

NRL Report 6290

Optical Techniques for Electron Probe Analysis

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*X-Ray Optics Branch
Optics Division*

May 28, 1965

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U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

This study is concerned with two techniques in optical microscopy which exploit the principle of light interference to enhance optical contrast in metallurgical specimens.

The first method achieves this through interference layers formed within the specimen by anodization in an electrolyte. A variety of experimental arrangements are suggested for carrying out the anodization. It is also noted that the optical effects of anodization can be adjusted by overlaying the specimen with films of nitrocellulose.

The second method produces optical contrast through interference layers formed by replicating the etched-out surface of the specimen. This latter technique has the advantage of being applicable to any specimen which can be etched, and it is not limited to anodizable species. Here too, the optical results of replication can be adjusted by exposing the replica to the vapors of its solvent.

PROBLEM STATUS

This is a final report on one phase of the problem; work on other phases is continuing.

AUTHORIZATION

NRL Problem P04-04
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OPTICAL TECHNIQUES FOR ELECTRON PROBE ANALYSIS

INTRODUCTION

Microscopy plays a vital role in electron probe microanalysis by being able to elucidate the surface geometry of metallurgical specimens. This it accomplishes not only by way of instrumental capability but also through a diversity of techniques aimed at enhancing optical contrast of the specimens.

Of particular interest is the technique of anodization, with its ability of produce color contrast in certain metallurgical species (1). For such specimens the effect amounts to a mapping out, in color, of the surface microstructure. The coloration results from the differential rate of oxidation of the component metals when they are made anodic in a specially formulated electrolytic reaction. It has been noted further that the color is related directly to grain orientations in a metal, as well as to phases in alloys.

Also under development is a technique which maps out in color the microstructure of any specimen, whether anodizable or not, and requires only that the specimen can be etched with respect to microstructure. The technique is an adaptation of the replication procedure used in electron microscopy, except that the replica thicknesses are chosen to be within the spectral range for light interference rather than for electron transmission. Granted this condition, then, the microstructure will replicate out in color, becoming visible when the replica is viewed after it has been stripped off the specimen.

ANODIZATION PROCEDURE

Description

Dish Setup - The anodization results illustrated in this report were obtained by the simplest means, as can be seen from Fig. 1. The essentials consist of

- a. the anode probe
- b. a platinum cathode
- c. a glass dish
- d. a dc power supply (0-300 volts)
- e. an electrolyte, such as the following used by Picklesimer (2):

60 ml ethyl alcohol
35 ml water
20 ml glycerin
10 ml lactic acid
5 ml phosphoric acid
2 gm citric acid.

The mechanical simplicity of this general purpose setup is made possible by using a probe point made of anodizable metal such as Nb. This permits contacting the completely submerged specimen without upsetting the conditions for anodization.

Jet Setup - This arrangement was considered for those occasions requiring the electrolyte to be supplied as a jet of fluid. In this setup the specimen is held in position by an anode clamp, as shown in Fig. 2.

