STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

COLLEGE OF ENGINEERING

Report No. 32

Strengthening of LiF Crystals by Magnesium-Diffused Surface Regions

by

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December 1964

Strengthening of LiF Crystals by Magnesium-Diffused Surface Regions

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Diffusion of magnesium into the surface of LiF crystals to controlled depths and subsequent heat treatments provided a wide range of surface zone hardnesses and structure. The bend strength of the LiF crystals was increased by as much as an order of magnitude. Ductility was achieved when dislocation generation occurred in the diffusion zone or when dislocations penetrated to the surface from the interior. A critical surface hardness of 130 to 140 kg per sq mm was found below which generation could take place in the diffusion zone and above which the zone was impenetrable. This hardness was obtainable by several methods, among them the aging of quenched MgF_2-LiF solutions to produce MgF_2 precipitation. Maximum hardness was obtained in quenched specimens with no visible evidence of MgF_2. Diffusion-zone formation followed a parabolic rate law and an activation energy of 20.9 kcal per mole was obtained for the process.

RECENTLY, the properties of ionic crystals as related to surface condition have been receiving much attention, specifically the transitions between ductile and brittle behavior. Originally Joffe[1] showed that NaCl crystals could be made ductile by immersion in water and related this to the elimination of surface microcracks. Aerts and DeKeyser[2] and Gorum[3] have subsequently shown that ionic crystals are inherently ductile and are embrittled through contact with air. Machlin and Murray[4] hypothesized that a layer of $NaClO_3$ produced by contact of ozone with NaCl induced embrittlement by acting as a barrier to outward dislocation flow. Westwood,[5] Rosenberg and Cadoff,[6] and Bilello and Cadoff[7] have reported surface strengthening of LiF crystals by coating with a magnesium compound and then heat treating for adherence. The major effect of the coat was to inhibit dislocation-slip lines from reaching the specimen surface. Westwood[5] showed microcrack formation and fracture to be caused by slip-band interactions at the surface.

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Manuscript submitted March 2, 1964. IMD

The material presented in this paper is an extension of the work reported earlier by Bilello, Rosenberg, and Cadoff[6,7] and illustrates the wide range of surface properties and bulk behavior obtainable by use of heat-treated magnesium-diffused surface regions in LiF crystals.

EXPERIMENTAL PROCEDURE

The LiF single crystals were obtained from the Harshaw Chemical Co. Some batch to batch variation was observed; therefore all specimens for a given test series were cleaved from the same crystal. The typical dimension used was 1 by 0.1 by 0.40 in. Surface damage resulting from cleavage was removed by chemically polishing in a 2 pct NH_4OH solution. Each group of specimens was given a vacuum anneal at 700°C for 4 hr to provide a base standard for measuring comparative effects of various surface treatments.

To produce the reacted surface zone, the annealed specimens were immersed in a boiling suspension of MgF_2 in doubly distilled H_2O, agitated slowly for 30 sec, removed, and dried at room temperature. Uniform coatings of MgF_2 were deposited with a thickness of approximately 5 mils. It should be noted that this technique can be modified for use with crystals which are soluble in water by using boiling absolute alcohol as the dissolving medium. This was found effective for the coating of NaCl with MgF_2. The diffused surface zone was obtained by annealing the coated samples at elevated temperatures in a vacuum of 10^{-4} mm Hg. Penetration depth was controlled by varying the annealing time from 1/2 to 28 hr. After heat treatment, the samples were tested for bend strength and hardness.

Load was applied by four-point bending in a hard-beam testing jig. Four-point rather than three-point bending was used to provide a wide area of constant stress and to minimize the effect of localized inhomogenities in the specimen. The deflection rate was 8×10^{-5} min^{-1} and the distance between knife edges was 1/4 in. Load-time curves were obtained from a chart recorder coupled to the machine and converted to resolved shear stress on the shear plane vs deflection, as plotted in the figures. The unstressed portions of the sample outside of the two outer knife edges were used for the microhardness studies. Microhardness measurements were made with a Bergsman tester attached to a Reichert metallograph. All hardness impres-

