Numerous bubbles formed under pressure sensitive tape applied to a stressed specimen of an aluminium alloy. The specimen had been stressed for 100,000 cycles in torsion fatigue before the tape was applied and several fatigue cracks had developed. The bubbles formed during an additional 2,000 cycles of stress. ×12

Specimens of these metals have been exposed to six different soils ranging in texture from fine sand to heavy clay, well to poor aerated, pH from 3·5 to 10 and electrical resistivity from 150 to 27,000 ohm-cm. The specimens, in the form of 1½ in. I. D. pipe, $\frac{1}{64}$ in. wall, 12 in. long, were sealed at both ends before exposure. Selected specimens of all these metals were removed from each of the soils after an exposure of two years and the corrosion attack was evaluated in terms of pitting and loss in weight.

The titanium was unaffected by corrosion in any of the soils.

The aluminium alloys behaved nearly alike in any one environment. All showed a relatively low resistance to attack as many of the specimens were perforated by corrosion within the two-year exposure period.

The corrosion of the aluminium varied widely with the different soils. For example, it was severely attacked by local corrosion in a sandy loam of relatively low electrical resistivity and high pH and practically unattacked in another loam of high resistivity and low pH.

Fatigue

Fatigue cracks usually start in pre-existing slip bands within the grains of a metal. It is therefore difficult to study the condition under which the crack is started and to determine the exact position of the nucleus (i.e. in boundary or interior of the grain) in commercial metals because of their small-size grains. The Division, therefore, produced aluminium alloy specimens (2·5% Mg, 0·25% Cr, 0·2% Zn) with grains 2 to 3 mm in diameter in order to observe the behaviour of individual grains under reversed torsional stresses. The individual grains were found to act independently of their neighbours as is illustrated by the direction of the slip bands in Fig. 8. Furthermore, there was no evidence that grain boundaries or interaction of neighbouring grains promoted cracking. It appeared that the principal factor to be considered in the fatigue crack initiation of polycrystalline aluminium is the resolved shear stress on the plane of easy slip in the slip direction.[7]

Motion pictures made of a specimen of an aluminium alloy during the time of fracturing in torsional fatigue showed a surprisingly large amount of material being extruded from the crack. In an attempt to obtain some of this material for identification, a piece of transparent pressure-sensitive tape was applied to the surface of a specimen after a fatigue crack had already been induced. When the specimen was then stressed for an additional thousand cycles, small bubbles formed under the tape (Fig. 9). Subsequent investigations disclosed that the bubbles formed simultaneously with detectable cracks. These bubbles, caused by gas liberated as a result of surface reactions, are expected to provide a useful means for studying such reactions[8] and for detecting the onset of fatigue cracking.

Nitriding titanium

A study of the nitriding characteristics of commercially pure titanium and a titanium alloy (6% Al, 4% V) was undertaken in the Division (cooperation, Mineral Products Division) to evaluate the suitability of these materials for special components in aircraft[9]. The requirements in this application were resistance to corrosion attack in salt water, suitable resistance to galling and wear in sliding contact and good machinability.

Specimens of the two materials were nitrided at 1800°F (980°C) in purified nitrogen for periods ranging from 4 to 168 hours. The titanium formed a uniformly thick case (Fig. 10) that increased in depth with increase in nitriding time but a sharp line of demarcation was maintained between the case and core. Furthermore, the "uniform case" consisted of a surface film covering a thicker or principal layer as is illustrated in the photomicrograph of a specimen nitrided for 168 hours (Fig. 11). There was an abrupt change in the etching characteristics at the middle of the principal layer that is believed to be due to a concentration gradient of nitrogen in the case. The case also had a wide variation in hardness values as is shown by the range in Vickers numbers given at the edge of the micrograph.

The titanium alloy also had a uniform depth of case (Fig. 12) that increased in depth with increase in nitriding time. However, the nitrided specimens showed the presence of elongated nitrided grains that penetrated into the core at approximately 45° to the surface. These grains were below the uniform case but they

