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Editor(s)	
Citation	Bulletin of University of Osaka Prefecture. Series A, Engineering and natural sciences. 1964, 12(2), p.139-144
Issue Date	1964-03-30
URL	http://hdl.handle.net/10466/8055
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Preparation of NiO Specimens for Transmission Electronmicroscopy

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(Received November 30, 1963)

Descriptions are made on the preparation of NiO specimens for transmission electronmicroscopy, from a crystal of macroscopic size, a technique of ion bombardment being employed at the final stage of the thinning process. Thus, specimens prepared by the present method contain ion damages which can however be removed completely by a full annealing.

1. Introduction

Observations of lattice imperfections by transmission electronmicroscopy have so far been made mostly on metals and alloys[1] and also on ionic crystals.[2] However, oxides are few whose imperfections were subjected to direct observations,[3] because it is difficult to obtain thin foils from oxide crystals of macroscopic dimension. Therefore, it is intended to prepare electronmicroscopic specimens from large crystals of various oxides.

Among others, the preparation has been begun with NiO, which was investigated chiefly by x-ray diffraction methods in the present authors' laboratory. This oxide is an antiferromagnetic substance with its Néel temperature at 250°C. The cubic lattice in its paramagnetic state begins to distort rhombohedrally at the Néel point on cooling and the origin of this distortion is considered to be purely magnetic. The critical difficulty in preparing NiO specimens for transmission electronmicroscopy arises mainly from the resistibility of the oxide to both chemical and electrochemical attacks by which the final thinning ot specimens can usually be attained.

The present paper reports a technique of thinning NiO crystal blocks, by ion bombardment, down to the thickness which enable one to perform a direct observation by transmission electronmicroscopy.

2. Apparatus of Ion Bombardment

Experiments of ion bombardment have hitherto been made mostly on metals and alloys and very few informations could be available for nonmetallic materials. Therefore, the present apparatus has tentatively been constructed following one[4] of the simplest techniques used for ionic etching of metallic specimens with some modifications. The electric circuit and the ion discharge tube of the apparatus are as shown respectively in Figs. 1 and 2. T in the former is a transformer to produce an electric potential necessary

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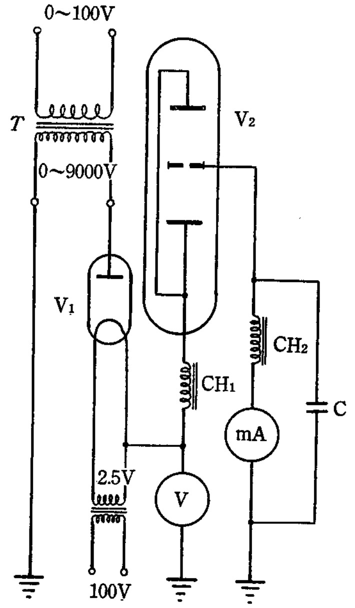


Fig. 1 Electric circuit employed for ion bombardment.

