December 1, 1965

INTERIM REPORT

Contract NASw-1203

AVCO/Tulsa Document TR 65-363-2

"A Study of the Blistering of Metal Surfaces
by Solar System Ions"

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FOREWORD

The material for this report was prepared in conjunction with Dr. Raymond D. Daniels and Mr. Leonard Milacek under a subcontract issued by the Avco Corporation/Tulsa Division to the Oklahoma University Research Institute, Norman, Oklahoma, under Contract NASw-1203. This work has been conducted jointly by Oklahoma University Research Institute and Avco Corporation/Tulsa Division.

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I. INTRODUCTION

The following interim report is submitted as a comprehensive summary of Contract NASw-1203, entitled "A Study of Radiation Induced Blistering by Solar System Ions." It presents an analysis of the work on the following basis.

A. Restatement of the problem.

B. Reason this problem is being studied.

C. Approach being used to study problem.

D. Prognosis of where we are going in coming months to solve the problems and arrive at a logical conclusion.

Contained in the following pages is a discussion of these four items.

II. BACKGROUND OF THE PROBLEM

In 1963, in the course of studying discolorations which appeared on aluminum samples subjected to proton radiation in the 100 KEV energy range under high vacuum in the AVCO/Tulsa space simulation chamber, it was noted that the surface of the metal, in addition to being discolored, contained numerous surface eruptions which were identified as blisters. Because the blistering phenomenon occurred on aluminum, a material used for various optical surfaces on spacecraft, and resulted from particle radiation of a type and energy to be found in space environments, the observation was of considerable practical importance as well as theoretical interest.

A few additional experiments showed the reproducibility of the blistering phenomenon and demonstrated, on 6061-T6 aluminum alloy sheet irradiated with 10^{17} protons/cm^2 at 200 KEV, that the surface did not blister during the irradiation, but that blistering occurred during subsequent annealing in the temperature range of 250-350°C. These experiments also indicated that the size, shape, and density of surface blisters obtained were sensitive to the processing history and the surface preparation of the aluminum samples.

At about this same time, results of studies of the agglomeration of hydrogen in aluminum and beryllium introduced by irradiation with 7 MEV protons appeared in the literature.[1,2] Although these investigations were concerned with evaluation of hydrogen agglomeration within the bulk material, because of the greater proton penetrations involved, the nature of proton penetration and the hydrogen behavior determined in these investigations was useful as a guide to analysis and interpretation of the blistering phenomenon observed at lower proton energies.

The present research program was initiated under NASA support in 1964 for the purpose of analyzing the processes which cause blistering in proton irradiated metals. The investigation is concerned not only with providing useful information on the conditions which cause blister formation; but, even more importantly, with gaining an understanding of the mechanisms involved.

Soon after the research program was initiated, it was learned that other investigators, concerned with the optical and thermal properties of spacecraft surface materials, had encountered the phenomenon of blistering on vapor deposited gold and aluminum coatings and on polished aluminum surfaces subjected to proton radiation in the energy range 1 to 10 KEV.[3,4] It was reported that blistering occurred during irradiation without the necessity of post-irradiation annealing. These results further emphasized the need for a detailed study of the problem and suggested that the blistering phenomenon may be the observable result of some rather complex interactions involving the structure and surface characteristics of materials and the radiation parameters.

III. REASONS FOR STUDYING THE PROBLEM

The problem of hydrogen blistering of aluminum and its alloys predates the specific problem of hydrogen pickup through proton irradiation in outer space environments by many years. The problem of formation of internal bubbles and surface blisters has been of concern to aluminum fabricators since the birth of the industry. The processes generally responsible for excess hydrogen in aluminum are retention in the solid of hydrogen dissolved in the liquid phase and the absorption in the solid of hydrogen produced at the surface in corrosion reactions.[5,6] Although improved industrial practice has overcome many of the difficulties encountered with hydrogen in commercial aluminum alloys, there is continuing interest in the subject because of the potential for hydrogen pickup in the various phases of fabrication of aluminum and because a detailed knowledge of the processes involved is still lacking.

The aim of the present work is to specify the conditions under which hydrogen in aluminum, introduced by proton irradiation, will produce surface blistering and to ascertain the mechanisms of the processes involved and the dependence of the phenomenon on material structure and preparation procedures.

Basic parameters which may play an important role in the blistering process are the penetration depth and distribution of protons in aluminum, the solubility of hydrogen in aluminum, the mobility of hydrogen in aluminum, and effects of lattice defects, impurities, and the oxide surface film on the distribution and transport of hydrogen in aluminum. Theoretical questions involved are the mechanisms of transport of hydrogen in the metal and evolution of this gas from the metal, the role of lattice defects, impurities and the oxide surface film in the transport and evolution processes, and the mechanism of blister formation.

IV. EXPERIMENTAL APPROACH AND TECHNIQUES

The experimental approach used in this investigation centers on the fact that observable surface blistering can be produced in aluminum under appropriate conditions of irradiation and thermal treatment of the metal, and that these conditions are sensitive to certain basic microstructural characteristics of the metal itself. The primary tool of analysis has been optical metallography. Techniques of electron metallography are being developed to supplement the optical techniques. These techniques make it possible to qualitatively describe the blister phenomenon and its relationship to microstructural features of aluminum. Annealing treatments used to promote blistering provide additional information on the influence of microstructure on blister formation and help to establish the growth kinetics of the microscopically observed blisters.

