1961

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Recommended Citation

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ELECTRON MICROSCOPE STUDY OF THE SYSTEMS CADMIUM-CADMIUM CHLORIDE AND LEAD-LEAD CHLORIDE

BY

DENNIS O'NEILL

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1961

Approved by

Andrew Larson (advisor) A W Schlechten

ABSTRACT

The nature of the dispersed phase in the cadmium-cadmium chloride and lead-lead chloride systems were investigated with the electron microscope.

Preliminary experiments on preparing and examining the dispersed phase showed that it was most feasible to study the material by electron-microscopic examination of replicas made from the surfaces of the fractured materials. Melting apparatus and methods were chosen so that samples of the melts could be easily quenched to different temperatures and so that the samples could be easily fractured with a minimum of surface contamination. Of the conventional replicating techniques tried, that of carbon replicas pre-shadowed with chromium was found to be the most suitable.

Electron micrographs of these surface replicas showed the presence of particles whose size varies over a large range. The larger particles are approximately spherical and may show partially developed facets, whereas many of the smaller particles depict an almost perfect hexagonal outline. The orientation of the particles appears to be related to the structure of the chloride samples.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Mr. J. W. Jensen, Physicist, Rolla Metallurgy Research Center, U. S. Bureau of Mines, under whose supervision the laboratory work was performed, and to Dr. A. H. Larson, Associate Professor of Metallurgy, who was the faculty advisor for this research project.

Special thanks are expressed to Mr. J. A. Rowland, Research Director of the Rolla Metallurgy Research Center, and others who made it possible for this investigation to be conducted under a Fellowship from the U. S. Bureau of Mines. Under this fellowship, the Bureau of Mines furnished the financial support, the space, and the equipment for this investigation. Excellent cooperation and assistance were received from the Bureau of Mines employees.

The author is also indebted to various members of the Metallurgical Engineering and Ceramic Engineering Departments for their advice and assistance.

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I. INTRODUCTION

A. Statement of Problem

This thesis is the result of an investigation undertaken to make electron microscope studies of the solidified cadmium-cadmium chloride and lead-lead chloride systems. The major topics of interest in this investigation were (1) to determine methods of specimen preparation which would meet the special requirements of the electron microscope, and (2) to determine if a dispersed phase of colloidal dimensions exists in these solidified systems.

B. Selection of Problem

It has been known for a long time that a number of metals form apparent solutions with their molten salts, for example, potassium in potassium chloride, lead in lead chloride and cadmium in cadmium chloride. Effects of this apparent solubility such as the formation of intensely colored melts, the repression of the metal solution by foreign salt additions, and the occurrence of small particles in the quenched salt were all interpreted by Lorenz[1] as due to colloid formation. Lorenz called these solutions and dispersions of metals in their molten salts "pyrosols." He considered the phenomenon of pyrosols to be a complex one which is to be compared with the complex phenomena of the colloidal chemistry of aqueous solutions. Also, Lorenz regarded these pyrosols, or fluid-dispersoid systems, as analogous to glass colored by metals (for example, gold ruby glass) and to substances like obsidian and pitchstone, which are found in nature. Other investigators in the field have suggested that these solutions and dispersions result from the possible formation of lower valent chemical compounds such as subchlorides or from the formation of true solutions.

Early investigations of these metal-metal salt systems were studied mainly in connection with phenomena exhibited during the electrolysis of these fused salts, and by solubility measurements and ultramicroscopic examination of the molten and solidified material. In the lead-lead chloride system, ultramicroscopic investigation of the solidified material indicated the presence of a dispersed phase consisting of metal particles of colloidal dimensions.[2] The solidified cadmium-cadmium chloride system will in some cases exhibit a dispersed phase which is microscopically visible.

From the great wealth of information gained by applying the electron microscope to the field of colloid science, it appears that some knowledge of the dispersed phase in solidified systems of metals in their molten salts could be obtained by using this instrument for examination of these systems.

II. REVIEW OF LITERATURE

A. History

By observing the electrolysis of a molten salt such as pure anhydrous cadmium chloride through a glass test tube, Richard Lorenz[3], in 1893, found that gaseous chlorine forms at the anode and a dark brown cloud forms at the cathode. This dark cloud or metal-fog moves about in the melt and finally colors it completely brown, whereas the pure cadmium chloride melt is colorless. Some of the reduced cadmium metal falls to the bottom of the test tube, but the major portion goes to form the brown cloud in the melt. Solidification of the melt yields a gray fused mass, and after extraction with water, a very fine crystalline powder is obtained which proves to be metallic cadmium.

This fogging phenomenon produced during the electrolysis of a molten metal halide may be obtained by adding a metal to its respective molten metal halide or by partial reduction of a molten metal halide with a reducing agent.

As a result of numerous investigations by Lorenz and co-workers on the fogging phenomena of different metal halide salts, the name "pyrosol" was proposed by Lorenz to describe these dispersions and solutions of a metal in its molten salt.

In 1926, Lorenz summarized many of the earlier investigations which were related or analogous to the complex phenomena of "pyrosol" formation.[4] Among these investigations are included such works as the ultramicroscopic studies of gold ruby glass by Zsigmondy, of natural blue rock salt by Siedentopf, and of fog particles in chilled halide melts by Lorenz, Eitel, and Hiege.

Eitel and Lange[5] investigated molten solutions of cadmium in cadmium chloride and lead in lead chloride with an ultramicroscope, and they found no particles of ultramicroscopic visibility. Hollens and Spencer[6] confirmed earlier work in showing that the molten cadmium-cadmium chloride system when cooled slowly contains particles of microscopic dimensions, and Heymann and Friedlaender[7] showed that this is true when the melt has been quenched in carbon tetrachloride. It has been stated by Terrey[8] that the cadmium particles have approximately colloidal dimensions when the melt is quenched in water.

Heymann, Martin, and Mulcahy[9] found that the solubility of cadmium in its chloride is 15 mole percent after equilibration at 690° C. Cubicciotti[10] gave values of 13, 14, and 15 mole percent cadmium in its chloride for three determinations at 740° C. Topol and Landis[11] determined the solubility of cadmium in cadmium chloride to about 1000° C by thermal analysis and decantation techniques and found results which are in good agreement with earlier reported values.

The solubility of lead in lead chloride at 600, 700, and 800° C of 0.020, 0.052, and 0.123 mole percent, respectively, was determined be Corbett and von Winbush[12] in a manner similar to the solubility determination made by Lorenz[13], whereby the excess metal is separated from the remainder of the melt before quenching.

Amelinckx, Van der Vorst, Gevers, and Dekeyser[14] were able to reveal dislocation lines in the interior of melt-grown and natural rock salt crystals through additive coloration by means of sodium metal and by means of small additions of barium chloride. After suitable heat treatment, colloidal sodium metal segregated out along certain surfaces or lines within the crystal, and similar results were obtained with the barium chloride. This segregation was observed by means of the ultramicroscope.

Recently, Simon and Sproull[15] published electron microscope studies of colloids in potassium chloride single crystals. These studies were made on the replicated fractured surfaces of potassium chloride single crystals containing excess potassium. For each heat treatment reported, colloids of a distinct size, rather than of a large range of sizes, were observed, and slower cooling rates resulted in larger colloids.

D. Electron Microscopy Techniques

In its present state of development, the electron microscope is relatively simple to operate, so that given a suitable specimen, no difficulty is encountered in obtaining an image on a fluorescent screen or on a photographic plate. The main problem in using this instrument in a new field of research lies in preparing specimens which will meet its special requirements. In striving to develop a technique for preparing suitable specimens for this investigation, the investigations cited below have been of considerable value.

Wyckoff[16], Cosslett[17], and Hall[18] have each reported on a number of methods and limitations for preparing specimens in electron microscopy. Holland[19] gives extensive theoretical and experimental data on the vacuum deposition of thin films, much of which applies to methods of electron microscopy. Bradley[20] developed a method of depositing carbon by evaporation in a vacuum, which has resulted in a series of new techniques for producing replicas and support films of carbon. Hibi[21] has proposed a nozzle system for improving metallic shadow-casting. An interpretation of electron micrographs produced from inorganic replication techniques has been given by Calbick[22]. The mechanical strength, structure, resolution, and contrast of replicas produced from high-density metals which are condensed in a vacuum have been investigated by Baillie[23]. A method for full and partial replication, utilizing a residual-gas scattering evaporation technique and an auxiliary strengthening layer of sublimed sulfur has been introduced by Leonhard, Cook, and Anderson[24]. Stiegler and Noggle[25] have investigated the use of sodium metaphosphate as a parting agent for stripping replicas from specimen surfaces, and they found that a parting layer as thin as 7A may give satisfactory stripping of replicas from some surfaces.

III. APPARATUS

The apparatus used in this investigation is divided into three divisions corresponding to the three major divisions of the experimental work:

(1) melting apparatus--for preparing solidified melts of metal-metal chloride systems;

(2) vacuum evaporating apparatus--for shadow-casting and for making evaporated inorganic surface replicas of solidified melt materials;

(3) analysis and recording apparatus--for obtaining data from replicas.

Specific information on reagents and materials used in this investigation is given in Appendix.

A. Melting Apparatus

Initially, the metal-metal chloride systems were melted in 18x150 mm Vycor test tubes, with a Fisher burner for the heating source. After preliminary tests with this apparatus, it was found desirable to obtain a crucible-type furnace which would give a more uniform temperature gradient in the melt. The crucible furnace selected as the most feasible was a Hoskins type, capable of operating up to 950° C. The furnace chamber is 6 inches deep, and it has a diameter of 1.5 inches. Vycor test tubes, 25-mm OD and smaller, were used as crucibles for containing the melts in this furnace.

From observations made on the molten and solidified melts prepared in Vycor test tubes in the crucible furnace, a number of changes were deemed necessary. Instead of removing and quenching the melt contained in the crucible, it appeared that more representative specimens of the melt would be obtained by extracting portions of the melt from the crucible and then quenching these portions at different temperatures. Also, the best method found for examining the melt specimens with the electron microscope was by replicating the fractured surface of solidified melt material. Therefore, it was desirable to obtain pieces of the melt material with the least amount of contamination and of a shape that could be readily replicated. These changes in the melting apparatus were achieved by using a 25-mm OD Vycor test tube as the crucible from which individual portions of the melt were extracted with 7-mm OD Vycor tubes, sealed at one end and provided with an opening in the side at approximately 4 inches from the bottom. A simplified cross section of the furnace and crucible assembly is given in Figure 1. The extraction tubes were of a diameter small enough that short sections (approximately 0.5 inches) could be easily broken off to allow replication of the fractured surface of the contained solidified melt.

The furnace and crucible assembly were placed in a Fisher Isolator/Lab in which a helium atmosphere was maintained during heating and quenching of the metal-metal chloride material. Figures 2 and 3 show the arrangement of the melting apparatus. A Chromel-Alumel thermocouple connected to a Leeds and Northrup No. 8686 millivolt potentiometer was used for determining the temperature of the melt. A heated vacuum desiccator preserved the chemical reagents that were used in the Isolator/Lab.

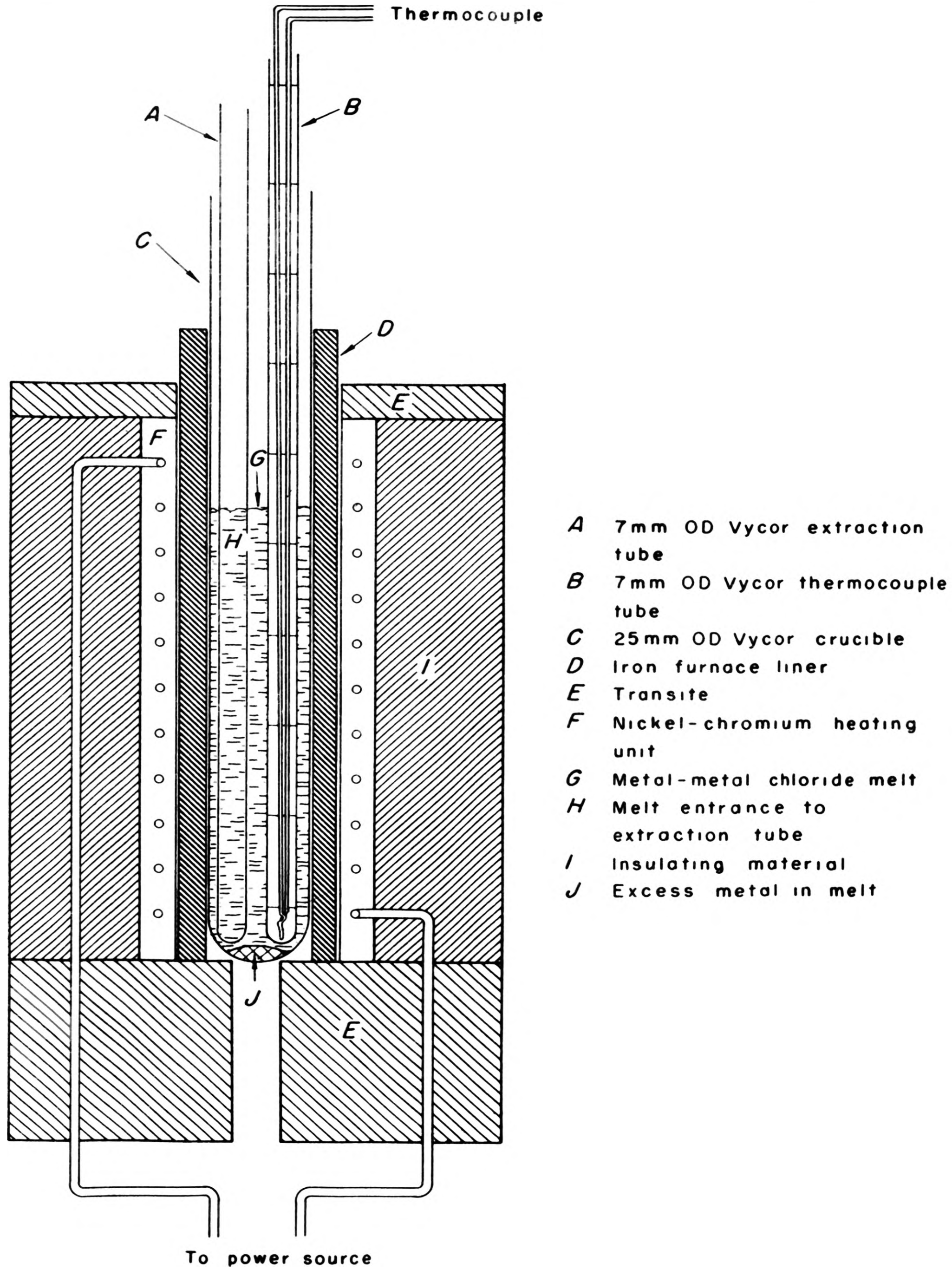

FIGURE I

Simplified Cross Section of Furnace and Crucible Assembly

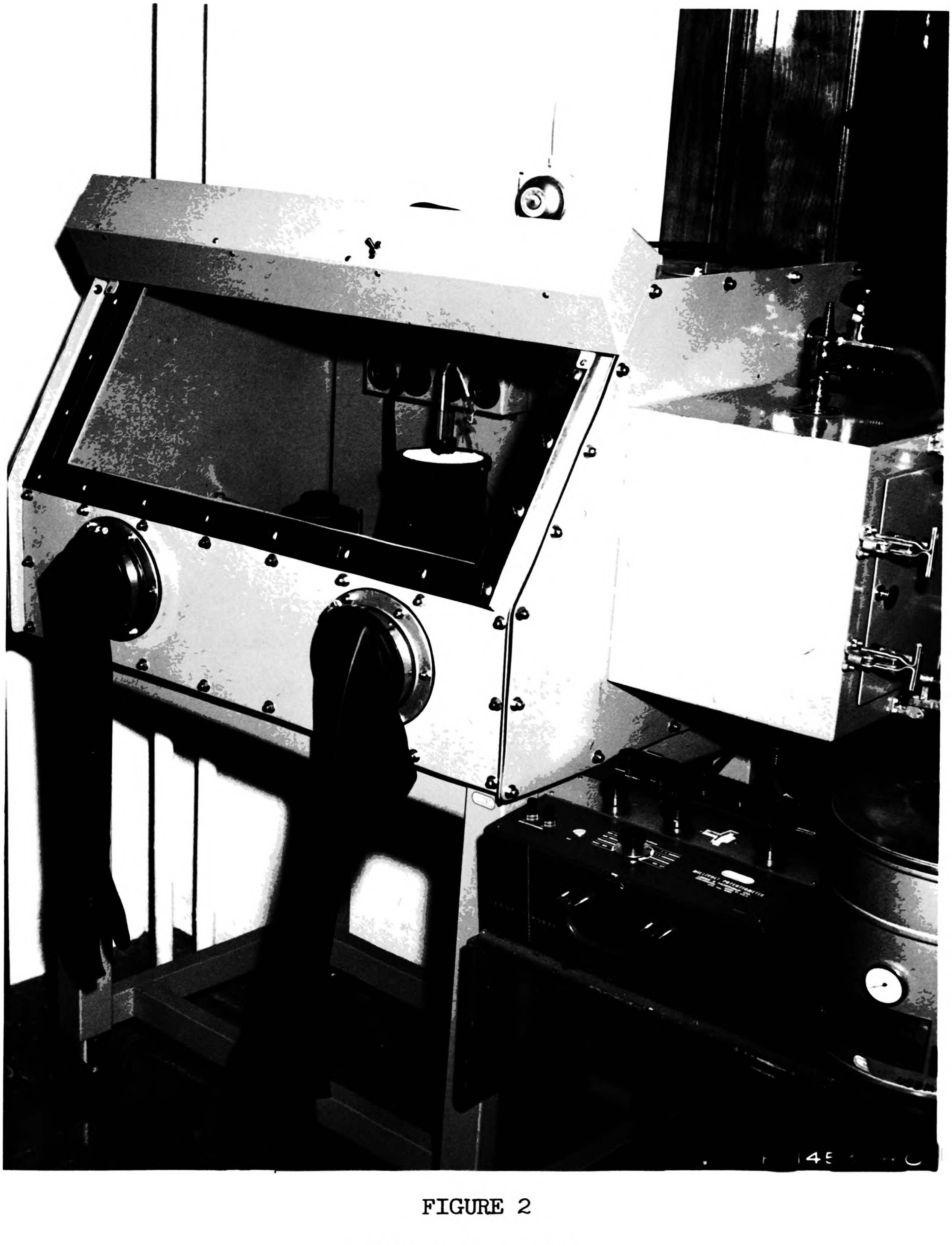

FIGURE 2

Melting Apparatus

FIGURE 3

Arrangement of Melting Apparatus in Isolator/lab

B. Vacuum Evaporation Apparatus

Vacuum evaporators or coaters are considered as indispensable accessory equipment in all electron-microscope laboratories, and in this investigation a Distillation Products LC1-12 Vacuum Coater was used for shadow-casting and for other coating techniques requiring the evaporation of substances in a high vacuum.

