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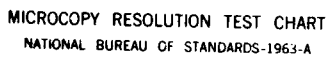UNCLASSIFIED   DEC 83 N00014-82-K-2050   F/G 20/12   NL

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FINAL TECHNICAL REPORT:

GROWTH OF CADMIUM TELLURIDE BY PULLING

UNDER LIQUID ENCAPSULATION

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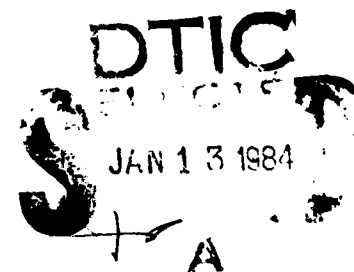
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Final Report on:

GROWTH OF CADMIUM TELLURIDE BY
PULLING UNDER LIQUID ENCAPSULATION

I. RESEARCH SUMMARY

This research effort was aimed at re-examining the potential of the LEC technique for growth of CdTe. The study was conducted in two ADL systems, type MP and MP-II, suitable for growth at pressures up to 75 and 600 psi respectively. Investigations of the optical and thermal properties of B_2O_3 were carried out in a modified conventional low pressure puller.

This study established the suitability of the LEC technique for growth of CdTe in single crystal form. The following results were obtained.

1. **High Pressure (30 atm) LEC Growth of CdTe.**

   Using a precast charge (5N, II-VI, Inc.) and B_2O_3 (Rasa Type D) as encapsulant it was possible to growth at a pulling rate of 4 μm/s a CdTe crystal of about 5 mm diameter which contained four lamellar twins, no grain boundaries, no low angle grain boundaries, and no optically visible precipitates. Bubble formation at the CdTe-PBN-B_2O_3 interface was absent (only one bubble was observed during the run); the seed remained specular throughout the experiment (i.e., no loss of seed material was observed).

2. **Low Pressure (4.3 atm) LEC Growth of CdTe.**

   LEC growth was investigated using a 5N, tellurium-rich (II-VI, Inc.) charge and B_2O_3 (Rasa, grade D) as encapuslant in quartz and PBN

crucibles. During melt down and growth, extensive bubble formation was observed at the crucible-CdTe-B_2O_3 boundary. Crystallites formed instantaneously within the bubbles and grew in size during their migration to the center of the melt. Upon establishment of seed-bubble contact, crystallite formation on the seed is initiated, seed-melt contact is disrupted, and single crystal growth is prevented.

3. Wetting Characteristics of Solid CdTe in Contact with B_2O_3
    at a Pressure of 4 atm and Temperatures Ranging from 660-930°C.

It was found that B_2O_3, at seed withdrawal rates ranging from 1 μm/s to 50 μm/s, forms a maximum meniscus height of 3 mm. In no instance did the withdrawn seed crystals exhibit a B_2O_3 coating. The forced wetting condition relaxes immediately upon arrest of seed withdrawal and a contact angle of 90° (planar B_2O_3 interface) is established within minutes. Significant evaporative loss of seed material was observed.

4. Optical and Thermal Characterization of B_2O_3.

The thermal characteristics of B_2O_3 layers were investigated at growth temperatures. Vertical thermal gradients were determined and a theoretical study of the heat transfer characteristics was performed. It was found that the encapsulation layer exhibits significant optical transparancy in the near infrared which suggests that the optical measurement of melt surface temperatures by IR imaging techniques may be feasible.

2

1. Introduction

Deficiencies in presently obtainable bulk CdTe (eg., precipitates, twins, low angle grain boundaries, dislocations, etc.) have frequently been attributed to inadequate control of heat and mass transfer during and following the liquid-solid phase transformation. In addition, the chemistry of the system exhibits characteristics which appear to make the implementation of growth in LEC configuration problematical. Previous investigators (1) observed a loss of Cd from the melt which occurred around the periphery of the growing crystal when overpressures of less than 13 atm were employed (2). It has also been reported (3) that a coherent encapsulating film cannot be maintained on the growing crystal due to insufficient chemical wetting by the encapsulant (B_2O_3) and that dissolution of Cd, Te and CdTe in the encapsulant occurs which reduces its optical clarity and changes the composition of the melt. Material obtained to date by LEC growth is characterized by extensive grain boundaries, low angle grain boundaries, lamellar twins and precipitates.