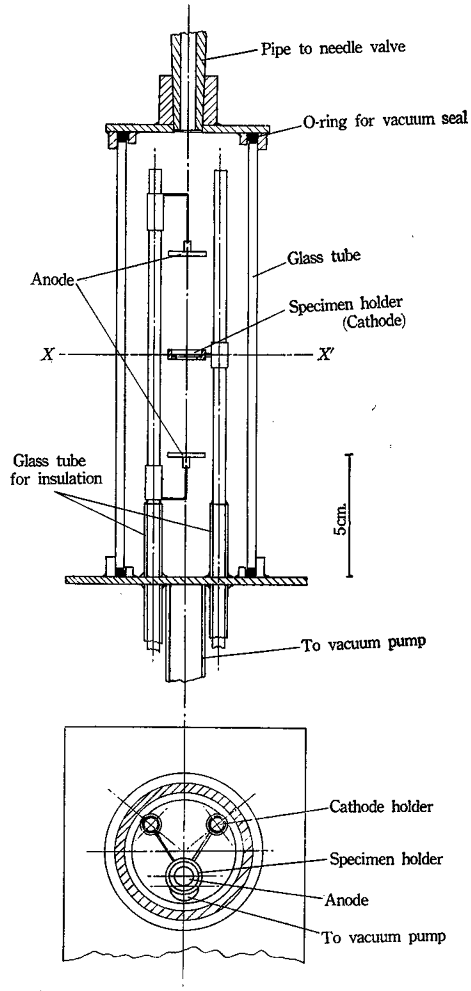


Fig. 2 Schematic drawing of ion discharge tube.

for the ionic discharge. This has been made by taking an iron-sheet core for magnetic flux leakage off from a neon-lamp transformer of standard type with capacity of 20 ma. at 9 kv. The current rectification is made by a valve, V_1, and is therefore simply a half-wave rectification. The resulting pulsating dc voltage is lead, through a choke coil CH_1, to the anodes of discharge tube. It is given up, for the moment, to smooth out the voltage pulsation by earthing each or one end of the choke coil CH_1 through a condenser, because such a connection seems to have a tendency of inducing very severe current pulses of low frequency. The reason is not clear at present, and even without the condenser for getting a nearly constant potential, the milliammeter, mA, must be protected, by both a condenser, C, and a choke coil, CH_2, from the current pulses which arise occasionally at lower gas pressures in the discharge tube.

Almost no special care was paid to the design of the discharge tube except for the

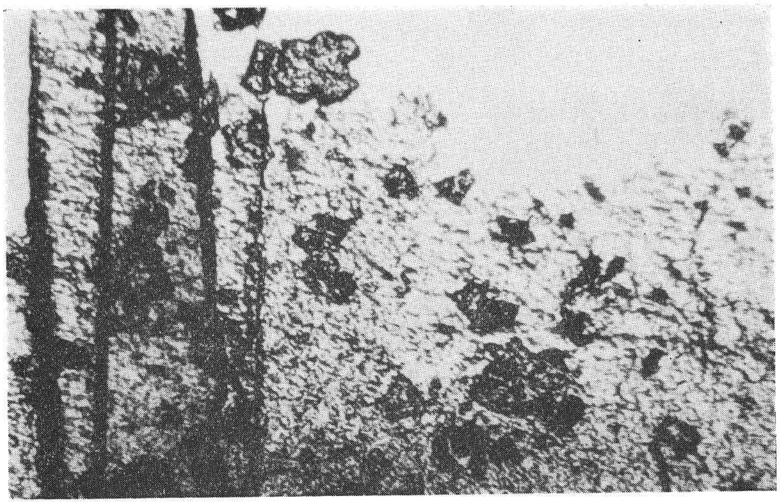
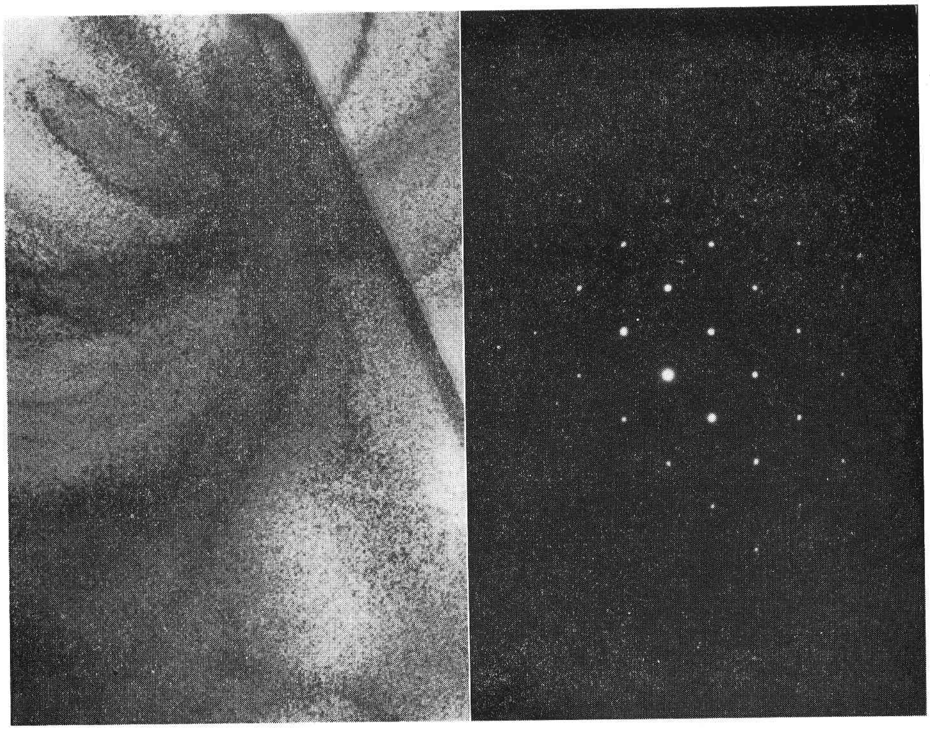


