Effect of Anodic Surface Films on the Plastic Deformation of Aluminium Crystals*

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I. Introduction

Effects of the surface film of crystals on the plastic behaviour have been studied by many investigators. Roscoe[1] published the pioneering work on the effect in cadmium crystals. Further studies on cadmium crystals were made by Cottrell and Gibbons[2], and Phillips and Thompson[3]. On zinc crystals studies were made by Harper and Cottrell[4], Pickus and Parker[5], Gilman and Read[6], and Coffin and Weiman[7]. A striking effect of the surface contamination on "easy glide" of pure silver and gold crystals has been reported by Andrade and Henderson[7]. These experiments have shown that crystals are strengthened by the presence of thin surface layers, i.e. the surface film has been found to increase the critical shear stress of crystals to more than twice the normal value.

Many works on the effect of surface active reagents, on the one hand, have been carried out by Rehbinder, Lichtman and Maslennikov[9], Andrade and Randall[10], Andrade[11], Andrade, Randall and Makin[12], Harper and Cottrell[4], Mentor and Hall[13], Phillips and Thompson[3], Masing[14], and Coffin and Weiman[7]. It has been demonstrated by these works that surface active reagents increase the rate of flow of metal.

And it is also evident metallographically that surface conditions affect slip bands of crystals. Wilms[15] reported the abnormal slip markings in aluminium polycrystals having thick anodic films.

The experiments which will be described in this paper pertain to: (1) the structure of anodic surface films produced by electropolishing, and (2) effects of the surface film on the yielding stress, stress-strain curve, crystal twisting produced during extension, fine structure of slip bands, abnormal slip markings, development of kink bands, and the crystal rotation, which were studied collectively.

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II. Experimental Procedure

Long single crystals of aluminium of 99.99 pct purity made by strain-annealing technique were employed in this investigation. They were 1 to 1.5 mm thick and 10 to 15 mm wide. The original orientations are illustrated stereographically in Fig. 1.
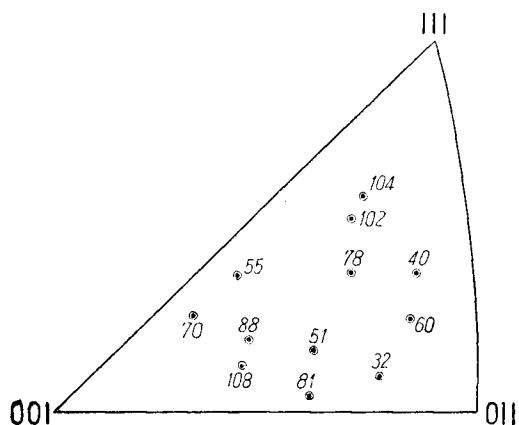

Fig. 1. Stereographic projection of the crystal axes.

The crystal was cut into two sections by a thin saw having the fine teeth so that each section would be more than 70 mm long. One of them was electropolished in Jacquet's bath[16] of perchloric acid=acetic anhydride, and the other section was electropolished in a solution of orthophosphoric acid. If the case is necessary, the one section was etched in a 4 pct hydrochloric acid solution and the other section was anodically oxidized in a solution of 1 pct ammonium borate. The surface of each specimen was not subjected to any mechanical polishing prior to the chemical treatment. Examples of the condition of surface preparation are presented in Table I and the orientation of the crystals given in this table is shown in Table II.

Specimens, whose surfaces thus prepared, were deformed in tension at room temperature. Each of the sections 'A' and 'B' obtained from the same specimen had the equal gauge length which was in most cases 50 mm. In the present tensile test, the lower end of the crystal was suspended freely while the load was gradually increased at a definite rate by continuously pouring water into the vessel hung from the grip at the lower end of the specimen. Any rate of elongation would

Table I. Conditions of Surface Preparation in Main Specimens

Specimen No.	Solution of anodic treatment	Voltage	Current density (A/dm²)	Temperature (°C)	Mean thickness of the film (Å)
55–A	Jacquet's bath	33–35	9–10	<30	<100
55–B	65% orthophosphoric acid	35–37	23	<60	ca. 500
88–A	Jacquet's bath	34–36	9–10	<30	ca. 100
88–B	70% orthophosphoric acid	35–39	22–23	<45	ca. 400
78–A	Etched by 4% HCl	2	—	25	< 50
78–B	1% ammonium borate (after polishing in Jacquet's bath)	115	4–0.005	28	ca. 1500

Table II. Original Crystal Orientation of Main Specimens

Specimen No.	Primary slip plane	Slip direction	θ_0	λ_0	η_0
55-A and -B	$(\bar{1}11)$	[101]	55.2°	34.8°	0°
88-A and -B	$(\bar{1}11)$	[101]	49.4°	41.0°	3°
78-A and -B	$(\bar{1}11)$	[101]	51.2°	41.5°	15°

θ_0: Angle between the normal to the slip plane and the specimen axis.
λ_0: Angle between the slip direction and the specimen axis.
η_0: Angle between the slip direction and the the maximum slope on the slip plane.

suffice, but the rate was in most cases 10^{-2} to 10^{-4} pct per second. As the lower end of the specimen was suspended freely, the crystal twisting about the tension axis, if it occured, could be measured by the mirror attached to the specimen. The details of the tensile apparatus have been described in the previous paper[17].

Electron-micrographs were taken by the technique of oxide-replica or positive-replica. The positive-replica method requires a two-stage process. In the present investigation, the methylmetacrylate-aluminium method for the specimen electropolished in Jacquet's bath and the polyvinyl alcohol=aluminium method for the specimen electropolished in phosphoric acid were employed. Shadow casting with chromium vapours was utilized on the positive replica and, if necessary, on the oxide replica also.

Laue transmission patterns taken before and after extension were analyzed by the use of the crystallographic globe.

III. Anodic Films Produced by Electropolishing

The anodic film formed on the surface of aluminium during electropolishing can be removed by the method of scratching squares on the surface of the specimen and immerging it in a saturated solution of mercuric chloride. Films are lifted free by attacking chemically the metal through the scratch. The films are washed in 5 pct hydrochloric acid and water, and then mounted on the specimen screen of electron-microscope.

Anodic films made by the electropolishing in Jacquet's bath were very thin and they in most cases came into fine pieces in a solution of mercuric chloride. On the other hand, films produced in a solution of orthophosphoric acid were relatively thick and they were easy to take up with the screen.

Mean thickness of anodic films, indicated in Table I, was estimated by comparing the penetrating power of electron beams between the film in question and the standard film, in the same field of vision of the electron microscope, as shown in Fig. 2. The standard films of various thickness were made by anodic oxidation in a solution of 1 pct ammonium borate which is believed to produce the anodic film of relatively
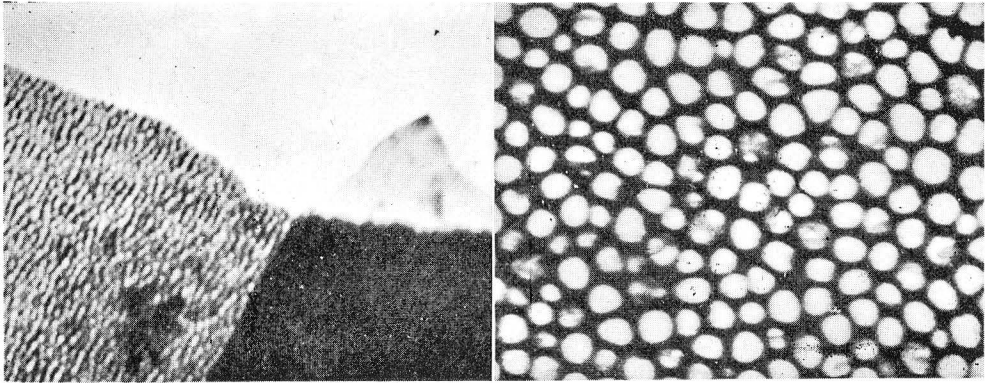
Fig. 2. Comparison of the penetrating power of electron beams between two kinds of films. The thicker film on the left-hand of the picture is that of specimen No. 88–B and the thin film on the right the standard.   ×10,000

