MLM-2887(OP)

A NEW TECHNIQUE FOR MICROAUTORADIOGRAPHY AND TRITIUM PROFILING

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Abstract

A new technique has been developed for high magnification examination of autoradiographic emulsions. The technique enables a relatively quick examination of autoradiographic emulsions from large areas of metallographically prepared samples at magnifications of up to 50,000X. The technique also allows for profiling of the tritium distribution with the promise of quantitative profiling, all on a microscale.

Introduction

Autoradiography has been used for many years to detect the presence and location of radioactive species in materials. Actually, the technique was used before radioactivity was discovered, however, the understanding of what was happening was somewhat questionable. Most of the developments and improvements in autoradiographic emulsions and techniques have occurred only in the last fifty years. A reasonably comprehensive text covering the history and development of autoradiographic techniques has been written by Rogers(1) and is recommended to anyone attempting to utilize these techniques.

Autoradiography, in general, is any technique which utilizes radiation emitted from the subject of interest to expose a photographic emulsion and provide an image of the subject. There are several ways to accomplish this, the oldest being simply pressing the sample against a sheet or plate containing a photographic emulsion. After exposure, the emulsion is then processed like any photographic emulsion, and the image examined by appropriate techniques. Other techniques involve stripping a film of emulsion from a plate and placing it on the sample or applying a liquid emulsion directly on the sample, allowing it to dry, exposing and then processing the emulsion. The latter two techniques can be used to examine the emulsion in-situ on the sample and therefore identify the location of the radioactive species within the sample. The liquid

*Mound Facility is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. DE-AC04-76-DP00053.

emulsion technique can be medium to high resolution depending on the emulsion size and the technique used for examining the emulsion. The medium resolution is normally done by examination with a light microscope. The high resolution work previously required the use of a transmission microscope and the consequent reduction in available sample area for examination.

The Metallurgy Group at Mound Facility developed and has used autoradiography as an investigative technique for over 15 years. The technique developed has been used primarily to determine the depth of penetration of tritium into engineering materials and determine whether there are any segregation effects due to microstructural characteristics of these materials. Until recently, this technique utilized optical microscopy at magnifications limited to about 1500X and was relegated to qualitative evaluation only. Quantitative techniques were developed but were too tedious and complicated to be used on a routine basis and consequently have not been employed.

Recently, however, modifications of this technique have enabled in-situ autoradiographs to be examined at magnifications up to 50,000X on a metallographic sample. Preliminary work also indicates that a relatively simple technique should allow a reasonably quantitative determination of the amount of tritium present in microareas of the sample. Previous high resolution techniques required the counting of individual exposed grains of emulsion and correlating or calculating the concentration from this type of data.

Experimental Techniques and Results

The techniques developed at Mound utilized Kodak NTB-2 liquid emulsion which has a developed grain size of about 2000 angstroms. The emulsion is melted in a water bath ($\sim 60^{\circ}C$) and spread gently onto a metallographically prepared sample using a teflon rod. The original technique allowed for a twenty-four hour exposure. The emulsion was then processed in-situ on the sample and examined and photographed using a light metallograph. A typical sample, so prepared, is shown in Figure 1 at low magnification. The dark layer of developed Ag grains clearly shows the depth of penetration into this exposed sample. The optical appearance of a similar sample at somewhat higher magnification is shown in Figure 2.

A new technique has originated due to a discovery about five years ago but has been developed only in the last two years. This technique involves the examination and analysis of the normal autoradiographs, in-situ, in the scanning electron microscope (SEM). With modification of the emulsion, these can be examined at magnifications up to 50,000X.

The evolution of this technique was actually based on the serendipitous discovery of a little known phenomenon associated with scanning electron

