LA-3515

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Observation of the Microscopic Distribution of Oxygen and Carbon in Metals by He^3 Activation

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

LA-3515
UC-25, METALS, CERAMICS,
AND MATERIALS
TID-4500

H.C. $ 3.00 .65

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Report written: May 10, 1966

Report distributed: November 21, 1966

Observation of the Microscopic Distribution of Oxygen and Carbon in Metals by He^3 Activation

by

Dale M. Holm
John A. Basmajian
Wm. Mort Sanders

Blank Page

ABSTRACT

The microscopic distribution of oxygen and carbon has been observed by bombardment of metallographically polished samples with He^3 ions and autoradiography of the activated areas. Positrons from the activation products cause the exposure on nuclear track plates, and the positron annihilation radiation is used to determine both the proper exposure and the composite decay curve. Correlation of the unfolded decay curve with the autoradiograph indicates the isotope causing the exposure. Positional resolution of 0.0005 inch has been obtained in samples having bulk carbon concentrations of about 250 ppm.

ACKNOWLEDGMENTS

The authors wish to thank Mr. and Mrs. Wright Langham for their assistance and advice in carrying out the preliminary experiments with autoradiography. Particular thanks is given to Mr. R. K. Smith for special assistance in the irradiations with the Los Alamos Scientific Laboratory Van de Graaff.

Blank Page

INTRODUCTION

The interstitial elements carbon and oxygen are known to have significant effects on the behavior of body-centered cubic metals. Mechanical properties, recrystallization behavior, strain-aging characteristics, and diffusion are affected by the amount and distribution of the interstitial elements. The standard methods of chemical analysis are not suited to the measurement of the microscopic distribution of oxygen or carbon in metals. More sophisticated tools such as the electron-beam microprobe cannot resolve small variations in composition in materials containing concentrations of a few ppm of these elements. This paper describes a technique for obtaining data on the actual distribution of oxygen and carbon in metals, especially in the region of grain boundaries.

The method consists of activation of the carbon and oxygen by energetic He^3 ions and subsequent autoradiography of the metallographically polished sample. Adequate autoradiographs of specimens having an average bulk concentration of about 250 ppm of the interstitial element have been obtained, and it should be possible to obtain useful information from samples with concentrations of about 25 ppm. Outlines of grains 0.0005 inch in diameter have been observed, and, therefore, film density variations separated by 0.0001 inch could be measured.

Markowitz and Mahony[1] have shown that He^3 activation is an extremely sensitive method for measuring oxygen and carbon in metals of high atomic number, but is subject to certain restrictions because of the short range of the incident ions. The short range of the He^3 beam and the strong energy dependence of the cross sections make this method particularly

suitable for measuring surface phenomena. The activity is highest at the surface, and it decreases very rapidly with depth for 6-MeV ions. This fact makes the method ideally suited to high resolution autoradiography.

Table I lists the reactions employed and other pertinent information. As seen in the table, the half-lives are short enough to give good autoradiographs after a 30-minute irradiation, and the reaction products are all positron emitters. The positrons cause the emulsion exposure, and the associated annihilation radiation is detected with two NaI detectors connected in coincidence. Portions of the decay curve are obtained during the film exposures, and this curve is used to determine which isotopes caused the emulsion exposure.

TABLE I

Pertinent Information on the Reactions

Reaction	Half-Life	β^+ Energy
$O^{16}(He^3,He^4)O^{15}$	124 sec	1.7 MeV
$O^{16}(He^3,p)F^{18}$	110 min	0.65 "
$C^{12}(He^3,He^4)C^{11}$	20.4 min	0.97 "

METHOD

A flat, metallographically polished sample is irradiated in a uniform intensity He^3 beam for about thirty minutes. A beta-sensitive nuclear track plate with a 10-micron-thick emulsion is then placed on the sample and is left on long enough to produce a predetermined number of counts on a scaler which serves as an exposure meter. After development of the plate, an enlarged print is made on high contrast paper.