This research was aimed at re-examining the encapsulation conditions and their effects on the crystalline perfection of LEC grown material. It was also directed at the establishment of heat transfer control during and following growth, and at an assessment of its effect on crystal quality.

2. Wetting Behavior of B_2O_3-CdTe System

Wetting experiments were carried out under actual growth conditions. Charges of CdTe (5N, II-VI, Inc.) were melted beneath B_2O_3 (J.M. Puratronic) to ensure the attainment of growth temperature. Under these cir-

cumstances, significant evaporative loss ('fuming') of seed material was observed already prior to the establishment of seed contact with the liquid encapsulant. While the etched (1% Br in methanol, 5 min) surface of the seed was originally specular in appearance, after 15 min at 930°C the grain structure of the polycrystalline seed became easily recognizable (Fig. 1). With lowering of the seed close to the surface of the encapsulant, instantaneous formation of microcrystallites on the seed surface was observed (Fig. 2). The mass transport mechanism responsible for the formation of these crystallites, always encountered in low pressure LEC, is likely related to gas bubbles (see below). It was observed that the deposited phase disappears gradually after immersion of the seed into the encapsulant.

In a series of experiments at growth temperature with CdTe seeds immersed in B_2O_3, it was found that at withdrawal rates in excess of 50 µm/s the receding seed carries with it a layer of B_2O_3 to a meniscus height of about 3 mm. However, the encapsulating B_2O_3 films were unstable and dewetting began immediately upon arrest of pulling. The dewetting process is radially non-uniform with films showing least stability at the (rounded) corners of the seed (Fig. 3). In all instances the end result was a 90° contact angle between the B_2O_3 and the seed (Fig. 4) regardless of the content of the encapsulant. This final contact angle is not considered to reflect the equilibrium wetting conditions; rather, it constitutes a hysteresis condition related to the geometry. The absence of wetting ($\Theta = 0°$) cannot a priori be excluded, nor can the relationship between wetting and the chemical and physical condition of the seed be specified.

4

3. Seed Encapsulation by Forced Wetting

Enhancement of 'seed' wetting was pursued by exploiting the physical and chemical properties of B_2O_3, namely the temperature dependence of the viscosity and the reported ability of the $B_2O_3-SiO_2$ system to phase-separate on cooling. A multi-component borate glass system (0.8 B_2O_3, 0.2 SiO_2) was investigated which exhibits a dual-phase microstructure at 750°C which is below the melting point of CdTe (1092°C). It remains a single phase liquid with a viscosity greater than that of pure B_2O_3 while in contact with the semiconductor melt. For this purpose the glass composition was formed by dissolving powdered high purity quartz glass in B_2O_3 at 1050°C. The effectiveness of this modified encapsulant was investigated in exploratory experiments using a polished steel rod as a seed substitute. At the increased viscosity of this liquid encapsulant, the wetting characteristics of this system were in essence identical with those of the CdTe-B_2O_3 system. Forced wetting was established through the use of a quartz sheath located co-axially about the 'seed'. In these experiments the sheath was contacted with the encapsulant; upon withdrawal, a coherent stable encapsulant film formed about the seed and could be withdrawn with the seed (Fig. 5). (Stainless steel was chosen as a model for CdTe since it is known not to be wet by molten borate glasses.)