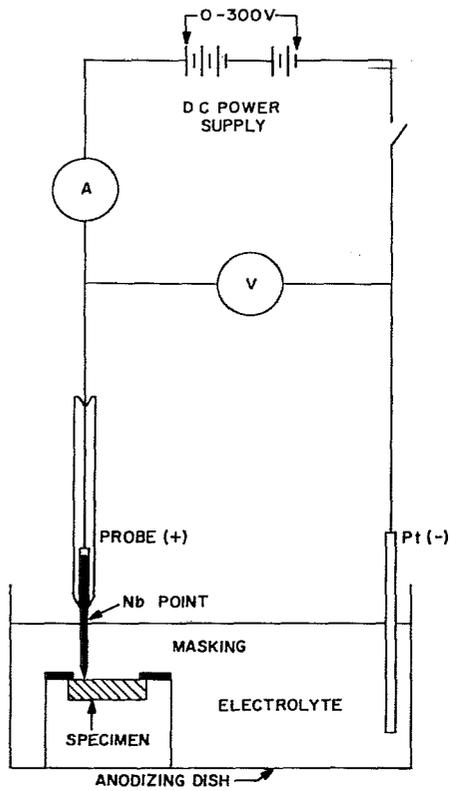


Fig. 1 - Dish setup for anodization with stationary electrolyte

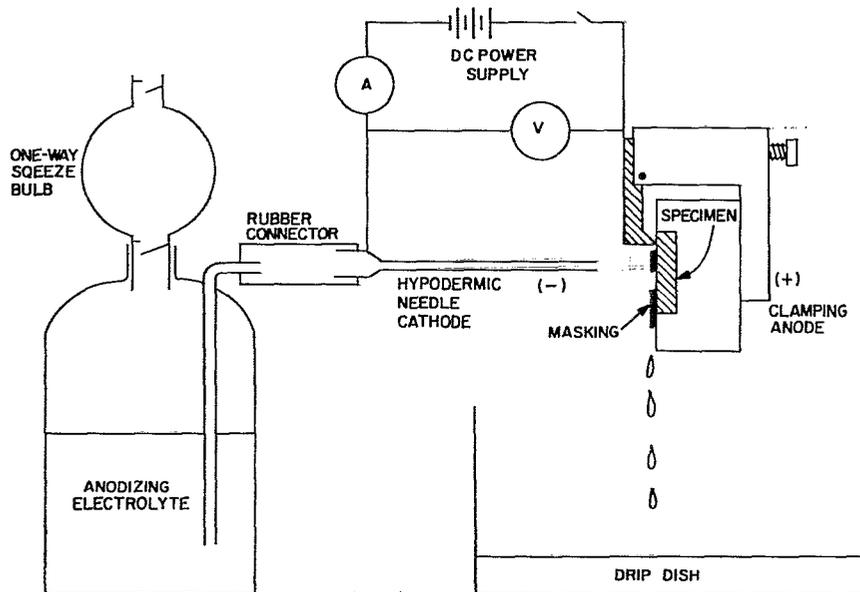


Fig. 2 - Jet setup for anodization with flowing electrolyte

Microscope Setup - Several arrangements were conceived which would permit the use of a microscope during the anodization of the specimen. These variations occur because of the particular facility each offers in containing the anodizing electrolyte. The arrangements are shown in Fig. 3.

Specimens

Preparation - In addition to the usual metallographic preparation of mounting in bakelite and polishing to a smooth finish, the specimen requires only to be masked completely,

