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INTERACTION OF A SURFACE COATING WITH EDGE AND SCREW DISLOCATIONS
IN ZINC CRYSTALS*

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ABSTRACT

Square 45° zinc crystals were oriented so that polycrystalline copper or chromium coating on $(1\bar{1}00)$ or $(33\bar{6} 11)$ faces would serve as obstacles to primary dislocations in screw or edge orientation. Evidence indicated that in general the surface layers of zinc under the coating were distorted more than the interior and the observed effects on strength and ductility were connected with the presence of a hard external layer. Distinction was made between "thin" coatings, where basal slip penetrated this layer, and "thick" ones, where the mode of deformation in the layer (not generally identified) was different. A classification based on this distinction was given of the complex variation of strengthening and loss of ductility with edge and screw obstacles and with coating type and thickness. Some of the differences between the effects for edge and screw dislocations were attributed to differences in mean free path.

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I. INTRODUCTION

Some previous studies¹⁻⁴ in which soft crystals were coated with thin oxide or plated metal films have indicated that in a tension test the coating strengthens the specimen greatly in excess of the direct load-carrying capacity of the coating and thus that the main effect of the coating is to influence the deformation of the substrate. In this case, a coating may hopefully be used as a conveniently variable perturbation of the state of the specimen for investigating certain mechanisms of strain hardening. In the present work, coated zinc crystals were studied under conditions designed to examine separately the effects of an obstacle to dislocations in edge and in screw orientation.

As indicated by the relevant previous work on zinc, the general effect of the coating is perhaps best described as an increase in the initial rate of strain hardening^{3,4} (electroplated $\sim 0.1 \mu$ metal coatings). It was shown (for hydroxide films) that the hardening begins to develop at small strains ($\sim 10^{-3}$) and that it is substantial at high but not at low strain rates.² The strain rate dependence^{2,4} explained why coating effects observed in creep tests were much

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1. R. Roscoe: Phil. Mag., 21 (1936), 399
 2. S. Harper and A. H. Cottrell: Proc. Phys. Soc. (Lond.) 63B (1950), 331
 3. J. J. Gilman and T. A. Read: Trans. AIME 194 (1952), 263
 4. J. J. Gilman: ASTM Special Publication No. 171 (1955), 3

smaller. It is known that solid coatings can reduce the ductility of zinc crystals of intermediate orientation.^{5,6}

The present work attempted to differentiate between the effects involving edge and screw dislocations through use of crystals oriented as in Fig. 1. The $(1\bar{1}00)$ faces contain the Burgers vector of dislocations of the primary basal slip system so that the segments of expanding primary dislocation loops approaching a coating on these faces are in screw orientation. The segments blocked by a coating on $(33\bar{6} \ 11)$ are in edge orientation. One examines the effects produced by coating only one pair of faces. Adherent electroplated metal coatings were suitable for this work being readily applied in a range of thicknesses. The results were in many respects bewildering, and attention was directed to their description and classification in macroscopic terms.

II. EXPERIMENTAL

0.3x0.3x20 cm seeded crystals of the orientation shown in Fig. 1 were grown from American Smelting and Refining Company 99.999% zinc in a high-purity graphite mold under argon in Pyrex capsules using a furnace with a steep gradient. With repeated use, the seed developed one or two subboundaries of increasing severity. This substructure was inherited by the crystal and was rather uniform along its length; it was monitored by Laue photographs using a fine

5. J. J. Gilman: Trans. AIME 191, (1951), 1148.

6. G. B. Greenough and D. A. Ryder: J. Inst. Met. (Lond.) 84 (1956), 467

(40 μ) focus tube and by examination of cleavage surfaces. When subboundaries of misorientation about $\frac{1}{2}^\circ$ appeared, a new seed was used.

Electrolytically cut specimen lengths were soldered in steel ball grips in an alignment jig with a 2.5 cm gage length after allowance for grip constraints. A one-hour anneal at 100°C was used prior to surface preparation. Tension tests were made at a rate of extension of 0.05 per minute on an Instron machine, using a toluene bath for tests below 25°C. The tendency for cleavage near the grips in coated specimens at lower temperatures was not diminished by mounting with epoxy cement or by applying the load through a 0.1 mm steel wire attached to a short sleeve grip, after Greenough and Ryder,⁶ instead of the rigid ball and seat arrangement.