In order to facilitate the evaporation of carbon in this unit, a carbon evaporation apparatus was inserted in the coating chamber and connected to one pair of electrodes, as sketched in Figure 4.

C. Analysis and Recording Apparatus

A Philips, EM-100, electron microscope was used for analysis of the replicas of the fractured samples. The essential components of the instrument comprise the following four major parts:

(1) the microscope tube with the electron source, electron lenses (magnetic type), specimen holder, 8-inch viewing screen (possible magnifications of 1,000x to 60,000x), and the device for photographing (incorporates an internal 35-mm roll film camera);

(2) a high-tension generator for supplying the voltage for accelerating the electrons and which allows an accelerating voltage selection of 40, 60, 80, and 100 kilovolts;

(3) the apparatus for energizing the lenses;

(4) a system of pumps for evacuating the microscope tube.

Figure 5 depicts the desk of this electron microscope, showing the viewing screen of the electron microscope tube and various control knobs. A simplified cross section of a portion of the electron microscope tube is shown in Figure 6.

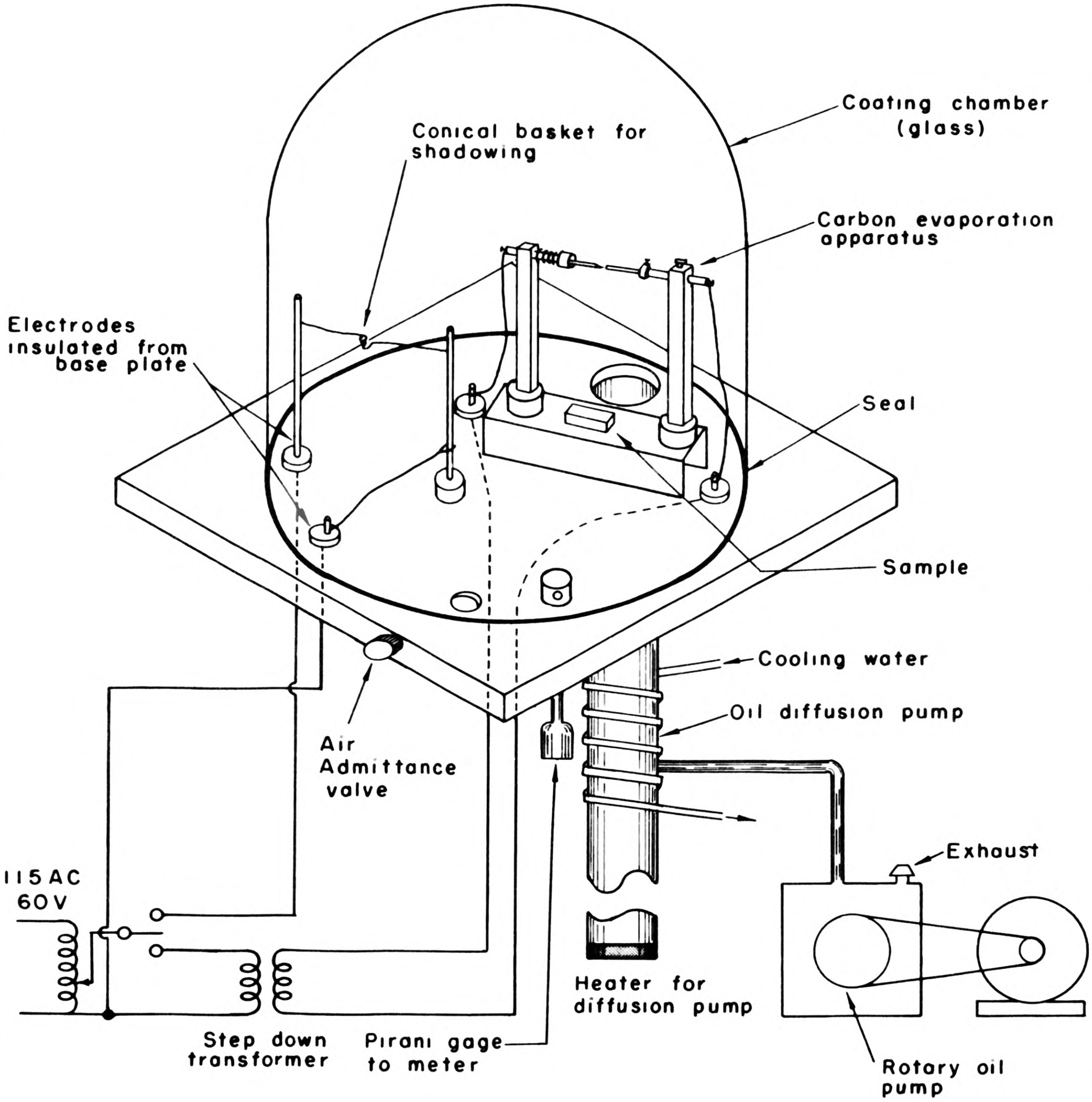

FIGURE 4
Sketch of Vacuum Coater and Carbon Evaporation Apparatus.

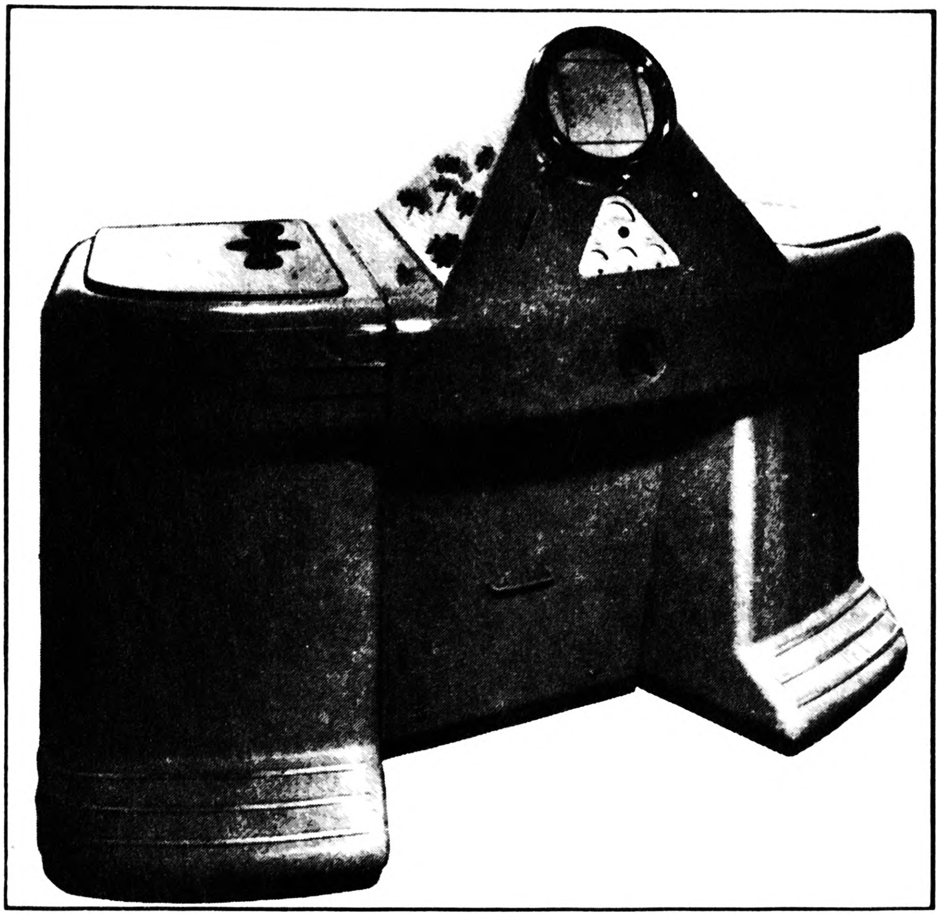

FIGURE 5

Philips EM-100 Electron Microscope
(from Hall, p. 211, Ref. 18.)

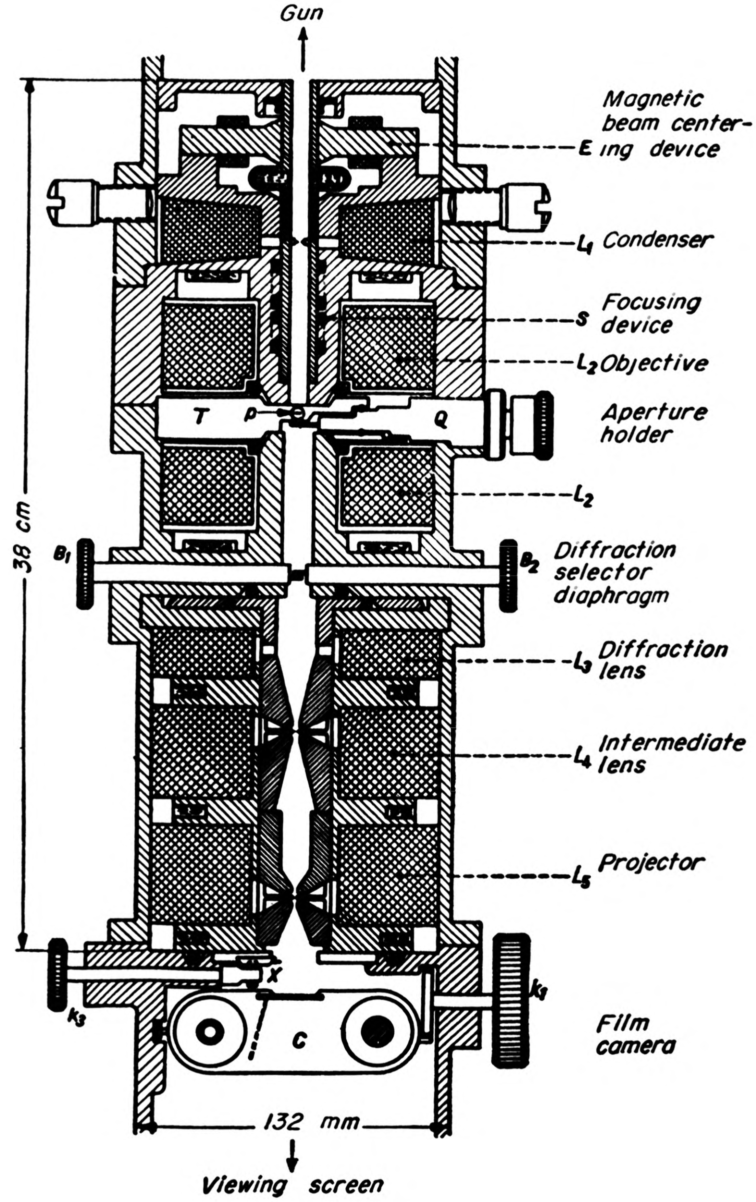

FIGURE 6

Simplified Cross Section of Electron Microscope Tube (from Hall, p. 212, Ref. 18.)

The roll film camera uses standard 35-mm high-contrast film permitting up to 40 exposures at enlargements to more than 15,000x. As a result of the location of the camera in the microscope tube, the film is capable of recording the screen image at a reduced scale of 4 times. Photographically, magnifications well beyond 250,000x may be obtained. The resolving power of this instrument is given as 30A or less.

A vacuum oven was used for dehumidifying an extra loaded camera to decrease the pump-down time for the microscope tube.

IV. METHODS AND PROCEDURE

A. Formation of Samples

At the beginning of this investigation, some of the melts were made by melting the lead or cadmium with the respective chloride in air in Vycor test tubes. These melts were quenched in air at room temperature or in an ice water mixture from approximately 600° C. After some experimentation in preparing specimens from these solidified melts or samples, a more suitable method for producing the samples was developed.

A 25-mm OD Vycor furnace crucible, as shown in Figure 1, was filled with approximately 200 grams of anhydrous cadmium chloride* or with approximately 250 grams of lead chloride to give a melt height about 5 inches from the bottom of the crucible. Because of the decrease in volume resulting from the change of powdered chloride to molten chloride, it was necessary to melt part of the charge before adding the remainder of the powdered chloride to the crucible. This addition was made by pouring the powdered chloride through a Vycor funnel, with a 45-mm diameter opening at the top and a stem opening about 12 mm in diameter. The powdered chloride was forced into the melt from the Vycor funnel by means of a glass rod.

The 7-mm OD Vycor tube containing the Chromel-Alumel thermocouple was placed in the crucible after the charge was melted. Samples of the pure chloride were obtained by extracting portions of the crucible

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*Specifications on chemical reagents are given in the Appendix. Before they were used, all chemical reagents were placed in a heated vacuum desiccator.

melt with the extraction tubes. It was noted that the melt temperature was decreased as much as 10° C when an extraction tube was placed in the melt; therefore, an additional 15 minutes or so were required for the melt to return to the temperature at which it was equilibrated. The metal of the particular chloride was added to the crucible melt to saturate it so that fogged chloride melts could be obtained; hence, an excess of molten metal was present at the bottom of the crucible in these fogged melts.

All samples extracted from the crucible melts were quenched in the helium atmosphere surrounding the apparatus or in a cold bath of kerosene under this helium atmosphere. The temperature of the helium atmosphere varied from room temperature to about 40° C, depending on the temperature of the melt and the length of time the melt had been heated. Higher temperatures of the atmosphere were prevented by maintaining a continuous flow of helium through the Isolator/Lab. The cold bath of kerosene was cooled to approximately -20° C before it was placed in the Isolator/Lab by immersion in a mixture of dry ice and acetone. The exact temperature of the kerosene at the time of quenching of each sample is listed with the melt data in the section on results.

The helium entering the Isolator/Lab flowed over a desiccant of calcium chloride, and bubbled under a given head of water, a head of 2 inches for melt 14 and 0.5 inches for the rest of the melts, 15 through 33.

After a number of samples were extracted, the remainder of each crucible melt was allowed to cool in the furnace in the Isolator/Lab atmosphere of helium, and this material was then included as one of the samples for analysis.

Samples were preserved in a desiccator containing calcium chloride as the desiccant.

B. Unsuccessful Methods for Preparing Samples

The specimen mount used in this investigation, and which is also most widely used in this country, consists of a grid provided with holes small enough to support very thin films and large enough to give an optimum sized unobstructed field at low magnification. For most purposes, satisfactory openings were provided by a grid having a count of 200 openings per linear inch. Electroplated grids of copper and nickel, woven wire grids of stainless steel, which cannot be electroplated, and many special-purpose grids were available. The copper and stainless steel grids were obtained either cut-to-size, approximately 3 mm in diameter, or in sheet form which measured 5 to 6 inches on a side. The stainless steel grid is thicker and more resistant to chemical attack than the copper grid, but because of weave convolutions, it has the disadvantage of providing a poor support for the thinnest films.

Usually, the specimen which is mounted on a grid consists of (1) particles suspended in or on a thin film; (2) an ultra-thin section of the sample material; (3) replicas of the sample. These thin films and replicas may be composed of plastics or evaporated inorganic materials (such as SiO, Cr, or C). In this investigation, numerous methods for preparing and mounting specimens of the sample material have been tried, some of which will be briefly mentioned.

1. Particle Suspensions. The examination of specimens of suspended and dispersed sample material gave rise to complications, such as contamination, poor resolution and contrast, and agglomeration of particles, which resulted in insufficient data for warranting further use of these methods at this time.

One technique used for mounting the suspended material was to let an air dispersion of the powdered material settle over a dry film or substrate mounted on a grid, whereby the particles are supposedly held to the substrate by electrostatic attraction; another method involved applying a drop of an aqueous dispersion of the material to the substrate with a medicine dropper. One of the disadvantages in using an aqueous dispersion resulted from contamination caused by the cadmium chloride, which is very soluble in water; also, there is no proof that the sought cadmium particles would not be chemically altered. Substrates on which these particles were placed consisted of evaporated carbon or plastic films. The carbon is much more resistant to the electron beam, but it readily breaks up when a drop of water is placed on it. The plastics used were 1- or 2-percent solutions of Parlodion (nitrocellulose) in amyl or butyl acetate and Formvar (polyvinyl formal) in dioxane or ethylene dichloride. A satisfactory thickness for the plastic substrates is probably about 200 A.

Another method involved grinding the material in a solution of Formvar in dioxane and then forming a thin film from this plastic for mounting on a grid. With this method the contrast and resolution from the embedded particles were poor, and it was not possible to employ the shadow-casting process.

