Lawrence Berkeley National Laboratory

Recent Work

Title

AN IMPROVED PHOTOGRAPHIC PROCESS FOR CONVERGENT BEAM ELECTRON
DIFFRACTION APPLICATIONS

Permalink

<https://escholarship.org/uc/item/8mn6f4pd>

Authors

Turner, J.H.
Krishnan, K.M.

Publication Date

1986-05-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

AUG 12 1986

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to Journal of Electron
Microscopy Technique

AN IMPROVED PHOTOGRAPHIC PROCESS FOR CONVERGENT
BEAM ELECTRON DIFFRACTION APPLICATIONS

J.H. Turner and K.M. Krishnan

May 1986

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks*

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

AN IMPROVED PHOTOGRAPHIC PROCESS FOR CONVERGENT BEAM ELECTRON DIFFRACTION APPLICATIONS

John H. Turner and Kannan M. Krishnan
National Center for Electron Microscopy
University of California
Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

The use of a surface developer, pyrocatechol, to process transmission electron microscope negatives has been shown to have significant advantages over the conventional D-19 process. The process described here is tolerant of a large margin of error in the electron exposure and produces a negative that not only retains details both in the highlight as well as the faint regions, but also preserves local contrast. These characteristics are particularly useful in convergent beam electron diffraction applications where one encounters a wide contrast range. Improved acuteness and an enhanced signal to noise ratio due to the prolonged exposures associated with this process have also been observed.

Introduction

It is recognized that the use of the conventional D-19* process to develop photographic negatives used in transmission electron microscopes for convergent beam electron diffraction suffers from two inherent limitations: the wide intensity range in the actual electron exposure and the narrow latitude of film development. Further, the exposure meters in the microscope are unreliable for these applications. Hence it is necessary to estimate the required exposure accurately, as this conventional process is very sensitive

to incorrect exposures and allows little room for correction once the exposed film is developed. In principle then, for best results, this procedure requires a set of different and accurate exposures that are determined for the intensity of the different regions of interest in the diffraction pattern.

Ideally one would like to use a processing mechanism that is tolerant of a large margin of error in the electron exposure and which produces in a single negative, fainter details as well as details in the highlights. A popular photographic method of approximating this ideal requirement is to resort to the use of a mixture of sodium thiosulphate and potassium fericyanide (Farmers* reducer) to etch the surface of the negative after the film is processed, thereby thinning the dense regions, and altering the negative permanently. Since this is a subtractive reducer, it also completely eliminates the fainter regions of the negative before reducing the highlights. Alternatively, some finer details in the over-exposed regions of the negative can be brought out by "burning-in" during the printing process.

This paper describes a series of experiments using three other development solutions to find a good alternative to the D-19 process. Our aim has been to develop a process in which (a) the actual electron exposure is not critical, (b) the negative is reasonably easy to print, (c) there is a large development time latitude, and (d) a negative that retains details both in the highlight as well as the faint regions is obtained.

Experimental Details and Results

A thin electron transparent specimen of MgAl_2O_4 (spinel) was made by ion-milling. The specimen was tilted to a [100] zone-axis orientation and a series of convergent beam electron diffraction patterns with exposures ranging from 0.12s to 64s were taken. This orientation was chosen because the [100] zone-axis pattern in spinels exhibits one of the widest contrast ranges possible. In addition, the presence of subtle detail in and around the two faint excess lines at the kinematically forbidden 200 positions due to double diffraction from the first order Laue zone (Steeds and Evans, 1980) would provide a good test for the quality of the development process. All experiments were performed on a JEOL 200 CX transmission electron microscope operating at an acceleration voltage of 100kV and at normal bias with a beam current of 50 μA . A low temperature (approximately -165°C) double tilt holder was also used.

Three different processes (Jacobson and Jacobson, 1978; Kodak, 1983) were tried, with varying results. First, a commercially available phenidone developer (Technidol LC*) was tried. This is an extremely low-contrast developer used generally for slow films with inherent high contrast. It was found that the contrast indeed was flattened. However, contrast among fine details was also destroyed. Next, we tried a split developer, using a mixture of Metol (Elon*) and sodium sulphite as the first solution and sodium carbonate as the second. In this process the negative is first saturated with the developing agent in solution after which it is immersed in the alkali bath to accelerate the development. The developing agent exhausts quickly in the highlight regions and halts development there, while the fainter regions continue to develop with a slower exhaustion rate, thereby balancing the overall contrast of the negative. The overall contrast of the negative was good but the local contrast of the finer details was again insufficient.

A radically different approach, using a surface or tanning developer, Pyrocatechol (Table 1), produced remarkably improved results. This is a slow working fine-grain developer. In such developers the initial surface reaction product from the development in the highlight regions considerably slows down further development in the deeper regions of the emulsion relative to other fainter regions of the negative. A typical negative following this development appears brown instead of black, due to the staining of the reaction product. The color of the stain works very much like a safelight filter to prevent print exposure and thus produces printing contrast with good gradation over the entire range of exposure. This stained negative continues to be transparent in the most dense highlight regions, unlike the opaque highlights of the D-19 process. It is precisely this transparency that allows us to contain the entire range of exposure on a single sheet of film, and retain good contrast throughout the negative. The effective speed of the film is reduced; i.e., much longer exposures than normal are required (an exposure of 16 seconds produced good results for a pattern that required an approximate exposure of 1 second for D-19 development). The ability to monitor the development of this film in the dark room under safelight conditions, and a large development time latitude, allows one to accommodate a much larger exposure range (i.e., 8-64 seconds with appropriate adjustment in developer strength or development time).