The specimens, with balls stopped off, were chemically polished in the nitric acid-hydrogen peroxide-ethanol bath⁷ and then dipped for 3 seconds into 5% KCN, rinsed and dried. This produced a smooth bright surface with no significant film as evidenced by the instant complete wetting of the surface on contact with liquid mercury. For coating a specimen, one pair of faces was carefully stopped off and the other pair plated for the requisite time with either copper (CuCN 22.5 g/l, NaCN 33.8 g/l and Na₂CO₃ 15 g/l, 20 ma/cm²) or crack-free chromium (proprietary bath, Unichrome CF-500, at 65°C, 460 ma/cm²), the plating rates being known accurately. The copper represented a

7. J. J. Gilman and V. J. DeCarlo: Trans. AIME 206 (1956), 511

relatively soft and the chromium a strong coating. Both were semi-matte, chosen in preference to bright deposits for greater ductility. Both remained adherent under severe deformation.

III. RESULTS

Figs. 2-6 give examples of mechanical behavior, the coated specimen being compared with an uncoated specimen (U) from the same crystal (except for the curves at the left of Fig. 2). The intercept on the stress axis corresponds to a shear strain of 5×10^{-4} . Plastic flow commenced much below this value, as has been demonstrated by Tinder.⁸ In general uncoated specimens deformed with uniform shape change while many coated specimens showing substantial strengthening developed a few inhomogeneities apparently similar to tensile kink bands⁹ after substantial strains.

A. Copper coatings -- 0.1 μ coatings on the E-face had no effect and on the S-face produced a strengthening reaching only a few g/mm^2 , less than expected from the data of Ref. 3. For the S-face, increasing the thickness to 0.4 μ gave an effect reaching about 10 g/mm^2 (Fig. 2), to 2.0 μ (not shown) an effect reaching about 30 g/mm^2 , and to 10.0 μ a rapid initial strengthening but cleavage failure after $\sim 10^{-2}$ glide. Effects for the E-face are discussed later.

8. R. F. Tinder: Acta Met. 13 (1965), 136

9. J. J. Gilman and T. A. Read: Trans. AIME 197 (1953), 49

Attention is limited for the moment to the 0.4μ coating on S-faces. The effect at room temperature or lower (Fig. 3) could be described as a transient increase in the strain hardening rate. Significant strengthening had already developed before the initial observation at 5×10^{-4} . The strengthening was similar to that reported by Gilman and Read³ (who studied randomly oriented crystals with copper coatings from 0.07 to 0.5μ with stepwise loading). They found generally larger effects although the magnitudes varied considerably. The coating effects may be sensitive to a number of variables; several of these were investigated with results as follows:

1. Gilman⁴ reported the coating effect was enhanced after the was interrupted for a recovery treatment. A one hour recovery after glide of 0.54 or 0.87 was found not to affect the relative positions of the S and U curves (results for chromium coatings shown in Fig. 5).
2. A lapse of time between plating and testing may permit sufficient diffusion between coating and substrate to influence the mechanical behavior.^{3,6} That diffusion does occur was indicated by the detectable fading of the copper color after a month or more. Mechanical test behavior was found not to be substantially different for a test made after a one week aging period (Fig. 3).

3. Instead of checking directly the reported strain rate sensitivity of the coating effect,^{2,4} the test temperature was varied. The strengthening effect $\Delta\tau$ was similar in nature but the maximum value increased somewhat on passing from 25°C to -10°C to -40°C.

4. The strengthening effect of the coating was not substantially different when one or two lineage boundaries were present although the uncoated specimen was stronger.

For the E-face, a 0.4 μ copper coating had no significant effect (Fig. 2) and none of the variations in procedure described in 1-4 above (recovery, aging, reduced temperature or varying lineage) revealed any effect. However, increasing the thickness to only 1.0 μ produced a large initial strengthening and a drop in ductility and these were accentuated with thicker coatings. The abrupt transition for the E-face in strength and ductility contrasts with the progressive development of strength with thickness on the S-face.