Since separation of the emulsion and the beta-emitting atoms governs the spatial resolution of the autoradiograph, it is necessary to use samples with flat and highly polished surfaces for irradiation. They must be mounted so that oxygen or carbon will not be introduced from the mounting material, in a position which will be struck by the beam. Significant extraneous oxygen or carbon in the area irradiated creates an error in the exposure meter reading, making the decay curve meaningless.

The principal restrictions in selecting the irradiation conditions are the heat effects on the sample and the necessity of obtaining uniform irradiation over the area of interest. Although no measurements have been made to determine the effects of heat on the samples, an arbitrary figure of 2 watts has been chosen as the maximum energy deposition rate. The maximum surface activity for a given wattage occurs approximately where the slope of the cross section vs energy curve is unity. Since this value is about 6.5 MeV, a current of about 0.3 microamp is the maximum which should be used. In these experiments, singly-ionized He^3 was used.

Uniform beam intensity was obtained with the aid of a quartz disk placed in the path of the beam. The beam was focused to a 0.090-inch-diameter fluorescent spot on the quartz while the quartz was viewed through a glass window in the sample holder, shown in Fig. 1. The nuclear reactions do not present a hazard to the viewer during focusing. The quartz disk is removed from the beam path prior to sample irradiation.

Eastman NTB-10 nuclear track plates with 10-micron-thick emulsion were used for the autoradiographs. Since it is important that the sample be in intimate contact with the emulsion and yet not deform it, a simple holder has been designed to handle the nuclear track plate. The plate is placed on its holder and lowered onto the sample without lateral movement, thereby minimizing emulsion scratching; the weight of the plate gives proper contact with the sample. The plate holder is then further lowered below the plate to minimize absorption and scattering of the annihilation radiation by the holder. Figure 2 shows the plate holder lowered and the plate on the sample between the two scintillation detectors. The shielding and light-tight bag have been removed. After proper