Fig. 4. Anodic film produced by the electro-polishing in a solution of orthophos-phoric acid. Direct oxide-replica, un-shadowed. Specimen No. 88–B.
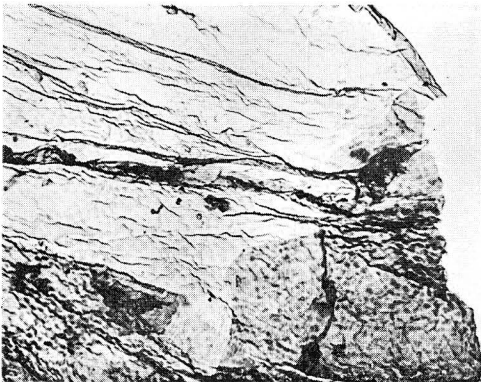   ×55,000

Fig. 6. Anodic film produced by the electro-polishing in Jacquet's bath. Direct oxide-replica, un-shadowed. Specimen No. 55–A.   ×10,000
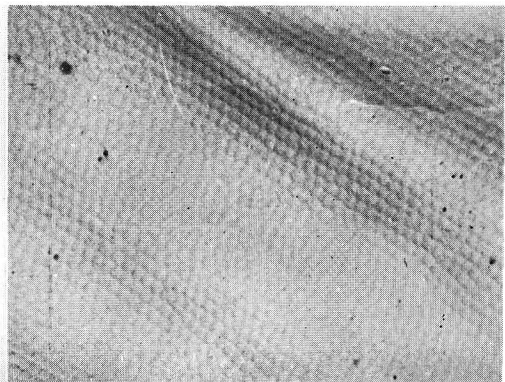
Fig. 7. Cell structure of the surface electro-polished in Jacquet's bath. Methyl methacrylate=aluminium raplica, chro-mium-shadowed. Specimen No. 114.
                                 ×10,000

uniform thickness[18]. They were removed also from the underlying aluminium by mercury method. Estimation of the thickness of the standard film was based on the experimental relation obtained by Nagase[19]. The relation is reproduced in Fig. 3.

In his experiment the thickness of films was measured by the multiple-beam interference method. The value found by extrapolating the curve to zero voltage is about 50 Å and this represents the thickness of the film formed on the clean surface of aluminium at room temperature. Mott[20] estimated the thickness at 40 Å.
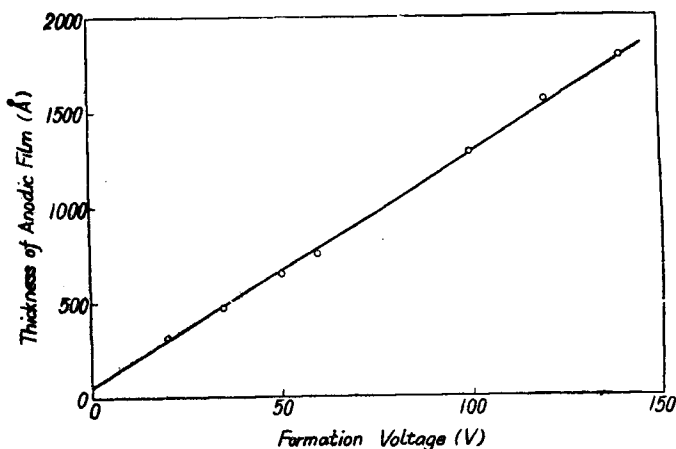

Fig. 3. A relation between the thickness of anodic film and the formation voltage (after Nagase).

The anodic film made by electropolishing in phosphoric acid is shown in Fig. 4. In the transparent part of the film, there can be observed extremely thin films to exist. The thin film, however, does not remain perfectly under the electron bombardment, as clearly observed in the picture. It stands to reason, therefore, that many workers have considered the structure of anodic films to be full of pores[21]. In contrast to Fig. 4, the pattern obtained by formvar-replica of one stage process shows the opposite blackening, as indicated in McLean and Tr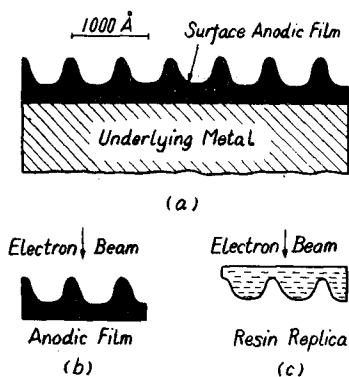otter's paper[22]. They employed the coarse-grained aluminium electropolished in a solution of phosphoric acid[23]. On the basis of these two facts, a schematic picture is given in Fig. 5. The black uneven part in this picture is the anodic film made by the electropolishing in phosphoric acid. The structure is very similar in appearance to the "micro-etch" structure of Brown[24].

Fig. 5. A schematic picture of the anodic surface film formed by the electropolishing in ortho-phosphoric acid.

Thus, the anodic film produced in phosphoric acid reveals the cell structure and it is composed of a thin part and a thicker part alternately. An accurate determination of the thickness of anodic films, accordingly, was very difficult because of the uneven thickness of the film. The thickness

presented in Table I, therefore, indicates only the mean value. In most specimens sufficiently polished in phosphoric acid, the thinner part of the film was 150 Å to 250 Å thick and the thicker part was more than 400 Å.

The anodic film produced in Jacquet's bath is shown in Fig. 6, where there can be seen onefold, twofold and manifold of the film. And the part of two or more fold film reveals slightly the orange-peel structure as observed also in the film made in phosphoric acid. In the part of onefold film, however, any cell-structure could not be detected on account of the extremely small thickness (ca. 100 Å). Positive replicas, however, sometimes reveal the cell-structure as clearly shown in Fig. 7. The furrow structure described in detail by Brown[24] was often observed in the positive replica shadowed with metal vapours, as indicated also in Fig. 17, but never in the oxide replica.

Thus, the anodic film formed by the electropolishing in Jacquet's bath has generally the uniform thickness in comparison with the film made by phosphoric acid.

Anodic films were examined also by the electron micro-diffraction, but they revealed only the very diffused halos.

IV. Results Obtained

A. Yielding Stress

The specimens electropolished in Jacquet's bath or etched by dilute hydrochloric acid had the critical shear stress of less than 100 g/mm². On the other hand, the specimens electropolished sufficiently in a solution of orthophosphoric acid had the stress of more than twice the normal value. The examples are shown in the fifth column of Table III. The yielding stress was obtained from both the stress-strain curve and the stress-twisting curve, by noting the value at which plastic flow commenced, as indicated by arrow markings in Figs. 8 and 9.