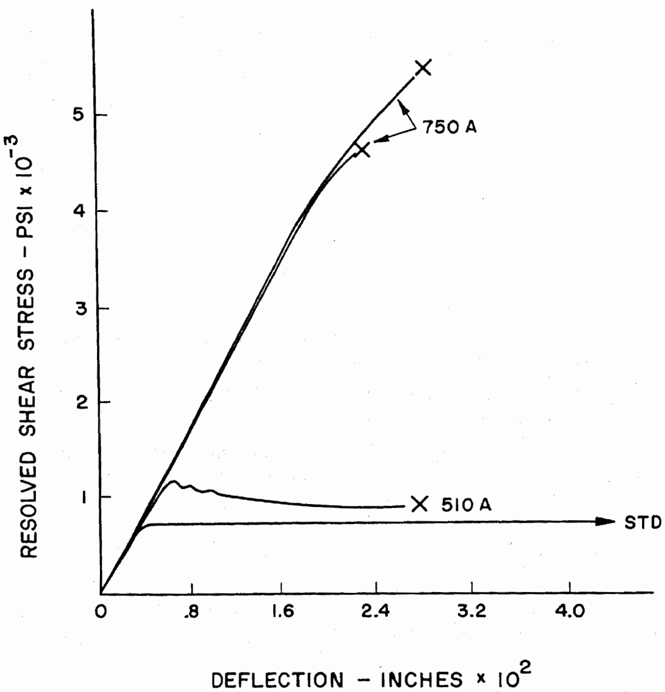


Fig. 1—Comparison of bend curves for standard, as-coated, and diffused Mg-LiF crystals.

Fig. 2—Fracture surface of LiF crystal diffused with magnesium. The diffused region, denoted by dense cleavage lines, is on the compression side. X170. Enlarged approximately 42 pct for reproduction.

sions were made on a fresh cleavage surface with the diagonal of the Vickers diamond indentor aligned parallel to either ⟨110⟩ or ⟨100⟩ directions to prevent distortion of the impression. Scratch tests were performed by indenting the sample under low loads (10 g) and moving the stage of the metallograph at a uniformly low rate (20.6 μ per sec) by means of a coupled motor.

Two methods were used to study deformation patterns. For preliminary observations the samples were cleaved to reveal fresh surface and then viewed under polarized light. For more detailed study of the dislocation patterns the polishing and etching techniques for LiF developed by Gilman and Johnston[8] were used.

Debye-Scherrer patterns were used for phase

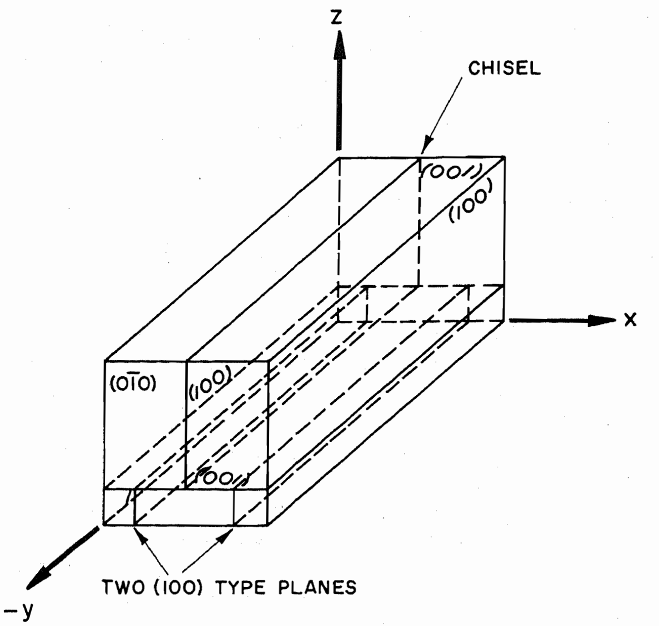
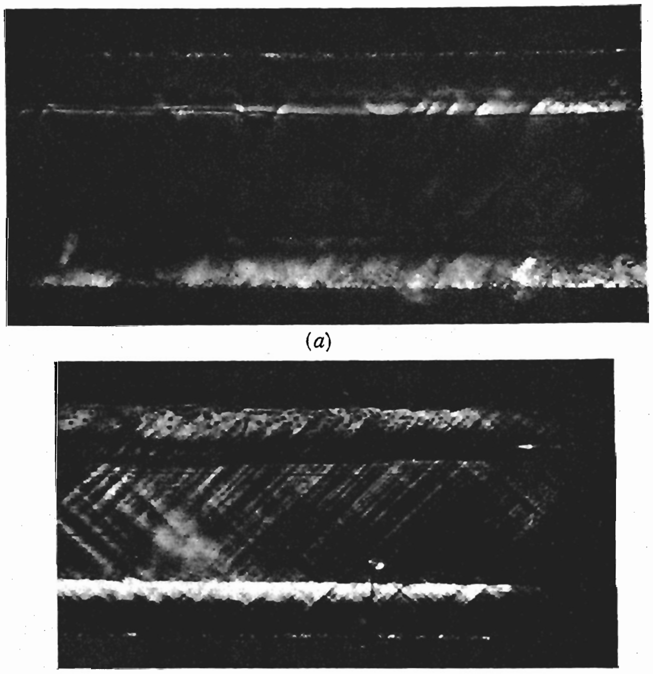


Fig. 3—Schematic diagram indicating orientation relationships for tests reported. Diffusion is from all faces. For bend tests, neutral axis is in *Y-Y* and load is in *Z* direction.