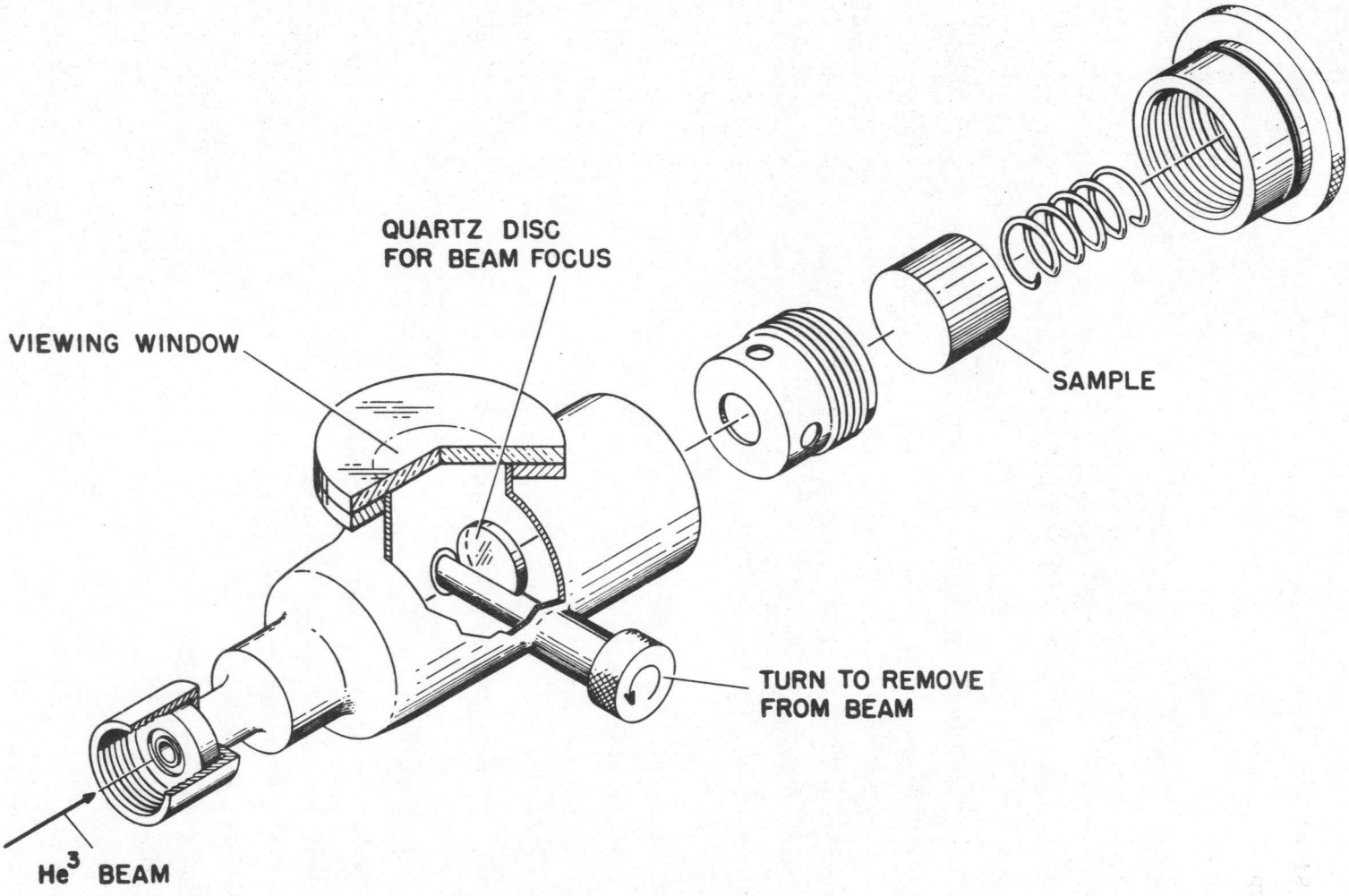

Fig. 1. Beam focusing port and sample holder for He^3 activation.