Table III. Several Experimental Results in Main Specimens

Specimen No.	Total elongation %	Mean rate of elongation % per sec.	Total load g/mm²	Critical shear stress g/mm²	Twisting angle ω '/cm	Number of kink bands per cm
55–A	11.5	6.5×10^{-4}	1871	76	-12.4	24
55–B	11.4	6.7×10^{-4}	1814	174	-5.1	14
88–A	20.0	9.6×10^{-4}	2013	91	$+6.8$	15
88–B	20.0	10.0×10^{-4}	2190	160	$+1.4$	8
78–A	2.1	1.3×10^{-4}	683	69	—	—
78–B	2.1	1.9×10^{-4}	756	150	—	—

Angle of axial twisting ω in minutes per cm is given by $\omega = [\omega]/(l + \Delta l)$, where $[\omega]$ is the total twisting angle at a certain stage of elongation, l the gauge length before extension and Δl the elongation. The positive and negative signs of the angle represent the left and right-handed twist respectively.
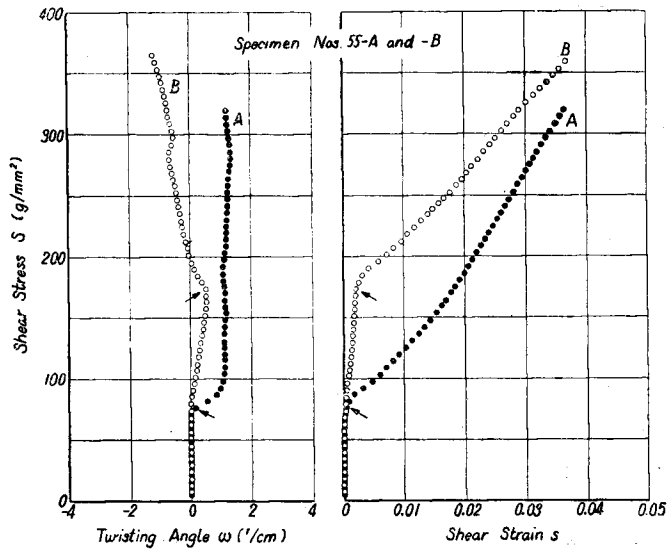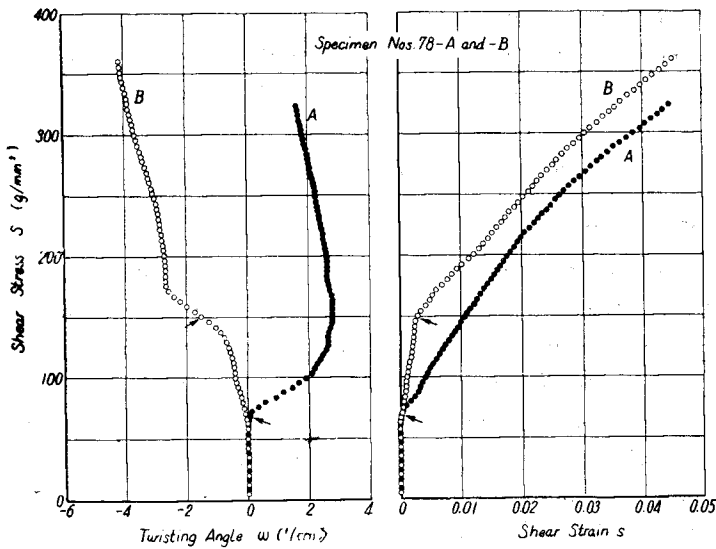
Fig. 8.

Fig. 9.

Figs. 8 and 9.　Correlation between stress-strain curves and
stress-twisting curves at the early stages of deforma-
tion.　Fig. 8: Specimen Nos. 55-A and 55-B.　Fig. 9:
Specimen Nos. 78-A and 78-B.

The magnitude of the increase in the critical shear stress did not always depend
on the increase in the thickness of the surface film, but it varied with specimens, as
understood from Table I and III.　Roscoe[1] found that for a particular thickness of

the surface film the critical shear stress decreased as the thickness of the specimen increased. The result obtained here is well understood in this connection, i.e., the effective thickness in the direction of slip in the specimens Nos. 55, 88 and 78 was respectively 2.3, 3.5 and 4.8 mm.

In the problem of how the presence of a thin surface film can increase the yielding stress, one cannot absolutely refuse the naive hypothesis that the film simply relieves the metal of part of tensile load. Roscoe[1], dealing with the effect of oxide films on the critical shear stress of cadmium crystals, deduced a value for the shear resistance of the film of the order of 3×10^9 to 3×10^{10} dynes/cm^2. The values obtained by Phillips and Thompson[3], dealing with the effect on the creep rate of cadmium, were the order of 10^9 dynes/cm^2. Gilman and Read[6] reported that a value of 9×10^8 dynes/cm^2 was obtained for the tensile strength of copper film in the creep test of zinc, and also a higher value of the order of 2.7×10^{11} dynes/cm^2 was deduced for the strength of a 700 Å copper film on a zinc crystal.

In this experiment, the specimens Nos. 55–A and 55–B had the films of the mean thickness of about 100 Å and 500 Å respectively, as presented in Table I. The difference in the critical tensile stresses for these two specimens was 208 g/mm^2. If the load difference were due to the film strength alone, the stress in the film would be 3×10^{11} dynes/cm^2. In the same way, the stress in the film of specimen No. 88–B was 2.5×10^{11} dynes/cm^2. A lower value of 8×10^{10} dynes/cm^2 was deduced for the strength of a 1500 Å anodic film of specimen No. 78–B.

B. Stress-Strain Curve

Stress-strain curves were raised entirely by anodic surface films in most cases, as shown in the right-hand diagram of Fig. 10. The fact has been established by a number of workers mentioned earlier. It was occasionally observed, however, that crystals lying near the boundary of the stereographic triangle through the $\langle 001 \rangle$ and $\langle 111 \rangle$ poles yielded stress-strain curves which crossed at certain strain values. The curves in the right-hand of Fig. 11 are typical. The curves labelled by ' A ' and ' B ' in these figures are those of the specimens electropolished in Jacquet's bath and in a solution of phosphoric acid respectively.

It was found also in this experiment that the stress-strain curve of the specimen covered with the thicker anodic film did not show the phenomenon of " easy glide " so clearly as the specimen having the surface film of less than 100 Å, as shown in Figs. 8, 9, 10 and 11.

C. Crystal Twisting

Aluminium single crystals experience the macroscopic twisting about the tension axis during the course of plastic extension[17]. This has been observed also by
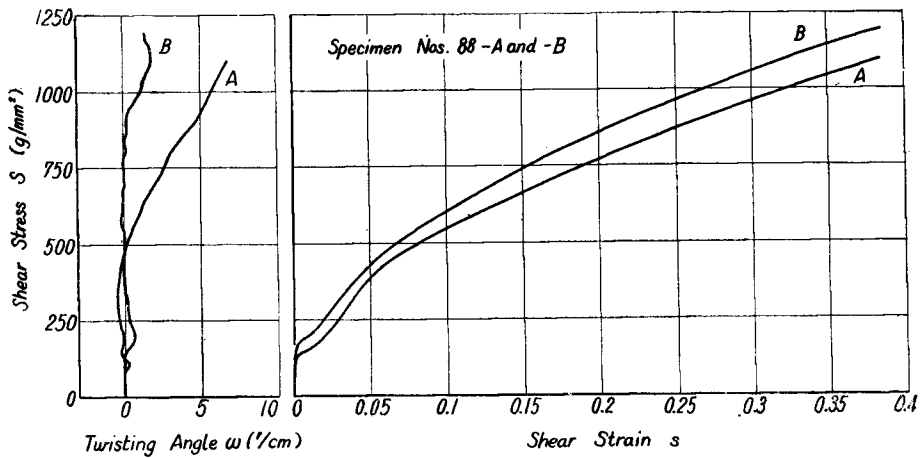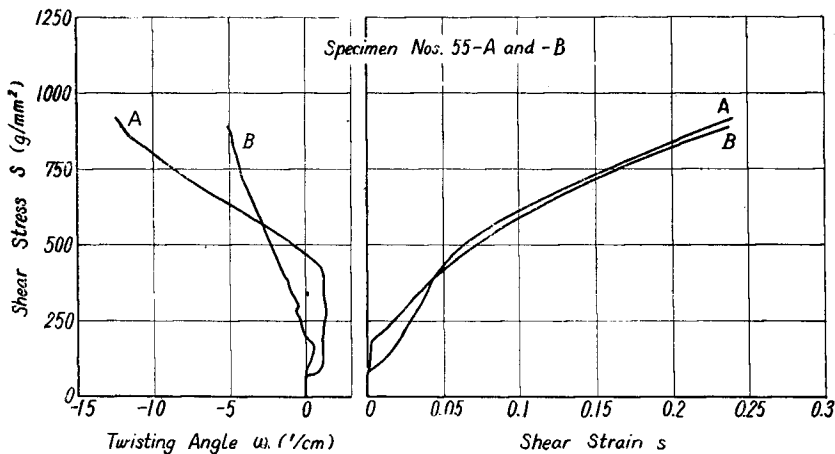
Fig. 10.