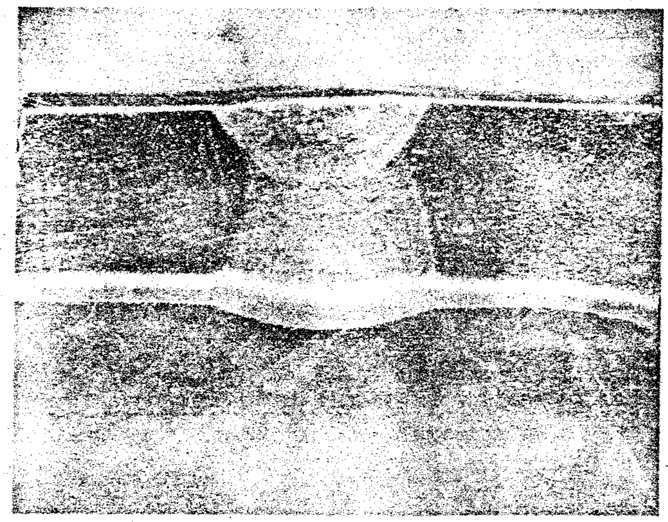


Figure 1. Low magnification (orig. 5X) optical photograph of a typical autoradiograph.

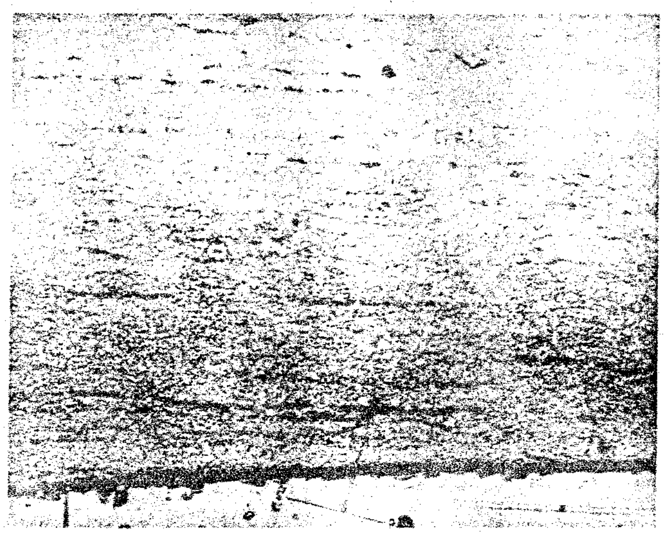


Figure 2. The appearance of a typical autoradiograph at higher magnification. (Orig. 100X)

microscopy. Samples of glass microballoons had been received with a request to measure the wall thickness. This was attempted by mounting the balloons on a SEM sample stub with silver paint. The balloons were broken and carbon coated for examination. The appearance of one of these balloons is shown in Figure 3. As can be seen, the silver particles

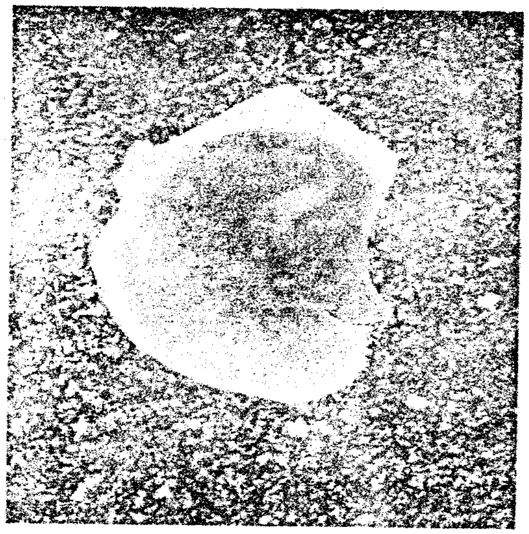


Figure 3

Transparency of a broken micro balloon (1.0 μm wall thickness) to the 20 Kv SEM electron beam. (Orig. 500X)

visible in the conductive paint are also visible through the wall of the glass balloon. These walls were measured to be about 1 μm thick. The appearance of the Ag particles through a crack in the glass and through the glass on either side of the crack is shown at higher magnification in Figure 4.

The reason for this apparent transparency to the electron beam is explained based on the penetrability of the glass to 20 Kv electrons. In this case, the electron beam strikes the top surface of the sample producing secondary electrons which are detected. Many of the primary beam electrons are able to penetrate completely through the wall where they strike the silver particles and are backscattered. These backscattered electrons are able to penetrate back through the glass wall and produce additional secondary electrons near the outer surface which are also detected. This transparency effect is limited to non-conductive, low density materials.

