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Abstract

A simple, routine method has been developed that allows ion-irradiated foils to be examined in cross-section. The method has been successfully demonstrated on three alloy systems (stainless steel, a low-chromium steel, and some high-strength copper alloys), and is generally applicable to most metals. The high success rate that is obtainable using this procedure allows several specimens to be examined from a single irradiated sample. This implies that statistically significant void and precipitate distributions may be obtained from irradiated specimens as a function of depth (damage level). This technique also allows multiple testing techniques (such as microscopy, scratch hardness and microhardness) to be simultaneously performed on a single irradiated sample. The preparation technique is described in detail and some typical applications are illustrated.

Introduction

Ion irradiation experiments have proven to be very useful as a radiation damage tool in fundamental materials studies.(1) The high displacement damage rates associated with heavy ion irradiations allow high damage levels to be achieved in a very short time. Two major uses of ion irradiation for radiation damage studies are readily evident: First, for scoping studies on new alloy systems to determine what sort of radiation damage effects occur for a given set of experimental conditions. If the alloy looks promising, then a full-scale neutron irradiation program may follow. Otherwise, only limited neutron studies may be necessary merely to confirm the trends established by the ion irradiation. A second use of ion irradiation studies is for detailed investigation of the effect of changing various experimental parameters (temperature, alloy composition, etc.). These studies allow a single variable to be isolated, which is important for theoretical modeling of radiation damage.

Most ion irradiation studies to date have used conventional "back-thinning" methods for examining the microstructure of the irradiated region. A potentially more powerful technique is the cross-section method.(2) The cross-section procedure allows the entire ion damage region to be viewed at once. This is an important advantage since the damage rate (and therefore the final damage level) varies with depth for ion irradiation. Separate control samples are eliminated when using the cross-section technique -- one merely cuts a cross-sectioned specimen from the unirradiated portion of the sample. This results in the very desirable effect that the control specimens are from the same sample as the irradiated specimens.

A final potential advantage of the cross-section technique which has only recently been achieved in practice is multiplicity of irradiated specimens.

The radial flux across the 3 mm irradiation beam diameter varies by less than 5% according to profilimetry measurements. Proper use of the cross-section method therefore allows up to eight identical irradiated specimens to be obtained from a single sample. This enables favorable counting statistics to be obtained from the cross-section technique as compared to the back-thinning method.

Spurling and Rhodes(3) were the first researchers to apply the cross-section method to an ion-irradiated material. They successfully thinned proton-irradiated 316 stainless steel in cross-section by utilizing a nickel plating procedure. Unfortunately, their technique required a high-temperature (500°C) heat treatment in order to ensure an adequate bond at the foil-plate interface. A subsequent modification of their plating procedure by Whitley et al.(4) circumvented the high-temperature diffusion bond step, and therefore allowed lower irradiation temperatures to be investigated in cross-section. Whitley's method was only applied to ion-irradiated nickel which was electroplated with nickel. The cross-section procedure was extended to copper and copper alloys by Narayan et al.(5) and Knoll et al.(6) Recently, Shiraishi et al.(7) and Sindelar et al.(8) have demonstrated a cross-section technique for ion-irradiated 316 stainless steel which uses a low-temperature Ni plating.

The purpose of this report is to outline the procedure presently used at the University of Wisconsin for obtaining cross-section specimens. With one exception,(9) details of the experimental procedures followed for the cross-section technique have previously been available only in the form of unpublished documents.(10-12) We have recently expanded upon the techniques originally developed by Whitley(10) and Knoll,(11) and have developed a procedure which may be routinely applied to several alloy systems.

Experimental Procedures

The Cross-Section Technique

The basic steps followed to obtain a cross-sectioned transmission electron microscope (TEM) specimen from an ion-irradiated foil are outlined in Fig. 1. The critical points in the procedure are steps 2 and 4, where the irradiated foil is electroplated and thinned, respectively. Care prior to and during the electroplating step is required in order to obtain a uniform, thick deposit layer with good adhesion to the foil surface. Different plating procedures are followed depending on the particular metal that is being investigated. The cross-section technique described below has been successfully applied to pure nickel, pure copper and copper-based alloys, several austenitic stainless steel alloys, and some low chromium iron-based alloys. The plating conditions for each alloy class are given in Table 1.

Special pre-plating procedures are required in order to ensure a good plating bond. The plating anodes are cleaned in acid prior to the start of electroplating. All foils are thoroughly degreased using acetone after removal from the irradiation facility. The irradiated nickel foils are given an activation treatment in Wood's solution(13) (60 g $NiCl_2$, 31 ml HCl, 250 ml H_2O) by making the sample anodic for 3 seconds at a current density of 200 mA/cm^2. The purpose of this step is to remove the metal oxide layer, which is necessary in order to obtain a good bond. Less than 0.1 μm of material is estimated to be removed from the irradiated surface as determined by interference microscopy. After activation, the current is reversed in this same solution for 5 minutes in order to apply a thin nickel plating. In a similar procedure, the oxide layer on the austenitic stainless steels is removed in a solution of 60 g $NiCl_2$, 40 ml HCl, 250 ml H_2O at a current density of

250 mA/cm^2 for 2 seconds. The polarity on the sample is then reversed and the sample is plated in this solution for 5 minutes. The sample is then transferred into the plate bath where it is made anodic for 10 seconds with a current density of 200 mA/cm^2. The polarity is then reversed and the foil is plated until a 2 mm layer has been deposited. The electroplating process typically takes about 15 hours to be completed.