4. Low Pressure (4.3 atm) LEC Growth of CdTe

Tellurium-rich charge (5N, II-VI, Inc.) and B_2O_3 (Rasa Type D) in pyrolytic boron nitride (PBN) and quartz crucibles were used in the investigation of low pressure LEC growth. According to the literature, the maximum vapor pressure of tellurium, as indicated by the three phase boundary loop (4) (for the vapor pressure of Te coexisting in equilibrium with

5

solid and liquid CdTe), is 0.185 atm at 930°C; the vapor pressure of Te over pure Te at the melting point of CdTe is less than 2 atm. It was found, however, that upon melting of the CdTe charge at pressures up to 4.3 atm (50 psig), bubbles appear at the crucible-CdTe-B_2O_3 boundary. Furthermore, associated with bubble formation was the appearance of crystallites within the bubbles as they migrate to the center of the melt (Fig. 6). The bubbles were found to gradually rise to the surface of the B_2O_3. The crystallites remained behind as a residue which subsequently evaporated from the surface of the encapsulant. Presence of dissolved material within the B_2O_3 was indicated by clouding of the encapsulant, observed as the glass cooled following the completion of the experiment. A semiquantitative spectroscopic analysis of the B_2O_3 (100 ppm sensitivity for Cd and Te) revealed significant Si levels, but neither impurities nor the presence of Cd or Te in the glass matrix.

The experiments showed that upon seed-melt contact the rate of migration of bubbles from the periphery to the center of the melt is increased. With seed-bubble contact, vapor growth on the seed was initiated with the bubble providing a transport path. It was observed that vapor growth of crystallites extends to the exposed surface of the seed above the B_2O_3. In all instances it was found that the bubbles formed an effective sheath about the crystal and prevented the establishment of proper seed-melt contact. The dimensions of the seed after the experiment were reduced by as much as 25% due to evaporative loss of material (Fig. 7).

The complications encountered during low pressure LEC growth of CdTe are attributed primarily to inadequate (too low) axial thermal gradients in the system and to the massive formation of gas bubbles at the CdTe-

crucible-B_2O_3 contact line, encountered with three different crucible materials and with dry B_2O_3.

5. High Pressure (30 atm) LEC Growth of CdTe

The polycrystalline charges of CdTe (5N, II-IV Corp.) were precast in a PBN crucible under liquid encapsulation at low pressure (50 psig). The polycrystalline seed (3.2 x 3.2 x 20 mm) was cut from the original starting material. The charge and the seed were degreased and etched for 10 min in a 5% solution of bromine in methanol. A second 10 min etch in a 1% bromine solution was followed by three rinses in methanol and drying in a stream of prepurified helium.

The PBN crucible was decarburized in a gas torch flame and placed, with the mounted seed, into the high pressure RF heated Czochralski system. A 40 g disk of ultrahigh purity B_2O_3 was placed in the crucible, the system evacuated to roughing pump pressure and back filled with nitrogen. The B_2O_3 was melted and taken to 1000°C under a pressure of 200 psig. At this point the furnace power was turned off, the pressure reduced to 1 atm, the chamber opened, and the etched charge of CdTe (55 g) dropped into the molten B_2O_3. The chamber was resealed, pressurized to 450 psi and brought back to temperature with the crucible rotating at 3 rpm. Some of the pieces of charge material were not completely covered by B_2O_3 when they were inserted; consequently, the crucible shaft was tapped to reposition the charge, providing for complete coverage. By this time, however, dark powder had formed on the surface of the exposed CdTe and, when encapsulated by B_2O_3, became dispersed and limited the optical transparency of the encapsulant. During the heat up cycle it became apparent that, at the increased pressure, B_2O_3 was being subjected to stronger convective mixing

7

than previously observed at low pressures. This effect was reflected in the relatively fast dispersion of the powdered material on the exposed charge throughout the liquid encapsulant. (After approximately 3 hours the B_2O_3 had cleared.) It is noted that the time necessary for the encapsulant to clear was increased significantly under the high pressure growth conditions.