B. Chromium coatings -- 0.2 μ was the minimum thickness tested (Figs. 4 and 5a). For the S-face, the effects were close to those of 2 μ copper coatings. The effect on the E-face, shown at -10°C in Fig. 4 and at 25°C in Fig. 5a, involved an initially high hardening rate interrupted by a broad yield (the fine serrations in the chart record would not be visible in these figures) leading to a final hardening rate slightly above that of an uncoated crystal. After

interrupting the test for a one hour recovery, there was some increase in the difference between clean and coated strain hardening rates. The thickness on the E-face was increased to 1.0μ in the expectation of exaggerating these effects, but the strengthening was about the same (Fig. 5b). For the S-face, a 1.0μ coating led to the development of shallow surface cleavages and reduced ductility (Fig. 5b). Another such specimen, however, suffered a large glide without failure (see Fig. 5a). It was found as described later that both 0.2μ and 1.0μ E-face specimens in Figs. 4 and 5 also developed many shallow cleavages during the yielding at small strains, even when load drops were barely perceptible in the chart record. With coatings substantially thicker than 1μ on either face, the cleavages propagated across the specimen soon or immediately after formation, as with the thicker copper coatings in Fig. 2.

C. Lineage Structure -- Lineage boundaries, even for misorientations substantially less than $\frac{1}{2}^\circ$, produced a transient increase in strain hardening rate (as noted previously)¹⁰, similar to the effect of an S-face coating, but in addition a small persistent increase in strain hardening rate. The comparison is illustrated in Fig. 6 where Specimen 12U, with no lineage boundary or network within the $3'$ sensitivity of the X-ray method, was used as reference to display the effect of the boundaries in 7U and 8U.

10. E. H. Edwards, J. Washburn and E. R. Parker: Trans. AIME 197 (1953), 1525

The magnitude of the temperature sensitivity of the S-face coating effect may be seen from the 0.4 μ copper data in Fig. 6 together with the observation that in two tests at -40°C the strengthening saturated at 18 and 25 g/mm^2 .

Applying a coating often produced loss of ductility if lineage was present, as remarked by Gilman.⁵ The transition was sharp and not obscured by the variations in ductility and tendency for failure near the grip usually met in such observations.⁶ An illustration is given in Fig. 4. The crystal of the inset had a lineage boundary (near 1°) somewhat more severe than the crystal of the main part of the figure, as indicated by the higher uncoated flow curve. The ductility after coating was drastically reduced for these inset specimens only (both failed well within the gage length). The situation may be summarized in a general way by saying that a transition to low ductility occurred when the combined effects of coating, lineage and low temperature reached a certain threshold. The threshold could be reached by intensifying only one factor, such as making the coating thick at 25°C (Fig. 2), or by mild contributions from all three, as in the inset of Fig. 4. The grip influence is apparently a dislocation obstacle effect (the grip or the accompanying bend plane) like those of coating and lineage.

D. Microscopic observations -- One readily verified (from the slip bands and lattice rotations) that the coatings did not alter the

character of deformation in the interior of the crystal. Study of the zinc just beneath the coating had two limited objectives: (1) does the coating crack in such a way as to indicate basal slip breaks through to the surface (2) are the surface layers of zinc distorted more than the interior. Detailed information was not obtainable since (1) was to be determined by microscopy on rough surfaces and (2) by X-ray photographs taken through the coating. The relevant observations are summarized below. Those for the E-face are drawn mainly from a separate extensive study made by Mr. C-K. Li of our laboratory. Coatings were classified as "thin" when evidence of basal slip appeared at the surface and as "thick" otherwise.

"Thin" coatings - For the E face, there were cracks in the coating parallel to basal slip traces and none other; in some, the bright zinc surface was visible (Fig. 7a). Li found substantial distortion ($\sim 10^\circ$) under a $1\ \mu$ copper coating. Gilman had found surface distortion under a copper coating; his surface of observation was not stated.⁴ The S-face (Fig. 7b) showed slightly irregular cracks the general direction of which ran parallel to the calculated basal slip trace and rotated in the predicted manner with strain. The surface of observation contained the slip vector so that the markings became prominent only after substantial strain, apparently by cracking and tearing of the coating at boundaries between basal glide packets. In this case also, the X-ray evidence showed the surface layers of zinc

became considerably distorted; a detailed analysis is not yet available.