The pre-plating treatment for pure copper and copper alloys involves electropolishing for 2 seconds in a solution of 33% HNO_3/67% CH_3OH cooled to -50°C at an applied potential of 5 V. This process is intended to remove the oxide layer and any carbon contaminants which may be present on the foil surface. The irradiated foil is then transferred to the plating solution (180 g $CuSO_4$, 30 ml H_2SO_4, 950 ml H_2O), where it is made anodic for 1 second using a current density of 100 mA/cm^2. Interferometer measurements indicate that the total depth removed during the above electropolish and strike treatment is less than 0.1 μm. Following the strike treatment, the polarity of the plating cell is reversed and the foil is electroplated at a current density of 100-150 mA/cm^2 for about 20 hours.

The low chromium iron-based alloys are susceptible to corrosion during the oxide layer removal step, in which the sample is made anodic in an electrochemical cell. Therefore a pickling solution containing an inhibitor is used to remove the metal oxide layer while minimizing corrosion of the base metal. Samples of 2-1/4 Cr-1 Mo steel have been successfully electroplated after pickling in 15 ml H_2SO_4 in 85 ml H_2O to which 2 g of thiourea was added. The specimens are dipped in this pickling bath for 3 minutes followed by a thorough water rinse. At this point the foil is directly transferred to the plating bath where the sample is plated at a current density of 100 mA/cm^2.

A common plating apparatus which consists of a current-controlled power supply, a heater base, a gas bubbler device, and a foil holder is used to achieve smooth electro-deposited stratums on the 0.5 by 1 cm irradiated foils. Figure 2 is a photograph of the equipment used for electroplating. The key features to note in the figure are the sacrificial anodes and the plexiglas sample holder. The anodes are bagged during the plating process to prevent sludge from depositing on the foil. The sample holder has been designed so as to optimize the plating rate of the irradiated foils. A detailed schematic of the sample holder is shown in Fig. 3. The small 0.5 by 0.5 cm "window" in the holder serves to minimize foil edge effects on the plate layer, thereby allowing uniform deposition to occur. A common aquarium air stone is used to create a fine stream of nitrogen gas bubbles. The gas bubbles are directed through the channel in the sample holder and allowed to flow over the foil surface. The purpose of the fine gas stream is twofold: First, it ensures that hydrogen bubbles formed from electrolysis on the foil surface are swept away. Failure to remove these H_2 bubbles while electroplating would result in a porous plating. A second, related advantage of creating a turbulent layer near the foil surface is that the critical electroplating current density is inversely proportional to the film thickness. Therefore, higher current densities (and hence shorter plating periods) can be achieved when the plating solution is well agitated. However, too high an agitation rate will also cause a porous plating.

After a layer approximately 2 mm thick is deposited on each foil surface, the sample is removed from the plate bath and mounted in epoxy. Figure 4 shows a plated copper foil as it appears prior to being mounted in epoxy. The ion irradiation beam used at the University of Wisconsin Heavy-Ion Irradiation

Facility is 3 mm in diameter. The 3 mm diameter disk attached to the top of the electroplated foil in Fig. 4 defines the irradiated beam spot, and serves as an aid for determining whether a particular slice is from the irradiated or control region of the foil.

A diamond saw is used to slice specimens from the plated sample. With the use of a 150 μm-thick blade, it is possible to obtain as many as eight irradiated cross-section specimens of 200 μm thickness from a single sample. A virtually unlimited number of control cross-section specimens may be obtained from the same sample. As described later, these multiple specimens allow several different experimental analyses to be performed (e.g., extraction replicas, TEM, etc.). Figure 5 shows the control and irradiated cross-section specimens from a stainless steel sample as they appear immediately after being sliced by a diamond saw. The 3 mm TEM disks are either punched from the thin rectangular cross-section slices, or they are cut out using a circular saw.

Preparation of TEM Foils from Cross-Sectioned Specimens

Electropolishing techniques are generally used to prepare specimens for TEM analysis. Table 2 lists the solutions used for the jet-thinning of cross-sectioned TEM foils. Since the range of the incident ion is rather limited (~ 3 μm for 14-MeV Ni ions incident on nickel), it is essential that the irradiated boundary region of the specimen is transparent to electrons. One of the previous problems associated with the cross-section technique was the difficulty in obtaining adequate electron-transparent regions of the TEM foil at the irradiated boundary. Without utilizing special measures to force the thin area to occur at the irradiated boundary, a low success rate is obtained (typically $\lesssim 30\%$). This defeats the cross-section advantage of having multiple specimens. A further difficulty associated with many of the cross-sectioned alloy specimens is that the plating material thins at a different rate as compared to the alloy. In some cases, it is virtually impossible to obtain adequate thin area in the irradiated region of the cross-sectioned foil without a special experimental procedure. Two companion experimental methods have been developed to address this problem.

For most cross-sectioned materials, adequate thin area at the irradiated boundary may be obtained by simply using a protective lacquer to isolate the region of interest. The procedure is as follows: First both sides of the TEM disk are covered with a protective lacquer with the exception of a ~ 50 μm wide strip centered along the irradiated boundary. The specimen is then electropolished for a period of time ranging from 15 seconds to 2 minutes, depending on the foil thickness and the particular metal being investigated. Following this prepolish treatment, the lacquer is removed from the TEM disk and the specimen is electropolished until perforation occurs. Figure 6 is an optical micrograph that shows a typical result for an irradiated copper alloy following the above procedure. The parallel, dark bands running horizontally across the micrograph outline the residual step height change from the pre-polish treatment. Adequate thin area in the damage region has been obtained in greater than 80% of the cross-sectioned copper alloy specimens which were prepared using the above technique. Since six to eight irradiated specimens are generally available from each plated sample, this high success rate allows multiple specimens to be analyzed. Similar techniques have recently been successfully applied in the cross-section analysis of a commercial ferritic steel (HT-9) following ion irradiation.(14)

A somewhat more complicated procedure is employed to electrochemically thin cross-sectioned stainless steel specimens. A two-step polishing technique which utilizes two different electropolishing solutions is used in conjunction with the above prepolish lacquer technique. The first step involves the application of a protective lacquer which exposes only the irradiated boundary region. The specimen is then polished in solution 1 (see Table 2) which polishes the nickel plate at a slightly faster rate compared to the steel. After approximately two minutes (for an original specimen thickness of 250 μm), the lacquer is removed and the specimen is polished to perforation in solution 2 which polishes the steel at a more rapid rate compared to the nickel plate.