After clearing of the encapsulant, the seed was lowered to a position 3 cm above the encapsulation and maintained in this position for ten minutes. (In this condition it had been observed, at low pressure, that the seed instantaneously loses its specular nature and becomes subject to evaporative loss to an extent that window clouding occurs.) In the high pressure growth experiment, the seed exhibited no evaporative loss and remained specular for five hours.

After establishment of seed-melt contact, growth was initiated by pulling at 4 μm/s with seed rotation of 4 rpm; no temperature adjustments were made for 10 minutes. This seeding procedure resulted in the desired necking. Temperature reductions were subsequently made at 10 min intervals. When the growing crystal emerged from the encapsulant, it was not wet by the B_2O_3. However, as mentioned above, different from growth experiments conducted at low pressure, no loss of material (fuming) was observed. This difference in behavior is attributed to enhanced kinetic (convective) heat transfer by the high pressure ambient and the associated establishment of steep axial temperature gradients in and above the B_2O_3 layer as well as in the growing crystal.

Notable for high pressure growth was the pronounced reduction in the tendency for bubble formation. During the course of this particular growth experiment, only one bubble was observed; in comparison with low pressure

8

LEC, the time required for the bubble to migrate from the periphery of the melt to the seed-melt interface (about 45 min) was substantially reduced. Significant is the fact that upon bubble-seed contact no disruption of the liquid-solid phase transformation was observed. [It should be noted that, during low pressure LEC, bubble attachment to the seed resulted effectively in disrupting seed-melt contact and in our inability to achieve growth (Fig. 8).]

After growth for about 15 min, an attempt was made at increasing the crystal radius through a melt temperature decrease. The system responded with instantaneous uncontrollable freezing of the melt surface, indicative of the existence of very shallow radial thermal gradients.

Following suspension of crystal pulling, the surface of the melt was remelted and the system was reseeded on a portion of previously grown material. Pulling was again initiated at 4 μm/s. Necking was accomplished and one temperature reduction was made to increase the diameter; the crystal diameter increased; shouldering and constant diameter growth were achieved through temperature corrections. After growth of about 6 mm an increase in seed rotation (from 5 to 10 rpm) was initiated to correct the observed trend toward growth with a decreasing crystal diameter; this was followed 10 min later by a further increase in rotation rate to 25 rpm. The rotation effect on the melt temperature was small and temperature reductions were applied after 25 mm of growth.

The grown crystal was photographed (Fig. 9) and radial slices were cut out at 13 mm, 25 mm and 40 mm from the seed end (Fig. 10). The sections were cleaned and subsequently etched for 10 s in a 4:3:1 solution of 2% silver nitrate in water, nitric acid and hydrofluoric acid to reveal any

9

twins and grain boundaries. The analysis indicated that growth following the original seeding was associated with a grain selection process which resulted in a single crystal matrix with four lamellar twins. Breakdown of the matrix into several grains was observed as a result of the second seeding operation. Grain selection became operative again and significantly reduced the extent of polycrystallinity as growth proceeded from the second (Fig. 10b) to the third (Fig. 10c) sample position, a distance of 1.5 cm.
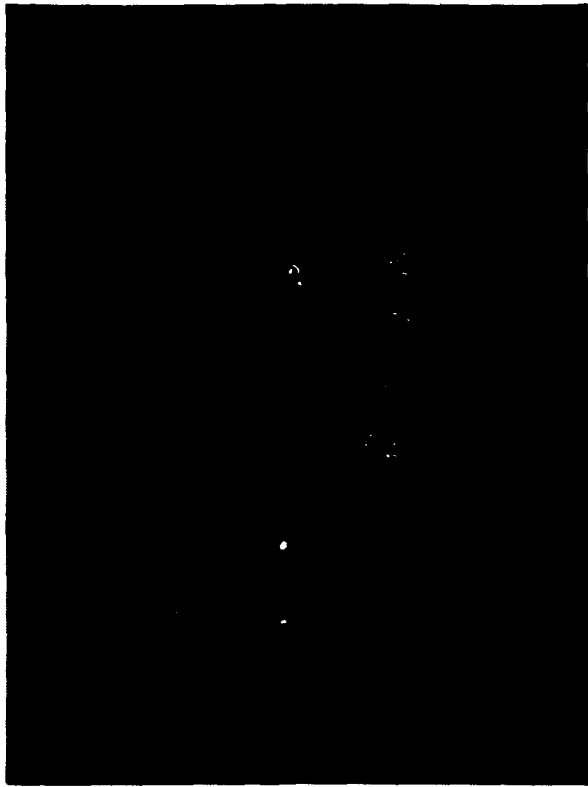
Notice:

In view of early termination of funding for this preliminary research effort, the last phase (High Pressure LEC Growth) was conducted with supplementary funding by the Department of the Army - U.S. Army Research Office, Contract No. DAAG29-82-K-0119.

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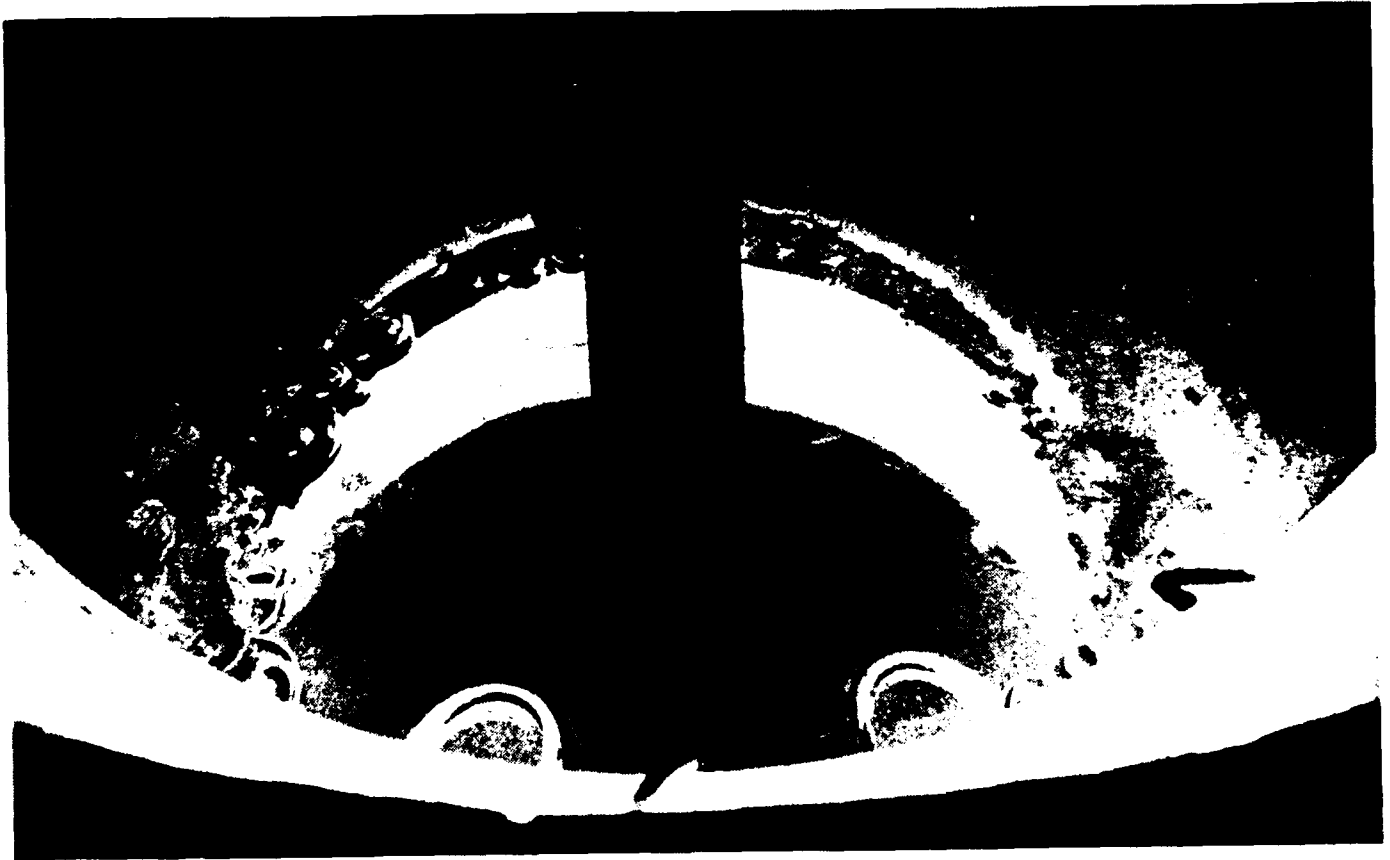4. A.J. Strauss, Proc. Int. Symp. on CdTe, Strasbourg, I-1 (1971).