(*a*)

(*b*)

Fig. 4—Slip-band configuration, under polarized light, in a magnesium-treated specimen. Bottom edge was under compression. (*a*) Low-stress region. (*b*) High-stress region. X25. Enlarged approximately 39 pct for reproduction.

identification. The specimen powders were placed in 0.03-mm quartz capillaries which were sealed under a vacuum of 10^{-4} mm Hg. Subsequent heat treatments were then performed on these sealed capillaries. The specimens were kept in the capillaries during exposure to the nickel-filtered copper radiation.

EXPERIMENTAL RESULTS

General Observations. The bend-deflection curves shown in Fig. 1 illustrate the basis for this study. The standard sample, polished and annealed at 700°C for 4 hr, showed a resolved yield of about 750 psi. Coating a similar sample with MgF_2 raised the yield stress to about 1200 psi with subsequent irregular drop-off in load. This result resembles the strengthening effect of surface coatings as reported by Westwood[5] who attributed the stress decrease to breakthrough of dislocation-slip bands through the coating to the surface. The samples 750A were coated, vacuum-annealed at 700°C for 3 hr, and furnace-cooled prior to testing. The bend-deflection curves showed some deviation from linearity at about 4500 psi and fracture at 5000 to 5500 psi. As will be seen, the increase in strength is related to the effect of the diffusion of magnesium into the LiF during the 700°C anneal.

The compression edge of a (100) fracture face of a section of specimen 750A is shown in Fig. 2. The orientation relationships are indicated schematically in Fig. 3. Cleavage lines normally associated with fracture in LiF are in evidence in the interior of the crystal, but the surface zone is delineated by a massive cross-cleavage pattern. Penetration of such a region by an advancing crack occurs with expenditure of a high elastic energy, thus resulting in the observed strengthening.

Slip-band configurations along a (100) face (Ref. Fig. 3) as observed under polarized light are shown in Fig. 4. In regions of low stress (left region, Fig. 4(*a*), away from cleavage surface) the density of slip lines is low and none penetrated the surface zone to the specimen surface. As the stress increases (moving right) the slip lines enter the zone to a limited extent and finally at the fracture face, extreme right of Fig. 4(*b*), penetration to the surface is noted. Although a high density of slip lines is present beneath the diffusion zone only a slight deviation from linearity in the bend-deflection curve for this specimen was observed. The small gross plastic deformation is related to the small extent of slip breakthrough to the surface. Fig. 5 shows the etch-pit configuration of the dislocations at the surface region in this specimen. In this figure, as in Fig. 4, the slip lines penetrate the treated surface zone but do not reach the specimen surface. The character of the surface resistance to dislocation movement will be discussed in a subsequent section. Some features to be noted from Figs. 2, 4, and 5 are: 1) the sharp delineation between the surface zone and the interior of the crystal; 2) the higher dislocation density beneath the surface zone even though the surface was subjected to a higher stress; 3) a profusion of pitting in the surface-zone region of the etched section of specimen 750A, Fig. 5; 4) also in Fig. 5, there is some indication that some of the slip lines found in the surface-zone region are not continuous with slip lines in the interior region just beneath the zone; and 5) there are indications of a transition region between the surface zone and the interior unreacted portion of the crystal, Fig. 4.

The general observations described above indicated that a more detailed study of the structure and properties of the surface region would be needed in order to explain its effect on the behavior of the LiF crystals. These studies are described in the following sections.

MgF_2 : LiF System—Heat-Treatment Effects. X-ray analysis of annealed and unannealed scrapings taken from the diffusion zone of specimen 750A showed the major constituent LiF plus a lesser amount of MgF_2. The equilibrium diagram for the MgF_2 : LiF system,[9] Fig. 6, shows limited retrograde solubility of MgF_2 in LiF. Thus, the pitting seen in the surface zone, Fig. 5, can be attributed to precipitates of MgF_2.

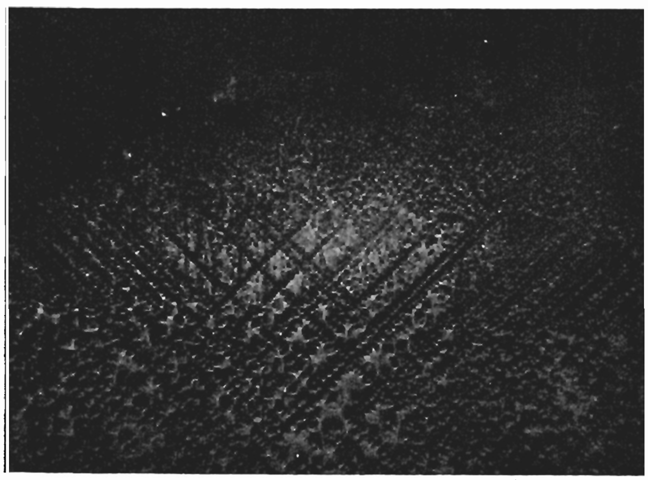


Fig. 5—Etch-pit delineation of dislocation-slip line penetration into the surface region of a magnesium-treated sample. Dense surface pitting represents MgF_2 formed during the furnace cooling from the diffusion temperature, 700°C. X250. Enlarged approximately 26 pct for reproduction.