Results and Applications

A variety of experimental techniques may be applied to the cross-sectioned specimen in order to obtain different pieces of information. A brief sampling of some typical results which may be obtained is presented below.

Extensive thin area for TEM analysis at the irradiated boundary is achievable using the preparation techniques previously outlined. Electron-transparent regions that extend along the irradiated boundary for distances up to 100 μm have been obtained under favorable conditions. Figure 7 shows a portion of the thin area that was obtained along the irradiated boundary of a Cu-Zr (AMZIRC) specimen irradiated with 14-MeV Cu ions at 300°C to a fluence of 3×10^{20} ions/m^2 (40 dpa peak damage). In this specimen, perforation during electropolishing occurred on the interface and there were roughly equal amounts of thin area on either side of the hole.

Optical microscopy may be performed on irradiated cross-section specimens in order to help characterize the effect of irradiation. Figure 8 is an optical micrograph of a 316 stainless steel specimen which has been irradiated with 14-MeV Ni ions at 650°C to a fluence of 3.3×10^{20} ions/m^2. The damage region is clearly visible in the micrograph as a ~ 3 μm wide band adjacent to the plated interface. The different etching behavior in the damage region was determined from TEM investigations to be due to iron phosphide precipitates. These precipitates were needle-shaped with an average length of 100 nm and density ~ 2×10^{20} m^{-3}.

Extraction replica techniques are often utilized in alloys where irradiation can enhance or induce precipitation events. It is essential that the precipitates be extracted from the matrix in order for accurate quantitative microchemical analysis results to be obtained.(15) Figure 9 shows an extraction replica obtained from a cross-sectioned 2-1/4 Cr-1 Mo steel specimen which had been ion-irradiated using 14 MeV nickel ions. This micrograph shows extracted chi phase, a radiation-induced phase, from the bainitic structure of the steel that had been plated with iron.

A qualitative assessment of the strength increase (or decrease) due to ion irradiation can be obtained by performing a scratch hardness test(16) on an irradiated cross-section specimen. Figure 10 shows the results of qualitative scratch hardness tests that were made on annealed copper and a high strength Cu-Zr alloy (AMZIRC) following 14-MeV Cu ion irradiation to a peak damage level of 40 dpa at 100°C. The indenter load was about 0.5 g in both cases. There is a strong indication of radiation hardening in the copper specimen as indicated by the narrow scratch width in the ion-irradiated region, compared to the scratch width in the nonirradiated region. There is either no strength change or perhaps a slight amount of radiation hardening in the AMZIRC specimen.

Summary

A routine procedure has been developed which allows ion-irradiated metals to be examined in cross-section. The high success rate that is obtainable using this procedure allows multiple specimens to be examined. This implies that statistically significant void and precipitate distributions may be obtained from irradiated samples as a function of depth (damage level). The many potential advantages of the cross-section technique over conventional back-thinning methods may now be realized in practice.

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Table 1. Electroplating Conditions for Various Metals

Metal	Electroplating Solutions	Experimental Conditions
Nickel	150 g $NiSO_4$ 150 g $NiCl_2$ 50 g boric acid 1000 ml H_2O	200 mA/cm^2 50°C nickel anodes
Stainless Steel	150 g $NiSO_4$ 150 g $NiCl_2$ 70 g boric acid 1000 ml H_2O	200 mA/cm^2 70°C nickel anodes
Copper/Cu Alloys	180 g $CuSO_4$ 30 ml H_2SO_4 950 ml H_2O	150 mA/cm^2 20°C copper anodes
Iron Alloys	200 g $FeCl_2$ 75 g NaCl 75 g $CaCl_2$ 750 ml H_2O	100 mA/cm^2 90°C low carbon iron anodes

Table 2. Parameters Used for Jet-Electropolishing of Cross-Sectioned Specimens

Alloy	Initial TEM Disc Thickness	Solution	Volts	Current	Temp
Cu-Zr, Cu-Cr-Zr	200 μm	33% HNO_3, 67% CH_3OH	15 V	90 mA	-30°C
300 Series Austenitic Stainless Steels	250 μm	Solution 1: 30% HNO_3, 70% Methanol, Time = 2 min	10 V	80-90 mA	0°C
		Solution 2: 10% Perchloric Acid, 90% Acetic Acid, 20 g/ℓ Cr_2O_3, 10 g/ℓ $NiCl_2$	45 V	80-90 mA	20°C
Low Cr (< 4 wt.%) Ferritic Steels	250 μm	5% Perchloric, 95% Ethanol	60 V	90 mA	0°C