The necessary conditions for blister formation and the characteristics of the blister patterns developed have been studied as a function of the radiation parameters and the properties and preparation of the material being irradiated. The radiation parameters under study are: proton energy, flux, total or integrated flux, and sample temperature during irradiation. Except for some preliminary experiments, the work to date involving radiation parameters has been concerned primarily with the effects of proton energy on the blister phenomenon. Substrate temperature has been held to $70^{o}F$, the total flux has been 10^{17} proton/cm^2 and the flux has been either 11×10^{12} p/cm^2 sec or 1.5×10^{12}p/cm^{2}sec. These values of flux were dictated on the one hand by the desire to minimize the time required to obtain 10^{17}p/cm^2 and on the other by limitations on the flux obtainable with the accelerator when used to obtain lower energy protons. Proton energies were varied between 200 KEV and 7 KEV.

The material employed, except for some auxiliary experiments on gold and vacuum evaporated gold films, has been aluminum, spectroscopically analyzed as being of 99.997 + % purity. The impurities present are iron .001% and magnesium .001%. All other possible impurities are below the limit of reliable analysis.

From a theoretical point of view, the ideal material with which to work would be a defect-free, impurity-free, single crystal of aluminum without an oxide film. The behavior of the material in this initial condition could be evaluated under proton irradiation for various crystallographic orientations of the surface, and the results obtained could then be compared with results obtained with controlled additions of impurities and defects and with the presence of a surface oxide film. From a practical point of view it is impossible to achieve the above conditions. Single crystals can be prepared, but they are neither defect-free nor impurity-free, and, although it is possible under ultra-high vacuum conditions to prepare film-free aluminum, this technique has not been exploited as yet.

Our approach thus far has been to attempt to evaluate the blistering phenomenon in aluminum crystals of relatively high purity under conditions where the defect structure and characteristics of the surface film are known and to an extent can be controlled. These samples have been, for the most part, single crystals or extremely large grain polycrystals on which the irradiated area is largely confined to one grain which can be treated like a single crystal.

The sample types and preparation procedures employed can be classified as follows:

A. Wrought Samples

1. Fine grained material prepared by recrystallization of swaged samples cut from a cast ingot.

2. Large grain material prepared by recrystallization of swaged samples coupled with a long time grain growth anneal.

B. Remelted Samples

1. Single crystals prepared by remelting and directional solidification in a Bridgeman type furnace.

2. Samples prepared in the Bridgeman furnace as described above, but containing two or three large grains running parallel to the direction of solidification.

Polycrystalline samples prepared by recrystallization of high purity aluminum have been utilized for two reasons. First, to compare blistering behavior in high purity polycrystals with that in wrought alloy samples, and, second, as a method for preparing large crystals by a technique which avoids the necessity of remelting the aluminum and the consequent development of subgrain structures associated with the growth from the melt.

Single crystals have been prepared by the Bridgeman technique in a graphite crucible under an argon atmosphere. Unseeded crystals all show a preferred growth direction of high indices. The average growth direction is approximately from (100) -34°, from (110) -22°, and from (111) -30° on a stereographic net. Attempts to seed low indices growth directions have been only partially successful in that the growth direction could be warped only about 15 degrees toward a major axis from the preferred high indices growth direction.

Most single crystal samples grown from the melt have contained observable substructures. The substructures are of two general types which can be denoted as cellular and lamellar.[7] Subgrain boundaries are believed to form as a consequence of impurities in the melt which give rise to constitutional supercooling. Microsegregation then occurs with the impurities concentrated at the subgrain boundaries.

Most studies of microsegregation have been conducted with impurities as chosen additives in purer metals, suggesting that the aluminum under study must be of lower purity than our analyses indicated or that impurities were being introduced in the melt process. A recent study of impurity segregation by electron microprobe analysis, however, demonstrates that the impurity level necessary for substructure formation is well within the impurity level of 99.997 + aluminum.[8] The study further indicates that the concentration enhancements in the regions of microsegregation can be as much as two orders of magnitude.

The surfaces of aluminum samples used in the irradiation studies are prepared by electropolishing. The samples are polished in a 2:1 methyl alcohol-nitric acid solution followed by rinsing in an

85 per cent orthophosphoric, 3.5 per cent nitric acid solution. Technique in the electropolishing process is critical in obtaining reproducible results. Solution temperature, current density, and polishing time have been found to be important factors in the process.

A tendency for pitting to occur in the electropolishing process, particularly on crystals grown from the melt by the Bridgeman technique, has been linked with the substructure of the aluminum. The pitting tends to be localized along boundaries which subsequent irradiation and annealing reveal to be regions of high blister content. These regions are believed to be subgrain boundaries formed during solidification, and the preferential etching response is to be expected. Attempts to eliminate this preferential etching by modification of the polishing procedure have been partially successful. The important thing is to keep the etching time short.

Although electropolishing techniques have been designed to substantially reduce pitting in samples being prepared for irradiation, the intentional development of pitting in grown crystals appears to be a useful technique for identifying substructures.

The thicknesses of the oxide films formed on the aluminum samples in the preparation process are determined by the technique developed by Hunter, Fowle, and Towner.[9, 10] The technique is based upon a combination of the characteristics of barrier layer type anodic coatings and interference color methods. The barrier layer has been found to be about ten angstroms and the total thickness of the oxide, including the porous layer, about 60 angstroms for the electropolished surfaces.

In addition to the radiation experiments on aluminum crystals, studies have been initiated on samples of gold and on vapor deposited gold coatings on aluminum substrates. These studies have been initiated to complement the work on aluminum using a material on which there is no oxide layer, and are an attempt to reproduce and interpret results reported elsewhere on the blistering of gold films.[3]

V. DISCUSSION OF RESULTS

Results obtained thus far in the investigation make possible a reasonably consistent qualitative description of the proton radiation induced blistering process in aluminum. The picture, however, is by no means complete, nor are all of the mechanisms explained.