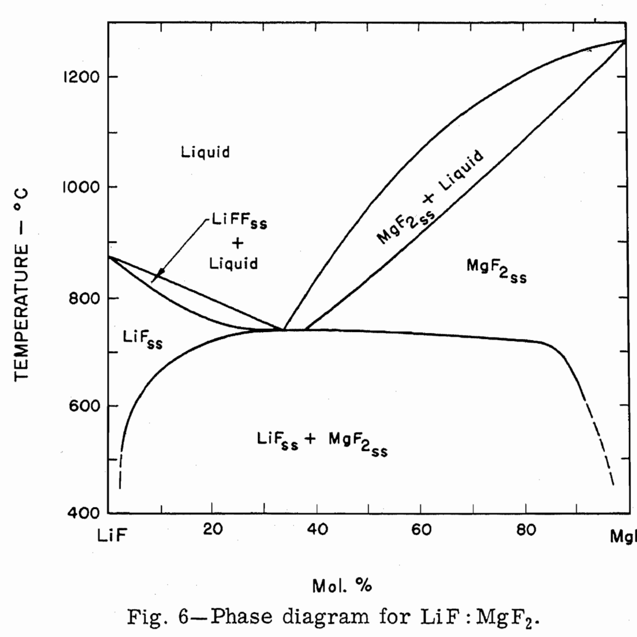


Fig. 6—Phase diagram for LiF : MgF_2.

Fig. 7—Clear surface region, after bending, resulting from quenching from the diffusion temperature, 700°C. X150. Enlarged approximately 30 pct for reproduction.

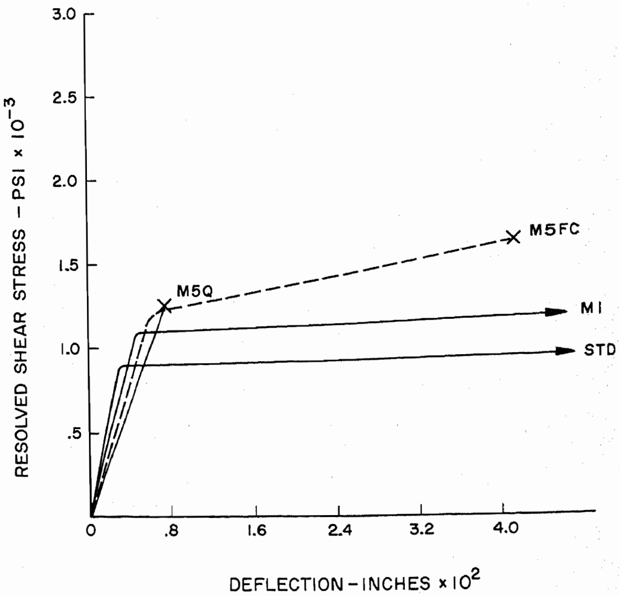


Fig. 8—Bend curves for 500°C-treated crystals (M5Q, quenched; M5FC, furnace-cooled) compared with standard (STD) and as-coated (M1) samples.