Photo. 1 Photomicrograph of NiO Specimen prepared by ion bombardment (×75)



(a) Electronmicrograph (b) The corresponding diffraction pattern

Photo. 2 NiO specimen prepared by ion bombardment conveniency of assembling and diassembling. However, as for the electrodes, several tests were performed on the effect of shape and separation and further of the employment of third electrode. A favourable condition was obtained by the setting as shown in Fig. 2. Electrodes, a negative one of which serves as a specimen holder, are made of aluminum that can hardly sputter on collision of charged particles. The sample on the cathode is placed at the middle of the two anodes, so that thinning of the specimen by ion bombardment would proceed at the both surfaces of the specimen plate. A needle valve is used to controle the gas pressure inside the discharge tube, air being employed as the gas to be ionized in the present experiment only for the reason of simplicity.

3. Preparation of Specimens

An NiO crystal grown by flame fusion method was cleaved into a thin plate less than 1 mm in thickness so that its both faces were flat and parallel, the plate being subjected to a treatment of thickness reduction. Before bombarded, thickness of the specimen plate should be reduced mechanically to several tens of microns to save the time necessary for ion bombardment. The procedure of the mechanical reduction is similar to that used in the preparation of a small sample for metallurigical micrography, in which a sample is mounted on a moulding material. However, the mounting material should be so transparent as to be able to see the thinning process, and further it should never require even a small pressure on moulding the specimen because a thin plate of NiO is very fragile. In the present case, a commercially available adhesive, "Araldite R", was employed as a moulding material with a glass tube as a moulding case, the approximate thickness of the specimen being estimated from its transparency to the visible light.

The thinned specimen was released from the mount by oxydizing the adhesive off with hot potassium dichromate solution containing concentrated sulphuric acid. The NiO flakes thus liberated were annealed at 1200°C in air for longer than 10 hours to remove stresses induced by the mechanical treatment, after being washed and dried by the same treatment as the usual one for samples for electronmicroscopy.

The bombardment was made under the ion discharge current ranging from 3 to 7 ma. at the working dc potentials confined between 1 and 2 kv., both the current and voltage being lowered with the progression of thinning. However, only a small fraction of the current must be effective for bombarding the specimen, because the majority of ions would be repelled to the metallic holder by positive charges accumulated on NiO. Therefore, to reach an adequate thickness, a bombardment for a fairly long time more than 100 hours is necessary under the conditions mentioned above. Photo. 1 is a photomicrograph of a sample thus prepared, taken by transmitted light. It shows that the flake has neither uniform thickness nor flat surfaces and therefore that the etching does not proceed uniformly by the ion bombardment and only the thinnest parts of such flakes could be available for the direct observation.