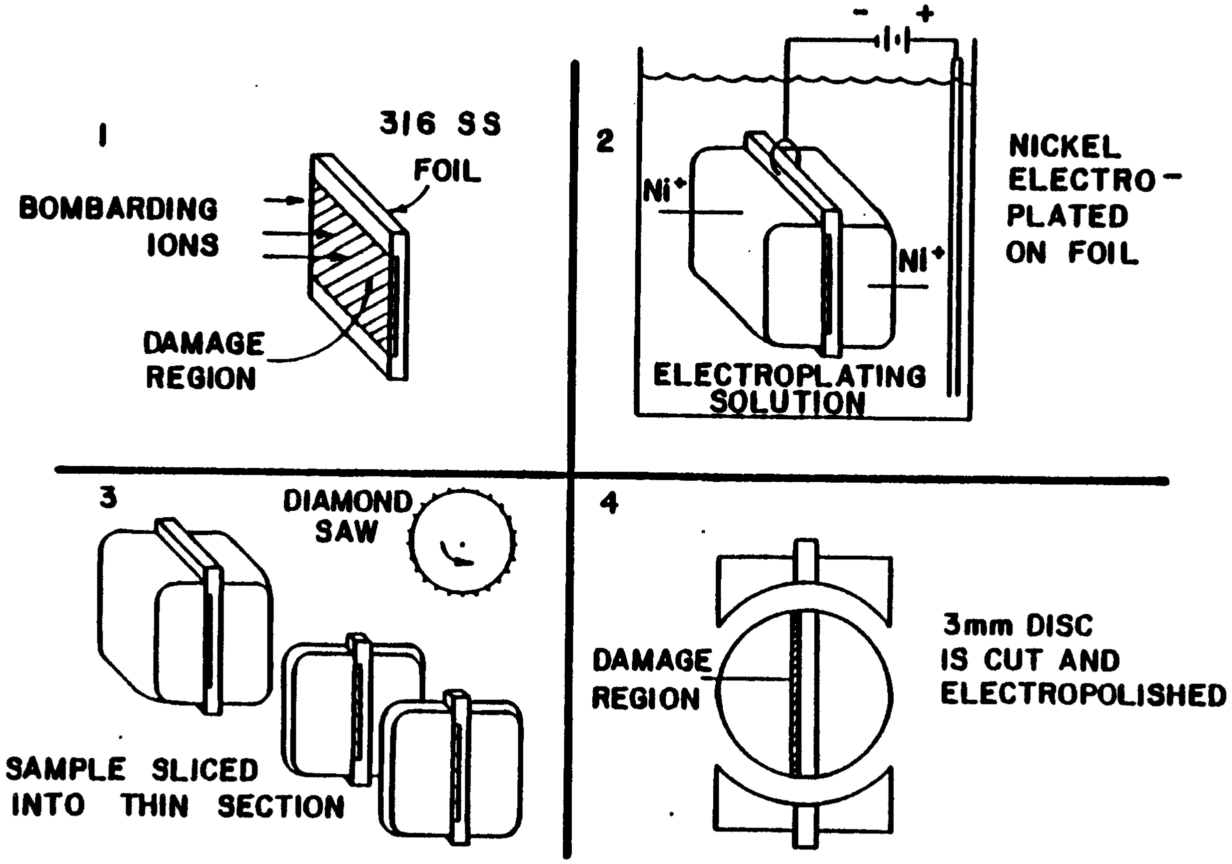

Figure 1. Procedure for preparing ion-irradiated foils in cross-section.

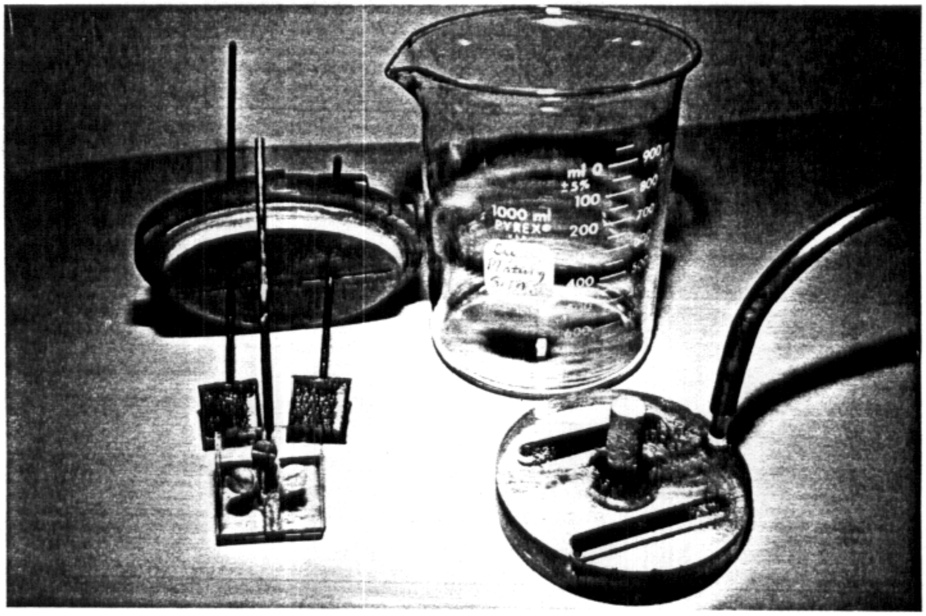

Figure 2. Apparatus used for electroplating ion-irradiated foils.