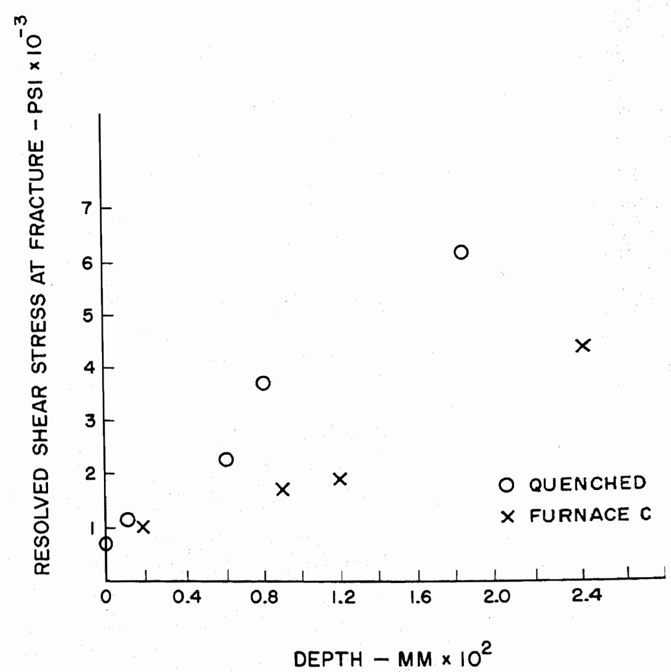
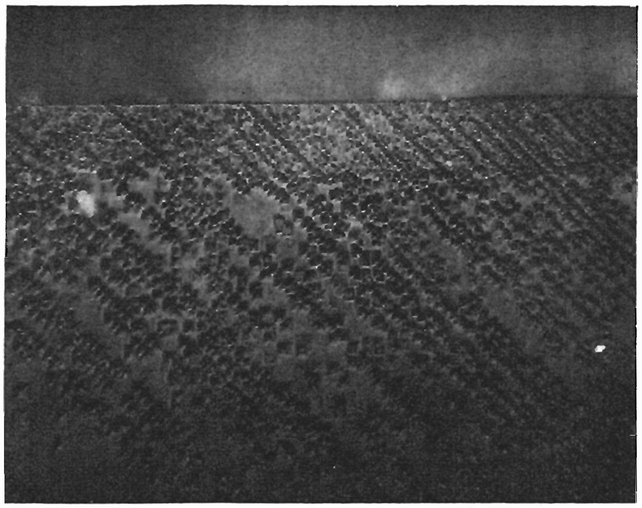


Fig. 9—Change in fracture stress with change in thickness of the surface diffusion zone. Diffusion at 600°C. Circle at zero depth represents standard undiffused sample.

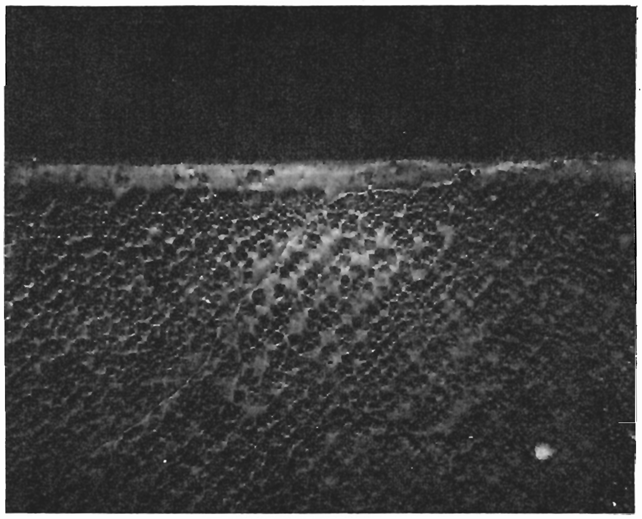
To verify this, a specimen was annealed similarly to 750A but was quenched from the diffusion temperature. The most rapid quench obtainable without shattering the specimen consisted of relieving the vacuum and spilling the specimen directly onto a watch glass floating on ice water. The slip configuration produced during a subsequent bend test is illustrated in Fig. 7. The surface region is comparatively free of the massive pitting observed in the furnace-cooled specimen, Fig. 5, suggesting either preservation of a supersaturated solution of magnesium in LiF or submicroscopic precipitation of MgF_2. X-ray analysis of the zone material indicated a significantly lower proportion of MgF_2 as compared with the furnace-cooled sample. As seen in Fig. 7 no dislocation penetration into the zone is observed. The specimens had a bend-fracture strength of about 6000 psi and showed no gross plastic deformation at fracture.

The data presented in Fig. 8 for samples diffused at 600°C summarize the typical effects of diffusion depth and quenching on the bend-fracture strength of magnesium diffused LiF crystals. Fracture strength increases with diffusion depth, a factor which was controlled by the diffusion time. The strength of quenched samples increased more rapidly with penetration depth than those which were furnace-cooled. All samples treated at 600°C or above fractured with little or no macroscopic deformation. However, one series, M5(FC), slow-cooled from 500°C exhibited considerable ductility in addition to a higher strength. The bend curve for this sample as compared with quenched and standard samples is in Fig. 9. The photomicrograph of this sample, Fig. 10(*a*), shows the surface zone containing precipitates but with slip lines crossing the zone. The appearance of slip lines across the diffusion zone correlates with the observed ductility. There is evidence again in this figure that the slip observed in the surface zone is not always continuous with the slip in the interior. The equivalent quenched sample, M5(Q), showed no ductility with complete absence of slip lines in the thin zone, as seen in Fig. 10(*b*). In comparing the ductility of M5FC with other furnace-cooled samples, it should be noted that the diffusion temperature for M5 was 500°C as compared with 600°C or higher for the others. From the phase diagram, it can be seen that the magnesium concentration of the M5 samples would be lower than that of the others in the series.