FIGURE CAPTIONS

Fig. 1   Polycrystalline CdTe seed in contact with B_2O_3 at 930°C. Note delineation of individual grains caused by evaporation.

Fig. 2   Formation of crystallites on the end of CdTe seed positioned above the liquid encapsulant (CdTe melt is beneath B_2O_3). Notice also bubbles at the periphery of the encapsulation layer.

Fig. 3   Radially non-uniform wetting condition of B_2O_3 on CdTe following arrest of seed pulling.

Fig. 4   Contact angle of 90° between the B_2O_3 encapsulant and the CdTe seed following relaxation. (Mirror reflection of seed confirms planarity of B_2O_3 layer.)

Fig. 5   Forced wetting of stainless steel seed by B_2O_3-SiO_2 at 1050°C.

Fig. 6   Bubbles containing crystallites in liquid B_2O_3. Note the residue left on the surface of the encapsulant following rupture of a bubble.

Fig. 7   CdTe seed after 8 hours exposure to low pressure growth conditions.

Fig. 8   Prevention of seed-melt contact by interaction of bubbles with the CdTe seed. (Note crystallites on exposed seed surface.)

Fig. 9   High pressure (450 psig) LEC grown CdTe.

Fig. 10   Radial slices from crystal shown in Fig. 9 taken at (a) 13 mm, (b) 25 mm and (c) 40 mm from the seed end (top to bottom). (See text.)
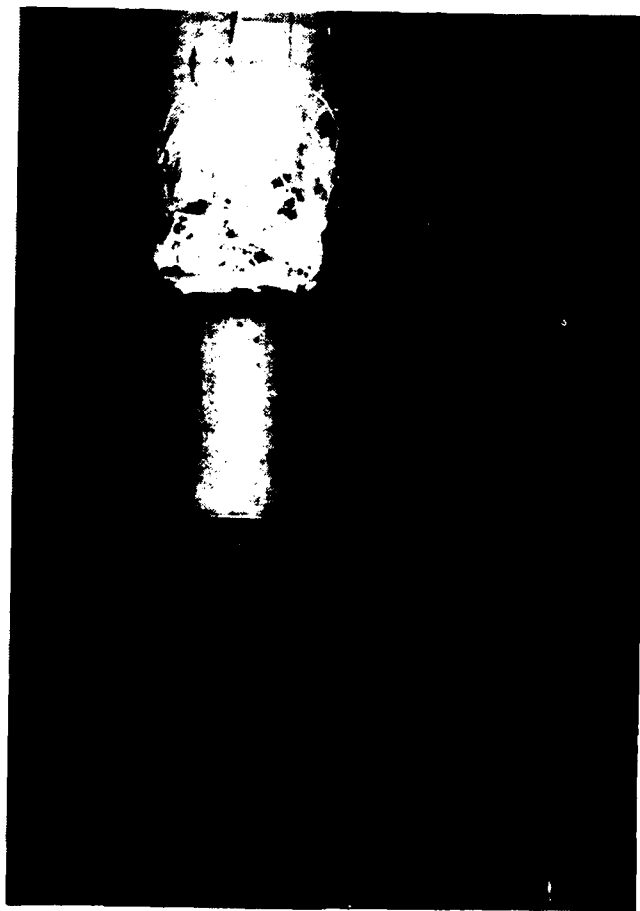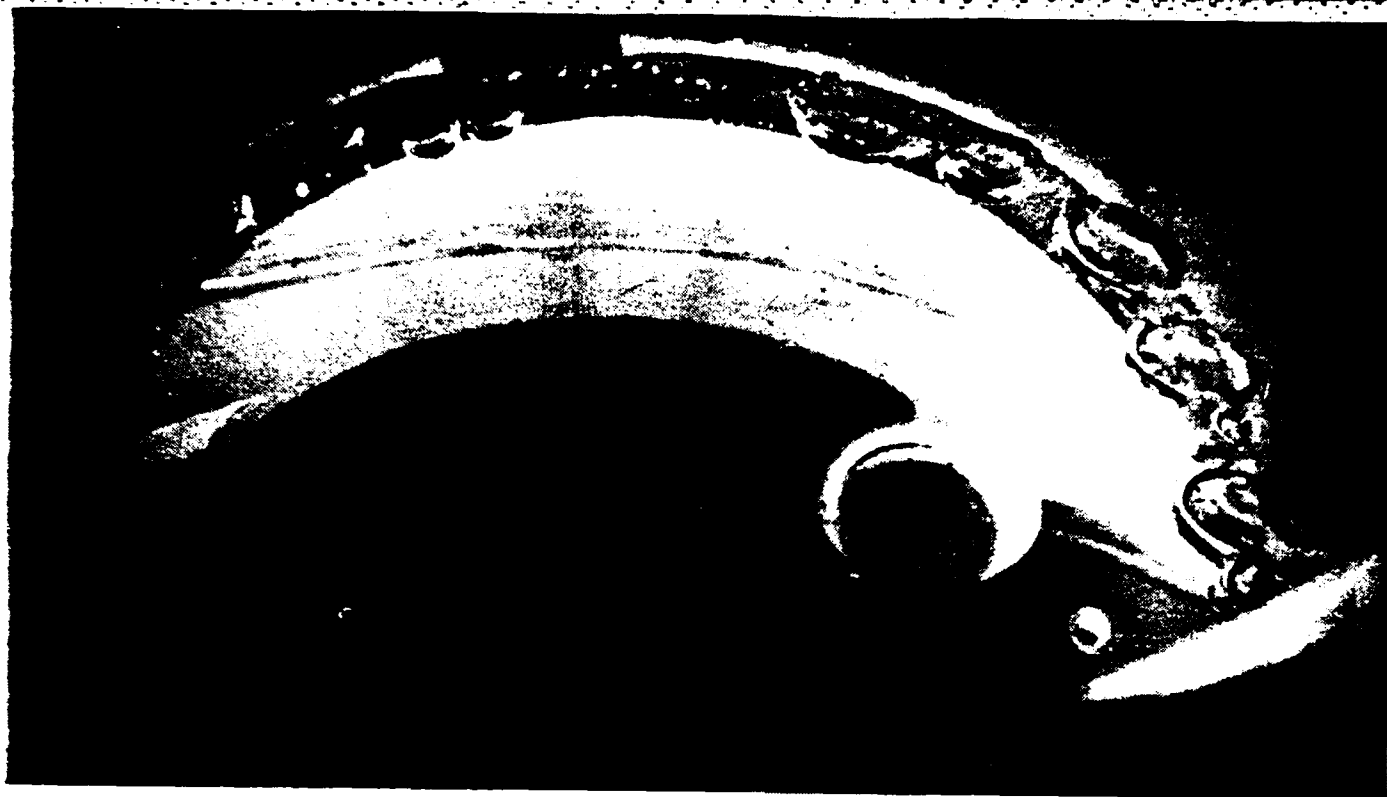
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