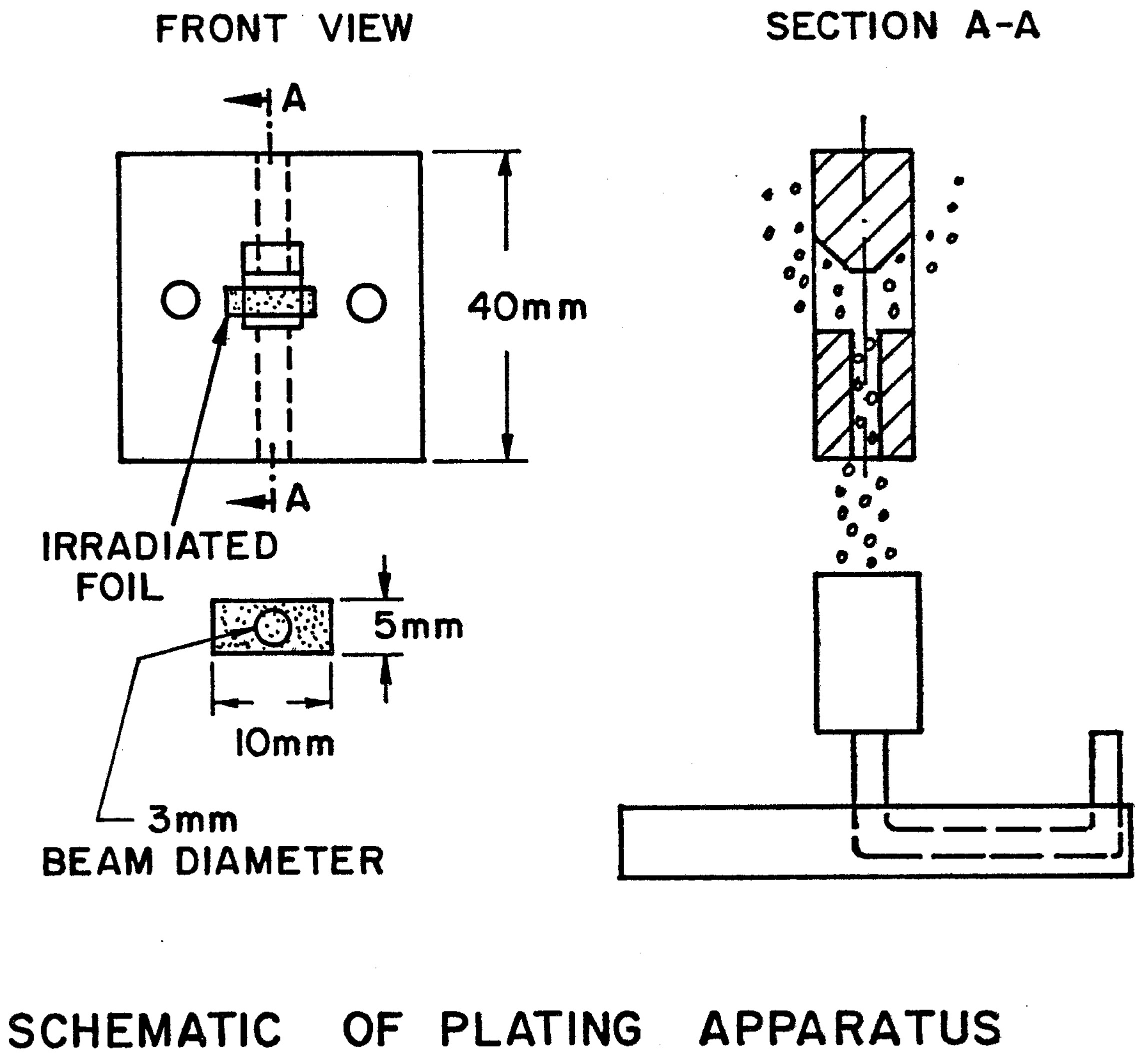

Figure 3. Schematic of sample holder and gas bubbler used for electroplating ion-irradiated foils.

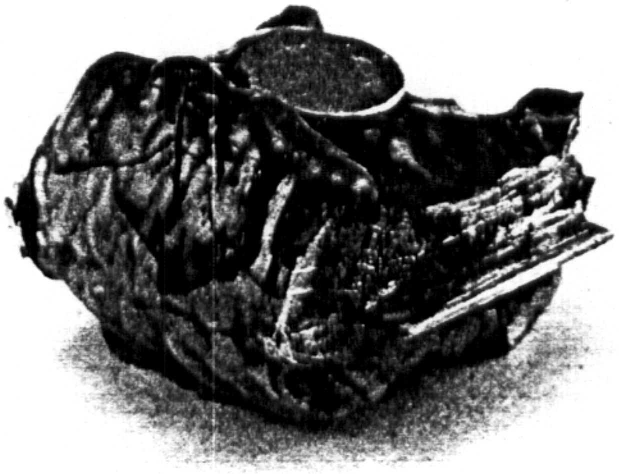

Figure 4. Photograph of an electroplated ion-irradiated copper foil.

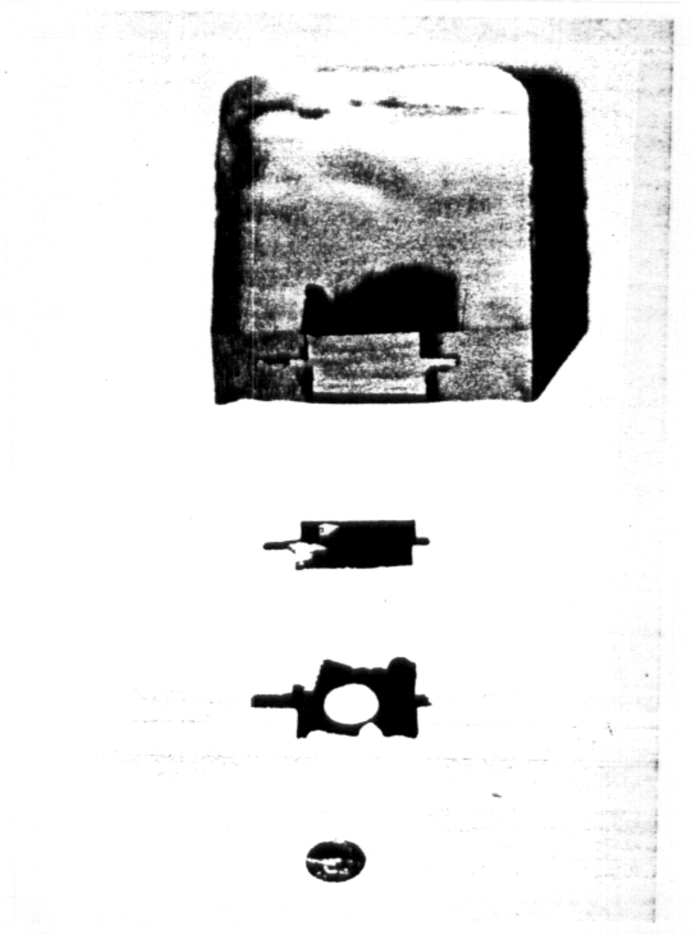

Figure 5. Control and ion-irradiated cross-section specimens from a stainless steel sample.