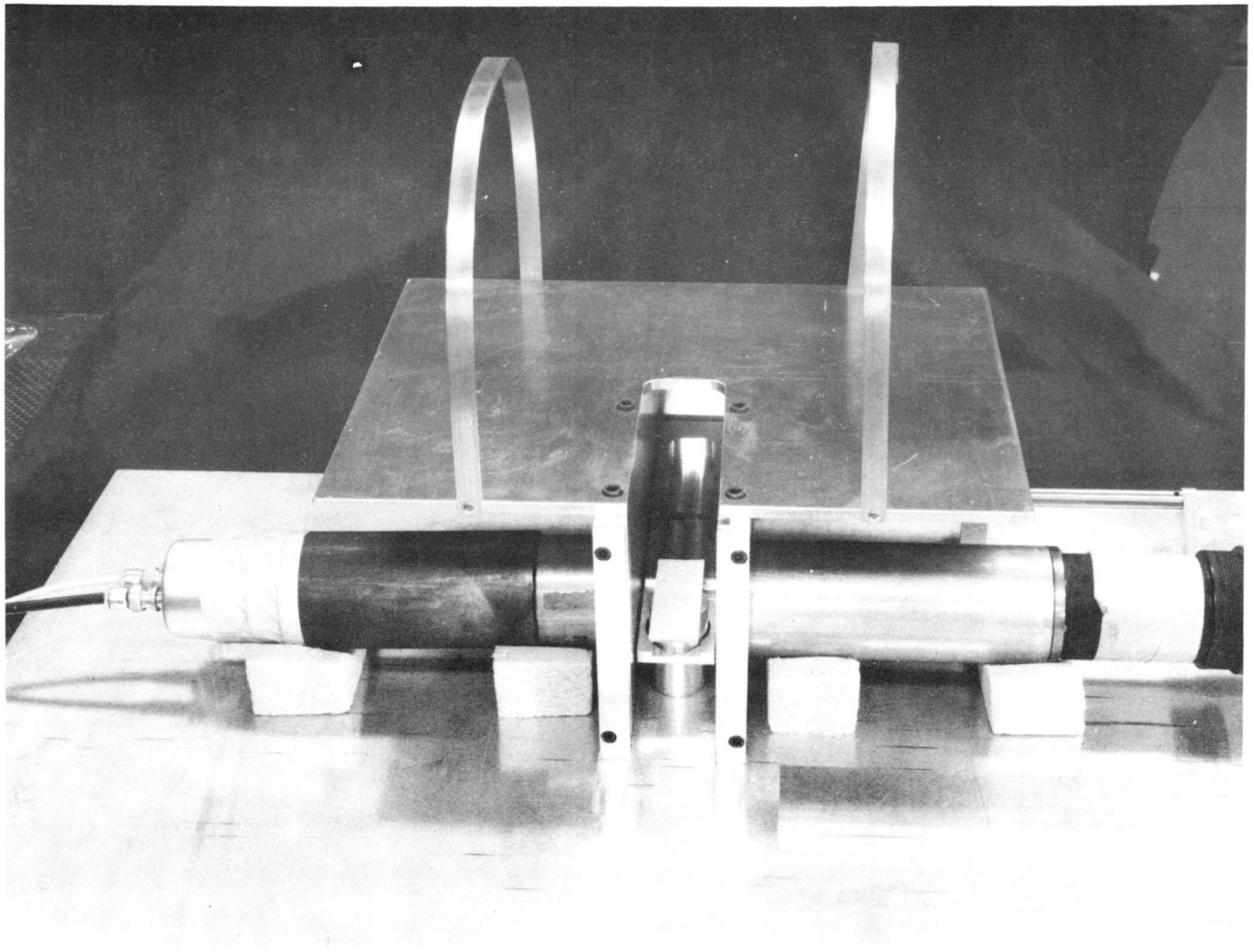

Fig. 2. Arrangement of sample, nuclear track plate, and scintillation detectors.

exposure, the plate is lifted from the sample by the holder and developed. The duration of the exposure is determined with the aid of the exposure meter-scaler and a calibrated Na^{22} source. A 10^8 dis/cm^2 ($\approx 3 \times 10^5$ counts from a 0.09-inch-diameter spot for our detector system) gives an adequate exposure for most samples. This is about ten times the value used for tritium autoradiography.[2] Beta rays from tritium expend all of their energy in the emulsion and have a high specific ionization compared to positrons of greater energy. The difference in sensitivity is primarily due to the difference in specific ionization.

ELECTRONIC CIRCUITRY

Figure 3 is a block diagram of the electronic circuitry used to obtain the decay curve and determine the duration of emulsion exposure. The NaI detectors were connected to detect coincidence events from the 0.51-MeV gamma rays associated with annihilation of the positrons. Coincidence counting minimizes background and improves the signal-to-noise ratio in the counts which comprise the decay curve. The decay curve shown in Fig. 4 was obtained with a multichannel analyzer operated in the multiscaler mode in which the counting time per channel was small compared to the instantaneous half-life.

RESULTS

The $O^{16}(He^3,p)F^{18}$ reaction was chosen for the first experiments because of the long half-life of F^{18} and large cross section of O^{16}. An internally oxidized sample of zirconium in silver was selected to give high contrast, although metal grains would probably not be visible. Figure 5 is a print of a 5-minute autoradiograph taken 1 hour after irradiation. The sample had been irradiated 40 minutes with 0.07 microamp of 6-MeV

