

Application of Extraction Replicas and Analytical
Electron Microscopy to Precipitate Phase Studies*

E. A. Kenik[†] and P. J. Maziasz[†]

CONF-840767--6

DE85 001253

When analytical electron microscopy (AEM) is applied to multiphase materials, the question of the relative dimensions of the excited volume and the phase being analyzed arises. If the excited volume is not significantly smaller than the second phase volume, in-foil analysis does not reveal the actual phase composition; compositional analyses can be far more accurate performing the same AEM analyses on extraction replicas. The preparation, advantages, and limitations of extraction replicas for AEM are discussed in this paper. Several applications are included in order to emphasize the benefits of employing extraction replicas in conjunction with in-foil analysis.

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Preparation of Extraction Replicas

Figure 1 illustrates the stages in the preparation of a direct, carbon extraction replica. The specimen is initially electropolished to provide a clean, smooth surface [Fig. 1(a)], subsequently electroetched to remove the matrix and leave lower conductivity or less reactive phases in relief [Fig. 1(b)]. A carbon film (30-100 nm thick) is deposited on the etched surface from a carbon arc source [Fig. 1(c)]. The replica is finally released from

*Research sponsored by the Division of Materials Sciences and the Office of Fusion Energy, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

[†]Authors Kenik and Maziasz are with the Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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the specimen by further electroetching, which dissolves the underlying matrix. For 316 stainless steel, electroetching in 10 vol % hydrochloric acid/ethanol at 5 to 10 V and near -20°C provides matrix-free extraction replicas. The replica floats away from the specimen surface in alcohol and is cleaned and then collected and dried on a beryllium grid.

Figure 2(a,b) compares the extraction replica and in-foil microstructure of a neutron-irradiated stainless steel which contains a high density of precipitates and voids. Though some particle agglomeration has occurred, the fidelity of the replica is quite good; impressions of voids are preserved, most phases are extracted well, and the void-precipitate association is captured by the replica. Precipitate sizes and shapes are similar for the replica and in-foil microstructure. Figure 3 shows an extraction replica of M_6C (η) precipitates from EBR-II irradiated 316 stainless steel (525°C , 31 dpa). The well-faceted nature of the precipitates suggests little or no dissolution during electroetching; furthermore, there is no indication of a surface film, confirmed by the independence of apparent composition with precipitate thickness.

Advantages of Extraction Replicas for AEM

The removal of the surrounding matrix provides several advantages for performing AEM on fine precipitates. If the excited volume contains no matrix, it is obvious that the composition measured by x-ray energy dispersive spectroscopy (XEDS) or electron energy loss spectroscopy (EELS) represents that of the precipitate.

However, it has been shown for in-foil XEDS analysis that, even when the primary excited volume contains no matrix, secondary fluorescence effects contribute matrix x-ray counts to the precipitate spectra. Extraction replicas become necessary to spatially resolve precipitate particles that are smaller than the minimum excited volume in-foil. Finally, the detection limits for trace elements in precipitates are also improved for extraction replicas because the minimum mass fraction is determined solely by the precipitate excited volume, even if the electron probe is not entirely contained inside the phase. The excited volume, for in-foil analyses, may contain some matrix, which requires higher trace element concentrations in the precipitate in order to exceed the minimum mass fraction required for detection.

For neutron-irradiated materials, the radioactivity of the specimen can also interfere with XEDS microanalysis. Figure 4 illustrates the magnitude of the problem for a highly activated (HFIR irradiated) stainless steel (specimen activity ~ 1000 μ -curie). Figure 4(a) shows the spectrum measured with the electron beam off, while Fig. 4(b) shows the spectrum with a large-diameter, high-current electron probe on a region of the TEM disk normally thin enough for AEM analysis. Because one must subtract two very similar spectra and analyze the small difference, precision of such an analysis is degraded. By significantly reducing the volume of radioactive material, an extraction replica allows high precision XEDS analysis of precipitates in irradiated material.

The "in-hole" XEDS spectrum arises from extraneous radiation, generated in the microscope illumination system, which fluoresces the

entire specimen. The reduced volume of a replica therefore also results in a reduced "in-hole" spectrum. Figure 5 compares the "on-replica (film)" background spectrum with an "in-hole" spectrum from a conventional TEM disk specimen of a mildly activated (EBR-II irradiated) stainless steel. The "in-hole" spectrum [Fig. 5(b)] exhibits x-ray peaks for the major alloy constituents of the specimen, while the "on-replica" spectrum [Fig. 5(a)] exhibits a uniformly low background. As a result of the lower intensity of the subtracted, background spectrum, the replica permits more precise and accurate analysis as well as better trace element detection.