OPTICAL MICROGRAPH OF AN ELECTROPOLISHED CROSS-SECTION SPECIMEN

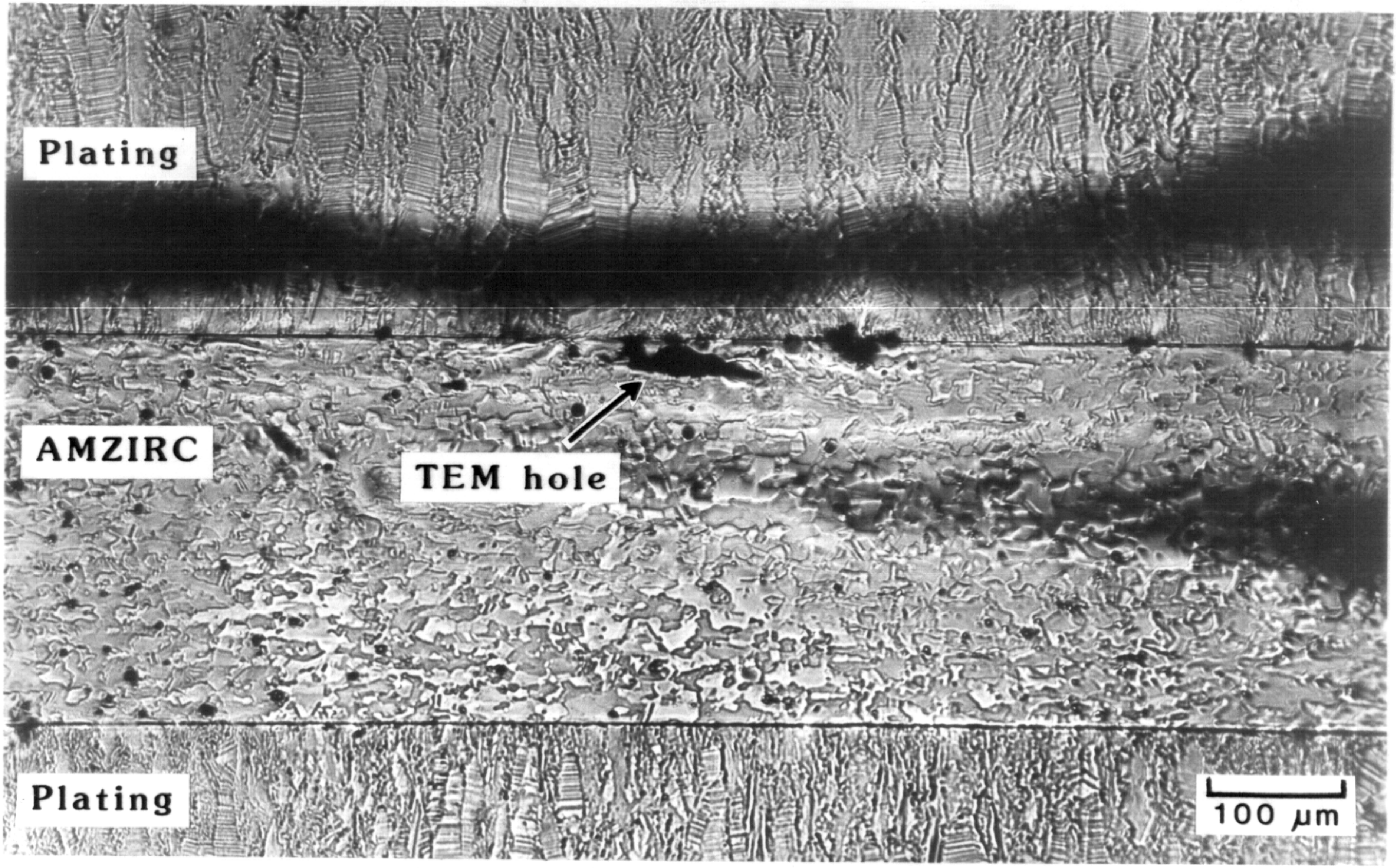

Figure 6. Optical micrograph of an electropolished copper alloy cross-section TEM specimen. The arrow points to the perforation in the foil next to the irradiated boundary.

REPRESENTATIVE THIN AREA IN A CROSS-SECTIONED AMZIRC SPECIMEN

Figure 7. TEM micrograph showing the extent of the electron-transparent region along the irradiated boundary of a cross-sectioned Cu-Zr specimen.