Fig. 11.

Figs. 10 and 11.　Stress-strain curves and stress-twisting curves.
Fig. 10: Specimen Nos. 88–A and 88–B.
Fig. 11: Specimen Nos. 55–A and 55–B.

Paxton and Cottrell[25] in rod crystals of aluminium. Heidenreich and Shockley[26] found in aluminium crystals the slight rotation of the laminae in a slip band relative to one another by means of electron-diffraction. Barrett[27] reported that a single crystal rod of zinc could be twisted, provided that the basal planes were nearly parallel to the cross-section plane. And Kawada[28] also found that the twisting occurred in the stretched zinc bicrystal having a grain boundary in the longitudinal axis of the specimen. Twisting was also observed by Gilman and Read[6] in zinc and tin mono-crystals of the triangular and the other special shapes of the cross section. Gilman

and Read attributed the axial twisting to the shape effect. Wilman[29] was the first to postulate the rotational slip as a real mode of deformation.

We should have expected the ease of twisting to be correlated with η which is the angle between the slip direction and the maximum slope on the slip plane ; the greater the η, the more twisting is needed near the grip in addition to ordinary bend gliding, in theory. But in practice, the specimen having the large angle of η did not always give the large twisting. In this connection, we had by mere chance a specimen, No. 55, whose angle of η was 0°. This specimen did undergo a relatively large twisting, as shown in the left-hand diagrams of Figs. 8 and 11. This led us to consider that the twisting is much influenced by inhomogeneities such as deformation bands arisen from the grip effect, as described in our previous paper[17].

The twisting is generally very sensitive at the beginning of slip and the occurrence of the secondary slip which plays an important role in the formation of inhomogeneities. This is the reason why the twisting does not progressively increase with increasing elongation ; the stress-twisting curve sometimes looks unsteady. And it is shown in the curves 'A' of Figs. 8, 9, 10, 11 that the stress at which the twisting begins corresponds exactly to the yielding stress obtained from the stress-strain curve given in the right-hand of these figures. Thus it may be said that the twisting gives the sensitive indication of slip.

In this connection, in the specimens Nos. 55–B and 78–B, slip bands could not be indeed detected microscopically up to the shear stresses of 174 and 150 g/mm² respectively, but the twisting was observed to have begun at the stress of about the same values for the specimens Nos. 55–A and 78–A, as clearly shown in Figs. 8 and 9.

If the twisting produced during tensile deformation is essential to the slip process, it is natural to assume that the amount of twisting should be equal in two of those specimens subjected to the equal shear which have the same gauge length and the same orientation. But in practice, the amount of twisting has been observed to decrease with the increase of thickness of the surface film as indicated in Table III and in the left-hand diagrams of Figs. 10 and 11. It appears, therefore, that the surface film affects the mode of deformation in the crystal.

The amount of twisting stated above gives only the mean value of the overall length of a specimen. But the twisting attributable to the grip effect in tensile deformation[30] does not occur uniformly along the overall length. To ascertain this fact, two mirrors, M_1 and M_2, were attached to a specimen in such a way as shown in Fig. 12, and the local twisting was measured. The third mirror, M_3, was attached to the lower grip as usual. The amounts of twisting between the upper grip M_0 and the mirror M_1, M_1 and M_2, M_2 and M_3, and M_0 and M_3 are given seperately in Figs. 13 and 14. The specimens Nos. 102 and 104 presented as examples in these figures
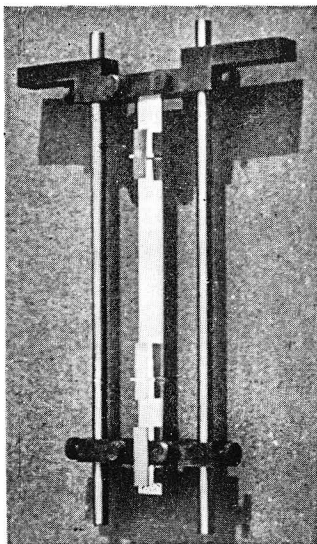
Fig. 12. Setting of three mirrors on the specimen and on the lower grip. Two bars for fastening the grips are removed when testing.
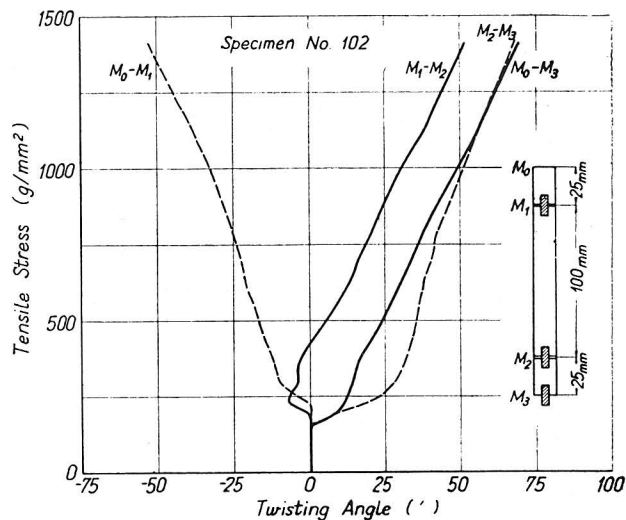

Fig. 13.

Figs. 13 and 14. Local crystal twisting along the length of crystals. M_0 indicates the upper grip, and M_1, M_2 and M_3 are the mirrors attached to the specimen and to the lower grip, as illustrated in the right-hand of the figures. Fig. 13: Specimen No. 102-A. Fig. 14: Specimen No. 104-A.

were both electropolished in Jacquet's bath and stretched in the ordinary manner. The specification is given in Table IV. The twisting angle of Table III shows only the mean value of twisting between M_0 and M_3. A detailed account for the local twisting will be published elsewhere.

D. Fine Structure of Slip Bands

It has been demonstrated by many workers that the surface finish of crystals affects the appearance of slip bands. Our previous work[31] showed that specimens coated with thicker anodic films formed by
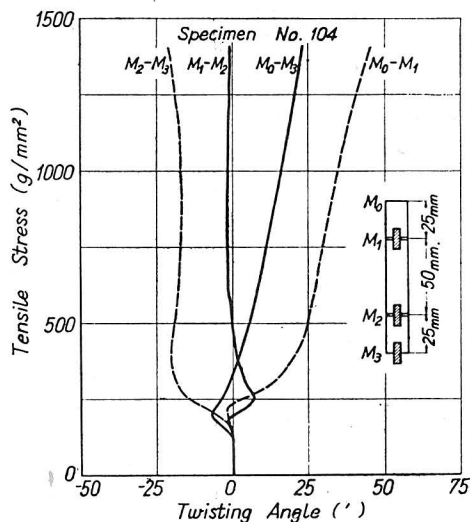

Fig. 14.