2. Polishing Techniques. Metallographic polishing techniques were unsuccessfully applied for preparing smooth sample surfaces which could be replicated free of artifacts.

The samples were mounted in Bakelite, Lucite, or a casting to facilitate handling of sample material during grinding and polishing. The grinding involved four individual stages through 240, 320, 400, and 600 grit, wet abrasive papers. Water could not be used as the grinding lubricant because of its chemical attack on the cadmium and lead chloride sample material. Also, the material readily clogged the dry abrasive papers. Some success was attained by using ethyl alchol as a lubricant for the lead chloride samples, but the solubility of the cadmium chloride in alchol discouraged the use of this lubricant. The most suitable lubricant found for grinding both types of sample material was a solution of paraffin dissolved in kerosene.

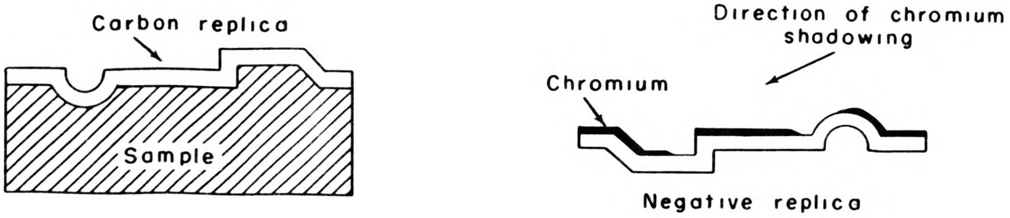
Polishing was performed on a bronze-disk polishing lap with a metcloth or a nylon cloth. Such polishing abrasives as diamond dust, of about 0.25 and 6 micron particle sizes, and alumina (Linde, grades A and B) were used. The diamond dust abrasive was not suitable because it readily embedded in the soft sample materials. From observations made under an optical microscope, the Linde B used with a solution of paraffin in kerosene appeared to give a nicely polished surface, but replicas made from the polished material always showed the presence of much foreign material.

3. Thin Sections. Very little consideration was given to preparing the material by means of thin sectioning, mainly as a result of numerous failures which have been encountered by other investigators in

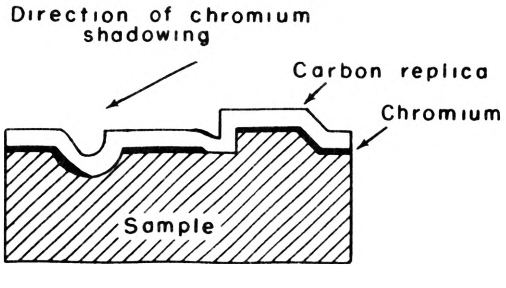
trying to cut thin sections of other materials of a similar nature. The cadmium chloride samples exhibited good basal cleavage, and an attempt was made to obtain thin sections parallel to this cleavage by repeated stripping with adhesive tape, as has been employed for obtaining thin sections of talc.[26] The few thin sections which were obtained by this method proved to be of no value. In sections that were thin enough for examination, the action of the electron beam in the microscope tube readily disintegrated the material.

C. Successful Methods for Preparing Samples

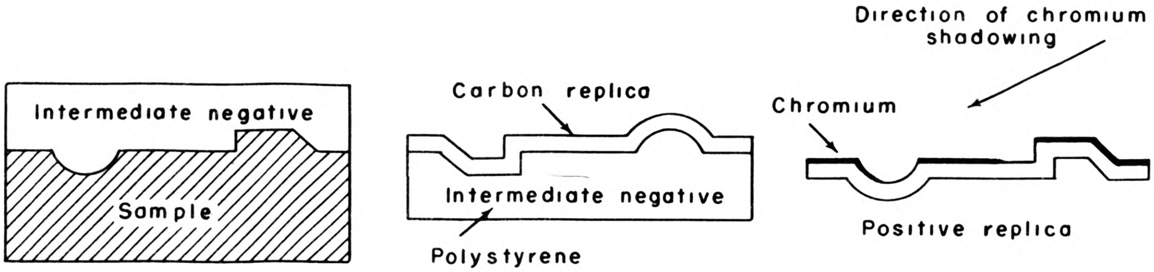
1. Replicas. Because of the difficulty encountered in trying to examine some materials directly by transmission, numerous replicating techniques have been developed. These techniques are all basically the same in that they depend on a film of varying thickness to provide a representation of the surface. A negative replica is made by applying a plastic or an evaporated inorganic film to the surface, and when the film is separated from the surface, it will show the heights and depressions as reversed with respect to the original surface. A positive replica is made by replicating an intermediate negative replica, and this positive shows the heights and depressions as they are on the original surface. Figure 7 depicts some of the stages during the negative and positive replicating technique. One of the advantages of the positive replica is that the intermediate negative replica can be quite thick for allowing easier separation from the sample, and then the intermediate negative can be dissolved away from the final positive.



(a) Shadowed negative replica



(b) Pre-shadowed negative replica



(c) Two-stage or positive replica

FIGURE 7
Development of Negative and Positive Replicas.

Both negative and positive replica techniques have been tried during the course of this investigation. The advantages and disadvantages of one over the other depend largely on the physical and chemical nature of the surface being replicated; when a new substance is examined, some variation in standard technique may be required. The techniques described below have all been applied during this investigation. Many of these which did not give satisfactory replicas could possibly have been employed with some degree of success if sufficient time were taken to work out the details of a particular technique and if the time required for preparing replicas were not of considerable importance.

The fractured surfaces of the cadmium chloride and lead chloride samples were quite rough, and conventional techniques for stripping thin films of plastic and evaporated materials could not be readily used. Plastic films such as those of Formvar, which are normally about 600 A thick for negative replicas, are not nearly as stable in the electron beam as are evaporated carbon replicas. Also, the shape of plastic replicas may be readily altered in the process of stripping and shadowing. Some thin plastic replicas were stripped from the samples by reinforcing the replicas with a backing layer of another plastic, chosen so that it could be dissolved in a solvent which would not dissolve the negative plastic replica. For example, the Formvar negative replica is not soluble in butyl acetate or water, and the backing layer was formed with either Parlodion, which dissolves in butyl acetate, or with polyvinyl alcohol, which dissolves in water. The main difficulty with this technique was that of removing all traces of the backing layer.

Another variation tried with plastics was to make a thick plastic replica of the sample which could be removed by stripping; with cadmium chloride samples, the plastic was removed by dissolving the sample in water. This replica was shadowed with chromium and coated with an evaporated carbon film approximately 100 A in thickness. With the carbon film up, it was then placed in a suitable solvent for removing the plastic. This technique did not prove very feasible, in that all traces of the plastic could not be removed without causing disintegration of the carbon film or positive replica.

The most successful technique found for replicating the cadmium chloride samples was that of producing a negative carbon replica. The samples, which were obtained by breaking off 1/2-inch sections from the Vycor extraction tube samples, were mounted vertically on a glass slide with a soft vacuum wax (Apiezon Q) to hold them in place. The sample material was pushed up inside each section of Vycor tubing until the fractured surface was even with the top of the tubing. This step was of importance in preventing the formation of a carbon film on the sides of the sample which would tend to contaminate the replica during subsequent stages of its removal. The mounted samples were placed in the vacuum coater and shadowed with evaporated chromium, followed with the evaporation of a carbon coating or negative replica.

Upon removal from the coating chamber, a sample was pushed out of the section of Vycor tubing and immersed in distilled water for removal of the replica by dissolution of the sample. During dissolution, swelling of the sample tended to break the replica into numerous fragments which floated on the water surface. To minimize this breakage, a saturated aqueous solution of calcium chloride was used, instead of the distilled water for slowing down the dissolution rate of the sample. However, the added advantage of using the saturated solution was offset by breakage caused during the additional washing which was required to remove all traces of the calcium chloride. The replica was readily washed in a Buchner type funnel which had a stopcock fitted to the stem. Hence, the sample rested on the perforated filter plate of the funnel until it was completely dissolved, and fresh distilled water was added at the top of the funnel while the used solution was drained through the stem. The washed replica fragments were dipped out of the water on grids for examination with the electron microscope.

The lead chloride samples were shadowed and replicated in the same way, but no suitable solvent was found for dissolving the samples away from the replicas. If the samples were allowed to stand in distilled water for a period of about 24 hours, it was sometimes possible to loosen a few fragments of the replicas, although these fragments were usually void of the rougher features of the fractured surface.

The technique which finally was most feasible consisted of applying a parting layer before shadowing the samples. Boron trioxide and Victawet have each been evaporated on samples as parting layers without any success. Recent investigators[27] introduced the use of sodium metaphosphate for Victawet. With this material, it was usually possible to remove the replicas after the samples had been standing in the distilled water for a few hours. The selection of a suitable evaporating source for giving a uniform parting layer of a desirable thickness on the fractured lead chloride samples still presents a problem.

2. Vacuum Evaporation. Vacuum evaporation was used to prepare

solid films on the sample material. When the vapor source is intentionally situated so that the evaporated material is deposited perpendicular to a sample surface, the process is referred to as vacuum coating; and when the material is deposited obliquely on a sample, the process is referred to as shadowing or shadow casting. An ultimate vacuum of between 3 and 7 microns was achieved during these evaporation processes.

The filament vapor source for evaporating the chromium was a conical basket formed from 20 mil tungsten wire. This type of filament works very well for evaporating chromium in the pellet form, and for all practical purposes, it may be classified as a point source type. The filament was placed about 5 inches from the sample, and orientated in such a manner that the vapor was deposited at an angle of approximately 60 degrees to the surface of the sample. (This angle was not determined accurately because the rough nature of the sample surface precluded measuring the height of objects from the shadow lengths.) Pellets of chromium of approximately 20 mg were selected for use in the filament, and by experience a current-versus-time value was determined for producing shadow films of optimum thickness. For establishing this optimum thickness, for which about 10 mg of the chromium pellet were required, the films were examined in the electron microscope.

Usually, the carbon evaporation followed the shadow-casting process; therefore, it was not necessary to open the vacuum chamber between the shadowing and carbon-coating processes. Carbon rods 1/8 inch in diameter were used for electrodes in the carbon-evaporation apparatus. The end of one of these rods was reduced to 0.05 inch in diameter for a length of 3/8 inch, while one end of the other carbon rod was square. The reduced length of carbon was found to be of sufficient size for producing a carbon replica of desirable thickness on most of the samples. The reduced end of one carbon rod and the square end of the other were held in contact by a spring under tension and attached to the moveable electrode holder. During evaporation of the carbon, current to the carbon electrodes was increased until an arc was generated at the point of contact; it was then held constant until the reduced length of carbon had been consumed, at which time the carbon evaporation ceased.

When an evaporated parting layer was used on the lead chloride samples, it was necessary to open the vacuum coater to arrange the electrodes for the final or replicating process, because the vacuum coater contained only two pairs of electrode terminals. The vapor sources were arranged in the vacuum coater so that after the parting layer of sodium metaphosphate was deposited vertically on the sample surface, the sample could be chromium shadowed. The coating chamber was then opened, and the sample was removed to avoid contamination by foreign material as the apparatus was prepared for the carbon evaporation. For a parting-layer filament vapor source, a tungsten ribbon filament approximately 1.5 inches long and 0.25 inch wide was used. One small drop of the sodium metaphosphate, in the form of a paste containing 25 percent water, was smeared on this ribbon filament with a needle. The filament was positioned about 4 inches above the sample with the parting material facing the sample.

D. Recording the Replica Image

Observation of an image formed on the screen of the electron microscope was made in a dark room. Even after the eyes are adapted to the darkness of the room, it is essential to make a compromise between having a high electron-beam intensity, which provides a sufficiently well illuminated screen image to the unaided eye, and having a low electron-beam intensity, which is less likely to destroy the specimen or to overexpose the film.

The correct film exposure was estimated by experience from the screen brightness, and exposures usually ranged between 1 and 5 seconds. For all practical purposes, a lower exposure limit of 0.5 second is imposed by the manually operated camera shutter, and an upper limit of 10 seconds is imposed by electrical variations in the electron optical system.

During the handling of the film, the darkroom was illuminated with a deep-red safelight. After the film was removed from the electron microscope it was developed in a daylight roll-film developing tank. The standardized procedure used for developing the film consisted of frequent agitation for 5 minutes in the developing solution, 1 minute in the acid stop, and 10 minutes in the fixer. The negative was then washed for approximately 30 minutes in running water, rinsed with a photoflo solution, and allowed to hang in air until dry.

Details of exposures on each roll of film were consecutively recorded in a log book, and after the film was developed, negatives were permanently numbered.

Enlargements of selected 35 mm negatives were made on 5x7-inch sheet film. Thus it was not necessary to handle a roll of negatives for producing a particular photograph, and the final prints made from these enlargements appeared as negatives, which are sometimes desirable for viewing photographs of shadowed specimens.

The exposure time for the 5x7-inch film was maintained constant at 1.5 seconds, while the light intensity of the enlarger was adjusted so as to produce a consistant visual brightness for each negative. The film was processed in open-top tanks with chemical reagents recommended by the film manufacturer.

V. RESULTS OF INVESTIGATION

The equilibrium temperature and quenching temperature used for producing each of the samples are given in Table 1. Microstructure data were obtained for some of these samples, but the remaining samples were consumed during the search for a suitable method for sample preparation.

The limits of error for the Chromel-Alumel thermocouple used in this investigation were ± 3/4 percent for temperatures of 277 to 1260° C.

The temperature of each chloride melt was recorded with the thermocouple tube resting in the bottom of the melt crucible. A calibration for determining the temperature gradient in a lead chloride melt showed that the maximum temperature was obtained at the center of the melt, which was 2.5 inches from the bottom. For example, if a melt measured about 600° C at the bottom, the temperature at the center of the melt would be about 4 percent higher, or 624° C, and the temperature 0.5 inches from the top would measure 600° C, or the same as that measured at the bottom.

Chromium, palladium, gold, silver, and platinum were used for shadowing metals. Chromium shadowing had good resistance to chemical attack, and displayed good contrast and resolution to the replicas. The palladium shadowing was less chemically resistant. Portions of the gold and silver shadowed films became detached from the carbon replicas, thus presenting a poor specimen for examination. Because of poorly designed vapor filament, the platinum did not give reproducible shadowing.

TABLE I

List of Samples

Sample No.	Composition	Temp. °C	Quenching Temp.°C	Quenching Medium	Remarks
1	Cd-$CdCl_2$	600	RT*	air	sample in 17-mm OD tube
2	Cd-$CdCl_2$	600	0	ice water	"
3	$CdCl_2$	647	RT	air	sample in 7-mm OD tube
4	$CdCl_2$	606	RT	air	"
5	Cd-$CdCl_2$	700	RT	air	"
6	Cd-$CdCl_2$	700	RT	air	"
7	Cd-$CdCl_2$	750	RT	air	"
8	Cd-$CdCl_2$	650	RT	air	"
9	Cd-$CdCl_2$	550	RT	air	"
10	Cd-$CdCl_2$	650	RT	air	sample in 17-mm OD tube
11	Cd-$CdCl_2$	600	RT	air	"
12	Cd-$CdCl_2$	600	RT	air	"
13	Pb-$PbCl_2$	515	RT	air	sample in 25-mm OD tube
14	$CdCl_2$	620	30	helium	sample in 7-mm OD tube
15	$CdCl_2$	591	32	helium	"
16	Cd-$CdCl_2$	561	35	helium	"
17	Cd-$CdCl_2$	602	37	helium	"
18	Cd-$CdCl_2$	644	39	helium	"
19	Cd-$CdCl_2$	644	---	cooling furnace	sample in 25-mm OD tube

TABLE I (continued)

List of Samples

Sample No.	Composition	Temp. °C	Quenching Temp.°C	Quenching Medium	Remarks
20	Cd-$CdCl_2$	652	32	helium	sample in 7-mm OD tube
21	Cd-$CdCl_2$	654	-3	kerosene	"
22	Cd-$CdCl_2$	712	39	helium	"
23	Cd-$CdCl_2$	712	0	kerosene	"
24	Cd-$CdCl_2$	690	39	helium	"
25	Cd-$CdCl_2$	690	39	helium	"
26	Cd-$CdCl_2$	690	--	furnace	sample in 25-mm OD tube
27	$PbCl_2$	700	30	helium	sample in 7-mm OD tube
28	Pb-$PbCl_2$	570	36	helium	"
29	Pb-$PbCl_2$	532	-15	kerosene	"
30	Pb-$PbCl_2$	532	37	helium	"
31	Pb-$PbCl_2$	720	-10	kerosene	"
32	Pb-$PbCl_2$	720	37	helium	"
33	Pb-$PbCl_2$	720	--	cooling furnace	sample in 25-mm OD tube

*Room temperature

No significant success was achieved in using plastic materials for preparing replicas of the fractured surfaces. The thickness of the carbon replicas was easily controlled, and they seemed to be the most feasible for examining the fractured surfaces.

A. Micrographs of Cadmium Chloride Samples

Table II lists the smallest and largest particle diameters observed on micrographs of the different samples.

Figure 8 depicts typical structure of the fractured surface of pure cadmium chloride from sample 15, which had been cooled by quenching from 591° C to 32° C in helium. Some features of the high surface relief show triangular arrangements. The microstructure in Figure 9 shows the fractured surface on another portion of sample 15.