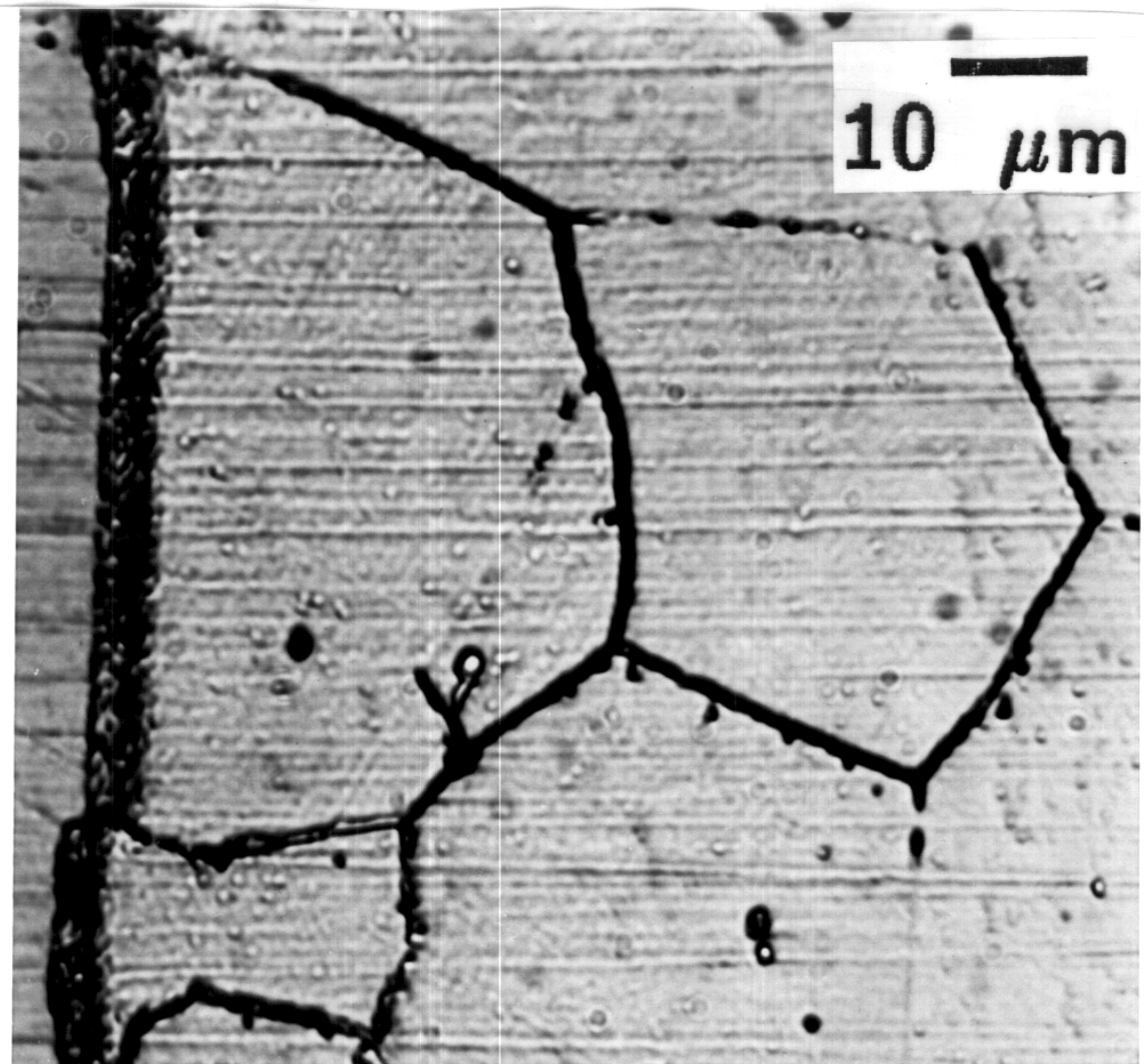

Figure 8. Optical micrograph of a 14-MeV Ni ion irradiated 316 stainless steel cross-section specimen (40 dpa peak damage). The 3 μm-wide band along the irradiated interface corresponds to the radiation damage region.