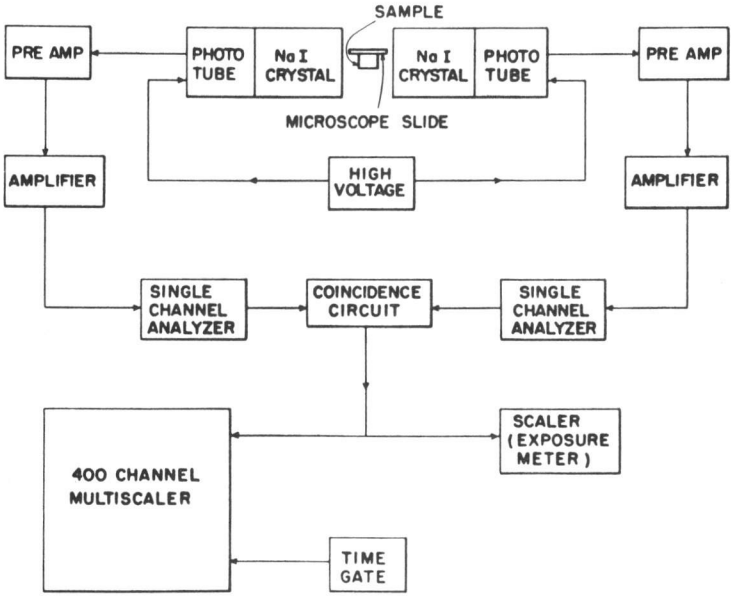

Fig. 3. Electronic circuitry used in He^3 autoradiography.

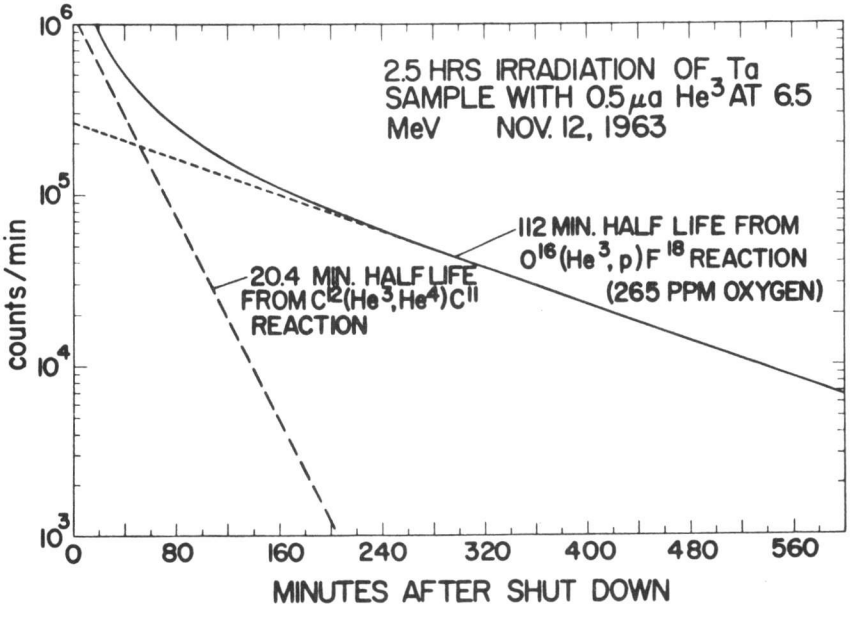

Fig. 4. Decay curve.