Figures 10, 11, and 12 are micrographs of fogged samples, and are void of visible particles of the dispersed phase. Figures 10 and 11 represent the structure of sample 1, which was prepared in an atmosphere of air at room temperature and quenched in a 17-mm OD Vycor test tube from 600° C to room temperature in air. The triangular shapes shown in these two figures have angles that measure approximately 60 degrees. Figure 12 represents the structure of sample 20, which had been quenched from 652° C to 32° C in helium.

The micrographs in Figures 13 through 17 show particles of the dispersed phase in sample 1. The spherical particles in Figure 13 range from 0.8 to 3.7 microns in diameter, and each displays one well developed facet, with other facets at different stages of development. Figures 14 and 15 show the orientation of the facets on the particles with respect to the hexagonal angles exhibited by the fractured surface

TABLE II

Range of Particle Diameters in Cadmium-Cadmium Chloride

Sample	Temp. °C	Quenching Temp. °C	Number Particles Observed	Apparent Diameter of Particles in Microns	
				Smallest	Largest
1	600	room temperature	92	0.57	6.1
2	600	0	119	0.67	3.0
5	700	room temperature	8	0.8	1.4
26	690	furnace	8	2.3	6.7
22	712	39	250	0.2	3.6
24	690	39	20	0.75	3.4
18	644	39	5	1.2	2.7
17	602	37	2	1.4	4.0
16	561	35	10	0.31	1.3
23	712	0	100	0.13	2.7
21	654	-3	170	0.13	2.4

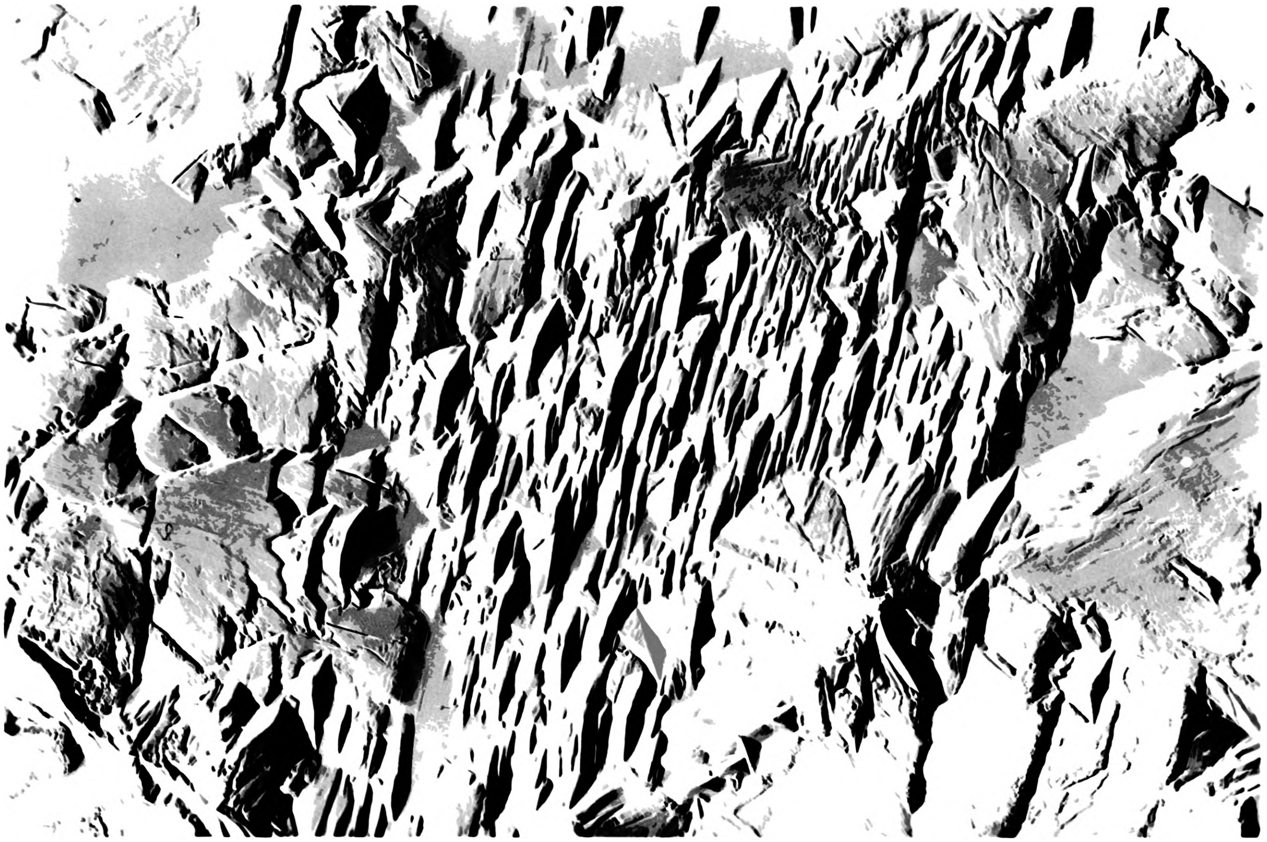


FIGURE 8

Electron Micrograph of the Fractured Surface of Cadmium Chloride; Sample 15; Quenched From 591° C to 32° C in Helium; 5,000X.

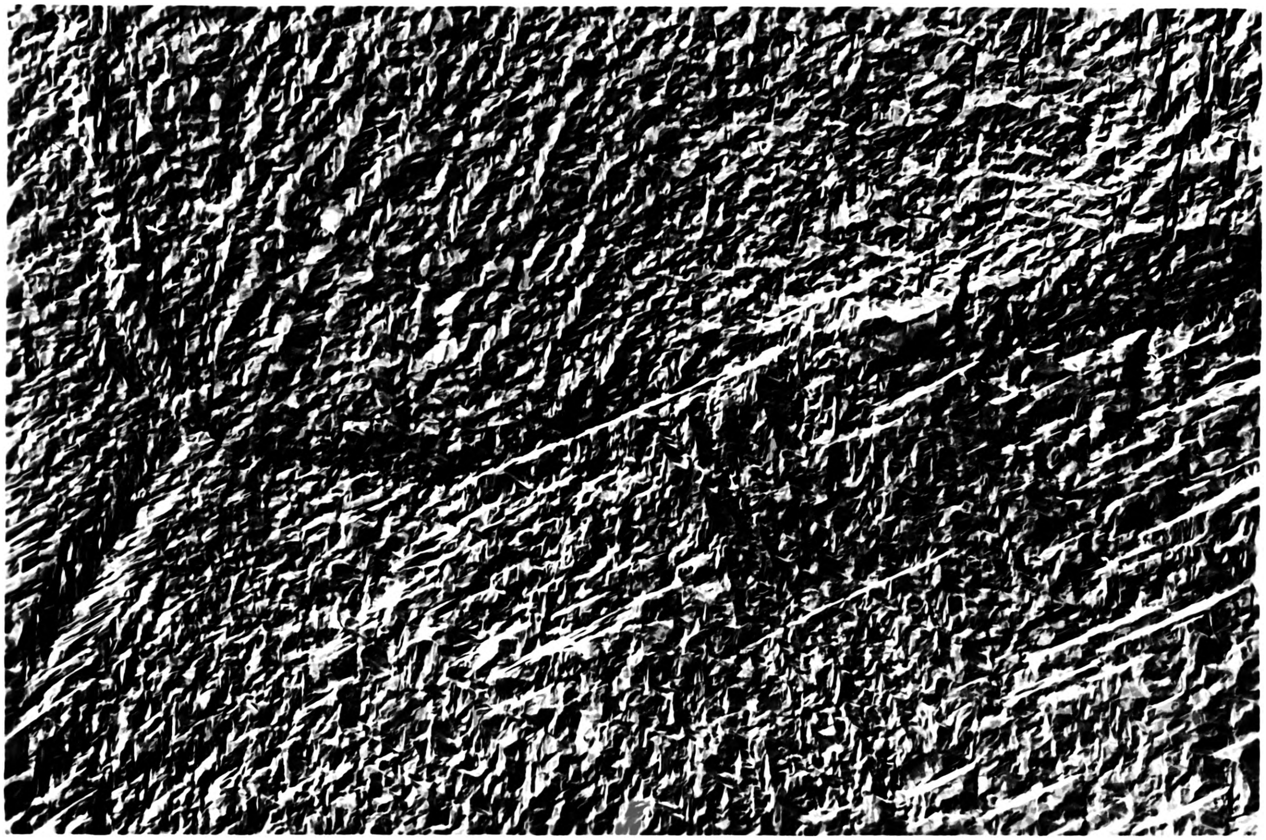


FIGURE 9

Electron Micrograph of the Fractured Surface of Cadmium Chloride; Sample 15; Quenched from 591° C to 32° C in Helium; 5,000X.

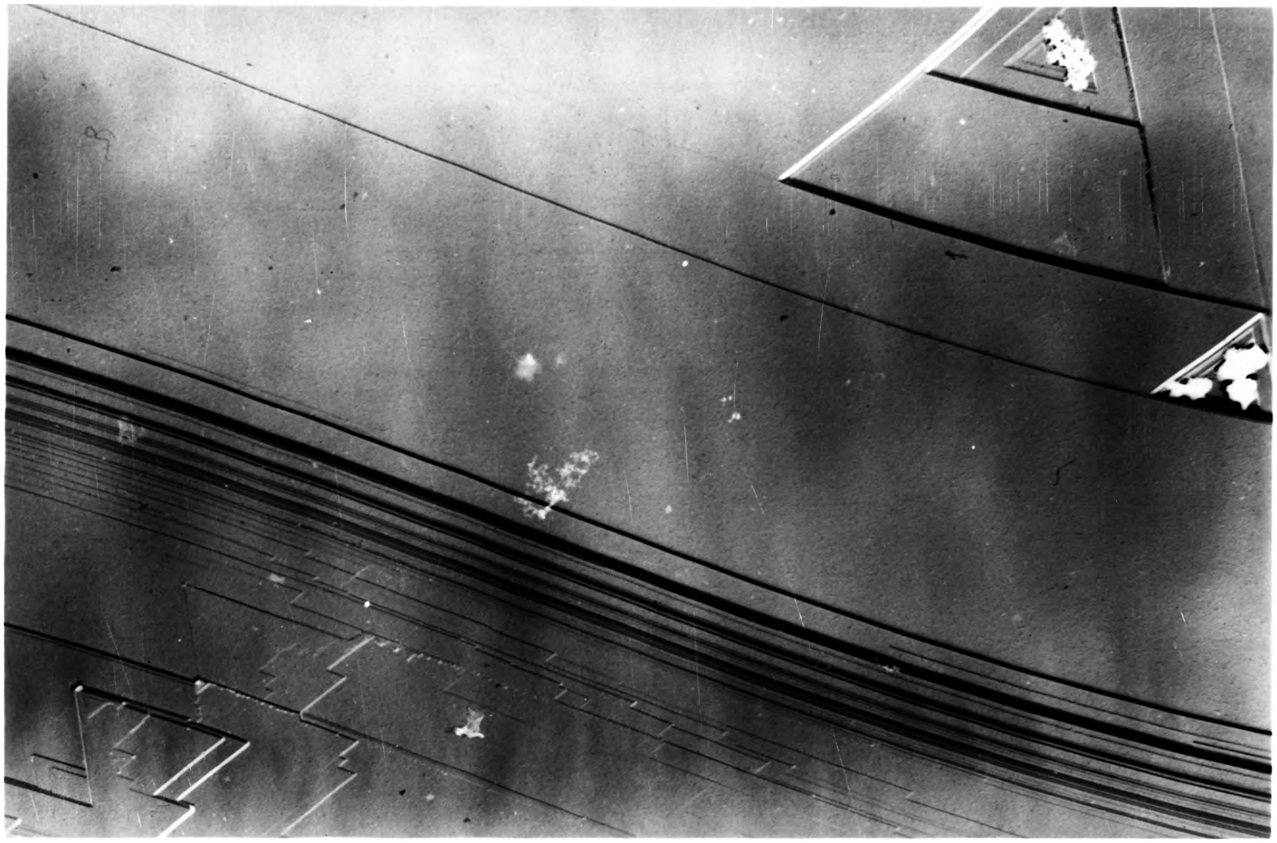


FIGURE 10

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperature in Air; 6,250X.

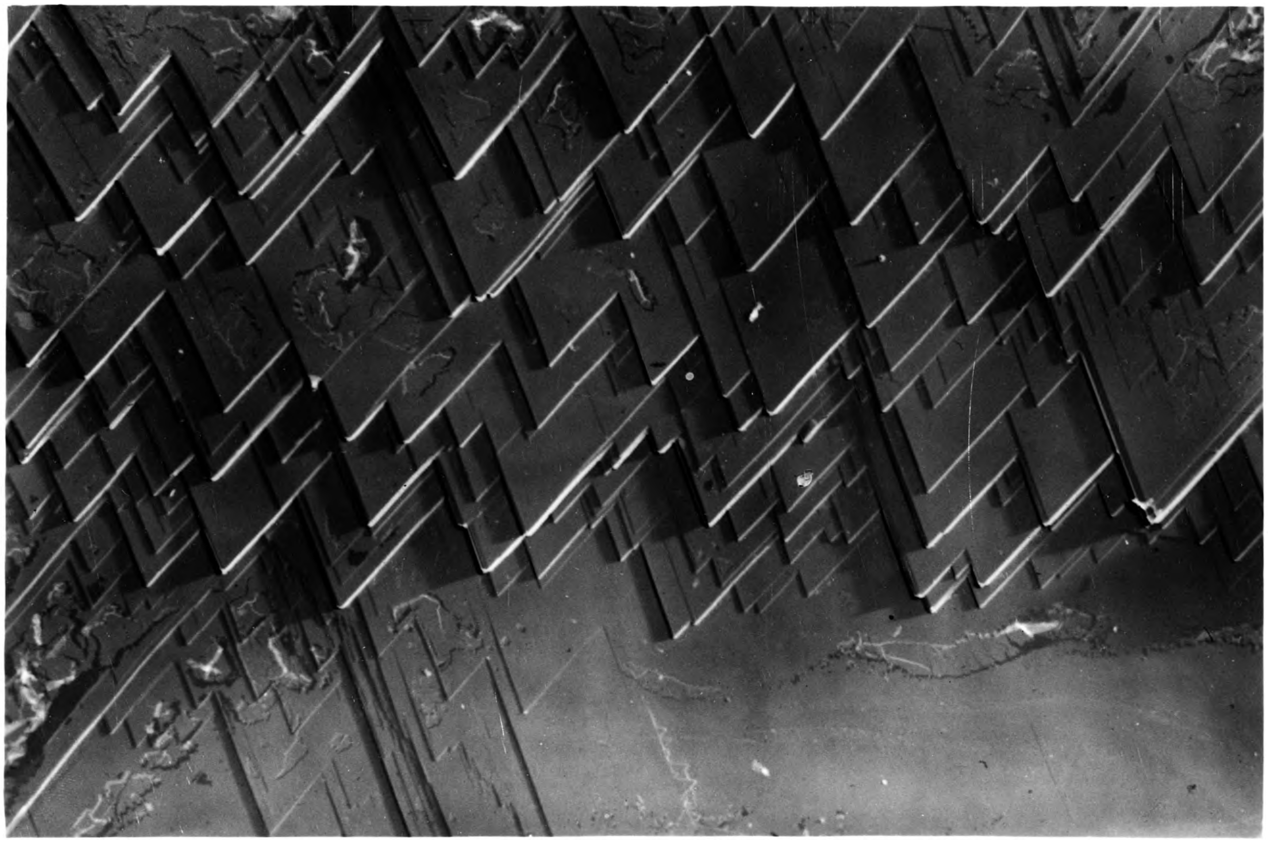


FIGURE 11

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperature in Air; 5,000X.

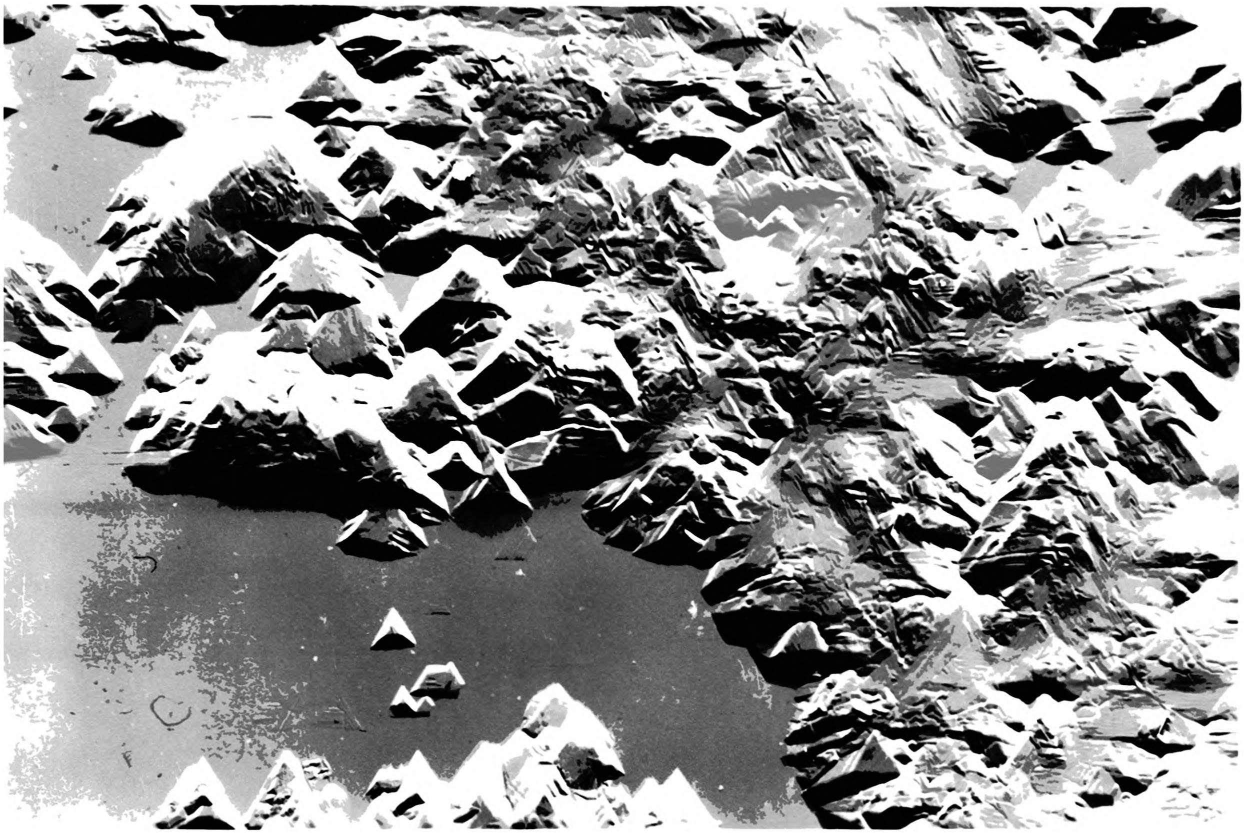


FIGURE 12

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 20; Quenched From 652° to 32° C in Helium; 5,000X.