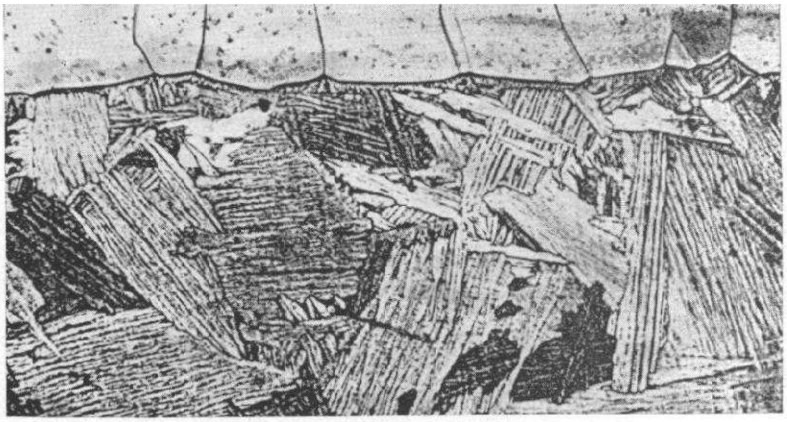

Fig. 10.
Structure and depth of case of titanium nitrided in purified nitrogen at 1800°F (980°C) for 48 hours. Etched in 1 part HF (48%), 12 parts HNO_3 (conc.) and 87 parts H_2O. ×200

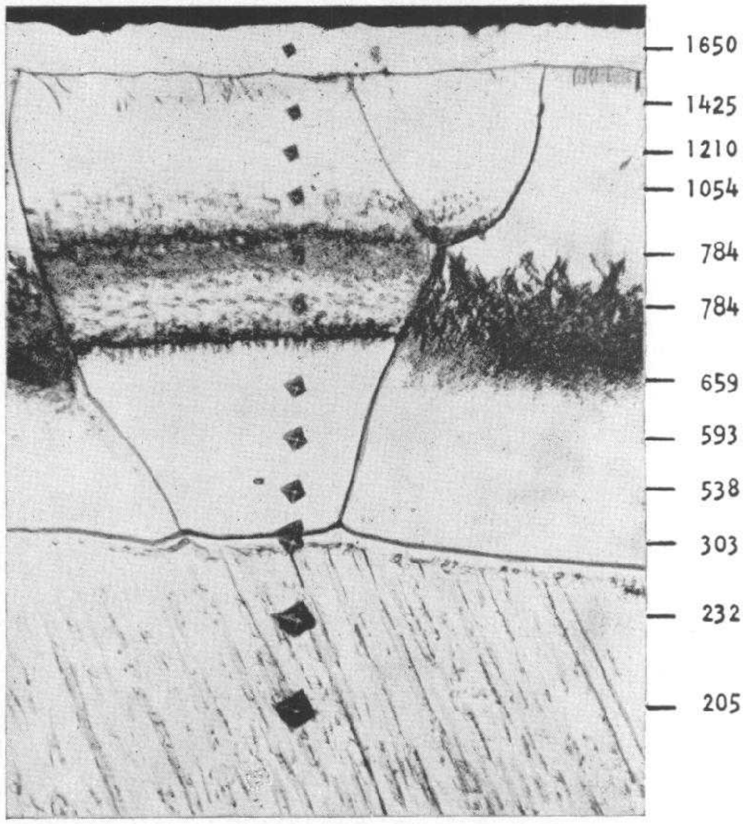

Fig. 11.
Microstructure and Vickers Microhardness indentations (50-g load) and corresponding Vickers hardness numbers across the case into the matrix of a titanium specimen nitrided in purified nitrogen at 1800°F (980°C) for 168 hours. Hardness range corresponds to Rockwell C 77 to C 12. Same etchant as for Fig. 10. ×350.

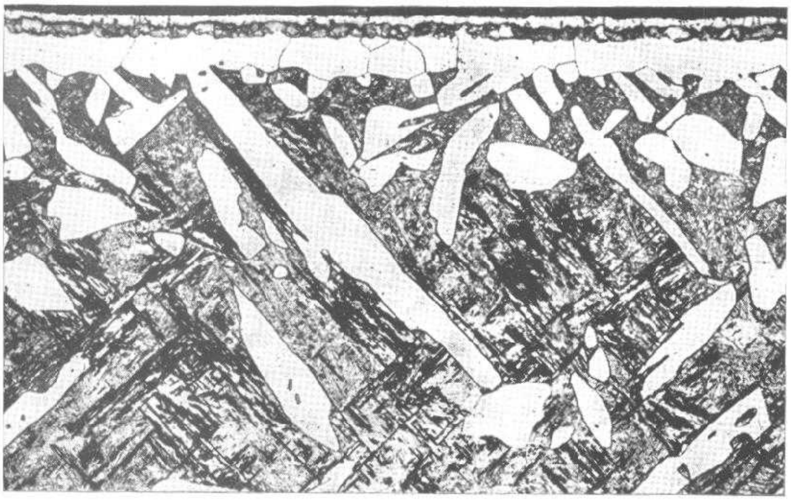

Fig. 12.
Structure and depth of case of titanium alloy (6% Al—14% V) nitrided in purified nitrogen at 1800°F (980°C) for 48 hours. Same etchant as for Fig. 10. ×200