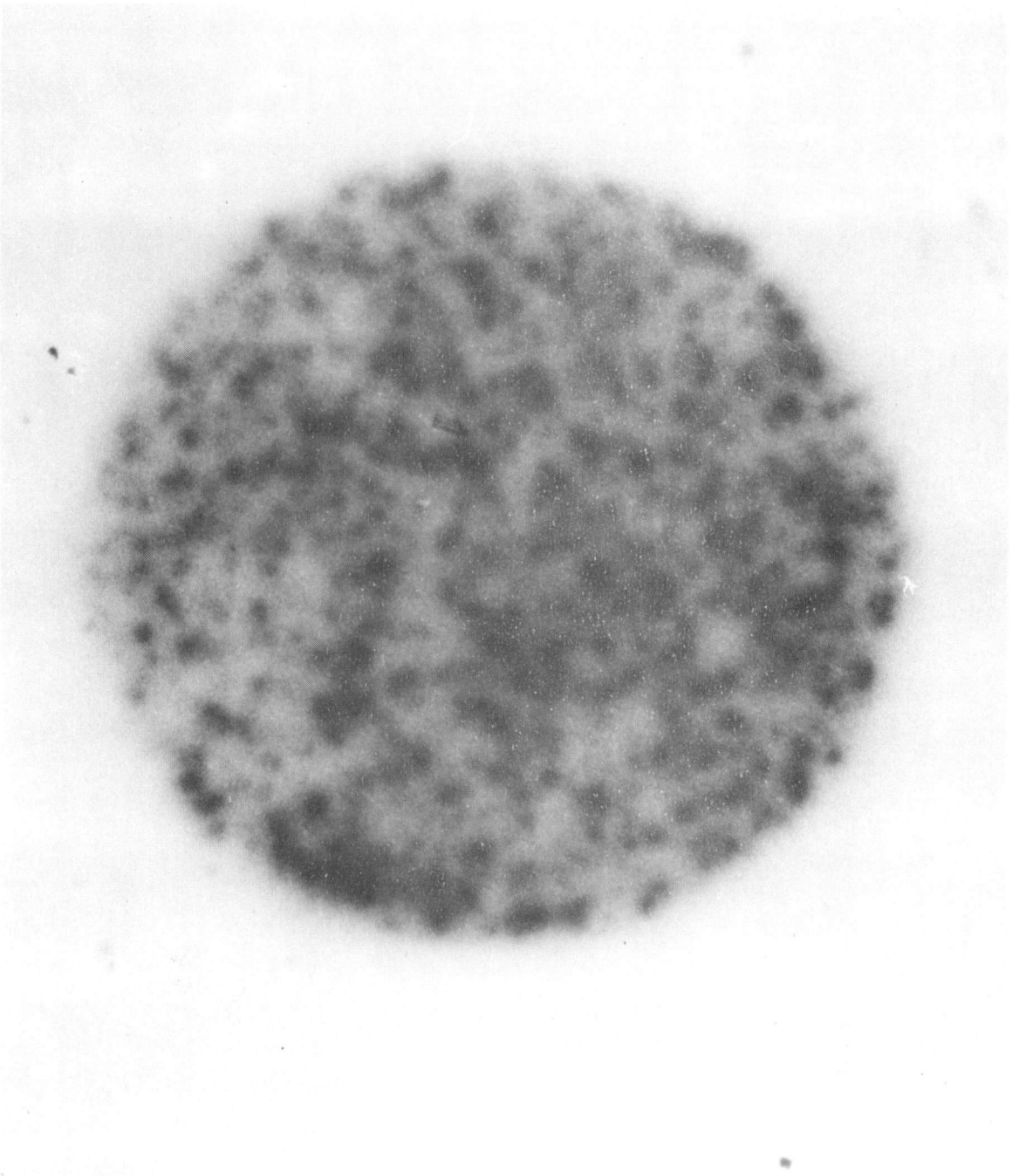

Fig. 5. Autoradiograph of oxidized silver-zirconium sample.

He^3. The black areas are the regions of high oxygen concentration. The diameter of the irradiated area was 0.090 inch. This picture demonstrated the feasibility of the technique, and some evidence of oxygen was observed in a few grain boundaries.