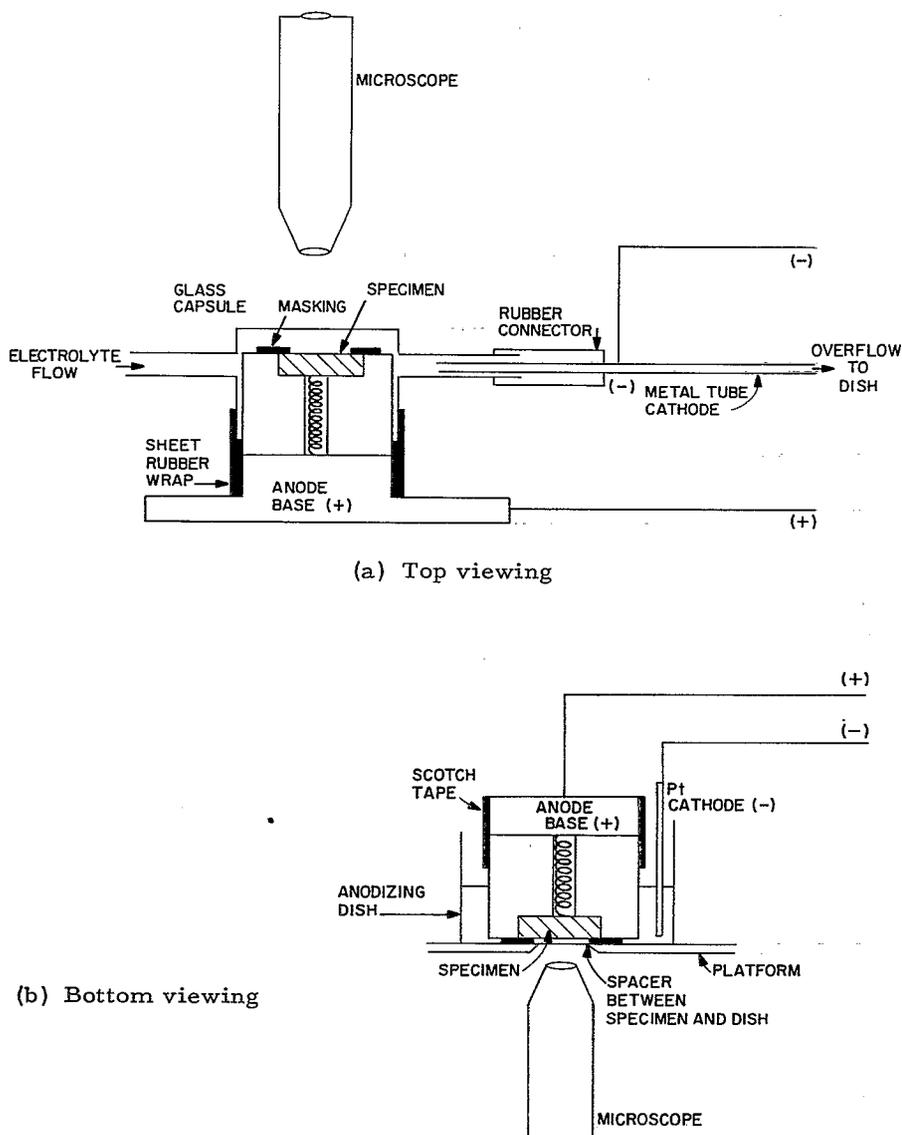
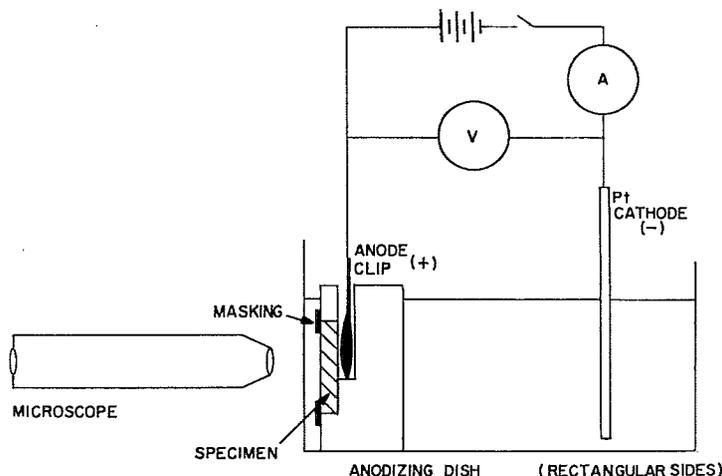


Fig. 3 - Microscope setup for monitoring anodization of metallurgical specimens



(c) Side viewing

Fig. 3 (cont'd) - Microscope setup for monitoring anodization of metallurgical specimens

except for the area to be anodized. The masking is especially important in preventing electrolytic breakdown at the metal/bakelite interface. A very suitable means of doing this is by using scotch tape. The stop-off lacquer used by electroplaters is also very effective.