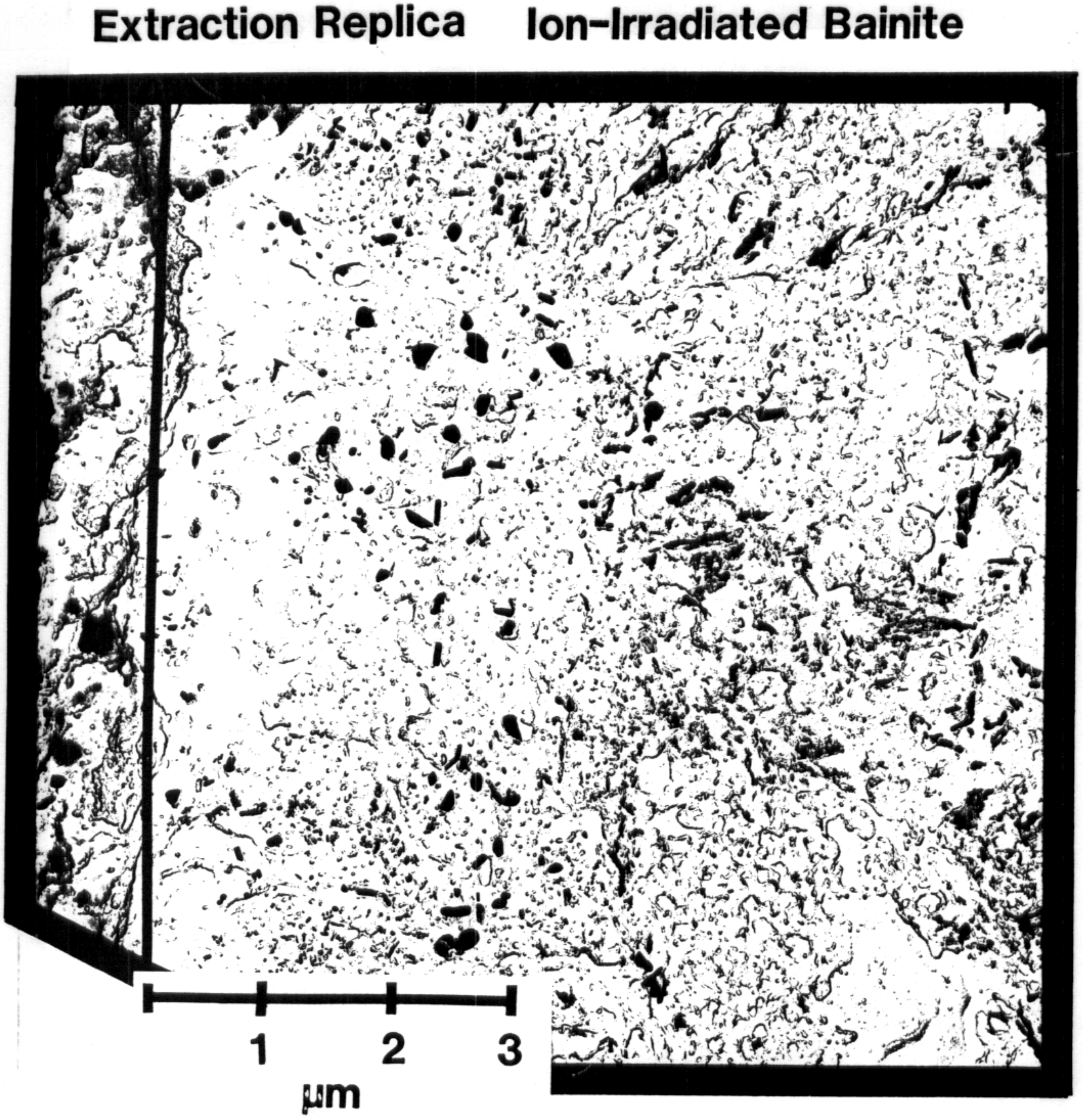

Figure 9. Extraction replica electron micrograph from a cross-sectioned 2-1/4 Cr-1 Mo steel specimen. Note the extracted chi phase precipitates which formed in the 3 µm damage zone during the 14-MeV Ni ion irradiation.

SCRATCH HARDNESS OF ION-IRRADIATED METALS

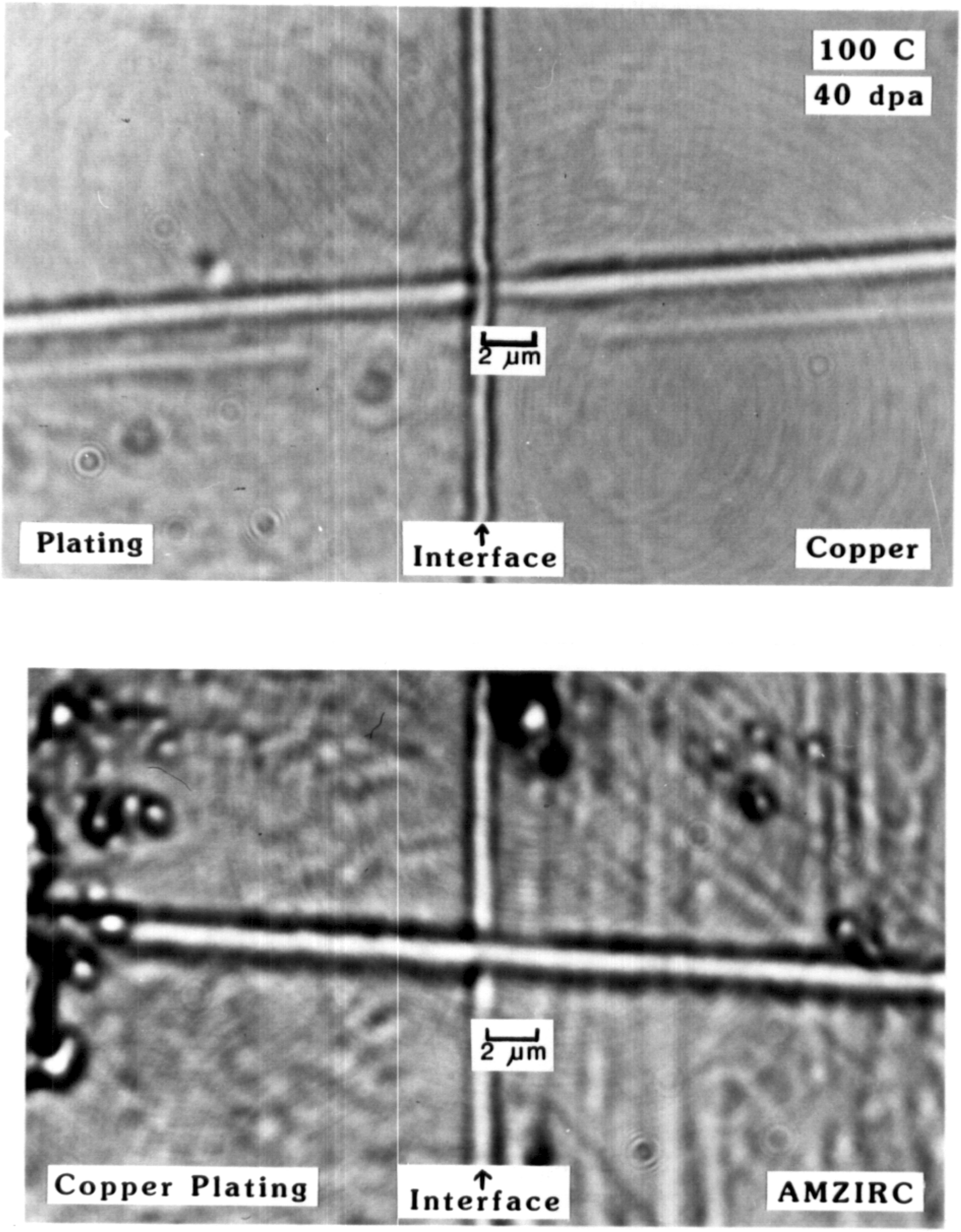

Figure 10. Scratch hardness of annealed copper (top) and cold-worked plus aged AMZIRC (bottom) following 14-MeV Cu ion irradiation to a peak damage level of 40 dpa at 100°C.