Table IV.

Specimen No.	Crystal Orientation			Critical shear stress g/mm²	Total elongation %	Total load g/mm²	Mean rate of loading g/mm²/min.
	θ_0	λ_0	η_0				
102–A	55.8°	37.9°	17°	65	6.0	1413	5.0
104–A	58.1°	36.9°	19°	59	4.0	1407	5.0

electropolishing in orthophosphoric acid had only the coarse and distinct slip bands on widely spaced slip planes when they were stretched at the rate of $10^{-4}\%$ per second. The slip bands had often the width of more than 5000 Å and they did not reveal the lamellar structure in most cases. Fig. 15 indicates the slip bands in the specimen No. 40 which was electropolished in phosphoric acid. In this picture, the slip bands are white. The technique of preparing oxide replicas was described in the previous paper[31]. Wilsdorf and Kuhlman-Wilsdorf[32] also reported of the wide slip bands in the crystal covered with a thicker surface film.

Thus, the specimen coated with a thicker anodic film, when stretched under creep conditions, develops only the coarse slip widely spaced and does not reveal such fine slip lines as can be usually observed in the specimen electropolished in Jacquet's bath.

In the case of a relatively rapid rate of elongation, however, the slip bands even in the specimen having a thicker surface film are resolved into the fine slip lines which are familiar in the specimen bearing a thin film, though they are still wider. Fig. 16 shows the slip bands in the same specimen No. 40, as presented in Fig. 15, which was stretched at the rate of elongation of $10^{-2}\%$ per second. The effect of strain rate on the appearance of slip bands in the specimen coated with a thicker film formed in phophoric acid has been reported previously[31].

Aluminium single crystals, whose surfaces are prepared solely by electropolishing in Jacquet's bath and coated with anodic films of less than 100 Å, when they are subjected to the extension at normal rates of more than $10^{-2}\%$ per second, develop isolated fine slip lines of 400 Å or less, and the cluster of the fine slip lines here and there, regardless of the orientation of crystal, as reported also by Kuhlman-Wilsdorf and Wildorf et al.[32][33] and Fujita, Suzuki and Yamamoto[34]. The maximum height found by Wilsdorf et al.[32] is 1200 Å.

In the extension test of crystals electropolished in Jacquet's bath under creep conditions, however, the mean spread of heights seems to increase in comparison with that of crystals subjected to the normal strain rate; the height ranging widely up to 2000 Å. The specimen with a thicker film shows the effect of strain rate more markedly, as stated above.

And it appears that the orientation of crystals affects the structure of slip bands; two kinds of slip bands are shown here. The one type generally consists of a few coarse slip lines of more than 1000 Å and a number of fine slip lines. The slip bands shown in Figs. 17 and 21 belong to this type. The slope of the slip plane towards the crystal surface in the specimen No. 60-A shown in Fig. 17 is 86°. The slip band
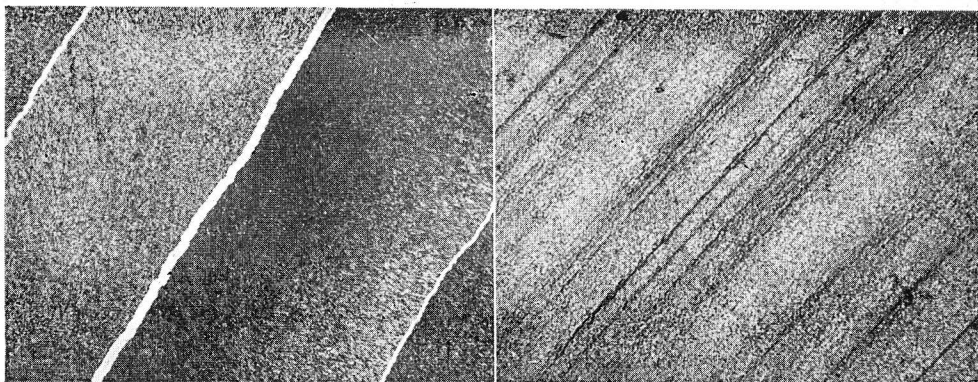
Fig. 15. Slip bands in specimen No. 40 electro-polished in phosphoric acid and stretched slowly by 4.3% of elongation. Oxide-replica, un-shadowed. ×1,300

Fig. 16. Slip bands in specimen No. 40 electro-polished in phosphoric acid and stretched rapidly by 5.2%. Oxide-replica, un-shadowed. ×1,600
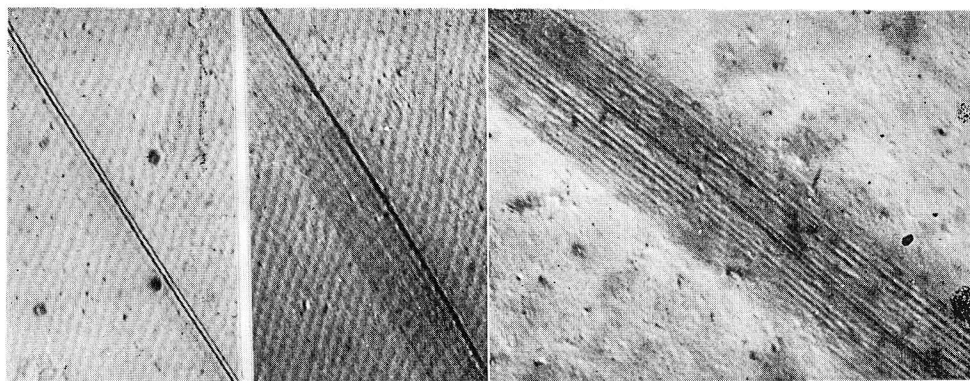

Fig. 17. Slip bands in specimen No. 60–A stretched by 10.0%. Methyl metha-crylate=aluminium replica, chromium-shadowed. ×10,000

Fig. 18. Slip bands in specimen No. 55–A stretched by 11.5%. Methyl metha-crylate=aluminium replica, chromium-shadowed. ×10,000
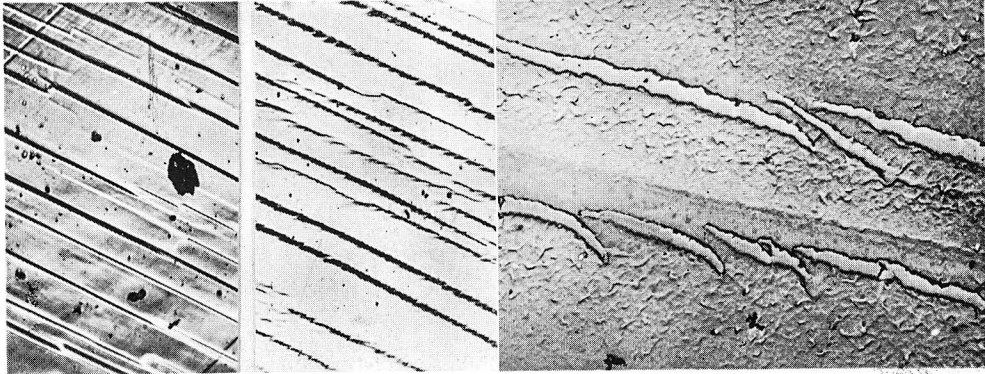
Fig. 19. Difference of the appearance of slip bands between specimens Nos. 55–A (left) and 55–B (right).   ×320