The elimination of the surrounding matrix provides several additional benefits for AEM analysis of precipitates. No additional absorption of low energy x rays occurs outside the precipitate, which may be important for light element analysis using ultrathin window or windowless XEDS detectors. The absence of matrix allows the use of a large-diameter probe to sample hundreds or thousands of precipitates in order to determine average precipitate composition, which indicates the effect of the total precipitation on the matrix composition. In some additional cases, the relative phase fraction (for multiple phase precipitation) could be calculated on the basis of average precipitate and individual phase compositions. The extraction replica should provide improved "signal-to-noise" in diffraction patterns of fine precipitates as a result of the low scattering power of the carbon film relative to that of typical metallic or ceramic matrices. Double-diffraction effects between the matrix and precipitate

are eliminated, thus reducing the complexity of the diffraction patterns and providing diffracted intensities for the precipitate which are more directly interpretable.

Disadvantages of Extraction Replicas for AEM

There are several limitations to the use of extraction replicas to the AEM of precipitates.

1. Information on crystallographic and morphological habits is lost.
2. There is a possibility of interference between elements in the replica film and those in the precipitate (e.g., carbon analysis of metal carbides on a carbon replica).
3. There are some precipitates which either do not extract or do not extract simultaneously with other phases [e.g., Ni_3Si (γ')]. In addition, large particles of certain phases (e.g., sigma phase in stainless steels) are too thick on the replica and are better analyzed in-foil where they are thinned to electron transparency together with the foil.
4. For larger particles, significant beam heating can produce precipitate modification, decomposition, or loss from the replica. Electrostatic charging can also produce the loss of precipitates or destruction of the replica.
5. Artifacts can occur, particularly if the extraction replicas are not carefully made. Several of these include surface films, partial precipitate dissolution, clustering of precipitates, and the presence of unexpected elements in the replica film (e.g., silicon contamination of evaporated carbon films).

Analysis of Phosphorus-Rich Phases in Neutron-Irradiated 316 Stainless Steel

In this application, precipitate analysis on extraction replicas was required to reduce the background resulting from the intrinsic radioactivity of the material and by the inability to excite only the precipitate, especially in the case of the lath phosphide. Figure 6 illustrates that both phases are phosphorus-rich and have different morphologies and different ratios of chromium, iron, and nickel. At higher fluence, the phosphide B contains ~28 wt % P. The appearance of these phosphorus-rich phases is somewhat surprising, as the phosphorus content of the stainless steel is only ~0.02 wt % P (hence a factor of $\sim 10^3$ enrichment).

Conclusions

Extraction replicas provide a powerful extension of AEM techniques for analysis of fine precipitates. In many cases, replicas allow more accurate analyses to be performed and, in some cases, allow unique analyses which cannot be performed in-foil. However, there are limitations to the use of extraction replicas in AEM, of which the analyst must be aware. Many can be eliminated by careful preparation. Often, combined AEM studies of precipitates in-foil and on extraction replicas provide complementary and corroborative information for the fullest analysis of precipitate phases.

FIGURES

FIG. 1.--Stages in the preparation of direct, carbon extraction replica. (a) Electropolishing, (b) electroetching, (c) carbon film deposition, (d) electroetching to release replica.

FIG. 2.--Precipitate microstructure of D0-heat 316 stainless steel neutron irradiated in EBR-II at 630°C to 36 dpa. (a) On-replica microstructure, (b) in-foil microstructure.

FIG. 3.--M₆C (eta) precipitates extracted from D0-heat 316 stainless steel neutron irradiated in EBR-II at 525°C to 31 dpa.

FIG. 4.--XEDS spectra from radioactive titanium-modified 316 stainless steel specimen (activity ~1000 μ -curie). (a) Intrinsic emission spectrum measured with electron beam off. (b) Total emission spectrum with electron probe excited thin matrix region.

FIG. 5.--(a) "On-replica" XEDS spectrum and (b) "in-hole" XEDS spectrum for specimens prepared from 316 stainless steel irradiated in EBR-II at 630°C to 36 dpa.

FIG. 6.--Morphology and XEDS spectra for phosphorus-rich phases found in 316 stainless steel neutron irradiated in EBR-II at 500°C to 8.4 dpa. (a) Lath-shaped phosphide A and (b) globular phosphide B.

(a) ELECTROPOLISHING

(b) ELECTROETCHING

ORIGINAL SAW CUT SURFACE

NEW ETCHED SURFACE

ppfs
VOID

NEW POLISHED SURFACE

(c) CARBON FILM DEPOSITION

(d) REPLICA REMOVAL BY FURTHER ELECTROETCHING

CARBON FILM

NEW ETCHED SURFACE

FREE-FLOATING CARBON FILM

FIG. 1.--Stages in the preparation of direct, carbon extraction replica. (a) Electropolishing, (b) electroetching, (c) carbon film deposition, (d) electroetching to release replica.