The results suggest that blistering is a consequence of the lifting of the oxide film on aluminum in the irradiated area. The blistering may be caused by the pressure of hydrogen trapped under the oxide, or from hydrogen agglomeration just under the metal surface. The latter causes localized swelling of the metal with consequent stresses on the oxide.

At energies of about 10 to 50 KEV, protons cause sputtering and removal of the oxide layer on the high purity aluminum, Figure 1. In the range 50 to 70 KEV, blistering occurs spontaneously upon irradiation. At 100 KEV, blistering occurs only after annealing at a temperature of at least 250^{o} C, and the distribution of blisters is sensitive to the substructure of the aluminum, Figure 2. At 200 KEV, blistering has not been observed at all, even after annealing.

These observations are considered typical; specific results will be greatly influenced by the purity and defect structure of the material. For example, 6061 alloy will blister upon annealing after irradiation at 200 KEV, Figure 3. Also, cold working will markedly influence the size and distribution of blisters obtained, Figure 4.

The influence of proton energy on blister formation must be explained on the basis of particle penetration in the aluminum lattice, although data on proton penetrations in these energy ranges are meager.

Penetration data in the literature are presented in the form of range energy curves by Young for 1 to 25 KEV protons in aluminum[11], and as energy loss versus proton energy for 50 to 400 KEV protons by Warshaw.[12] Wilcox has converted proton stopping power data into range-energy curves in the range 0 to 350 KEV for aluminum and gold.[13] These reported results indicate an expected penetration of approximately .1 to 1.5 microns for protons in the 10 to 200 KEV range.