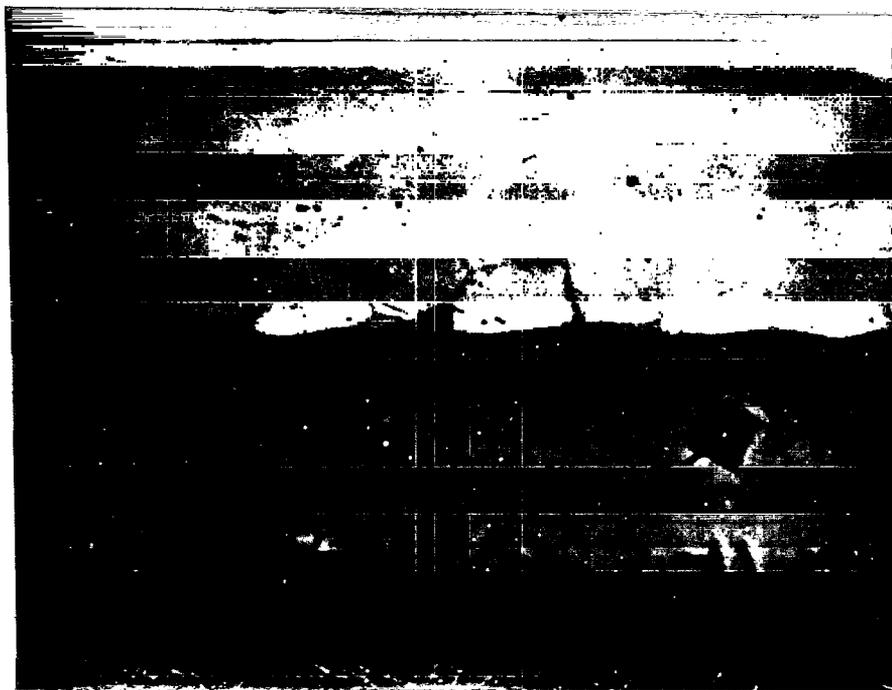
Species - The particular metallurgical species anodized in this study are diffusion couples representing two special categories in anodization. The Nb-Ti specimen is an example of a group whose metal constituents both anodize in an electrolyte. Figure 4(a) shows such a specimen as it appears without anodization, and Fig. 4(b) as it appears with anodization. The upper region of these figures is the Nb side of the diffusion couple, and the lower region is the Ti side. The Ni-Zr specimen is an example of a group whose metal constituents do not all anodize in an electrolyte. This specimen is seen in Fig. 5(a) when not anodized and in Fig. 5(b) after being anodized. In this latter case, Ni goes into solution while only the Zr anodizes (and then only with difficulty, depending on the effective area of the Ni).

The first specimen group mentioned above presents little difficulty, other than having to determine the proper voltage for obtaining the optimum in color contrast. This can be facilitated by making a color-voltage strip for each metal in the specimen and comparing the strips alongside each other. An easy way of doing this is to unmask and anodize successive intervals of each strip in a descending voltage sequence. In this way one takes advantage of the masking action of the preceding anodized intervals against the effects of anodization at the lower voltages.

The second specimen group calls for closer control of the electrolysis to minimize dissolving the nonanodizable metals. For the Ni-Zr diffusion couple this meant masking off the Ni wherever possible, raising the dc voltage until the Zr could anodize, and terminating the electrolysis at a point when anodization had ceased. This point can be recognized on the current meter as a leveling off of the current to a minimum value, which represents the dissolution current of the Ni. For this couple it was also possible to resort to ac voltage to minimize the dissolution of Ni. The extent to which this alternative can be taken with specimens other than Zr species remains to be investigated however.

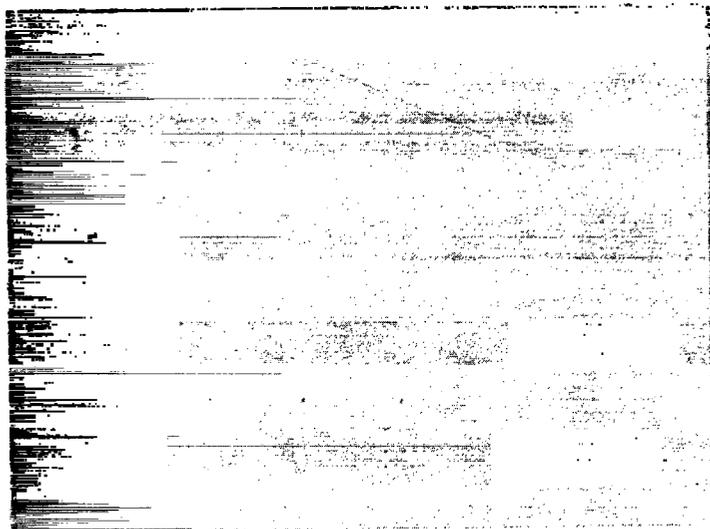


(a)