Microhardness. The phase equilibria and quenching effects showed wide variation in bulk properties



(*a*)



(*b*)

Fig. 10—Structure of slow-cooled (*a*) and quenched (*b*) LiF after diffusion at 500°C. X250. Enlarged approximately 30 pct for reproduction.

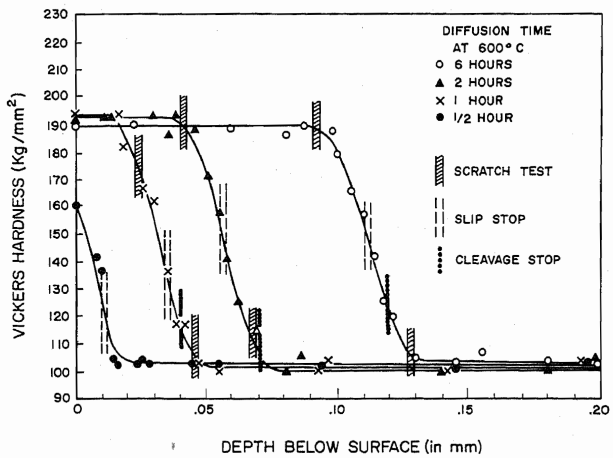


Fig. 11—Microhardness profiles for samples quenched after diffusion at 600°C. Data from scratch, bend, and cleavage are superimposed.

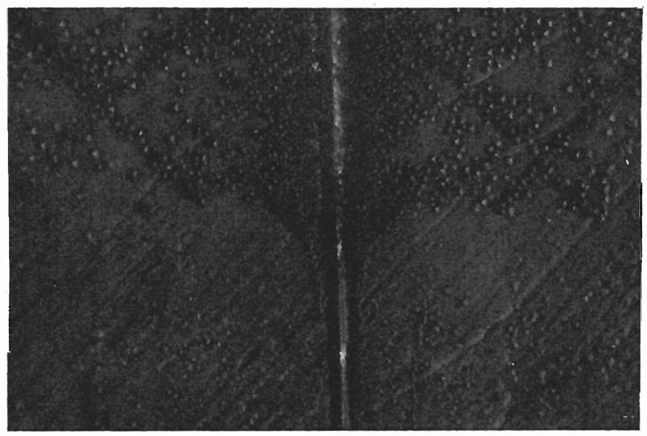


Fig. 12—Scratch test showing delineation of the interface region between interior and surface zone. Dislocation generation by the scratch disappears in the surface region. X850. Reduced approximately 1 pct for reproduction.

of the heat-treated crystals. Microhardness measurements were used to study the changes occurring within the diffusion zone. The changes in the diffusion zone were then correlated with the changes in bend strength of the composite crystals.

A typical set of microhardness profiles across diffusion zones of quenched specimens is shown in Fig. 11 for a 600°C anneal. Sets of curves were obtained at 50°C intervals between 500° and 700°C. The features of all are similar: 1) the surface zone shows constant hardness (after a minimum diffusion time); 2) the maximum hardness attained in the surface zone is higher for higher diffusion temperatures which correlates with the increased solubility of magnesium in LiF at higher temperatures; and 3) there is a narrow transition region between the diffusion zone and the unreacted part of the crystal. Some evidence of this transition region was seen in the earlier microstructures. Superimposed on the microhardness profiles are the diffusion-zone depths as measured from the microstructures based on the massive cleavage structure demarkation (marked cleavage stop) similar to Fig. 2 and the slip discontinuities (marked slip stop) similar to Figs. 4 and 5. In addition, the interface could be delineated using a scratch test. A typical photomicrograph showing the scratch as it runs into a diffused zone is shown in Fig. 12. The density of etch pits on either side of the scratch decreases as the scratch moves through the transition region into the diffused zone. Both sides of the transition zone are delineated by the scratch-induced markings. All the microstructural indicators fall within the transition zone obtained from the microhardness profiles.

The diffusion treatment carried out at 500°C provided some data which were not completely compatible with the results for the other temperatures. The microhardness profiles appear in Fig. 13. Here a different type of profile is obtained for the shorter annealing times; the lower times yielded a lower hardness "plateau". These curves also have superimposed the cleavage, slip, and scratch-test data used to delineate the diffusion zone. The important

