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ELECTRON MICROSCOPE STUDIES OF
SECOND PHASE PARTICLES IN DILUTE ALLOYS OF URANIUM

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INTRODUCTION

This report describes techniques of transmission electron microscopy for determining particle size and density in uranium rich alloys. Uranium that contains small amounts of alloying elements and that has had appropriate heat treatment offers remarkable resistance to swelling during irradiation.⁽¹⁾ An explanation is that alloying elements are present as precipitate particles, the number and size of which alter the swelling characteristics. Several investigators have utilized electron microscopy to examine replicas from which the size and density of second phase particles in uranium rich alloys were determined. The present study corroborates results obtained by the replica technique. In addition, the transmission microscopy technique reveals very small particles which are below the limit of resolution of the replica technique.

EXPERIMENTAL CONSIDERATIONS

The two alloys investigated were identical to those described previously by Woods.⁽²⁾ Second phase particles were delineated by an electropolish-electroetch followed by replication with cellulose acetate. The final electron micrographs were then analyzed with a Zeiss Particle Size Analyzer. The method used by Woods, et al., has several limitations because (1) surface roughening takes place during electropolishing and small particles are obscured by the background structure, (2) particles smaller than 800 Å, a reasonable lower limit of resolution, are neglected, and (3) lattice defects, such as dislocations, which may be associated with particles and possibly influence the properties of the metal are ignored by replica techniques. Transmission electron microscopy was therefore applied to the problem of determining the size and density of small particles in uranium.

Specimens for transmission electron microscopy are usually foils that are thinned just before final viewing. Bulk samples cannot be rolled into the more convenient thin sheet form without altering the size and distribution

of particles; therefore, electron microscope specimens for this study were prepared directly from the bulk samples. Rods, 3 mm in diameter, were machined from the bulk samples and embedded in a self-curing resin. The rods were sectioned into 0.5 mm thick wafers by a water-cooled diamond saw,⁽³⁾ and the wafers were made half as thick by mechanically polishing both sides through coarse diamond paste. Final thinning was performed with a fine electrolytic jet, because the small size of the wafers precluded use of the conventional window method for electrolytic thinning. During jet polishing, the specimen was held in a 3 mm diameter recess in a 20 cm long stainless steel holder. An insulating lacquer applied to the end of the holder and the edge of the wafer localized the action of the electrolyte. A drawn down glass tube containing a platinum cathode served as the jet. With the tip of the jet 1 cm from the sample and a current density of 0.2 amps/cm^2 , pitting was negligible. The electrolyte consisted of 85% orthophosphoric acid in water.⁽⁴⁾

A stationary jet tip produces a spherical dimple; whereas, a moving tip produces a flat dimple. After a dimple is formed on one side, jetting is stopped and the sample is removed from the holder. The dimpled surface is painted with insulating lacquer and reinserted in the holder so the undimpled surface can be jet polished. A strong light source is focused on the specimen which is viewed by a low power stereo microscope. The electrolytic jetting is stopped as soon as light is transmitted through the insulating lacquer on the back of the sample. The wafer is then carefully cleaned in several washes of acetone and given a second electropolish. The second treatment removes the oxide layer formed on the specimen during thinning and passivates the surface with respect to oxidation.⁽⁴⁾

QUANTITATIVE MEASUREMENTS

Samples for transmission electron microscopy are thin foils 100 to 2000 Å thick depending on the material being investigated. From replica studies, it was apparent that the diameter of the larger particles would be greater than the foil thickness. On the other hand, small particles would be on either surface in addition to being enclosed within the foil. Special

considerations must therefore be given to the sample thickness. Consider a foil having thickness, t , which contains particles having identical radii, r .

Since the micrograph is a two-dimensional representation of a three-dimensional subject, it does not distinguish between particles enclosed within the foil and those on either surface. Therefore, the effective maximum sampling thickness must be twice the radius of the particle plus the thickness of the foil. Particles seldom have identical diameters, so it is necessary to separate the diameters into size classes. As is apparent from the figure, each size range i will have a thickness of foil of $D_i + t$. The total particle density is obtained by summarizing the i individual particle densities.