frequently exhibited common boundaries with nitrided grains of the surface layer. The growth of the elongated grains into the matrix appears to be associated with the cube planes of a beta phase at the nitriding temperature. The vanadium content of the elongated grains, as determined with an electron-probe micro-analyzer was approximately one-half of that in the matrix and no vanadium composition gradient was observed in the matrix in the immediate vicinity of these grains. The elongated grains had hardness values corresponding to about Rockwell C 50 whereas the adjacent matrix was about C 35. The hardness of the case ranged from C 77 at the surface to C 50 at the interface with the core.

The results of impact tests made on unnotched sheet specimens indicated that nitriding did not significantly affect the impact properties of the titanium but nitriding had a marked detrimental effect on the impact properties of the alloy. This adverse effect is believed to be due to the elongated grains in the alloy. Although the elongated nitrided grains were partly decomposed into a lamellar structure by heating in vacuum at 1750°F (950°C) for 1 hour followed by slowly cooling, the impact properties after this treatment were still too low for the nitrided alloy to be suitable in applications subject to shock loading.

The nitrided surfaces of the titanium had satisfactory coefficient of friction, wear and corrosion resistance for use in the intended application.

Acknowledgement

The author gratefully acknowledges the co-operation of his associates in the Metallurgy Division for the use of their data in preparing this manuscript. Special thanks are due to G. W. Geil, T. H. Orem, H. L. Logan, M. Romanoff, J. A. Bennett and J. R. Cuthill for their contributions.

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DISCUSSIONS

Mr. R. Choubey, NML: The author has mentioned that some surface reactions give rise to the appearance of bubbles and the consequent surface cracking in connection with the study of fatigue of aluminium alloys and I would like to know from Mr. Digges more about the nature of the surface reaction whether it is chemical or mechanical.

Mr. Thomas G. Digges (Author): We believe it is a chemical reaction. Mr. Bennett, who has done this work, is of the opinion that the bubbles are due to the liberation of hydrogen.

Mr. U. P. Mullick, Calcutta: I would request Mr. Digges to throw some light on the weldability of aluminium.

Mr. Digges (Author): We have not studied the weldability of aluminium. At present, we do not have a research project on welding of any metal.

Dr. B. R. Nijhawan, NML: I would like to compliment Mr. Digges on his masterly survey of the researches underway at the National Bureau of Standards. I have two specific enquiries to make to Mr. Digges. One is relating to the corrosion of metals where he mentioned, under the heading "Aluminium", that they were engaged in a study of the fundamental nature of the corrosion process and its relation to crystal structure as affected by deformation in tension. From the latest information it appears that the chemical theory of corrosion is being supplemented by the part played by "whisker" phenomenon, wherein it is claimed that "whiskers" growing at the surface promote corrosion. Perhaps Mr. Digges may be able to indicate to us how far this "whisker" phenomenon is applicable to the corrosion of aluminium and its alloys. The second query relates to the use of nitrided titanium for use in special components in aircraft. It was mentioned that the nitriding of titanium was done by purified nitrogen. We have considerable difficulties in purifying nitrogen and we experience difficulties in getting extra high-purity nitrogen in cylinder form, whilst we do purify it by employing suitable purifying trains. Could Mr. Digges indicate what was the purity of nitrogen employed for the test ?

Mr. Digges (Author): We are familiar with Gulbransen's theory on the promotion of corrosion of ferrous materials by the growth of whiskers but we have not conducted experiments along this line and we are not in a position to pass on its merits. We do not know of any similar work on aluminium. We do have a group working to establish the mechanisms of corrosion and due consideration will be given to all the current theories.

We did not make an analysis to determine the purity of the nitrogen used in nitriding titanium. However, we did use water-pumped grade nitrogen that was passed through a liquid oxygen trap to remove water and then over titanium at 980°C to remove oxygen before entering the nitriding chamber. With titanium as the getter, the oxide reaction is more rapid than the nitride and the titanium nitride that is formed eventually reverts to the oxide. To insure high efficiency in oxygen removal, the charge of titanium turnings was replaced before every run.