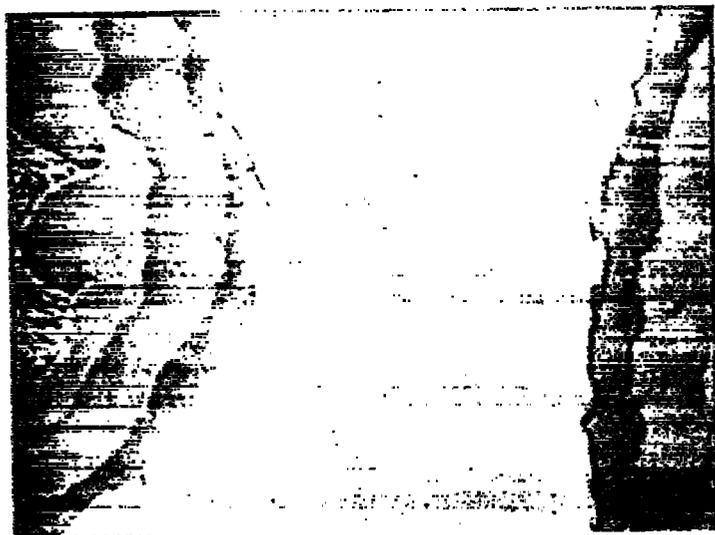


(b)

Fig. 4 - Nb-Ti specimen (a) without anodization and (b) with 90-v, dc anodization. (Original magnifications 500X.)



(a)

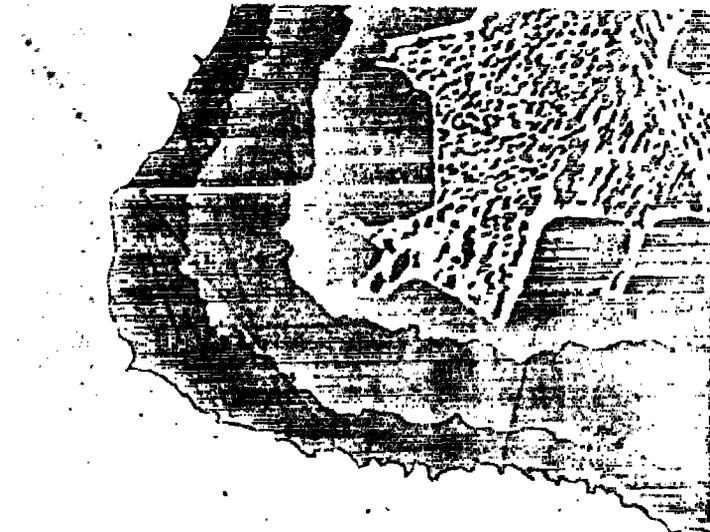


(b)

Fig. 5 - Ni-Zr specimen (a) without anodization and (b) with 90-v, dc anodization. (Original magnifications 1000X.)

Color Maneuvering

A realization that the coloration in anodization results from the optical interference caused by the oxide layer led naturally to the concept of adjusting the optical thickness by overlaying the specimen with a film of nitrocellulose. Figure 6(b) shows the same specimen area as Fig. 6(a), but with a nitrocellulose film added to reverse the contrast of the precipitates and surrounding matrix.



(a)



(b)

Fig. 6 - Ni-Zr specimen (a) anodized and (b) anodized, but with about 1000A nitrocellulose film added. Note the reversal in contrast of the precipitates. (Original magnifications 1000X.)

REPLICATION PROCEDURE

Description

It was soon apparent that the use of films in producing color could be exploited still further by an adaptation of the replication technique used in electron microscopy. Replication in electron microscopy is a means of transferring the surface geometry of any specimen to a media more suited to examination by electron transmission. This same means can be adapted to replicating the microstructure etched out of any specimen, whether anodizable or not. The replica thickness can be chosen to bring the specimen geometry within the optical range of light interference with the result of producing color contrast. This technique was first applied to the anodized surface of the above Ni-Zr specimen to test the effectiveness of the method. Figure 7(a) shows the surface that was replicated and Fig. 7(b) shows the replica itself, on a grid support, with its mirror image of the surface features.