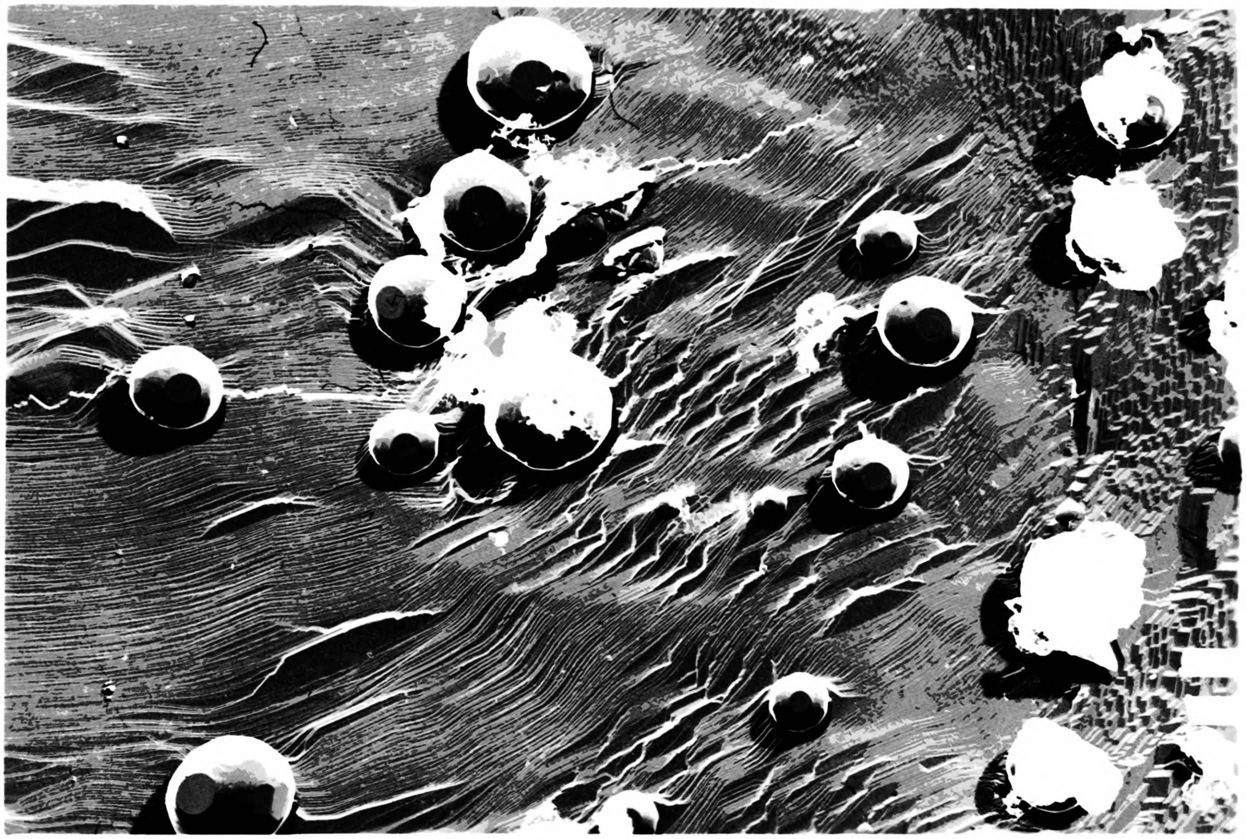


FIGURE 13

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperature in Air; 4,375X.

FIGURE 14

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperatures in Air; 6,250X.

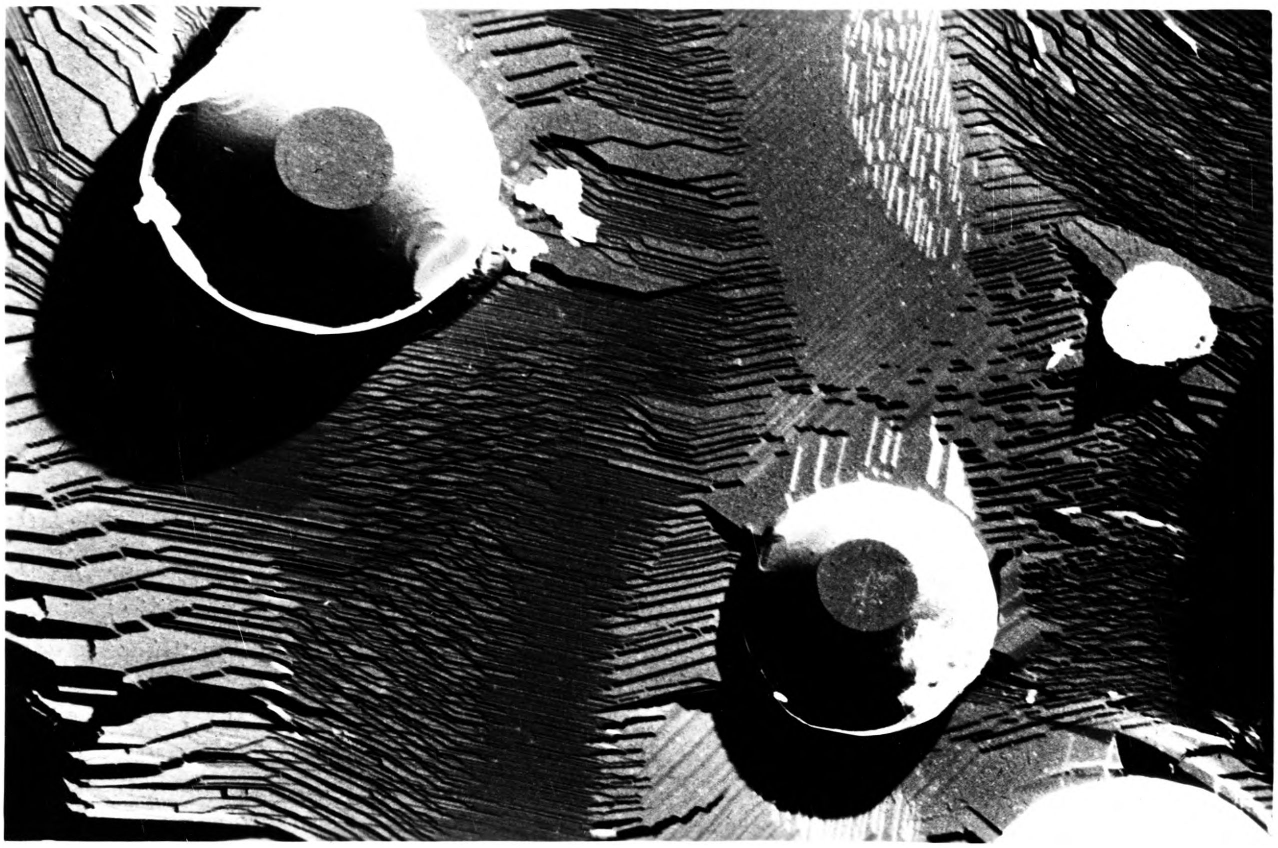


FIGURE 15

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperature in Air; 10,000X.

FIGURE 16

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched from 600° C to Room Temperature in Air; 5,000X.

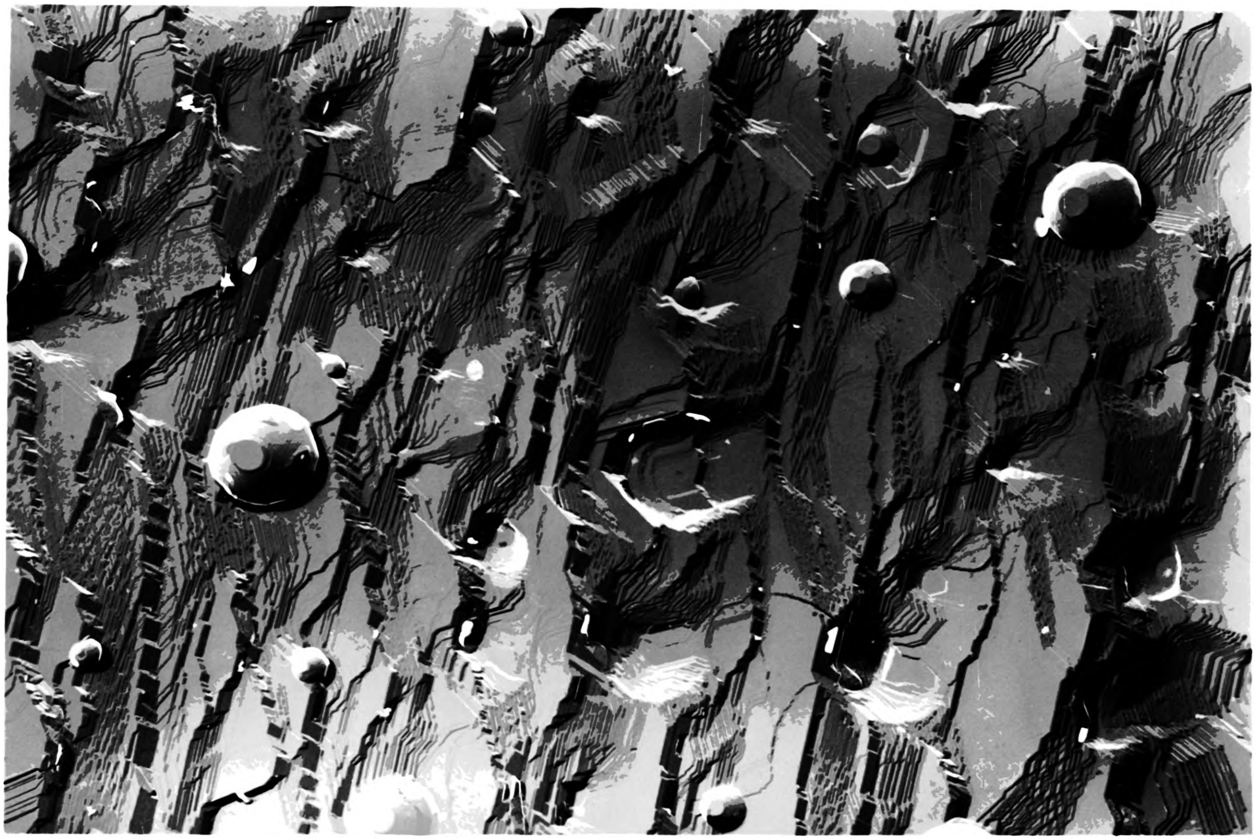


FIGURE 17

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 1; Quenched From 600° C to Room Temperature in Air; 5,000X.

structure. The facets on the particle shown in Figure 16 depict a hexagonal symmetry, and it appears that the lines of intersection of these projected facets with the surface would define a hexagonal arrangement aligned with that of the surface. Figure 17 shows particles ranging from about 0.6 to 2.7 microns in diameter. Certain facets on each of these particles seem to be orientated in the same direction, and the apparent hexagonal symmetry of the particles tends to be aligned with that depicted by the fractured surface. The surface structure does not show any changes in relief that would be indicative of a grain boundary.

The micrographs in Figures 18 and 19 represent different portions of sample 22, which was quenched from 712° C to 39° C in helium. Figure 18 depicts a surface densely populated with particles that appear to be sitting on surface relief of approximately uniform elevation. A light-colored ring or halo encircles most of these particles. Figure 19 shows the microstructure of a rough surface which contains particles of various sizes.

Figures 20 through 22 are micrographs of sample 23, which was quenched from 712° C to 0° C in kerosene under a helium atmosphere. Figure 20 shows numerous particles located along an abrupt change in the surface structure. Features of these particles are not clearly defined; however, a large range of particle sizes can be noted. Figures 21 and 22 overlap the same area. The particles range from about 0.2 to 2 microns in diameter. With the exception of one particle in Figure 21, all the particles in this overlapped area appear to be situated on the elevated relief of the fractured surface, and most of them form a row with the particles of smaller diameter at the ends.

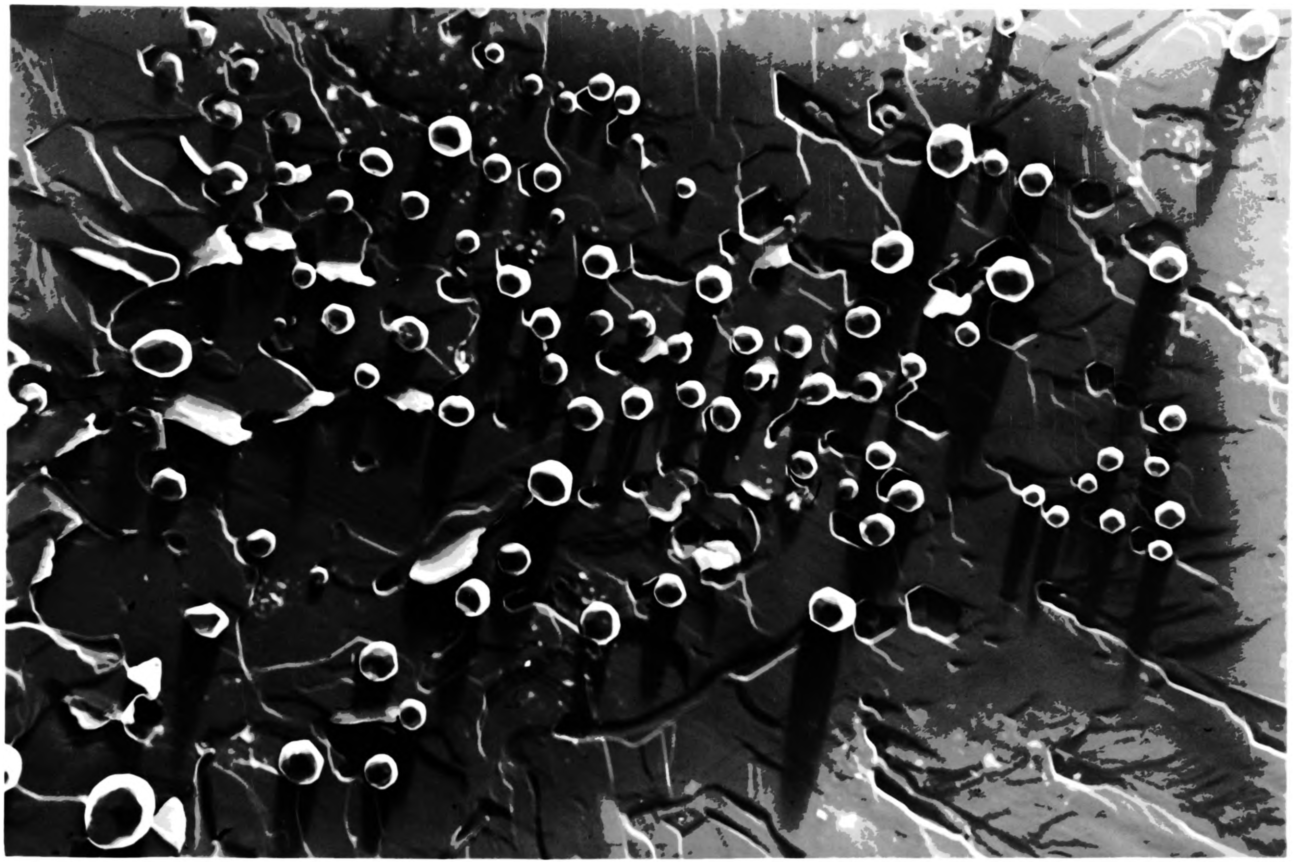


FIGURE 18

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 22; Quenched From 712° C to 39° C in Helium; 6,250X.