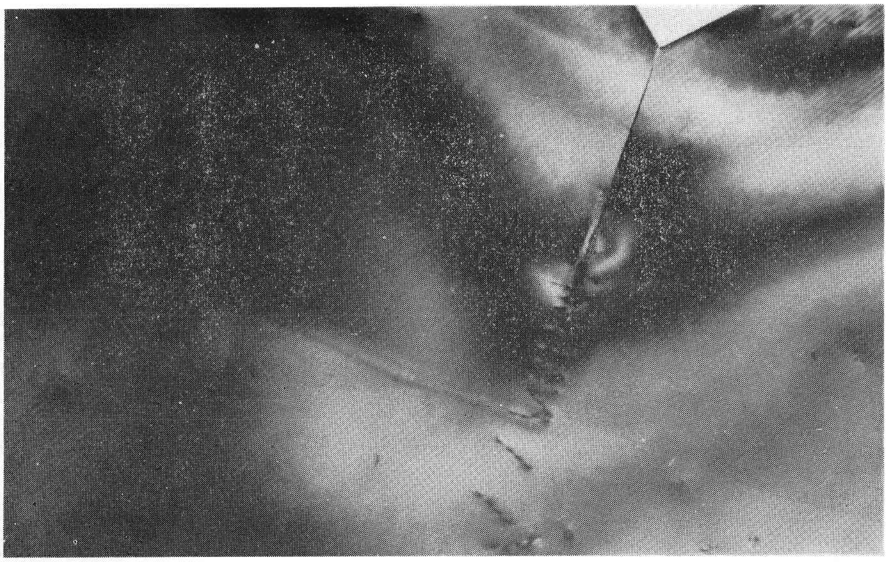


Photo. 3 NiO specimen annealed at 1200°C for c. a. 1 hr. in air.

4. Electronmicroscopic Examinations

Specimens prepared were examined in transmission in an electron microscope of HUII type at a magnification of 19,000 under an applied voltage of 100 kv., a photographic enlargement being 2. An example of electron micrographs of NiO specimens prepared by the present method is shown in Photo. 2 (a). The most characteristic feature of it is the presence of small spots (dots) finely dispersed throughout the whole region of the micrograph. But the corresponding diffraction pattern shown in Photo. 2 (b) shows no indication of the presence of substance other than NiO. Therefore, the dots may be considered to be images of damages formed by the ion bombardment in the course of the specimen preparation. Actually, no dots can be detected in micrograph of fully annealed specimen as shown in Photo. 3, where a crack along [*110*] and several dislocations are clearly observed. The results of the direct observations on many NiO specimens prepared by the present method will be published elsewhere.

5. Conclusion

It has become possible to prepare NiO specimens for transmission electron microscopy, from a crystal with macroscopic dimensions, by means of ion bombardment. At the present stage of technical dovelopment, the speed of thickness reduction by the bombardment is very low. Therefore, to save the time of specimen preparation it is necessary to make the specimen plate as thin as possible by some means before subjection to the ion bombardment

Unfortunately the introduction of ion damages into the final specimen can not be avoided because of the original nature of the preparation, though the damages can easily be swept out of the specimen by a full annealing.

The present technique could be applied to crystals of the other kinds which can hardly be attacked chemically or electrochemically.

Acknowledgements

The authors wish to express their sincere thanks to Prof. Z. Nishiyama who encourage them in the present work and allowed them to examine their specimens by the electron microscope of HUII type equipped in his Institute. Thanks must also be extended to Prof. S. Nagata, Prof. Y. Tomoda and Dr. Y. Watanabe who offered kind opinions based on their experiences on bombardment practices. Further, the authors are indebted to Dr. Y. Nakazumi for his kind offering of NiO crystals.

The cost of this investigation was partly defrayed from the Grants from Scientific Research in the Ministry of Education.

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