Fig. 20. Abnormal slip markings in specimen No. 55–B. Polyvinyl alcohol=aluminium replica, chromium-shadowed.   ×5,000
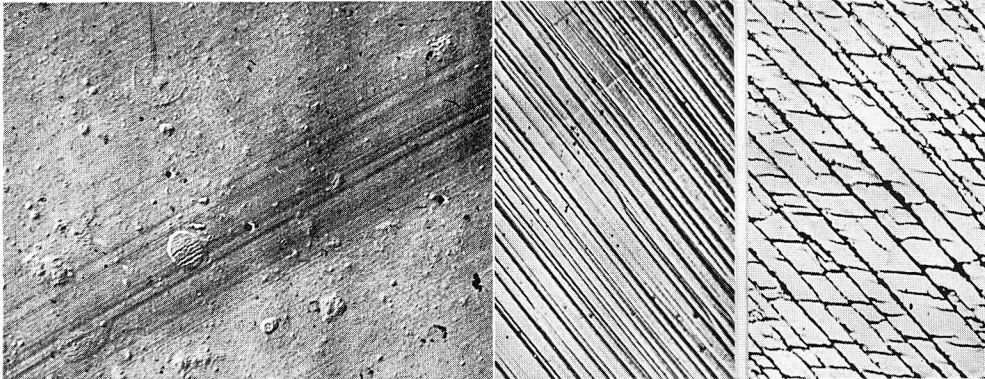

Fig. 21. Abnormal slip markings at a thick and round oxide particle retained on the surface of specimen No. 108 which was electropolished in Jacquet's bath and stretched by 4.5%. Methyl methacrylate-aluminium replica, chromium-shadowed.   ×10,000

Fig. 22. Difference of the appearance of slip bands between specimens Nos. 88–A (left) and 88–B (right).   ×320

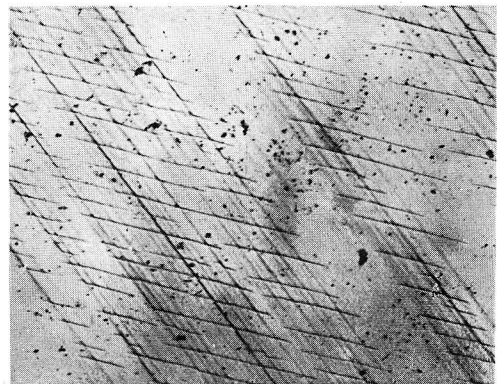Fig. 23. Abnormal slip markings in specimen No. 70–B which was electropolished in phosphoric acid and stretched by 14%.   ×100

given in the right-hand of Fig. 17 consists of a coarse slip line and the wide slip zone extended over about a micron. This shows that the coarse slip might occur on one or a few adjacent slip planes, but the greater part of the slip band was formed by rather homogeneous fine slip on several thousands of slip planes. The left-hand picture also indicates the similar structure, i.e. two coarse slip lines and the rather homogeneous slip zone, though it is indistinct. The furrow structure will serve the purpose for the confirmation. The slip bands of this type were observed also in the specimen No. 81-A and others which had the relatively small angle of θ and, hence, in which the interaction among different slip systems would not readily occur.

The other type of slip bands is such as can be resolved into the slip lines having the almost equal spacing and width. This was found for the first time by Heidenreich and Shockley[26] and confirmed later by Brown[25]. This is well known as the lamellar slip. Fig. 18 shows the lamellar slip in the specimen No. 55-A, although the spacing between elementary slip lines is wider than usual. The specimen was stretched slowly and the slope of the slip plane towards the crystal surface was 33°. The axis of this specimen lies near the boundary of stereographic triangle through the $\langle 111 \rangle$ and $\langle 001 \rangle$ poles and, therefore, the interaction among different slip systems will frequently occur in the crystal. Lamellar slip of this type can be often observed in single crystals stretched rapidly regardless of the orientation and is more general in polycrystals, although the mean spacing between elementary slip lines appears smaller than that of slowly stretched crystals. The case has been given in the beautiful works made by Wilsdorf and Kuhlman-Wilsdorf[32][33].

There is considerable disagreement on observations of the slip bands among different authors as pointed out by Mott[36]. This may be attributable to the strain rate and the crystal orientation, except the surface finish, as stated above.

E. Abnormal Slip Markings

Abnormal slip markings often appeared on the aluminium single crystal coated with a thick surface film. Wilms[15] also reported on the abnormal slip markings in aluminium polycrystals electropolished in phosphoric acid. Here, we shall call the slip markings which do not coincide with the usual slip along the octahedral plane as "abnormal slip markings".

The difference in the appearance of slip bands between the specimens Nos. 55-A and 55-B under the light microscope is shown in the left-hand and right-hand of Fig. 19 respectively. The surface preparation of these specimens is presented in Table I. "Cross slip", which was found first in aluminium crystals by Cahn[37], was clearly observed in the specimen No. 55-A. The slip bands in the specimen No. 55-B, on the other hand, look like the "saw teeth". The slip markings under an

electron-microscope are shown in Fig. 20. The picture indicates unconnected cracks of the anodic film along the slip. Similar case was obtained by mere chance, as shown in Fig. 21. It is observed in this picture that a thick oxide particle retained on the electropolished surface was broken along the underlying slip.

Another case in the specimen No. 88–B is shown in Fig. 22. In this case the abnormal slip markings developed into long bands reaching the normal slip traces of the octahedral plane. An extreme case was obtained from the specimen No. 70–B, as indicated in Fig. 23. Under the microscope, it was observed that the abnormal slip markings occured first at a place of the existing slip trace of the octahedral plane, as shown in Fig. 24, and then grew gradually into long bands.

There was some tendency that the abnormal slip markings appeared frequently in crystals whose axes lay near the boundary of stereographic triangle through the $\langle 100 \rangle$ and $\langle 111 \rangle$ poles and that they occurred markedly in the slow extension rather than the rapid extension.

A special case of abnormal slip markings, which looked like "cross slip", was found in the specimen No. 51–B. This is shown in Fig. 25 under the light-microscope and in Fig. 24 under the electron microscope.

When the traces of abnormal slip markings were checked with the crystallographic planes having simple indices, it was found that the traces coincided fairly well with the intersection of the (001) plane on the surface of specimen. However, in the specimens covered with a films of more than 1000 Å thick, it does not hold true and the abnormal markings develop in the direction nearly perpendicular to the tension axis, strictly speaking, perpendicular to the maximum strain.

F. Development of Kink Bands and the Crystal Rotation

It was found that the development of kink bands in crystals was affected by the surface anodic film. The number of kink bands developed on crystals decreases with the increase in thickness of the surface films, as indicated in the last column of Table III. Fig. 26 shows the difference of macroscopic structure between the specimens Nos. 88–A and 88–B. It is clearly observed in the picture that the specimen No. 88–A has a larger number of kink bands than the specimen No. 88–B. The surface treatment of these specimens is given in Table I. Thus, the surface film supresses the development of kink bands.