"Thick" coatings - That basal glide did not reach the surface was evident on the S-face in Fig. 7c from prominent transverse cracks visible in this chromium coating after a small strain. When such a specimen tolerated a larger strain, there were many such cracks together with shallow basal cleavages but no evidence similar to Fig. 7b to indicate basal glide (Fig. 9, discussed further below). On the E-face, the only cracks in the coating were those produced by a series of shallow basal cleavages. These are best observed in sections, which are difficult to prepare by conventional means (Fig. 8). They have been studied in some detail.¹¹ Depths ranged from $<10 \mu$ to 150μ . They formed after ≤ 0.04 glide and did not deepen but the tongue of the cleavage rotated backward with strain by trapping of interior edge dislocations in the bend plane which joined the base of the cleavage to the surface. Tongue rotation was described by Gilman and Read⁹ in a crystal of unspecified surface condition. A noteworthy observation made by Li is that in addition to the structure change near the surface, there was a detectable change (glide polygonization) extending to a depth of at least 0.5 mm.

That the surface layers under a "thick" coating on the S-face did not deform by normal basal glide is graphically shown by the two-zone shape change of the specimen shown in Fig. 9. This is the 1μ

11. C-K. Li and M. Metzger: To be published.

specimen of Fig. 5a.) The mechanism of deformation in the hard surface zones is not known. The central zone of this specimen deformed as would a well-behaved uncoated crystal with respect to thinning, lattice rotation and slip band appearance. This zone was thus not aware of the presence nearby of the hard S-face zones, and this indicates that the mean free path of screw dislocations was quite short.

IV. DISCUSSION

One seeks at this stage a generalized macroscopic scheme for classifying the various coating effects. One basis for this is the coating classification. Note that this classification, as "thin" when basal slip breaks through to the surface and "thick" when it does not, puts the copper coatings in the "thin" category on both faces up to several microns while $0.2\ \mu$ chromium was "thin" on S, but mainly "thick" on E, and $1\ \mu$ chromium was "thick" on both.

The structure observations indicated that the deformation of the zinc beneath the coated surface was disturbed or grossly altered by the presence of the coating. One then expects a hard zone or hardness gradient beneath the coating. A broad view of the strengthening phenomenon is then as follows. Dislocations are blocked by the coating long enough to accumulate and react producing after a small strain a harder layer beneath the coating. This layer then replaces the coating as the significant "second phase." As this layer forms and becomes stronger, it acquires a progressively larger share of the load -

this appears as the enhanced initial strain hardening rate. When the strength and extent of the layer reach saturation, the enhancement of the strain-hardening rate disappears. The effect of the harder zinc layer will persist after the coating cracks (although the continued presence of the coating may be required for its stability). The coating alone could provide persistent strengthening only where it deforms with the substrate and does not crack; this occurs only under very specific conditions.¹² The view advanced here is similar to one given by Basinski and Jackson¹³ with reference to copper..

The strength variations on the E-face were unusual. (a) The effect was small with a "thick" coating, say $0.2\ \mu$ or $1.0\ \mu$ chromium. Here the initial rapid hardening is interrupted by the formation of the shallow cleavage cracks each connected to the surface by a bend plane. For edge dislocations from the interior, these bend planes act as sinks as well as obstacles⁹ and they screen the coating so the hardening at this point is low and is not a function of coating thickness, as seen in Fig. 5a and b. The presence of bend planes, together with any interior glide polygonization that has occurred, represents the introduction of what may be regarded as a variety of lineage structure and, like the original lineage (Fig. 6), produces a small persistent enhancement of the strain hardening rate. This can be enhanced somewhat more by a recovery anneal permitting additional

12. T. Evans and D. R. Schwarzenberger: Phil. Mag. 4 (1959), 889

13. Z. S. Basinski and P. J. Jackson: Phys. Stat. Sol. 10 (1965), 45

polygonization (Fig. 5). (b) "Thin" copper coatings were remarkable in that 0.4μ produced no effect on E although it did on S while increasing the thickness only to 1μ produced a large effect on E. The absence of strengthening at 0.4μ on E may have the following explanation. In the earliest stages of deformation when dislocations are piling up beneath the coating, they may crack the coating before the reactions producing the hardened layer are able to occur. This is favored by a large dislocation mean free path with pile-ups over substantial lengths of the glide plane producing high stress concentrations. This is then more likely to happen on the E-face if the deductions concerning the longer mean free paths of edge dislocations are correct. Making the coating thicker allows it to sustain sufficient pile-up for the hardened layer to form.