Figure 4

Resolution of Ag particles in silver paint through 1 μm of glass. (Orig. 1400X)

The applicability of this observed phenomenon to examining autoradiographs in the SEM was immediately realized. The autoradiographic emulsion in use was known to be about 3 μm of gelatin with the exposed silver grains primarily in the first 1 μm layer next to the sample. For examination in the SEM, the autoradiograph need only be treated like a regular metallographic sample, grounded with conductive paint and carbon coated to provide conductivity on the plastic and the gelatin of the emulsion.

The appearance of the microstructure through the autoradiograph for an exposed sample of 304L stainless steel is shown in Figure 5. The appearance of the same sample at high magnification to show the location of exposed Ag grains relative to grain boundaries is shown in Figure 6.

Tritium Profiling

The ability to use energy dispersive x-ray analysis (EDX) in the SEM now allows for a simple technique for determining the amount of tritium present and determining segregation effects if they exist. Since the number of exposed Ag grains in the emulsion is a function of the amount of tritium present, the area under the Ag peak in the x-ray spectra can be used to determine a tritium profile. The line profile for Ag showing

Figure 5

Appearance of the micro structure through the autoradiographic emulsion in the SEM. (Orig. 500X)

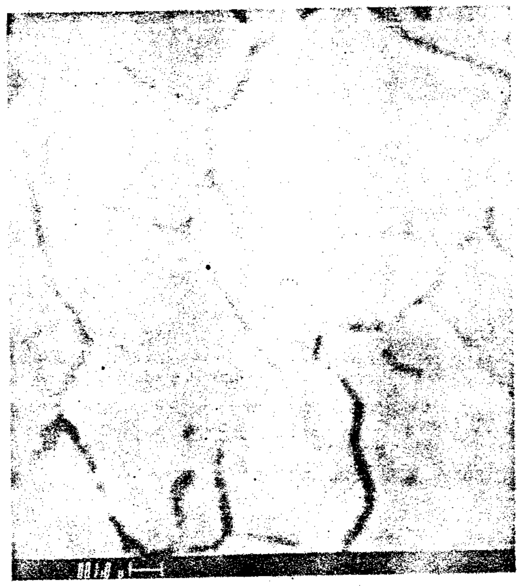


Figure 6

Resolution of Ag emulsion grains through a 3.0 μm gelatin coating in the SEM. (Orig. 5000X) tritium penetration into a 304L stainless steel sample is shown in Figure 7. This profile plots the peak intensity for Ag as a function of location as the electron beam slowly traverses the sample.

Figure 7

A line profile for Ag along the line shown illustrating the depth of tritium penetration. (Orig. 50X)

The above technique provides a relative profile; however, more accurate data can be obtained by counting for extended periods in a reduced area and plotting these counts as a function of depth or location. This technique is illustrated in Figure 8. An area 10 μm wide is shown in reduced area for the Ag counts next to an exposed surface of a sample.

The above technique can be made relatively quantitative by using a standard determined by another quantitative technique. This has been done using an exposed tubular 304L stainless steel specimen. One section of the tube was sectioned and machined at 50 to 250 μm increments. The turnings were weighed, dissolved and the amounts of tritium present determined by liquid scintillation counting. An adjacent section of the tube was quartered and each quarter mounted separately for autoradiography of the cross section.

The depth profile from radiocounting of this sample is shown in Figure 9. The depth profile from one of the autoradiograph samples is shown in Figure 10 based on counts for Ag in a 10 μm wide area for 20 seconds versus the depth of the area counted. Several areas on each of the four samples were counted, and the counts for a given depth varied by less than 2%.

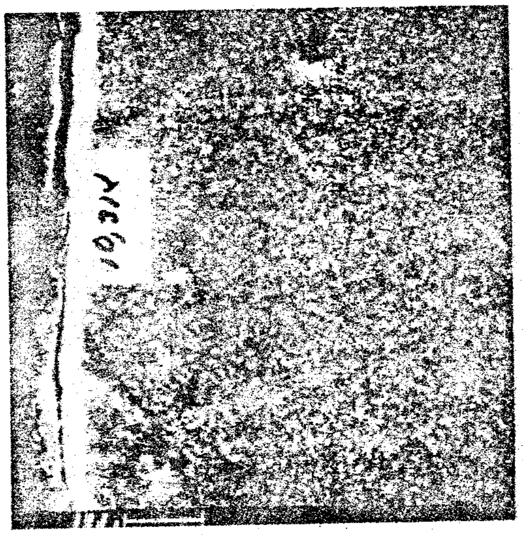


Figure 8

Illustration of the counting technique used for quantitative determination of tritium. The counts in the area shown were for a 10 sec interval. (Orig 1300X)