Crystal rotation in the simply slipped matrix between kink bands was examined by X–ray with a fine beam obtained from a capillary slit system, as reported previously[17]. Fig. 27 indicates the stereographic projection of the movement of crystal axes in the slipped matrices of the specimens Nos. 88–A and 88–B both of which were elongated by 20.0%. It was found that the crystal rotation of the matrices was
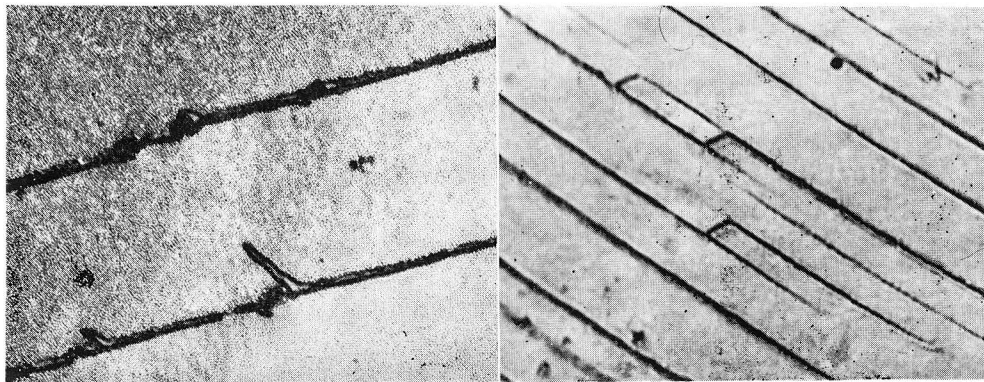
Fig. 24. Abnormal slip markings in specimen
No. 51–B which was electropolished
in phosphoric acid and stretched by
12%. Oxide-replica, un-shadowed.
×5,000

Fig. 25. Abnormal slip markings under the
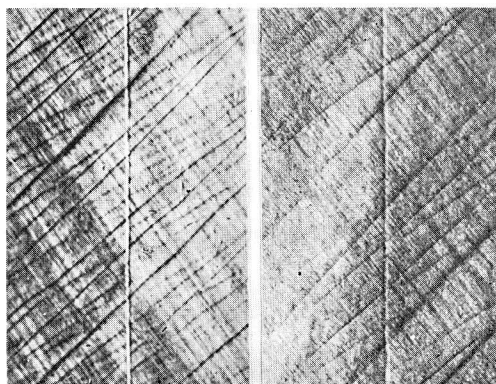pretence of cross slip in specimen
No. 51–B stretched by 12%.
×950

Fig. 26. Difference of the macroscopic struc-
ture between specimens Nos. 88–A
(left) and 88–B (right).   ×5

larger in the specimen No. 88-B than in the specimen No. 88-A and the amounts of "partial" elongation in the slipped matrices of the specimens Nos. 88-A and 88-B were measured from the local rotation of crystal to 23.5 and 24.2% respectively.

Thus, the "partial" elongation in the slipped matrix derived from X-ray examination was larger than the "total" elongation directly obtained from the gauge length. This means that kink bands have supressed the rotation of crystal in these

Fig. 27. Stereographic projection of the movement of the crystal axes in the simply slipped matrices of specimen Nos. 88-A (S_A) and 88-B (S_B), both of which were stretched by 20.0% of elongation.

specimens; hence, it is only natural that the smaller the number of kink bands, the more the rotation of crystal in the slipped matrix is expected at a definite "total" elongation. Accordingly, the effects of anodic surface films on the development of kink bands and on the crystal rotation are entirely consistent.

V. Discussion

A. Yielding Stress and Crystal Twisting

In the explanation of how the presence of a surface film can increase the yielding stress, one cannot absolutely refuse the naive hypothesis that the film simply relieves the metal from the part of tensile load. The film strength obtained in this experiment is about 10^{11} dynes/cm^2 as described in Section IV and it is so high as to make the explanation improbable. Accordingly, the effect of anodic films on the yielding stress must be accounted for by some other theory.

A theory of dislocations piling up beneath a surface film was postulated by Philips and Thompson[3] and independently by Cottrell[38]. An indication of the pressure of piled up dislocations against the oxide coat has been given by Barrett[39]. He found that if the oxide layer was suddenly removed from a plastically twisted metal wire, the wire would spontaneously twist a little further as the piled up dislocations
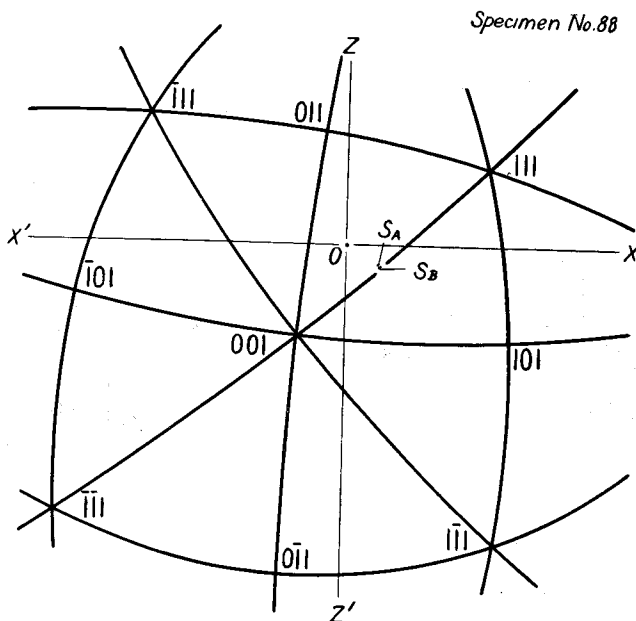
were allowed to escape from the metal.

In this experiment it was found that the crystal twisting occurred spontaneously during the plastic extension and it gave a very sensitive indication of slip. And in the specimen coated with a thicker anodic film, slip bands could not be indeed detected microscopically up to the yielding stress, but the twisting was observed to have begun at far below the yielding stress, as illustrated in Figs. 8 and 9. This is considered strong evidence for the belief that submicroscopic fine slip has already occurred far below the yielding stress, but the dislocations approaching a free surface have been held up by the presence of a surface film. Accordingly, yielding point is interpreted as the stress at which the surface film can not hold any longer to the pressure of piled up dislocations.

B. Stress-Strain Curve

It was found that the stress-strain curve of the crystal covered with the thicker anodic film did not show the region of "easy glide" so clearly as the crystal having the thin film, as illustrated in Figs. 8, 9, 10 and 11.

"Easy glide" in cubic crystals has been reported in α-brass crystals by Maddin, Mathewson and Hibbard[40], in copper crystals by Blewitt[41], and in aluminium crystals by Masing and Raffelsieper[42], Röhm and Kochendörfer[43], Crussard and Jaoul[44], Lücke and Lange[45], and Rosi[46]. Andrade and Henderson[8] found that exposure of the clean surface to air had a remarkable hardening effect on silver crystals. Considering these results, it may be said that easy glide occurs in crystals which have a suitable orientation for single slip and is absent from oxide layers.

Jaoul and Crussard[47] reported of easy glide only in the case of single crystals of aluminium, but not in polycrystals. And they found that the initial part of the stress-strain curve of polycrystals was raised with a decrease in the grain size. And Mott[48] has suggested that, in crystals showing easy glide, the dislocations are not retained in crystals but they pass out of the crystals. In appears, therefore, that the grain size effect is due to the large number of grain boundaries by which the importance of the free surface of the metal is diminished greatly. Accordingly, it may safely be said that the surface film can act as a barrier that permits dislocations to escape from the metal and, as a result, the crystal is strengthened apparently.

The unusual effect of the crossing of stress-strain curves illustrated in Fig. 11 may be attributable to the difference between the two specimens in the development of the inhomogeneities such as kink bands and, especially, "bands of secondary slip"[49] which cause the intense work-hardening; the surface film suppresses the development of those inhomogeneities. This will be described also later.

C. Effect of Surface Finish on the Fine Structure of Slip Bands

The crystal coated with a thicker anodic film, when stretched under creep conditions, develops only the coarse slip widely spaced and does not reveal such fine slip lines as are usually observed in the crystal bearing a thin surface film of less than 100 Å. In the case of a relatively rapid strain rate, however, the slip band, even in crystals covered with thicker films, can be also resolved into the fine slip lines, though they are still wider than those of crystals having thin films.