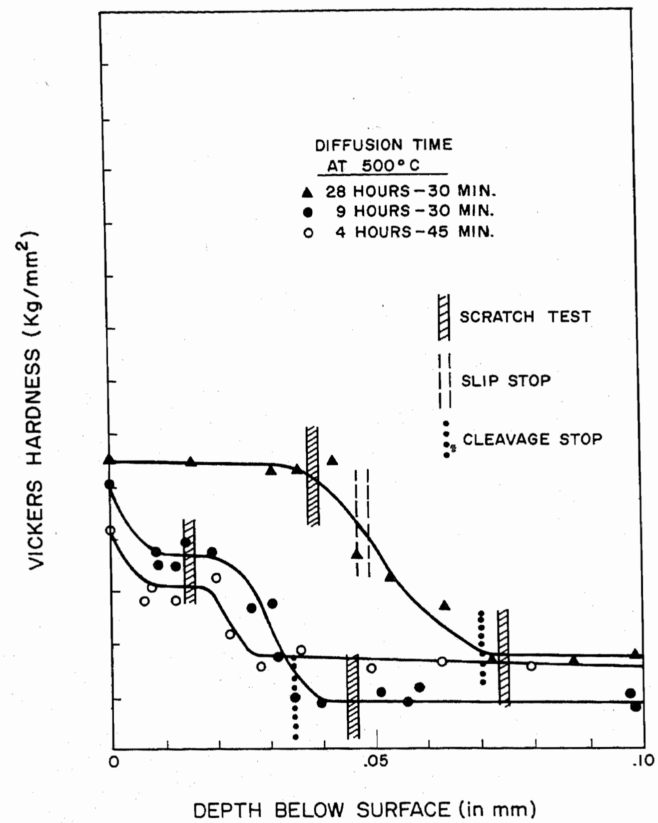


Fig. 13—Microhardness profiles for samples quenched after diffusion at 500°C. Data from scratch, bend, and cleavage are superimposed.

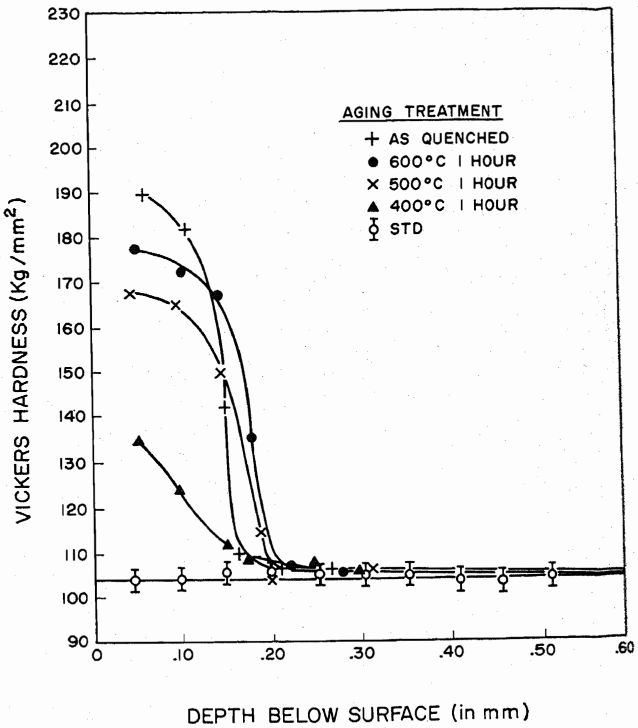


Fig. 14—Microhardness profiles for samples aged after quench from solution treatment at 700°C for 1 hr.

feature here is that the 4- and 9-hr profiles have no "slip stop" marking.

These samples exhibited ductility in the bend test and the dislocation patterns were found to penetrate the surface zone although the hardness, scratch, and cleavage patterns did indicate the presence of a zone. The significant parameter is the hardness in this region which is about 124 kg per sq mm. Referring back to Fig. 11, it is seen that the "slip stop" hardness is about 140 kg per sq mm. A similar hardness value for "slip stop" is observed on the other diffusion-temperature profiles. The question raised by these observations is whether the critical hardness is one which prevents slip breakthrough from the interior or whether the critical hardness restricts slip generation within the surface zone itself. Additional data described in the following section supports the latter model.

Aging. As indicated by the property variations between furnace-cooled and quenched samples, the $MgF_2:LiF$ system should be amenable to aging treatments. A series of specimens were coated with MgF_2, heated to 700°C for 1 hr, quenched, and then aged at various temperatures for 1 hr. Microhardness profiles, shown in Fig. 14, indicate decreasing hardness with decreasing aging temperatures.