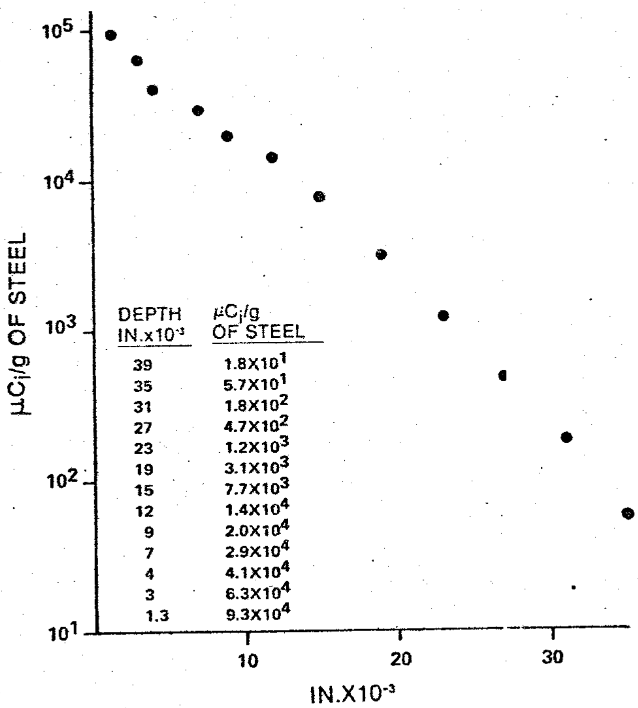
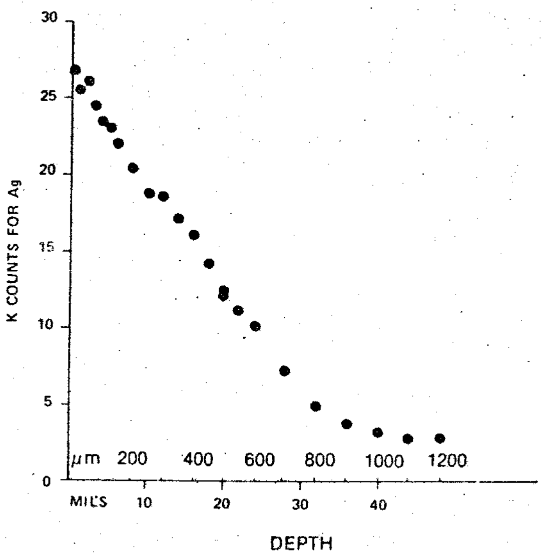


Figure 9

Depth profile of tritium as determined for a standard using liquid scintillation counting.
(10^4 μC_i/GM = 1 ppm by weight)

Figure 10

Depth profile for tritium in the standard sample based on Ag counts from the EDX in the SEM.



It is now possible to correlate the EDX Ag counts with the measured tritium concentration and establish a standard for comparing similar concentration ranges in similar materials. This is also dependent on exposure time of the autoradiograph and requires similar counting times and beam currents for the SEM as in quantitative microprobe studies. The calibration curve for a typical 24-hour exposure for this standard is shown in Figure 11. The best fit for these data for a linear plot in the range of concentration encountered was the log of tritium concentration versus the square root of the (Ag counts-background). The detectability limit for tritium using a 24-hour exposure was 1 ppb.

Higher Resolution

The preceding studies were all done using the straight Kodak NTB-2 emulsion which is about 3 μm thick. These samples could not be examined above 5000X without deterioration of the gelatin. Also, through the emulsion, the resolution of the Ag particles was not good enough to warrant examination above 5000X. However, recent experiments indicate that a gelatin thickness less than the developed Ag grain size is obtained with a dilution of the NTB-2 with distilled water. The dilution factor is 2:1 water to emulsion. A dilution of 2:1 emulsion to water gives a gelatin thickness of about 1 μm which would stop most of the tritium betas. The appearance of a sample using the former dilution is shown in Figure 12. This emulsion could be examined and analyzed at magnification up to 50,000X with no apparent deterioration.