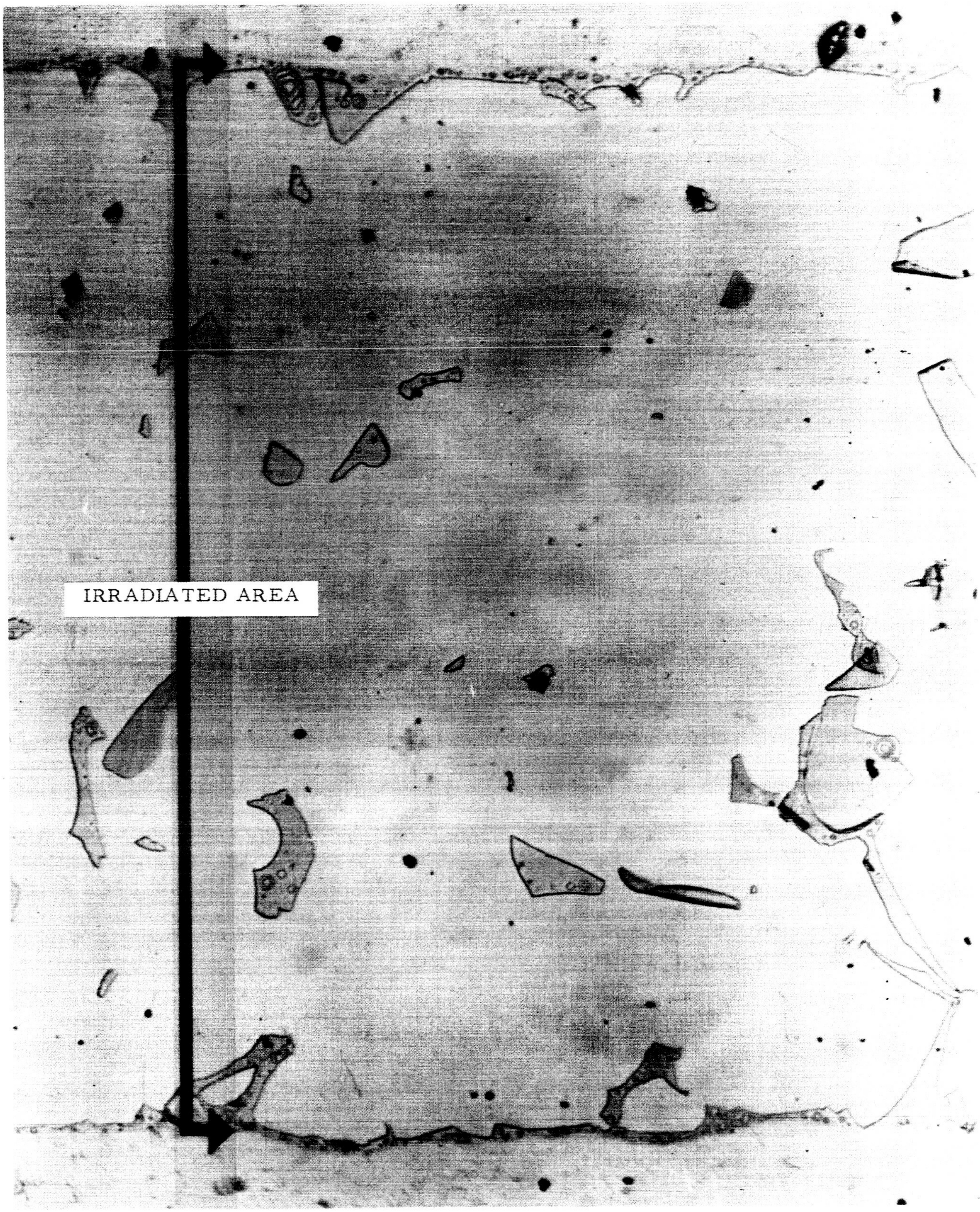

Figure 1 -- Sample Showing Oxide Removal

Magnification 270X

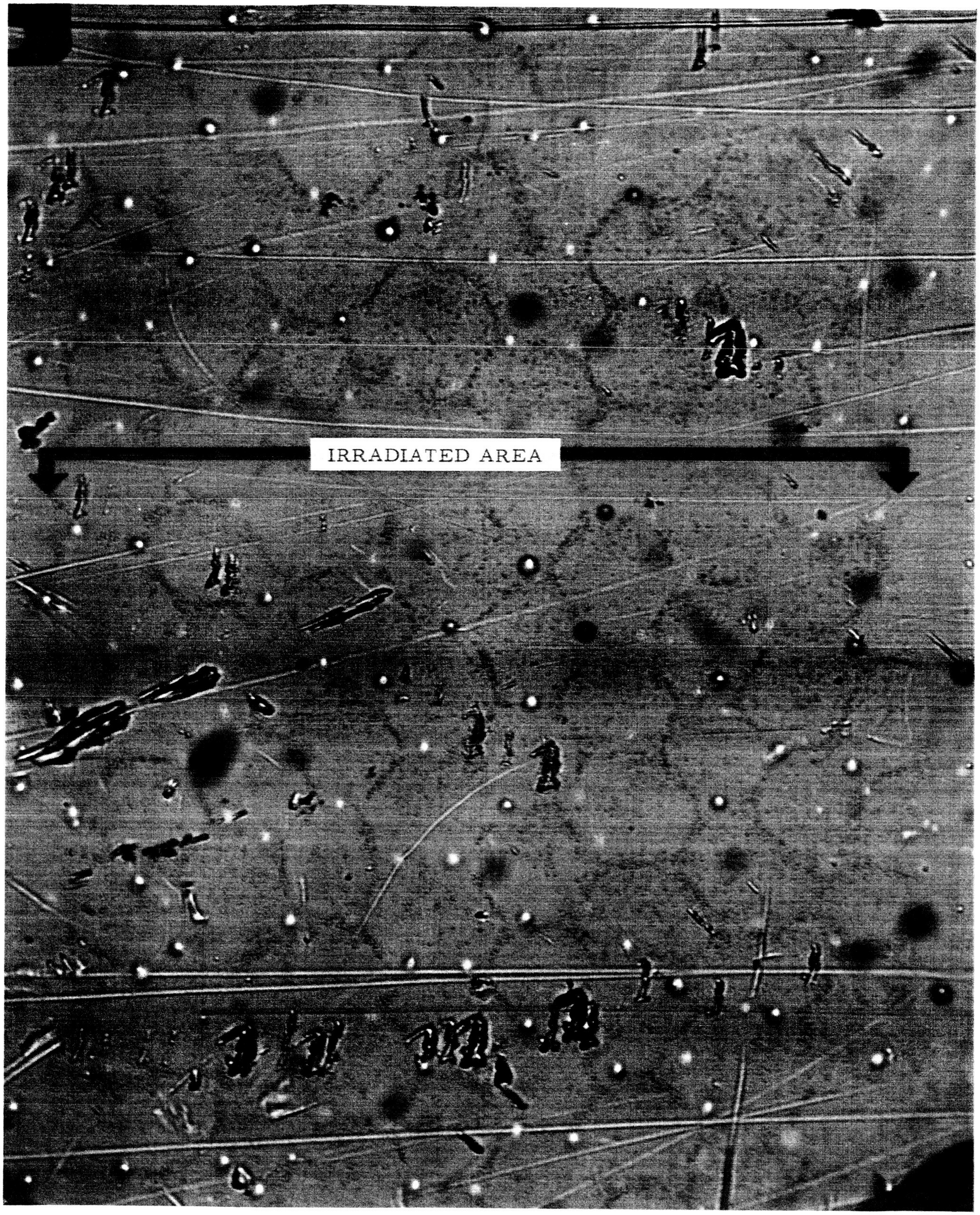

Figure 2 -- Hexagonal Blister Distribution with Normal Illumination
Magnification: 173X

Figure 3 -- 6061 Alloy Annealed After Irradiation with 200 Kev Protons
Magnification: 390X