If the particles are spherical, if the particles do not change size during electropolishing, and if a foil thickness can be assigned to the thinned foil, then the total number of particles per unit volume, PD , may be derived from the number with an observed diameter D_i from the relationship

$$PD = \sum_i \frac{N_i}{(D_i + t)A} \dots$$

where PD = the total number of particles per unit volume,

N_i = the number of particles with diameters within size range i revealed by the micrograph,

$\hat{D}_i$ = the average diameter of particles in an arbitrary but specific size range i ,

t = the foil thickness,

A = the area of one of the surfaces of the foil portrayed by the micrograph,

and the summation is made over the i classes. A simpler solution for obtaining particle density from transmission micrographs has been proposed by Hilliard in which particles are considered as being enclosed within the foil only.⁽⁵⁾ This solution is valid only when the particle diameter is small in relation to the foil thickness.

RESULTS

Samples of high purity uranium that have been thinned by the method described are similar to those described by other investigators.⁽⁶⁾ Second phase particles are not observed. However, the alloyed uranium specimens did disclose the presence of particles. Figure 1 is a transmission electron micrograph of an alpha rolled alloy that contains 185 ppm Fe and 95 ppm Si. The large precipitated particles appear dark, and are frequently surrounded by a network of dislocations. The shape of the particles cannot be determined unambiguously by transmission electron microscopy. It is inferred that the particles are spherical, because rod and plate-like particles are not observed. Attempts to identify the particles by electron diffraction failed; presumably the particles are rounded and do not permit sufficient penetration of the electron beam. Particle size-frequency determinations by replica techniques showed that the most prevalent diameter of particles in this alloy is approximately 0.2 micron. This was confirmed by transmission microscopy. The average diameter of a total of 50 spherical particles measured on transmission micrographs was 0.21 micron, and all diameters were 0.1 to 0.3 micron. For a foil thickness of 250 A, a density of 4.4×10^{11} particles/cc was calculated from transmission micrographs prepared from the above described alloy. This value agrees very well with the value 5.1×10^{11} particles/cc determined from replicas.

Figure 2 is a transmission micrograph of an alloy with an identical composition, but with a different heat treatment. The alloy was beta-quenched and aged 1 hour at 590 C. Quantitative metallography, based on replica techniques, predicted the presence of many particles having diameters less than 800 A, the lower limit of resolution of the technique. The diameter of the particles observed by transmission microscopy ranged from 100 A to 3000 A.

In fact, most particles had diameters less than 1000 A, in good agreement with the predictions based on replica results. Unfortunately, small particles are of the same size as dislocations and loops, and differentiation of these small particles is difficult. Because most particles were opaque to the electron beam, they were not tilt sensitive. Several micrographs of a given area of the specimen at various orientations were obtained and analyzed. Only those spots or particles were measured which were not tilt sensitive.

The particle density of this specimen had been estimated at 4.2×10^{11} particles/cc by replica techniques. The density of particles with diameters greater than 800 A derived from transmission electron micrographs and the mathematical relationship given above yielded a value of 3.2×10^{11} particles/cc, again in good agreement with the value derived from replicas. In a similar fashion the density of particles with diameters smaller than 800 A was estimated from the transmission micrographs and a value of 4.3×10^{14} particles/cc was obtained. This density is three orders of magnitude greater than the density ascribable to particles with diameters greater than 800 A. This difference most certainly emphasizes the value of high resolution electron transmission microscopy in the determination of particle size and frequency.

SUMMARY AND CONCLUSIONS

Transmission electron microscopy has been successfully utilized to study particle-size density distributions in dilute alloys of uranium. The results of a quantitative metallographic procedure used for determining particle size-density distributions from transmission electron micrographs agree well with that derived from replica electron micrography. The increase in resolution inherent in transmission techniques permits inclusion of particles normally too small to be resolved by replica methods.

75,000X

FIGURE 1

Transmission Electron Micrograph of Alpha Rolled Uranium Containing
185 ppm Fe and 95 ppm Si Showing Second Phase Particles and
Dislocation Networks

100,000X

FIGURE 2

Transmission Electron Micrograph of Uranium Containing 185 ppm Fe and 95 ppm Si Showing Second Phase Particles After the Alloy Had Been Alpha Rolled, Beta-Quenched, and then Aged 1 hr at 590 C Prior to Thinning

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