Procedure

The procedure worked out thus far takes into account the need to intensify the colors in the replica and also the need to restore the replica to its original shape so as to fall within the depth of focus of the microscope. The etched specimen is coated with a solution of collodion of such concentration as to form a coating thick enough to produce colors

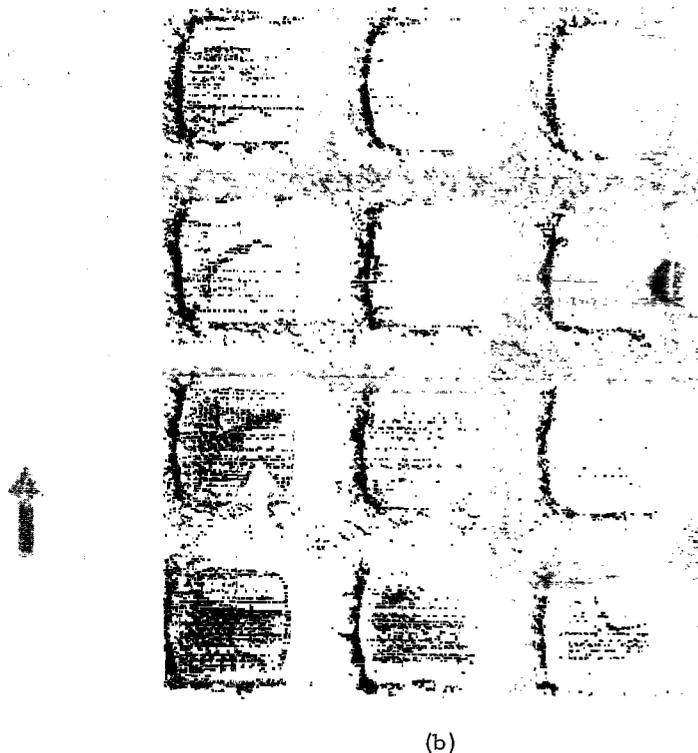


Fig. 7 - Ni-Zr specimen (a) anodized with 90-v dc and (b) its mirror image in the replica resting on a grid support. (Original magnification 200X.)

visually. The coated specimen is then coated in a vacuum with a semitransparent layer of Al. In this way the specimen helps to dissipate any heat that might disfigure the replica. The surface is then prepared for stripping by adding a layer of gelatin to reinforce the replica. Scotch tape is then applied over this surface to permit stripping off the replica. The collodion-gelatin is then separated from the tape and floated over warm water to dissolve away the gelatin. This permits the replica to mount the grid support without wrinkling and to assume its original shape as much as possible. The replica is then ready for microscopic examination.

Color Maneuvering

The color results in this technique can also be maneuvered merely by arranging an enclosure over the replica so as to hold an atmosphere of amyl acetate vapor. Figure 8 illustrates one such arrangement using a wooden flat wetted with amyl acetate and held directly over the mounted replica at some fixed distance. As the amyl acetate vapor causes the nitrocellulose to swell, the interference colors progress through the spectrum. The operator can adjust the amount of vapor to keep the color at some desired condition long enough to make a photograph.

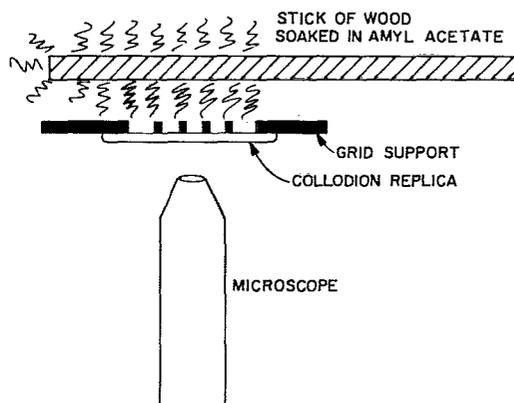


Fig. 8 - Replica setup for color maneuvering

ACKNOWLEDGMENT

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2. Picklesimer, M.L., "Anodizing as a Metallographic Technique for Zirconium Base Alloys," ORNL Report 2296, Oak Ridge National Laboratory, May 27, 1957

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