The $C^{12}(He^3,He^4)C^{11}$ reaction[3] was chosen for the second set of experiments. A tantalum rod was carburized with a carbon arc, and the polished sample was irradiated with 6-MeV He^3 ions for 33 minutes at 0.3 microamp. The autoradiograph shown in Fig. 6A was a 5-minute exposure started 5 minutes after the end of the irradiation. The general background is due to oxygen. Since the sample was not etched immediately after irradiation, it is impossible to distinguish between surface contamination and uniform volumetric distribution of oxygen that constitutes the general surface darkness. The diameter of the image is 0.090 inch, and grains 0.003 inch in diameter can easily be seen. Figure 6B is a photomicrograph of the sample area depicted in 6A. The irradiated region is enclosed in the dashed curve. By reference to the scale on Fig. 6B, one can determine that two grain boundaries containing carbon can be resolved if separated by 0.0005 inch. Nonuniformity of the beam intensity accounts for the lack of definition in part of the irradiated region.

From the photomicrograph, one can obtain only the effect of the etchant on the material, namely, the degree to which the etchant attacks the various portions of the structure. However, the autoradiograph shows definite areas of heavy carbon concentration in the grain boundaries, at junctions of grain boundaries (triple points), and within the grains themselves as substructure. More important is the fact that gradations in the density of the high carbon areas exist, and proper analysis under standardized conditions can lead to quantitative determination of carbon content variations over small distances.

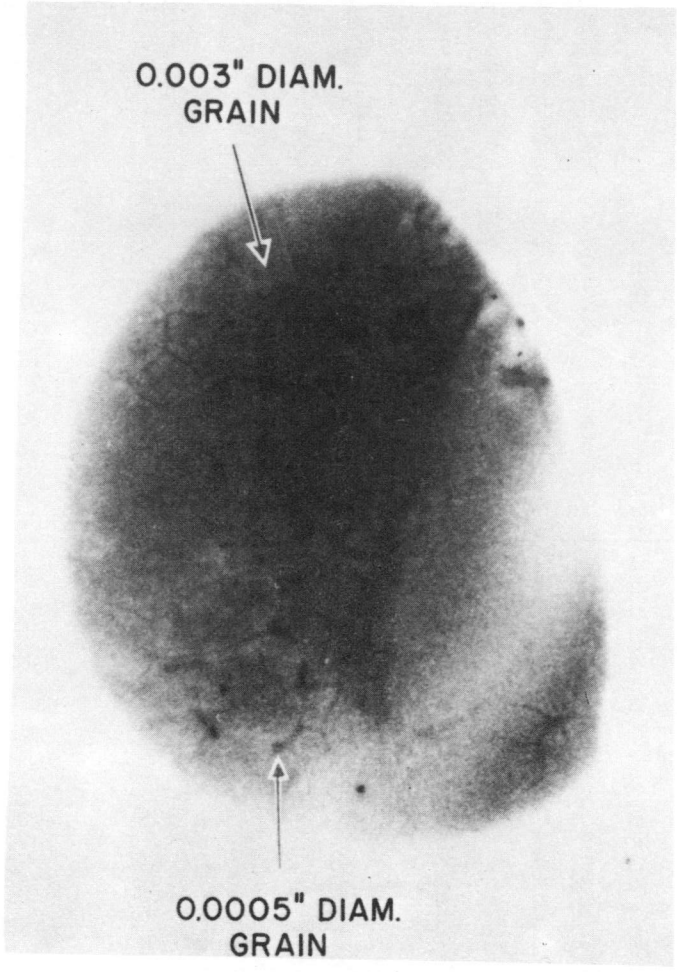

Fig. 6A. Autoradiograph
of carburized tantalum sample.