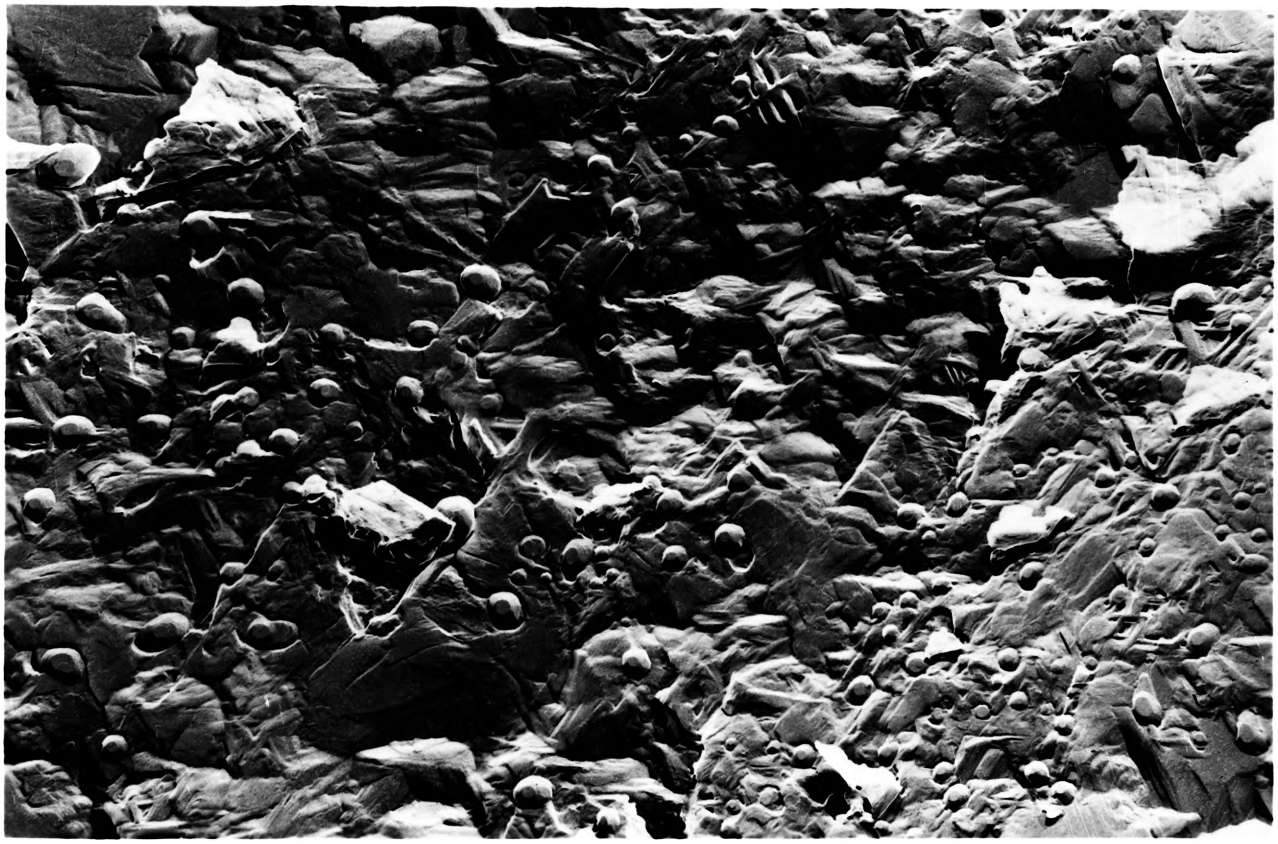


FIGURE 19

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 22; Quenched From 712° C to 39° C in Helium; 6,250X.

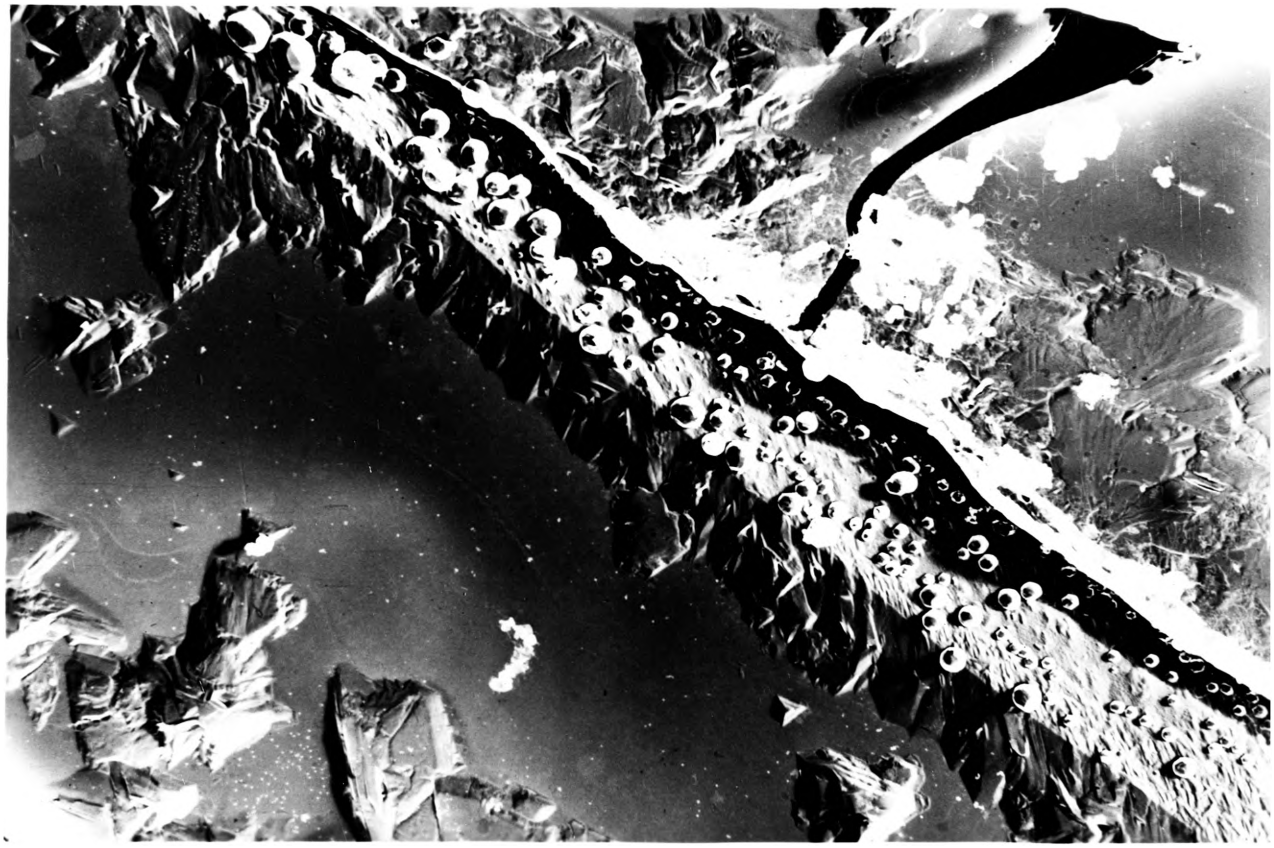


FIGURE 20

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 23; Quenched From 712° C to 0° C in Kerosene Under a Helium Atmosphere; 5,000X.

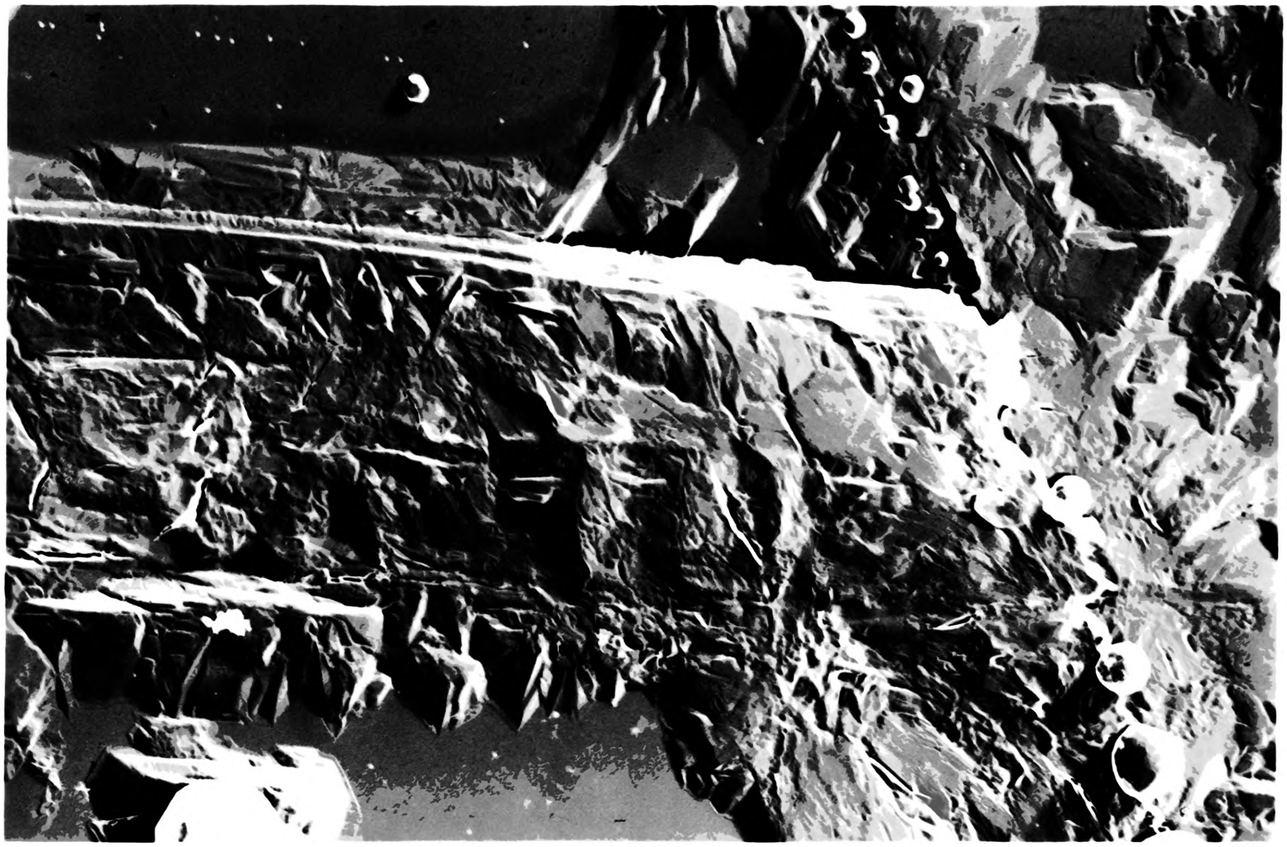


FIGURE 21

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 23; Quenched From 712° C to 0° C in Kerosene Under a Helium Atmosphere; 8,000X.

FIGURE 22

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 23; Quenched From 712° C to 0° C in Kerosene Under a Helium Atmosphere; 5,000X.

Figures 23 through 25 are micrographs of sample 21. This sample was quenched from 645° C to -3° C in kerosene under a helium atmosphere. Figure 23 shows a row of particles each of which has an almost characteristic diameter size of 0.4 microns. Adjacent to this row is a group of randomly located particles which exhibit large variations in particle sizes. Figure 24, at a high magnification, shows the hexagonal symmetry of this group. Figure 25 contrasts the difference between the large spherical particle and the small hexagonal particles in the row. The large particle has a 1.2-micron diameter, whereas the diameter of the smallest particle in the row is about 0.13 microns.

B. Micrographs of Lead Chloride Samples

Figures 26 and 27 are micrographs of sample 32. This sample was quenched from 720° C to 37° C in helium. Both these micrographs show irregular surface relief which was often noted on the lead chloride samples.

Figures 28 through 30 are micrographs of sample 31. This sample was quenched from 720° C to -10° C in kerosene under a helium atmosphere. Figure 28 shows a spherical particle which measures 2.8 microns in diameter. Figure 29 shows rounded relief features and a row of irregularly shaped particles. Figure 30 appears to be void of surface structure, but it shows a spherical particle which measures 1.0 microns in diameter.

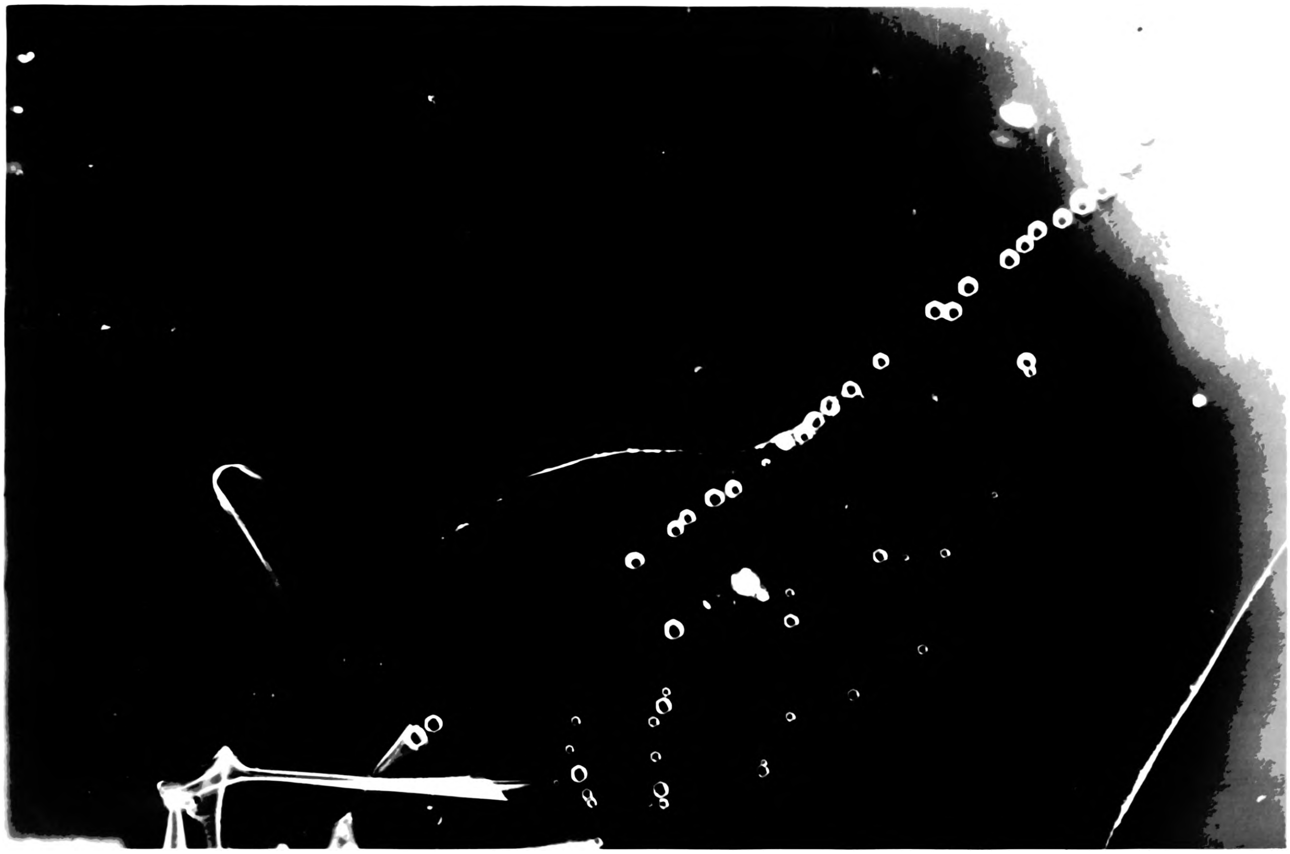


FIGURE 23

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 21; Quenched From 654° C to -3° C in Kerosene Under a Helium Atmosphere; 5,000X.

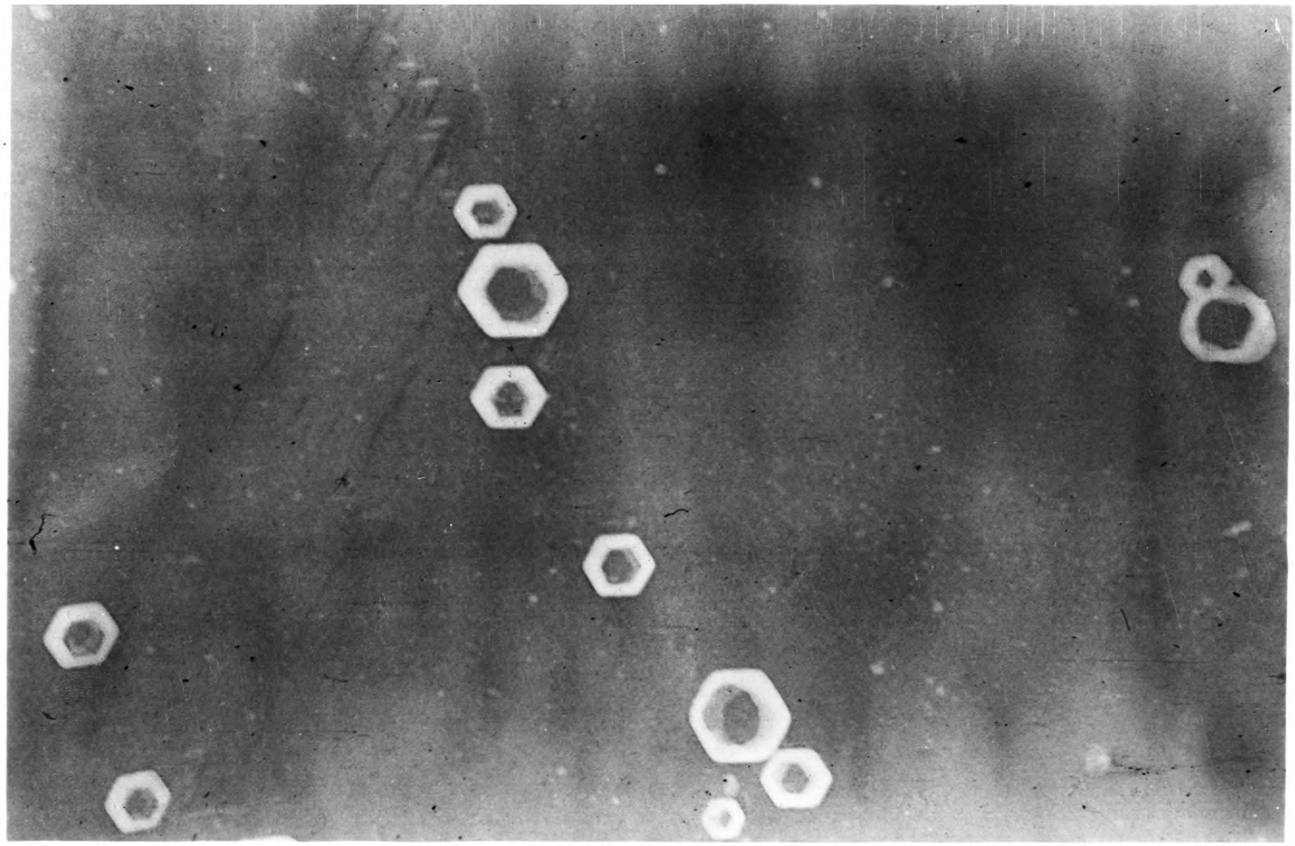


FIGURE 24

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 21; Quenched From 654° C to -3° in Kerosene Under a Helium Atmosphere; 25,000X.