These unusual strength variations are perhaps a peculiarity of zinc. Chromium-coated copper crystals show simple progressive increases in strength parameters with thickness.¹⁴

Effects on cleavage and ductility can be accounted for within the same framework. The hard surface zone will acquire a disproportionate share of the load and the local stress may reach levels high enough to initiate cleavage. For screw dislocations, cleavages formed only after this layer was well developed and considerable hardening was observed (the 1μ chromium curves in Fig. 5). A screw dislocation obstacle can initiate cleavages at relatively low applied stresses in this manner (note that some obstacles are not effective¹⁵) while it

14. R. J. Block and M. Metzger: To be published.

15. J. J. Gilman: Trans. Met. Soc. AIME 212 (1958), 783

could not do this through pile-up of screw dislocations in the soft interior because of the short mean free path and insufficient stress concentration. In the case of edge dislocations, cleavage could apparently be initiated by interior pile-ups as evidenced by the formation of cleavages at 0.2μ and 1μ chromium-coated E-faces at low stress (40 g/mm^2) before much hardening was observed (Fig. 5). The formation of the series of cleavages and bend planes then altered the mode of deformation. For 0.2μ chromium on the S-face however, where interior pile-ups are presumed unable to initiate cleavage, the surface layer would accept local stress build-up to the level required for basal slip to break through, hence this coating was "thin" on S although "thick" on E. The rather different behavior on the E-face of coatings of copper, which is elastically and plastically softer than the chromium, is consistent with the observation that the copper remained "thin", i.e. the interior pile-ups were relieved by slip rather than cleavage. The one or two cleavages responsible for loss of ductility at 1μ and thicker were formed after considerable strengthening and attainment of high local stress in the surface zone. The existence of the abrupt ductility transition is not surprising under these circumstances.

These considerations are necessarily speculative. The work is continuing.

V. ACKNOWLEDGEMENTS

The authors are indebted to C-K. Li and R. J. Block for advice and comment.

Fig. 1. Specimen orientation.

Fig. 2. Effects of some copper coatings at 25°C.

Fig. 3. Aging the plated specimen at room temperature for one week does not produce a strengthening much larger than that observed immediately after plating.

Fig. 4. Effects of 0.2 μ chromium coatings at -10°C . The set shown in the inset had somewhat more severe lineage.

Fig. 5. . The effects produced by 0.2 μ and 1.0 μ chromium coatings at 25°C.

Fig. 6. The strengthening produced by 0.4μ copper and 0.2μ chromium coatings on the S-face tends to saturate after a certain strain while lineage boundaries (Specimens 7 and 8) produce a small persistent increase in strain hardening rate.

Fig. 7. Appearance of some coatings after deformation at 25°C. The mark is 10 μ .

- a) E-face, 0.4 μ copper ("thin"), 0.5 glide. Side of photograph parallel to specimen axis.
- b) S-face, 0.2 μ chromium ("thin"), 1.0 glide. Top edge parallel to specimen axis.
- c) S-face, 1.0 μ chromium ("thick"), 0.2 glide. Top edge parallel to specimen axis.

Fig. 8. View of the edge of a spark-cut section parallel to the S-face showing tongues and shallow cleavage cracks on the E-face coated with 0.2 μ chromium ("thick") after 1.0 glide. Some of the faint scalloping of the profile of the S-face represents small tongues which terminated below the plane of the section. The mark is 100 μ .

Fig. 9. Crystal with a 1.0 μ chromium coating on the S-face illuminated to show the lip at the edge of the E-face formed after 1.0 glide at 25°C. X5. The viewing direction is indicated by the arrow in the sketch showing the specimen cross section.

a

b

c

FIG. 7

FIG. 8

FIG. 9