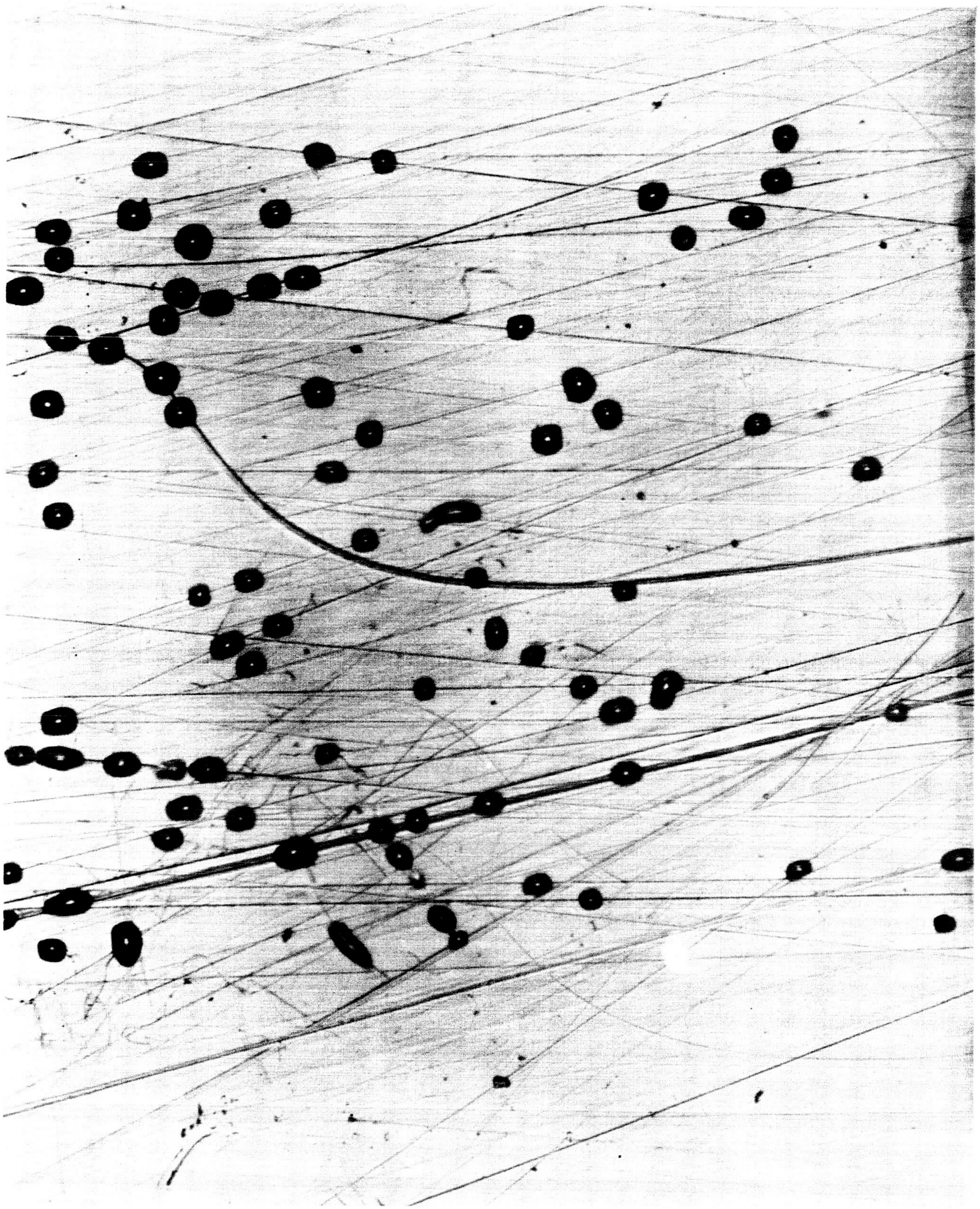

Figure 4 -- Blisters on Cold Worked Surface
Magnification: 260X

The reasonableness of some of our conclusions can be evaluated from a critical analysis of the work of Ells and Evans with 7 MEV protons.[1] They reported that samples irradiated at temperatures less than 100° C exhibited fine agglomerates, pockets of hydrogen, in the as-irradiated conditions. The protons penetrated the aluminum to a depth of about 0.033 cm and the agglomerates were evident upon etching cross-sections of the specimen perpendicular to the irradiated plane. The intragranular agglomerates rarely had radii less than 0.5 micron and most were greater than 1.0 micron. Annealing at 300° C for one hour produced a general coarsening of the agglomerates within the main hydrogen-containing layer and some dispersal of agglomerates at the edges of this layer and in grain boundaries in locations outside the main layer.

The initial width of the hydrogen-containing layer for the 7 MEV protons was estimated to be 0.004 cm (40 microns). The integrated fluxes were of the order of 0.01×10^{17} to 1.0×10^{17} protons/cm^2. Assuming a uniform distribution of protons within the layer, the hydrogen content was 0.16 to 22 ppm by weight.

An analysis, similar to that above, indicates that for the present work the hydrogen concentrations could be of the order of 1000 ppm or more. The calculation assumes an integrated flux of 10^{17} protons/cm^2 and a hydrogen containing layer 0.1 to 0.5 micron thick at mean depths of 0.1 to 1.5 microns below the surface.

Since Ells and Evans report fine agglomerates in as-irradiated samples containing 16 ppm hydrogen in the hydrogen containing layer, it is expected that our samples with a higher concentration of hydrogen near the surface would show similar voids. But these agglomerates may appear as blisters, since their size at low energies is of the order of the penetration depth. Alternately, hydrogen may merely be trapped under the oxide film. The spontaneous blistering observed can be explained by either of these processes. At 100 KEV the hydrogen containing layer is apparently too deep to cause spontaneous blistering. Annealing will produce blistering because of agglomerate growth and dispersal, and the distribution of blisters will be sensitive to the substructure because of the favorable sites for nucleation that the subgrain boundaries provide.

The lack of observed blistering in high purity aluminum irradiated with 200 KEV protons could be due to the gradual solution of hydrogen in aluminum during annealing before agglomerates are able to coarsen and disperse to a degree that affects the surface. Hydrogen will start leaving the penetration produced layer by normal lattice diffusion processes at a significant rate above 300°C so that the agglomerates will contract rather than grow and will eventually disappear.[14]

The results reported thus far on the blistering of aluminum surfaces have been based primarily upon observations under the optical microscope under normal incident light. This technique is adequate where the blister size is large enough, but the limit of resolution of the optical microscope is approached for the small blisters formed in high purity aluminum. The techniques for obtaining replicas for study of the surfaces by electron microscopy are being developed. An electron micrograph of a replica obtained from an aluminum sample irradiated at 100 KEV is shown in Figure 5.

Normal techniques yield replicas of the surface of the oxide layer. A technique has also been developed for increasing the thickness of the oxide layer and then removing the oxide as a self-supporting replica.[15] These replicas are expected to provide information both on the structure of the oxide and the surface at the metal-metal oxide interface.