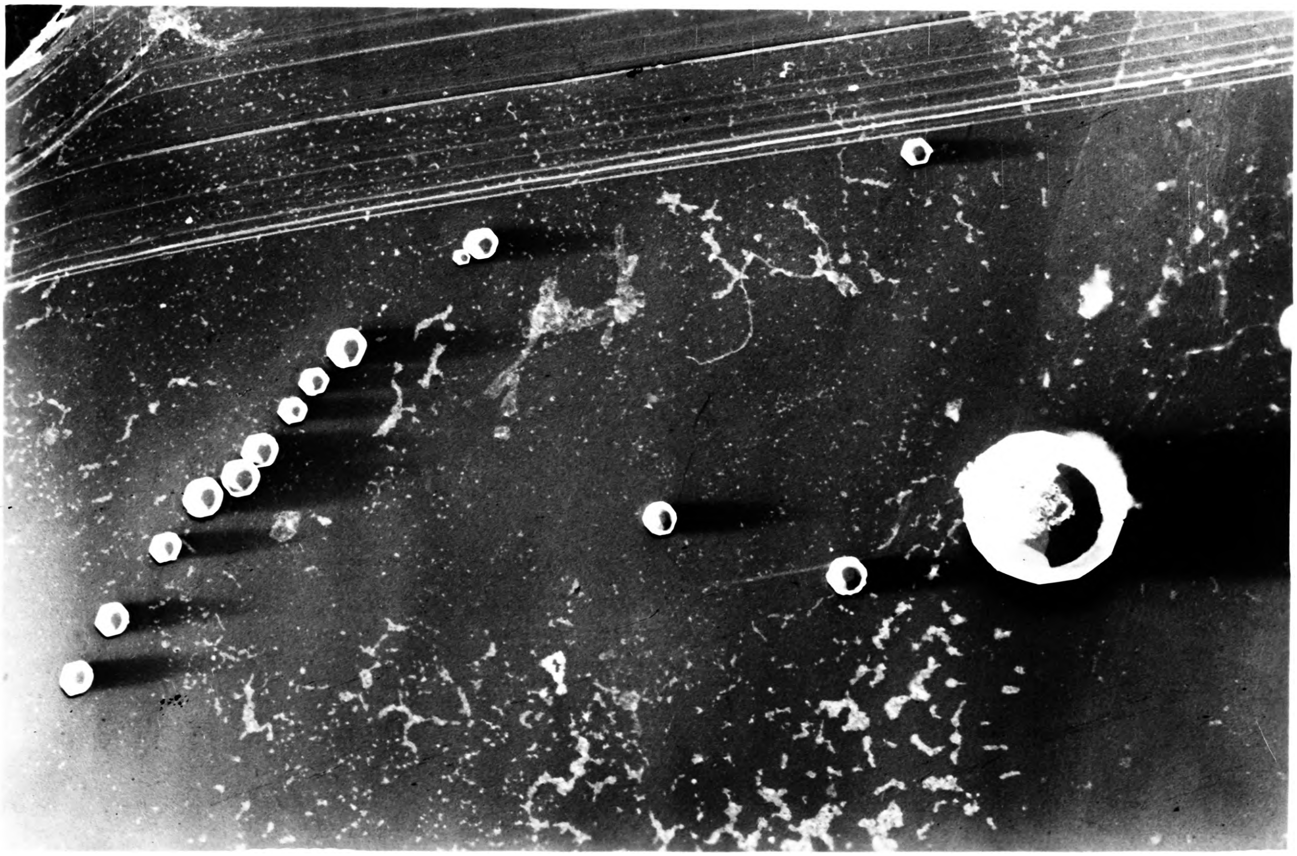


FIGURE 25

Electron Micrograph of the Fractured Surface of Cadmium-Cadmium Chloride; Sample 21; Quenched From 654° C to -3° C in Kerosene Under a Helium Atmosphere; 15,000X.

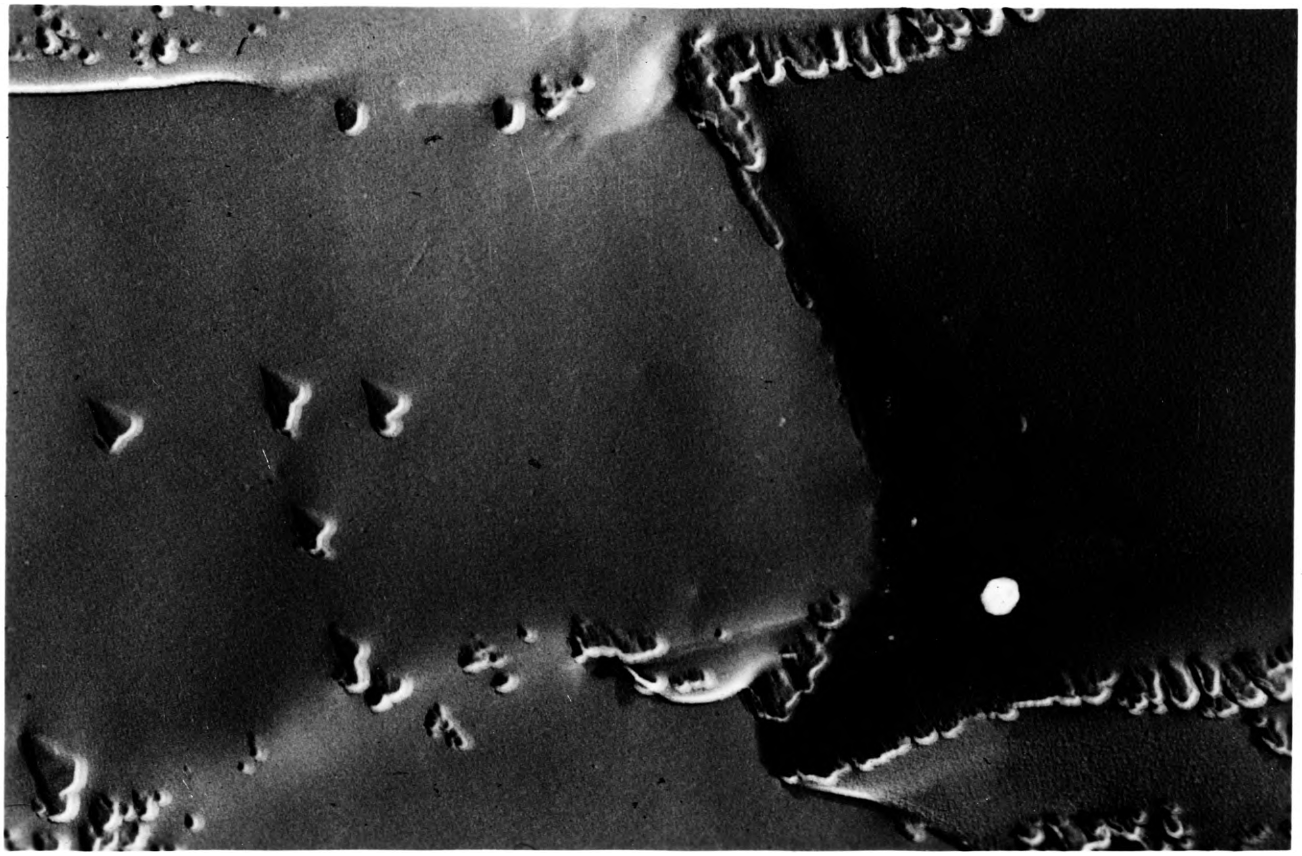


FIGURE 26

Electron Micrograph of the Fractured Surface of Lead-Lead Chloride; Sample 32; Quenched From 720° C to 37° C in Helium; 40,000X.

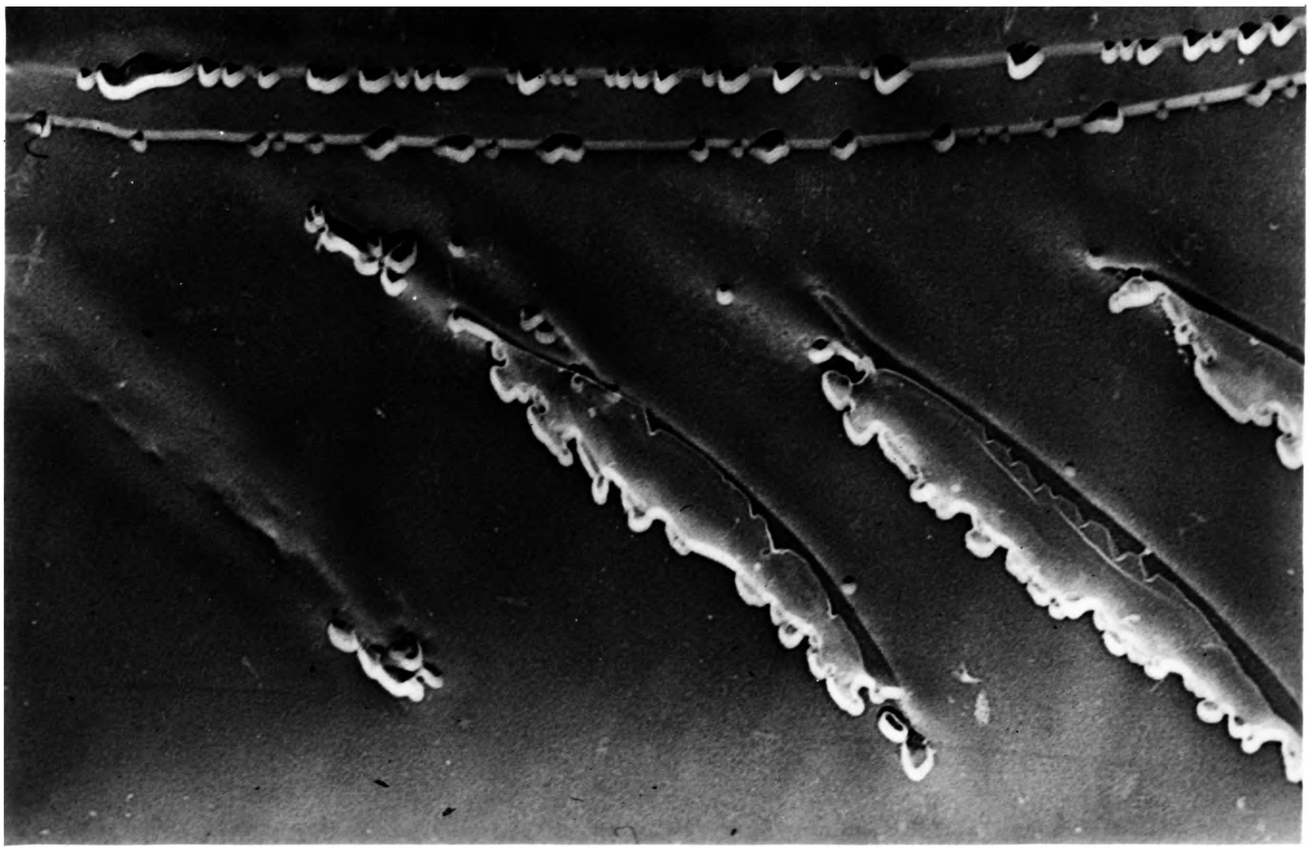


FIGURE 27

Electron Micrograph of the Fractured Surface of Lead-Lead Chloride; Sample 32; Quenched From 720° C to 37° C in Helium; 30,000X.

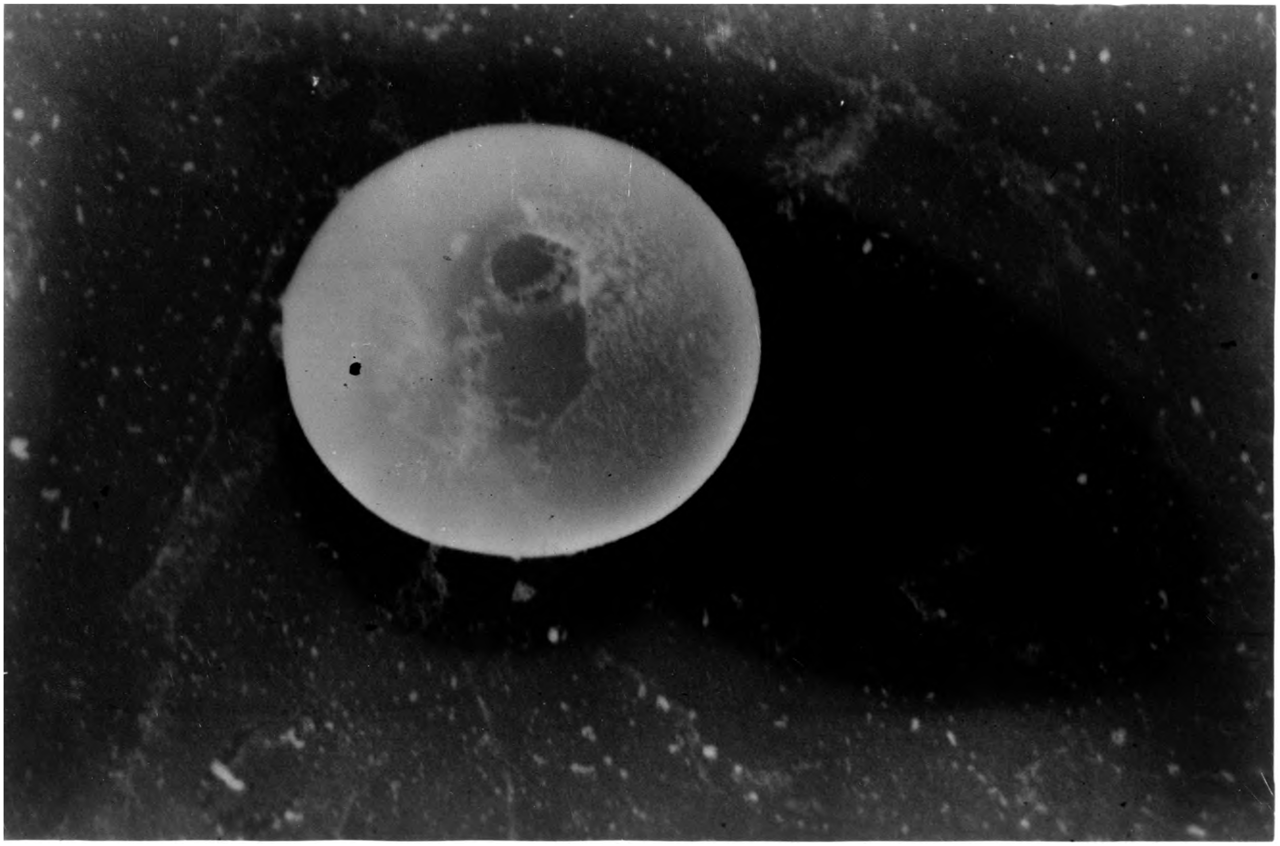


FIGURE 28

Electron Micrograph of the Fractured Surface of Lead-Lead Chloride; Sample 31; Quenched From 720° C to -10° C in Kerosene Under a Helium Atmosphere; 20,000X.