Bend-deflection characteristics of solution-treated, quenched, and aged samples are shown in Fig. 15. The surface zones in these samples were formed by diffusing at 600°C for 1 hr prior to

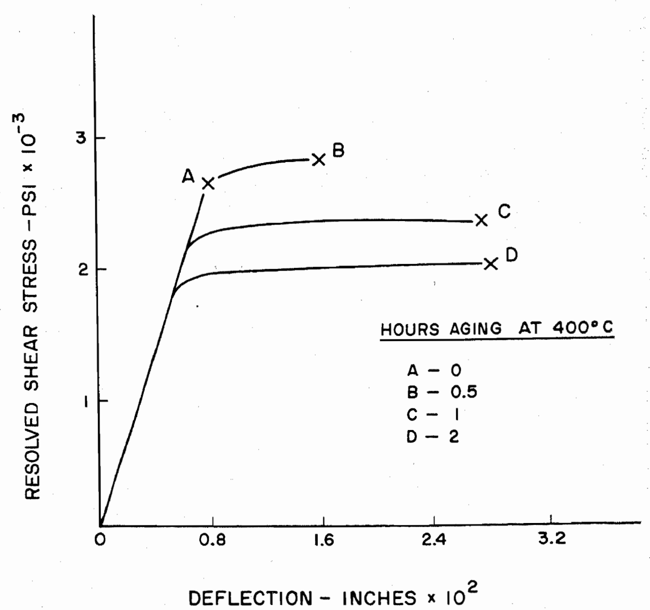


Fig. 15—Bend curves for samples aged at 400°C for times indicated following quench after solution treatment at 600°C for 1 hr.

quenching. This treatment was designed to provide surface hardnesses above the critical value for dislocation penetration and a zone depth shallow enough to allow penetration to the surface after some degree of precipitation. Aging at 400°C caused reduction in the yield strength and increase in ductility. Localized slip in the diffusion zone of the 0.5-hr-aged (400°C) sample was similar to the results found in samples quenched from 500°C, and again led to increased plastic flow. Specimens aged

Fig. 16—Slip-line generation in surface zone of specimen treated at 600°C for 24 hr, quenched, aged 2 hr at 400°C. Zone hardness, 125 kg per sq mm. Change in length of slip lines correlates with stress distribution in bending, maximum stress at right. X300. Enlarged approximately 6 pct for reproduction.

1 hr or more showed considerable surface pitting and homogeneous penetration of dislocations to the surface. One sample was given a longer diffusion time of 24 hr before aging for 1 hr at 400°C. As seen in Fig. 16 slip lines were generated and propagated in the surface zone itself, the occurrence that ultimately controls the mechanical behavior of the sample.

The microhardness values for the surface zones in these aged specimens are about 125 kg per sq mm which is comparable to the values of critical hardness for dislocation penetration previously obtained in samples quenched from 500°C after short diffusion times and those furnace-cooled from 500°C. The conclusion is that the appearance of slip markings in the diffusion zone is a result of generation of slip in the zone rather than the breakthrough of slip from the inner region. This would be particularly true in bending, since the maximum stress occurs in the outer fibers of the specimen. The critical hardness of 125 kg per mm for slip generation does not appear to be sensitive to the cause of hardening, since the same threshold is observed in quenched, slow-cooled, and quenched and aged specimens. An additional study of the precipitation mechanism is being carried out and will be reported subsequently.

Diffusion-Zone Formation. Microhardness profiles obtained as a function of temperature and time of diffusion indicate that the diffusion follows a parabolic rate law. Typical rate constants are 5.8×10^{-9} and 2×10^{-9} sq cm per sec at 600° and 550°C, respectively. The activation energy for the zone formation was found to be 20.9 kcal per mole. Inasmuch as the diffusion process could involve diffusion of magnesium, lithium, and vacancies it is difficult, with this data, to attribute the activation energy to a particular process. Further investigation in this area is needed.

SUMMARY AND CONCLUSIONS

A wide range of bend properties can be developed in LiF single crystals by the formation of magnesium diffusion zones at the crystal surfaces. Yield strengths can be increased by as much as an order of magnitude. The increase in bend strength is proportional to the depth and hardness of the diffusion zone. Ductibility in the diffused crystals is dependent upon the penetration of slip lines to the surface. For as-deposited coating and narrow diffusion zones it appears that ductility is dependent upon the breakthrough of internally generated dislocations.[5] For wide diffusion zones it was found that ductility was dependent upon the generation of slip within the diffusion zone itself. Slip generation was found to occur only when the zone hardness was below about 130 kg per sq mm. The critical hardness was independent of each of three methods used to achieve it:

1) quenching from 500°C after a short time diffusion which apparently restricted the amount of magnesium dissolved in the LiF;

2) slow cooling from 500°C which permitted precipitation of excess MgF_2;

3) aging at 400°C after quenching from higher temperatures (above 500°C).

From the above, it appears that the principal hardening is derived from supersaturation of LiF with magnesium. However, further study on the kinetics and morphology of the MgF_2-LiF precipitation reaction is needed to substantiate this.

The formation of the diffusion zone was found to follow a parabolic rate law with an activation energy of 20.9 kcal per mole.

ACKNOWLEDGMENT

The work presented in this paper is based on research sponsored by the Office of Naval Research, Metallurgy Branch, under contract NONR 285(43). Permission to publish the results is gratefully acknowledged.

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