A cellular substructure has been detected in the oxide. The cell size is similar to the size of the blisters formed after proton irradiation, but no direct correlation between oxide cell size and blister size has been established. Examples of the cellular structure can be seen in Figure 6.

A number of investigators have studied the development of cellular substructures in aluminum oxide.[16, 17] Apparently, the structure is sensitive to the manner in which the film is formed. There may be a relationship between the substructure of the oxide formed in chemical polishing and the substructure of the base material.

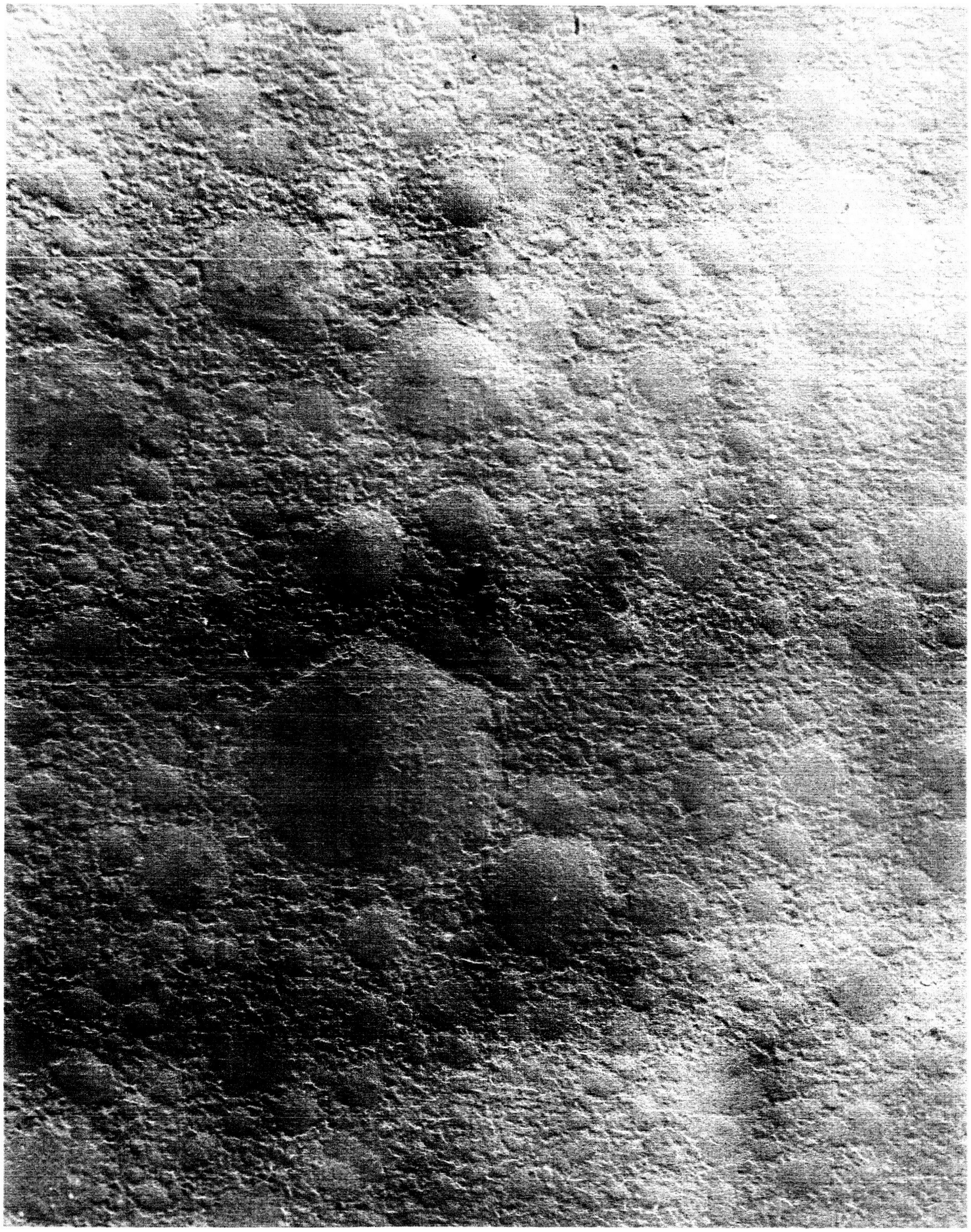

Figure 5 -- Electron Photomicrograph of Blistered Aluminum
Magnification: 22,500X