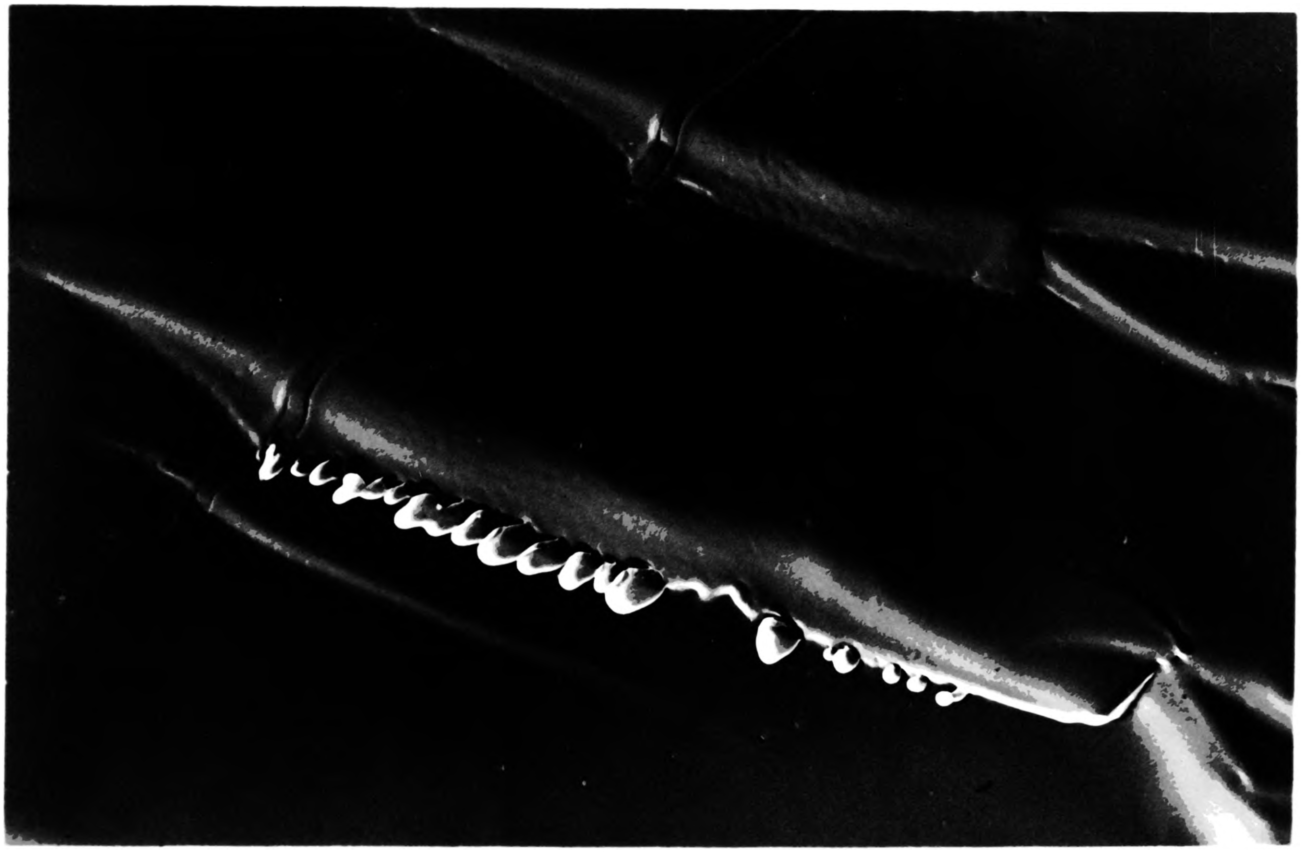


FIGURE 29

Electron Micrograph of the Fractured Surface of Lead-Lead Chloride; Sample 31; Quenched From 720° C to -10° C in Kerosene Under a Helium Atmosphere; 10,000X.

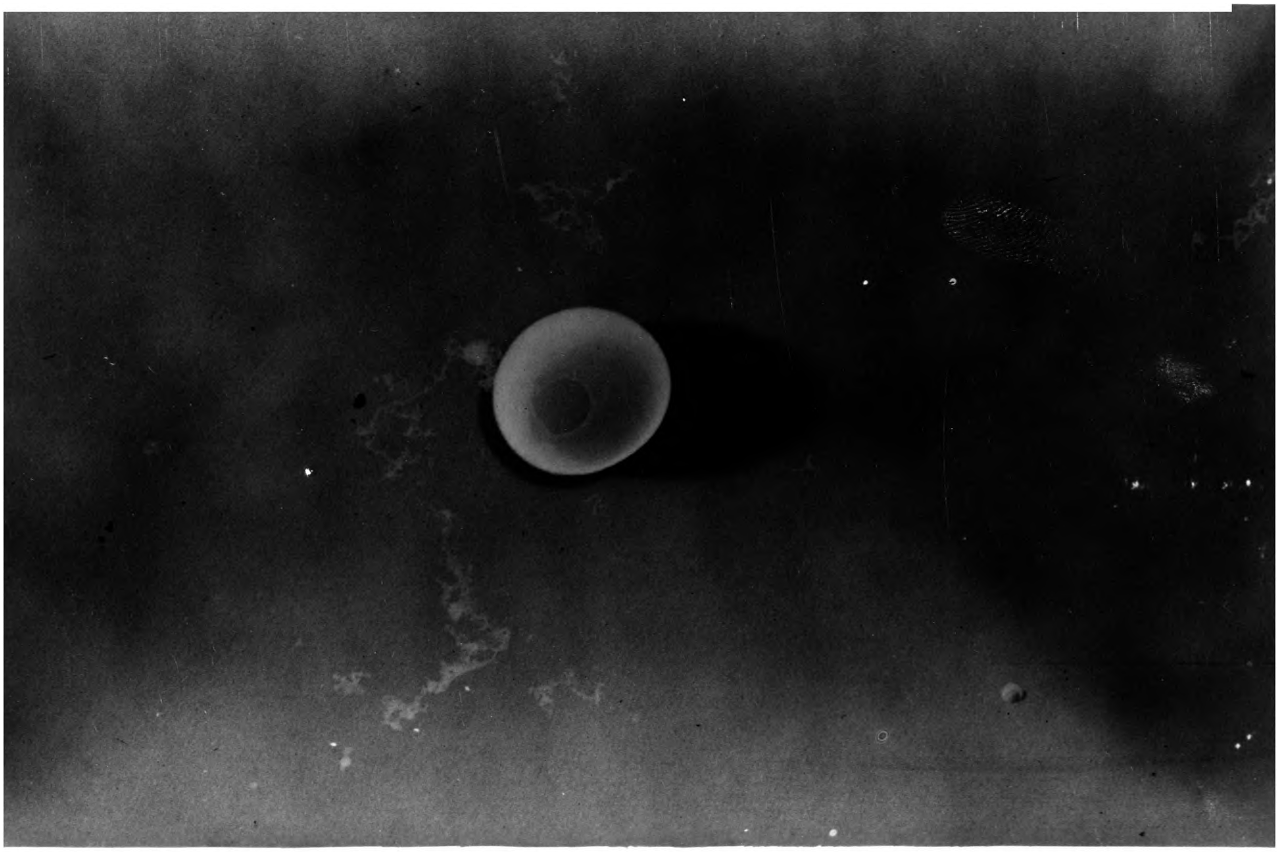


FIGURE 30

Electron Micrograph of the Fractured Surface of Lead-Lead Chloride; Sample 31; Quenched From 720° C to -10° C in Kerosene Under a Helium Atmosphere; 20,000X.

VI. DISCUSSION

A. Specimen Preparation

The melting apparatus provided means for extracting samples of a desirable dimension from the melts. The 7-mm OD Vycor extraction tubes were small enough in diameter so that only a small volume displacement resulted when the samples were extracted from the melt crucible, and the tubes containing solidified sample material were easily broken into short sections. The fractured surfaces prepared by this method were relatively free of artifacts.

In the past, chromium has probably been used oftener than any other shadowing material, mainly because it can be evaporated easily. It was considered the best shadowing material for use in this investigation.

In the selection of material and method for shadowing, it was necessary to consider such factors as contrast, resolution, chemical resistance, stability in the electron beam, adhesion to replica and sample, and ease of evaporation.

Platinum shadowing provides better contrast and resolution than does shadowing by a metal of lower density such as chromium, but the difficulty encountered in evaporating the platinum did not warrant its use. It is generally stated that a good chromium shadow, which will produce sufficient contrast and resolution, is obtained with a film thickness of about 50 A; the quality of the images observed during this search suggests that shadow films of about this thickness were obtained.

The chromium shadowing offered good resistance to chemical attack during the washing of the shadowed replicas. Also, this shadowing was quite stable in the electron beam with an accelerating voltage of 60 or 80 kilovolts.

The adhesion of the chromium shadow film to the carbon replica was very good. If this adhesion had been poor, discontinuities in the electron microscope images would have been observed.

Only limited information is available on interfacial adhesive forces between different types of shadow films and sample surfaces. This adhesion is attributed to both mechanical and molecular bonding. Relative values of the bonding were determined by noting the ease with which films could be stripped from the sample surfaces. Consequently, films that showed small adhesive forces were generally void of much detail.

The carbon replicas were considered quite suitable because of their great strength and the ease with which reproducible thicknesses were obtained. These replicas, which are of relatively low density, normally give limited contrast and resolution, and when they were preshadowed with the more dense chromium, the image details were considered to be primarily that of shadowing film.

A carbon coating or replica formed on a surface of low relief usually has a uniform thickness, whereas the coating on a surface of high relief, such as was encountered on the fractured chloride samples, is of varying thickness. Although some scattering of the carbon atoms results from their rebounding from objects within the coating chamber, the side of a surface element facing the evaporating source will have a thicker coating than a side facing away from the source. As a consequence, the forces exerted on the replicas during dissolution of the attached sample are sufficient to cause much collapse and breakage.

This breakage probably could have been minimized by using a less directional evaporating process and by using an appropriate replica-backing layer. Such a backing layer when being removed from the replica should exert less force on the replica than is exerted during dissolution of the sample from the replica.

The sodium metaphosphate should warrant further investigation for use as a parting layer. It was almost impossible to strip off replicas of the lead chloride surfaces with conventional techniques, and no suitable solvent was found for dissolving the sample away from the replica. The parting layer, however, permitted easy removal. The thickness of the parting layer should represent a compromise between that of obtaining good resolution and that of providing easy removal of replicas. Hence, the technique of applying a drop of the sodium metaphosphate paste to the vapor filament did not provide suitable control of the parting layer thickness.

B. Micrographs

The micrographs showed that particles on the surfaces of many of the cadmium chloride samples appeared to be identically oriented with respect to each other, and that there is a parallelism between the symmetry of the particles and the hexagonal symmetry of the fractured surfaces. This orientation is illustrated in Figures 16 and 17. Also, the normal melting point of the cadmium is below that of the cadmium chloride. This information suggests that the orientation of the particles is determined by the chloride which crystallizes before the metal.

Crystal habits may be influenced by many factors, some of which are the degree of undercooling, surface tension of crystals against the melt, and interference by neighboring crystals.

Examination of the different fogged samples showed a variation in particle shapes with changes in the degree of undercooling. For example, Figure 13 depicts almost spherical particles in a sample quenched to room temperature, and Figure 24 shows hexagonal particles in a sample quenched to -3° C. The crystallization rate for slightly undercooled melts is approximately equal in all directions and should give rise to the more spherical shapes; whereas, increased undercooling should result in preferred crystallization along certain directions and gives rise to polyhedral forms.

Micrographs, such as those in Figures 17, 19, 21, 22, 24, and 25, show particles of a large range of sizes relatively close together. A possible explanation for this size variation is that these particles may exhibit fusion temperatures which depend on the degree of dispersion and on external conditions such as thermal contraction of the chloride. For instance, the surface fusion temperature of a copper film about 10^{-3} or 10^{-4} mm thick may be about 380° C lower than the fusion temperature of the massive metal.[28]

Table II lists values for the smallest and largest particle diameters observed in micrographs of the fogged cadmium chloride samples. These values were calculated from enlarged images of the micrographs, and the diameters represent the average of the shortest and longest dimensions of each particle. The only significant information obtained from these values is that a large range of particle sizes may occur in the sample, and that the largest particle was produced in a furnace-cooled sample, whereas the smallest was produced in a rather rapidly cooled sample.

Particles from 0.04 to 2.8 microns in diameter have been observed in the fogged lead chloride micrographs. However, many irregularly shaped particles, somewhat similar to those shown in Figure 29, have been noted. Because of the uncertainty as to whether or not these were the dispersed phase sought, very few data were obtained.

VII. CONCLUSIONS AND SUMMARY

From preliminary experiments on preparing and examining the dispersed phase in the cadmium-cadmium chloride and lead-lead chloride systems, the electron-microscopic examination of replicas made from the surfaces of the fractured material proved to be the most feasible method of study.

Of the various replicating techniques tried, that using carbon replicas preshadowed with chromium was found most suitable. Considerable breakage was encountered when the replicas were removed by dissolution of the cadmium chloride samples. This breakage could possibly be prevented by use of a carbon replica of a more uniform thickness and a backing layer, such as sulfur, to strengthen the replica during removal from the rough sample surfaces. The water-soluble sodium metaphosphate parting layer should be investigated further as a means of removing replicas from relatively insoluble materials such as lead chloride.

Electron micrographs of the surface replicas show the presence of particles whose sizes vary over a large range. Because of this large variation, it was difficult to show any significant values for particle sizes with the different quenching temperatures. The larger particles (similar to 2 microns in diameter) are approximately spherical and may show partially developed facets, whereas the smaller particles (similar to 0.5 microns in diameter) depict an almost perfect hexagonal outline. This change in particle shape is considered to be related to such factors as the degree of undercooling, surface tension of crystallizing phase against the melt, and interference by neighboring crystals.

The micrographs showed that the more spherical particles were formed in the more slowly cooled melts; therefore, it appears that undercooling plays an important part in determining particle shape.

The appearance of particles identically oriented with respect to each other and oriented with respect to the hexagonal symmetry of the sample surfaces suggests that the orientation of the particles is determined by the chloride which crystallizes before the metal in the cadmium-cadmium chloride system.

BIBLIOGRAPHY

1. Alexander, J. (1926) Colloid chemistry. Vol. 1, Chemical Catalog Company, New York, p. 681-706.

2. Lorenz, R. (1915) Uber Bleinebel in Bleichlorid (Concerning lead vapor in lead chloride.) Z. Anorg. Chem. 91, p. 46-56.

3. Alexander, <u>op. cit.</u>, p. 681.

4. <u>Ibid</u>., p. 681-706

5. Eitel, W. (1928) Uber die Losung von Metallen in Salzschmelzen (Concerning solutions of metals in molten salts.) Z. Anorg. Chem. 171, p. 168-180.

6. Hollens, W. R. A. (1934) The nonexistence of cadmous compounds. J. Chem. Soc., p. 1062-1063.

7. Farquharson, J. (1935) Magnetic properties of solutions of cadmium in molten cadmium chloride and of molten calomel. Trans. Faraday Soc. 31, p. 1004.

8. <u>Ibid</u>.

9. Heymann, E. (1943) Distribution equilibria between molten metals and molten salts, with reference to the stability of intermetallic compounds in the molten state. J. Phys. Chem. 47, p. 473-484.

10. Cubicciotti, D. (1952) The solubility of cadmium in mixtures of cadmium chloride with other chlorides. J. Am. Chem. Soc. 74, p. 1199.

11. Topol, L. E. (1960) The cadmium-cadmium halide systems. J. Am. Chem. Soc. 82, p. 6291.

12. Corbett, J. D. (1955) The solubility of some metals in their molten halides. J. Am. Chem. Soc. 77, p. 3964-3966.

13. Alexander, <u>op</u>. <u>cit</u>., p. 687.

14. Amelinckx, S. (1955) Interaction of dislocations and f-centres in sodium chloride single crystals. Phil. Mag. 46, p. 450-451.

15. Simon, R. E. (1960) Electron microscope studies of colloids in KCl. J. Appl. Phys. 31, p. 2224-2225.

16. Wyckoff, R. W. G. (1949) Electron Microscopy. Interscience Publishers, New York, 248 p.

17. Cosslett, V. E. (1951) Practical Electron Microscopy. Butterworths Scientific Publications, London, 299 p.

18. Hall, C. E. (1953) Introduction to Electron Microscopy. McGraw-Hill, New York, 451 p.

19. Holland, L. (1956) Vacuum Deposition of Thin Films. John Wiley and Sons, New York, 541 p.

20. Bradley, D. E. (1954) Evaporated carbon films for use in electron microscopy. Brit. J. Appl. Phys. 5, p. 65.

21. Hibi, T. (1952) A new device for metallic shadow-casting. Rev. Sci. Instr. 23, p. 383-385.

22. Calbick, C. J. (1953) Inorganic replication: interpretation of electron micrographs. A.S.T.M. Special Technical Publ. No. 155, p. 33-46.

23. Baillie, Y. (1956) Investigations on the properties of thin metal films used as electron microscope replicas for metallurgical applications. Proceed. 3rd International Conference on Electron Microscopy, London 1954, p. 351-359.

24. Leonhard, F. (1960) Full and partial particle replication technique for electron microscopy. Rev. Sci. Inst. 31, p. 1181-1185.

25. Stiegler, J. O. (1961) Victawet and sodium metaphosphate as parting agents for electron microscope replicas. Rev. Sci. Inst. 32, p. 406-408.

26. Amelinckx, S. (1961) Electron microscope observations of dislocations in talc. J. Appl. Phys. 32, p. 341-351.

27. Stiegler, op. cit., p. 406-408.

28. Eitel, W. (1954) Physical chemistry of the silicates. University of Chicago Press, Chicago, Illinois, p. 374.

APPENDIX

REAGENTS

Cadmium, Metal, Mossy, Granular, Purified; Fisher Scientific Company.

Cadmium Chloride, Anhydrous, Fisher Certified; Fisher Scientific Company.

Lead, Metal (Test Lead) (Ag and allied metals, low), Sticks, 1/4 inch Diameter, Fisher Certified; Fisher Scientific Company.

Lead Chloride, Fisher Certified; Fisher Scientific Company.

Calcium Chloride, Anhydrous, 4 Mesh, Granular, Fisher Certified; Fisher Scientific Company.

Helium, Grade A; U. S. Bureau of Mines

VITA

Dennis O'Neill was born March 18, 1933, in Detroit, Michigan. He received his elementary and secondary education in the public school system in Colorado.

In November, 1951, he entered military service, and spent four years in the U. S. Navy. At the time of his discharge, he held the rank of Fire Control Technician, 1st Class.

He entered the New Mexico Institute of Mining and Technology, Socorro, New Mexico, in January, 1956, and received the degree of Bachelor of Science in Mining Engineering in June, 1959. In September, 1959, he enrolled in the Graduate School of the University of Missouri School of Mines and Metallurgy. He was awarded a U. S. Bureau of Mines Fellowship in September, 1960, for a period of one year.

He is married and the father of two children.