Thus, the surface film suppresses the fine slip and affects the structure of slip bands, in connection with the strain rate. As long as crystals are stretched in air, one cannot completely avoid the effect of the surface oxide layer. Hence in observing the fine structure of slip bands, both film thickness and strain rate become problems. It appears likely that the effect of strain rate may be responsible for the piled up dislocations to escape from their own slip planes, although there remains some argument on the possibility of climbing process at room temperature as pointed out by Mott[50].

Microscopic examination of the surface alone will not decide whether the appearance of the surface is typical of conditions within the bulk of the crystal. Kuhlman-Wilsdorf and Wisdorf[33] have considered that fine slip is typical within the interior. Alternately, a promising suggestion made by Mott[50] is that the surface layer will be subjected only to slow hardening due to the isolated fine slip, and a cluster of fine slip lines is formed as a result of relief of the stress due to a coarse slip in the interior. Following Hollomon[51], dislocation lines ending in the surface have the lower threshold stress than those in the interior. And H. Suzuki[52] has suggested that the three-fold node, in Thompson's[53] sense, climbs out from the surface layer of about 10 microns thickness in the crystal subjected to electropolishing and hence the source at the surface would act with first priority, because the source length is far longer than that of the interior. The non-uniformity of plastic behaviour in the surface layer obtained by Graham and Maddin[54] extends over from 25 to 50 microns in aluminium single crystals. In our previous paper[31] it has also been suggested from a different line of approach that the plastic flow of the surface layer seems to be easier than that of the interior and the tendency increases as the strain rate and strain are increased. In this connection, studies of electron diffraction on the surface effect made by Fujita, Watanabe and Ogawa[55], and Kimoto and Ueda[56], however, have not been consistent with each other.

The effect of anodic surface films resembles in some point to that of mechanical polishing on the appearance of slip bands made by Brown and Honeycombe[57] and Paxton, Adams and Massalski[58]. And Brown and Honeycombe have suggested that very small slip processes could appear on the surface as diffuse bulges without breaking

the film, but, as the deformation increased, the resistance of the film would be overcome occasionally, thus giving the opportunity for a coarse slip to develop.

D. Homogeneous Slip and Lamellar Slip

It was indicated that the orientation of crystals affected the structure of slip bands; two different kinds of slip bands in crystals electropolished in Jacquet's bath, were shown. One of them generally consists of a few coarse slip lines and the rather homogeneous slip zone extended over about a micron, as shown in Fig. 17. This type is most common in aluminium single crystals whose axes do not lie near the boundary of the stereographic triangle. The development of fine slip lines in a slip zone may be attributable to the effect of extremely thin surface films which cannot be eliminated from crystals pulled in air, or to the surface effect in Suzuki's or Mott's sense.

It is not evident up to the present whether the elementary slip in a slip band occurs on a isolated slip plane or on rather successive slip planes. Greenland[59] has reported of rather homogeneous slip zones in mercury crystals, although it is likely that the crystals had the skin preventing slip, as argued by Brown[24]. Yakutovitch et al.[60] assumed that the lamellar slip is formed by rather homogeneous fine slip. Some mechanism of homogeneous slip has been proposed independently by T. Suzuki[61] and H. Suzuki[52], though from different angles of approach.

The other type of slip bands is such as can be resolved into the slip lines having the roughly equal spacing and width. Lamellar slip of this type could be often observed in crystals in which the interaction among different slip systems would frequently occur. Hence it may safely be said that slip lamellae shown as in Fig. 18 are formed by the mechanism proposed by Fisher, Hart and Pry[62] and independently by Cottrell[38]; the formation is correlated with the interaction of different slip systems. If slip bands of this type were found also in hexagonal crystals which have one slip system only, an alternative theory of "annealing" mechanism proposed by Brown[63] and developed by Mott[50] should be considered. There are but few reports on the fine structure of slip bands in hexagonal crystals, but the picture given by Brown[24] does not belong to the lamellar slip of this type.

E. Abnormal Slip Markings

It was shown that abnormal slip markings often appeared on aluminium single crystals coated with anodic films of more than 300 Å thickness; four extreme cases were illustrated and one of them made the appearance of "cross slip" (Figs. 19-b, 22-b, 23 and 25).

It is only natural to consider that these slip markings may be attributable to the breaking of surface films, and also it will obliterate any evidence of slip of the

underlying metal, as pointed out by Wilms[15]. But one cannot reject out of hand the
supposition that as the deformation increases the resistance of the surface film will
be overcome by the pressure of piled up dislocations against the film and, as a result,
the film will crack along the slip giving the opportunity for piled up dislocations to
escape from the metal through the crack. However, in crystals bearing thick films
of more than 1000 Å, it does not hold true and abnormal slip markings occur in the
direction perpendicular to the maximum strain. Here the thickness of the surface
film is the problem.

When the traces of abnormal markings were checked with the crystallographic
plane having simple indices, it was found that most traces coincided fairly well with
those of the (001) plane. Accordingly, it appears likely that the formation of the slip
on the (001) plane reported by Boas and Schmid[64], the wavy, irregular branched
slip observed by Lacombe and Beaujard[65], and the prominent, wavy cross slip found
by Cahn[37], in aluminium crystals at high temperatures of more than 400°C, may be
ascribed to the effect of surface oxide films formed during heating.

F. Development of Kink Bands and the "partial" Rotation of Crystal

It was found that surface films suppressed the development of kink bands, and
the smaller the number of kink bands, the more "partial" rotation of crystal in the
matrix between kink bands was observed at a definite "total" elongation.

In the problem of how the presence of surface films inhibits the development of
kink bands, one can recollect at once the surface film suppressing the fine slip. In
this connection, Mott[50] has suggested that the dislocation wall in kink bands is formed
only by fine slip because of the difficulty of climbing process of dislocations at room
temperature. Hence the effect of surface film on the development of kink bands is
well explained by Mott's theory.

The effect resembles closely to the quenching effect. Maddin and Cottrell[66] have
reported recently that quenched aluminium single crystals reveal only the coarse slip,
but not fine slip. In our experiment[67], the aluminium single crystals quenched from
600°C did not develop kink bands so clearly as furnace-cooled crystals and it was
also shown by the study of electron-microscope that fine slip lines usually observed
in furnace-cooled crystals did not occur in quenched crystals.

It is expected also that the mechanical polishing of crystal surface, in Brown and
Honeycombe's sense[57], suppresses the development of kink bands.

VI. Summary

The anodic surface film of aluminium produced by the electropolishing in a
solution of orthophosphoric acid has the mean thickness of more than 300 Å and it is

composed of a thin part and a thicker part alternately, as shown in Fig. 5. The film made in Jacquet's bath, on the other hand, has the relatively uniform thickness of less than 100 Å.

These two kinds of surface films lead to the remarkable difference of plastic behaviours of the crystals : thicker anodic film raises the yielding stress and the flow stress, and suppresses the crystal twisting during extension and the development of fine slip and kink bands. Moreover, the surface film affects the fine structure of slip bands and gives rise to abnormal slip markings.

These effects are such as can be explained by assuming that dislocations pile up beneath a surface film : an evidence for dislocations being held up against the surface film has been given by the crystal twisting which is the sensitive indication of slip.

It was indicated that the crystal orientation and the strain rate affected the structure of slip bands in addition to the surface finish. Two typical kinds of slip bands were shown in connection with the crystal orientation.

And it was pointed out that abnormal markings under the pretence of slip often appeared on aluminium crystals coated with thick surface films and they might possibly occur in high temperature testing.

The effect that the surface film suppresses the development of fine slip and kink bands is well explained by Mott's theory. This effect resembles the quenching effect and it is expected also that the mechanical polishing of crystal surface suppresses the development of kink bands.

Acknowledgement

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