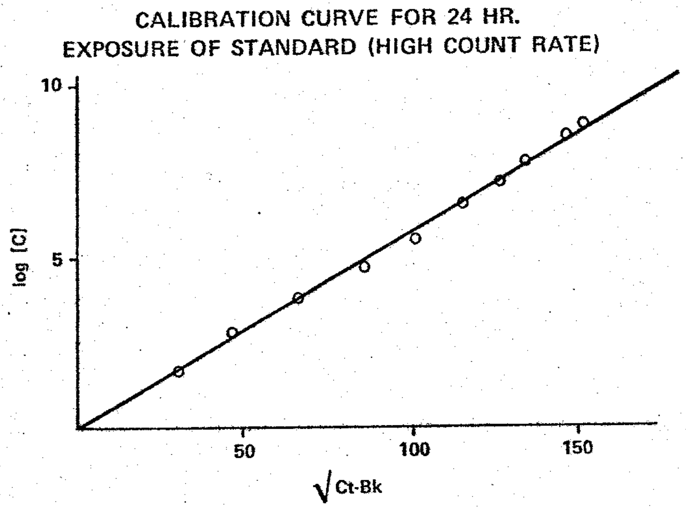


Figure 11. Calibration curve based on the $\log_e$ of the concentration of tritium in ppb as a function of the √counts under the Ag peak.

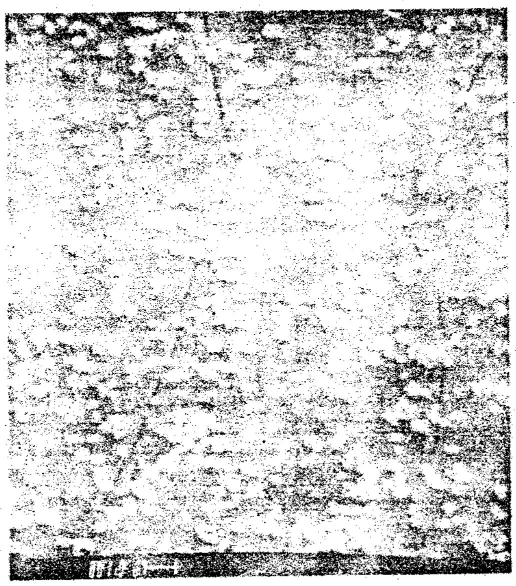


Figure 12. Greater resolution capabilities using diluted emulsion. (Orig. 5000X)

Discussion

Autoradiography techniques have been developed which provide an excellent technique for detecting the location and amount of radioactive isotopes in a material. This is especially valuable for hard to detect elements such as hydrogen or carbon. In general, this development has been limited to detecting tritium in austenitic stainless steel but other engineering materials can be investigated. It should be pointed out that the emulsions contain AgBr, which is a good oxidizing agent, and that potential chemical reactions resulting in reduced Ag grains are possible. All of the materials studied were passivated as part of sample preparation. If the chemical reactivity of the sample is not known, cold standards should be made to define background conditions.

The quantitative studies discussed were limited to the determination of one standard. The low levels of tritium present in this standard limit the range of quantitative work since the calibration curve does not extrapolate linearly beyond this level. If thinner emulsions are used for higher resolution, care must be taken to assure a uniform thickness for quantitative studies.

The newer NTE emulsions used for high resolution transmission studies should also be amenable to this technique and are currently under investigation. The particle size of the Kodak NTE or 129-01 is approximately 500 angstroms, which should allow higher resolution.

The accuracy of the quantitative work presented here has not been checked; and the work is offered only to indicate that the technique looks very promising. Much more extensive development would be required to determine the precision and accuracy of these measurements.

Acknowledgements

The author would like to acknowledge the contribution of several co-workers. Ken Chaney developed the machining and radiocounting technique and provided the data for the calibration curve. Dean Jones did all of the metallographic sample preparation for the autoradiographs. Good sample preparation is essential for reproducible results. Japnell Braun was the co-developer of the initial optical autoradiography technique and assisted in getting this manuscript completed.

References

1. Rogers, A. W., 1967, Techniques of Autoradiography, Elsevier Publishing Company, Amsterdam.