The electron microscope film (Kodak SO-163), used for this experiment, has an emulsion layer overcoated with a thin hardened gelatin layer. It was found that the use of this pyrocatechol solution causes the gelatin to swell excessively. This adverse characteristic can be eliminated by pre-hardening the gelatin for 10 minutes in a solution of sodium sulphate, sodium carbonate and formaldehyde (Table 1) prior to the development. This solution is best prepared immediately before use.

A comparison of the negatives obtained using the conventional undiluted D-19 process and the Pyrocatechol surface developer is shown in Figure 1. Because of the narrow range of the former, two different exposures are required, an extremely short one (0.2 seconds) for the highlights (a) and a substantially longer one (4 seconds) for the fine outer details (b). On the other hand, (Fig. 1c), a single exposure (16 seconds) followed by a prolonged development (10 minutes) using pyrocatechol yields optimum results. Figure 2 shows two regions printed from the same negative which was developed using the surface development process.

Figure 3 summarizes the nature of the development processes used in this experiment. The straight line segment of these characteristic curves determines the ideal exposure range of the film for the particular developments. In addition, contrast is directly proportional to the slope of the curve. A typical CBED pattern contains an extremely wide range of intensities which is beyond the limits set by the contrast of the D-19 developer. Split development and Technidol LC exhibit an ability to contain a wide exposure range but with poor contrast. The pyrocatechol curve indicates a longer straight line segment along with good contrast in the highlights as well as the faint regions. Note that in addition to a much larger exposure range compared to the D-19 process, the prints exhibit a very high resolution, particularly in the vicinity of the higher order lines in the double diffracted 200 spots. We believe that this is perhaps due to an increased signal to noise ratio in the course of such prolonged exposures coupled with this low activity developer. In fact, the improved resolution inherent in this image should shed some light on the controversial question of the space group of spinels (de Cooman and Carter, 1985).

Conclusion

We have shown that the use of a surface developer in conjunction with longer exposure to process convergent beam electron diffraction pattern negatives overcomes the limitations of the more commonly used D-19 process. The negative exhibits the ability to contain the entire range of electron exposure intensity as well as allowing for reasonable latitude in exposure time. Further, enhanced resolution and easy implementation of the process make this a very attractive alternative.

* Kodak Tradename.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. De Cooman, B.C. and Carter, C.B. (1985) On the point group of stoichiometric spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$. *Phil. Mag.*, 51, 175.
2. Jacobson, C.I. and Jacobson, R.E. (1978) *Developing*, Focal Press, London.
3. Kodak Trade Publication KP78838a 2-83 (1983).
4. Steeds, J.W. and Evans, N.S. (1980) Practical examples of point and space group determination in convergent beam diffraction. *Proceedings of the 38th Annual EMSA Meeting*, edited by G.W. Bailey (Baton Rouge: Claitors'), 188.

TABLE 1.

(Note: This process is for use with KODAK SO-163 film only).

1. Pre-Hardening Bath
(to make 1 liter)

Water	900 ml
Sodium sulphate	50 grams
Sodium carbonate	12 grams
Add water to make	1000 ml
Formaldehyde 37%	5 ml

Soak film in this hardening bath for 10 minutes. Rinse film before immersing in developer. (Without this bath, the gelatin will become swollen and damaged in the developer).

2. PYROCATECHOL DEVELOPER

Prepare solution A with:

Distilled water	200 ml
Pyrocatechol	16 grams
Sodium sulphite	2 1/2 grams

Solution B is a 10% solution of sodium hydroxide:

Water	100 ml
Sodium hydroxide	10 grams

(Store parts A and B in dark bottles).

Generally this solution can be used as follows in one liter of water:

Water	1000 ml
Part A	40 ml
Part B	10 ml

The strength of the developer is best altered by changing the amount of Part B. If you find that the developer is too strong, reduce Part B and conversely, if too weak, increase Part B. The solution should be used for one session and discarded as the solution does not keep well. This developer can be used for a development time range of 5-25 minutes. The film should then be fixed and washed as usual.

Figure Captions

- Figure 1. [100] zone axis pattern negatives of MgAl_2O_4 using the conventional D-19 process (a and b) and the pyrocatechol surface developers (c). Notice that the densities in the first order Laue zone and the zero order Laue zone are within printing limits.
- Figure 2. Details of the zero order Laue zone and a segment of the first order Laue zone including the (1, 21, 1) and (1, 21, 1) reflections. Both these regions were printed from the same negative (Figure 1c).
- Figure 3. Comparison of the effective printing density of the negative as a function of the exposure for the three different developments (arbitrary scales are used). It is obvious that the pyrocatechol surface developer saturates at a much higher electron exposure, thereby containing the entire range of electron intensities shown in Figure 2.

a

5507726

b

5507727

c

5507728

Figure 1.
XBB-864-2944

Figure 2.
XBB-864-2943

Figure 3.
XBL-864-1502

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*