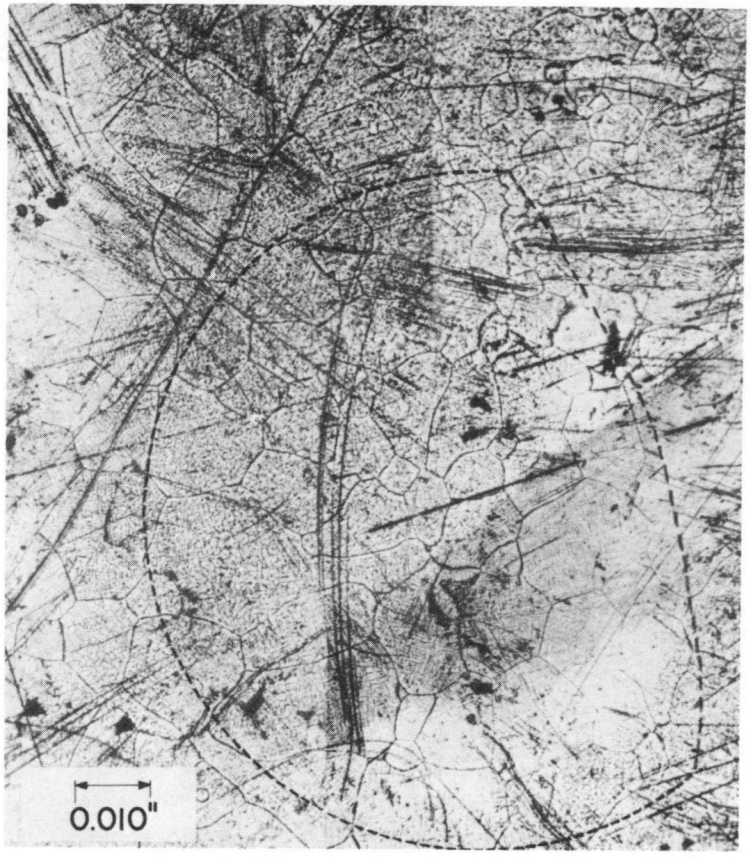

Fig. 6B. Photomicrograph
of carburized tantalum sample.

IMPROVEMENTS IN TECHNIQUE

The experiments described above do not represent the optimum conditions for sensitivity or resolution. Sensitivity can be improved by exposing the emulsion to weak light or by using NTB-2 or -3 plates. Optimizing irradiation conditions will also improve sensitivity. The resolution can be improved by using thinner emulsions and stripping techniques. Removal of surface after irradiation would reduce the surface contamination. Controlled etching as practiced by Albert[4] is the preferred method, but polishing would also reduce surface contamination.

More uniform beam intensity could be attained over a preselected area by a beam scanner to deflect the beam in the pattern required for the activation. For instance, the distributions of oxygen and carbon in germanium ingots could be obtained by irradiating a narrow region across the axis of the ingots.

CONCLUSIONS

Although the technique has not been optimized, the applicability of the method for measuring the microscopic distribution of oxygen and carbon in metal samples has been demonstrated. Resolution of 0.0005 inch has been attained on samples with bulk concentrations of 250 ppm. Reasonable extrapolations of the method should allow measurement on samples with bulk concentrations of about 25 ppm. Application of the technique will allow the determination of interstitial gradients in metals in a relatively simple manner. New experiments can be designed around this tool, and a better understanding of the role of oxygen and carbon in the properties of metals can be obtained.

REFERENCES

1. S. S. Markowitz and J. D. Mahony, "Activation Analysis for Oxygen and Other Elements by Helium-3-Induced Nuclear Reactions," Anal. Chem. 34, 329 (1962).

2. Dorothy A. Heller, "Radioautographic Techniques," p. 133 of "Advances in Biological and Medical Physics," vol. 2, J. H. Lawrence and J. G. Hamilton, eds., Academic Press, New York, 1951.

3. S. S. Markowitz and J. D. Mahony, " He^3 Activation Analysis for Carbon by $C^{12}(He^3,He^4)C^{11}$ Reaction," p. 419 of Radiochemical Methods of Analysis, vol. 1, IAEA, Vienna, 1965.

4. Philippe Albert, "Rapport de Mission Aux Etats-Unis," Voyage d'etude au Lawrence Radiation Laboratory et Berkeley du 2 Sept. au Oct. 1964. --- Directeur Scientifique au C.N.R.S. Laboratorie de Radiochimie Analytique du Centre d'Etudes de Chimie Metallurgique 15, Rue Georges Urbain, Vitry-sur-Seine, France.