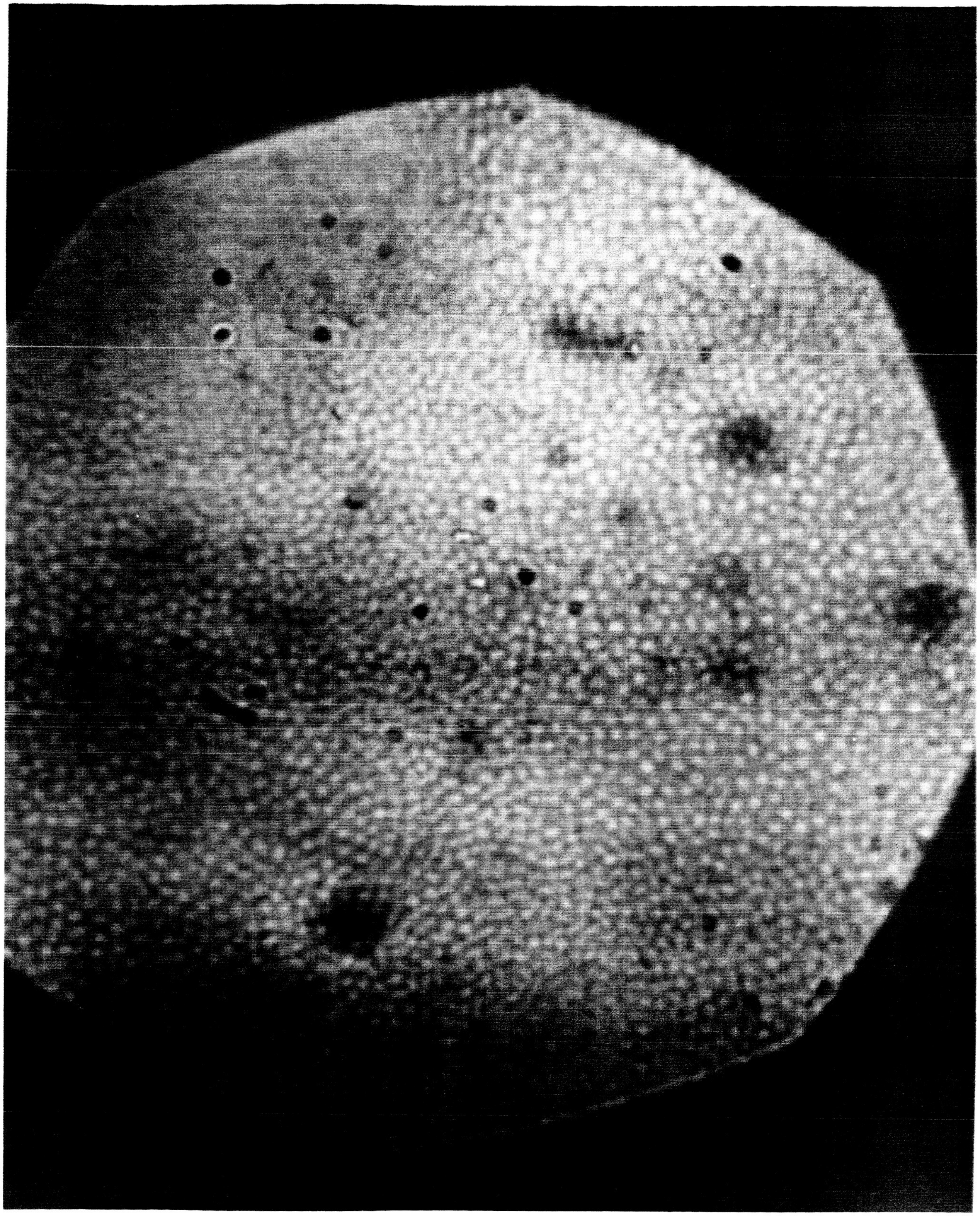

Figure 6 -- Cellular Substructure in Aluminum Oxide
Magnification: 173X

Oblique illumination has been found to provide a more sensitive means for detecting the effects of irradiation under the optical microscope than normal incident light. The irradiated areas are sites for diffused scattering of light and appear brighter under the microscope than unirradiated areas which reflect in a normal fashion. The advantages are indicated in Figure 7, where the irradiated area, the same area shown in Figure 2, is clearly visible because of diffuse reflection.

The sites for diffuse reflection may not always be blisters. There is evidence to indicate that some of the diffuse reflection is not caused by blisters, since diffuse reflection occurs in irradiated areas on samples bombarded with 200 KEV protons. The regions of diffuse reflection is caused, in part, by an accumulation of defects and debris in the oxide as a result of secondary emission.[18, 19, 20]

The experiments to determine the effects of proton bombardment on gold are thus far inconclusive. Six bulk samples of 99.999 per cent purity have been irradiated and two samples which consisted of vapor deposited gold films on aluminum substrates have been irradiated. Four of the bulk samples were mechanically polished and the remainder electropolished. One of the electropolished samples was irradiated at 15 KEV and appeared to be sputtered; the other, irradiated at 100 KEV, showed no apparent damage, even after annealing. There was no evidence of blistering on the mechanically polished samples. The proton energies were 10, 40, 70, 100 KEV.

Both samples with vapor deposited gold films blistered spontaneously. The film thicknesses were 2 microns and the proton energies 10 and 30 KEV. The appearance of the blisters, Figure 8, suggests that the protons penetrated the vapor deposited gold film and that pockets of hydrogen which formed separated the film from the substrate.

It is speculated that bulk gold will not blister in the way that aluminum does because of the absence of a brittle oxide film at the surface. Surface swelling in gold, if it occurs because of agglomeration of hydrogen under the surface, should appear during annealing by a process similar to sintering. The blistering of the vapor deposited gold films is assumed to be merely an adhesion problem.

Figure 7 -- Hexagonal Blister Distribution with Oblique Illumination
Magnification: 173X