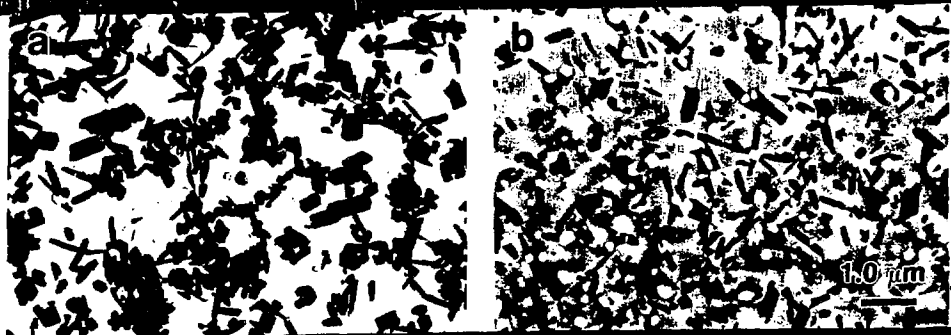


FIG. 2.--Precipitate microstructure of DO-heat 316 stainless steel neutron irradiated in EBR-II at 630°C to 36 dpa. (a) On-replica microstructure, (b) in-foil microstructure.

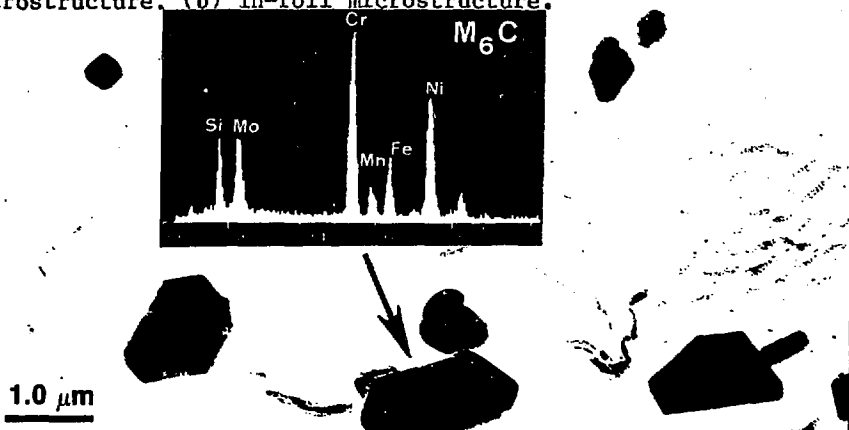


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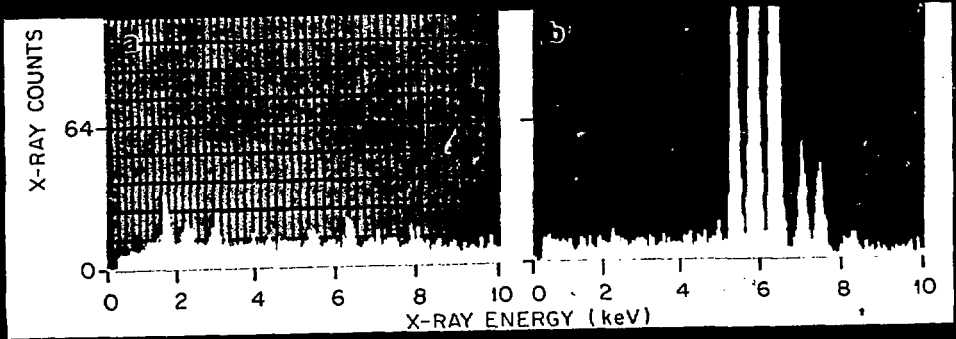


FIG. 5.--(a) "On-replica" XEDS spectrum and (b) "in-hole" XEDS spectrum for specimens prepared from 316 stainless steel irradiated in EBR-II at 630°C to 36 dpa.

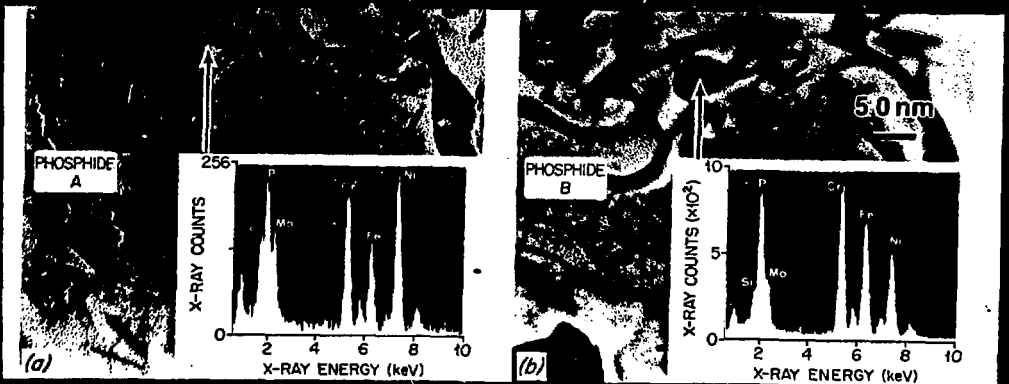


FIG. 6.--Morphology and XEDS spectra for phosphorus-rich phases found in 316 stainless steel neutron irradiated in EBR-II at 500°C to 8.4 dpa. (a) Lath-shaped phosphide A and (b) globular phosphide B.