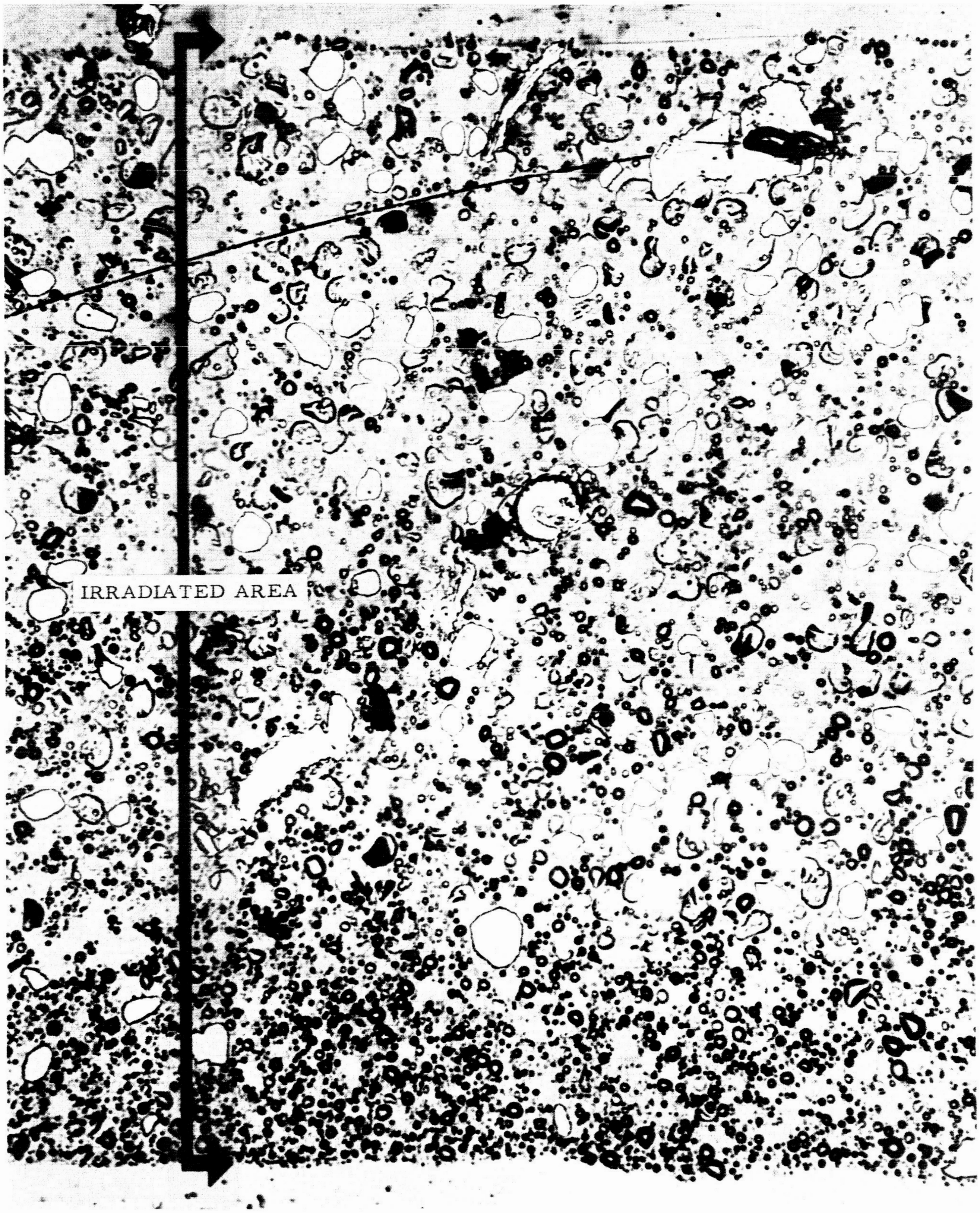

Figure 8 -- Vapor Deposited Au on Al After Irradiation with 10 Kev Protons
Magnification: 270X

VI. PLANNED FUTURE WORK

It is proposed to continue the research on proton radiation effects on aluminum with particular emphasis on experiments designed to provide more quantitative data and insight on the atomistic processes involved in blister formation. Work will be continued on development of more sensitive techniques for detecting blisters and on evaluation of the structural dependence of blister formation.

Primary objectives in the coming months will be to determine the relationship or importance of the metal oxide layer in aluminum to the blister phenomenon. To study this problem, the following approaches will be used:

A. The technique of Lewis and Plumb[21] for chemically stripping the oxide film from a sample without attacking the base material will be used to determine if the blisters present after annealing of proton bombarded aluminum are confined to the oxide layer or represent a swelling of the base material. From such a study, it should be possible to determine if blisters form because of void formation in the material or as a consequence of hydrogen accumulation under the oxide layer.

B. A complementary experiment will effect the possibility of blister formation on an oxide-free surface. Samples of proton bombarded aluminum will be annealed at ultra-high vacuum with the oxide layer intact in one case and with the oxide layer removed by ion bombardment in another case. These samples will be examined microscopically after annealing to determine if the oxide layer is a necessary requisite to surface blistering.

Experiments will be conducted to correlate the formation of blisters with the evolution of hydrogen from the metal. Optical studies of the rate of blister formation during isothermal annealing will be correlated with hydrogen evolved during vacuum annealing under similar conditions. The evolution of hydrogen will be monitored by a partial pressure analyzer.

The structural dependence of the blistering and diffuse scattering phenomena will be evaluated as a function of crystal orientation for a range of proton energies. Large-grain polycrystalline samples, for which the individual grain orientations and the effects of radiation on the individual grains can be determined, will be used in this study to facilitate the evaluation process.

Results obtained in the experimentation described above will contribute greatly toward a better understanding of the nature of the blistering phenomenon in terms of atomistic processes involved and their dependence on the structure of the aluminum. To construct an atomistic model for the blister process which can be quantitatively correlated with the observed effects, however, it will be necessary to have information on the initial distribution of protons within the material and on the solubility and mobility of hydrogen in aluminum. These data are not now available and cannot reasonably be deduced from the present work alone. It is possible that the hydrogen distribution can be determined by transmission electron microscopy and that the solubility and mobility of hydrogen can be determined by sophisticated diffusion measurements in a flow-calibrated mass spectrometer. Specific proposals for such studies will be made at a later date.

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