CONF-840767--13

THE UTILITY OF REPLICA TECHNIQUES FOR X-RAY MICROANALYSIS OF SECOND PHASE PARTICLES

CONF-840767--13

James Bentley

DE85 005564

X-ray microanalysis of second phase particles in ion-milled or electropolished thin foils is often complicated by the presence of the matrix nearby. Extraction replica techniques, revived from the early years of TEM investigations of materials, provide a means to avoid many of the complications of thin-foil analyses. The use of such techniques for x-ray microanalysis of precipitates is now well established in a number of laboratories. Improvements in qualitative analysis, in quantitative analysis, and in the analysis of radioactive specimens can be obtained with the use of extraction replicas. For small precipitates the x-ray signal from the matrix will often mask the x-ray signal from the precipitate for a thin-foil specimen. Thus the qualitative analysis (identification of elements present) of the precipitate is compromised or even precluded. For larger precipitates where a reliable qualitative analysis is possible in a thin-foil specimen, an accurate quantitative measurement of the composition is possible only with the use of replicas. The influence of beam spreading and secondary fluorescence, which can produce a significant x-ray signal from the matrix of a thin-foil specimen, are minimized or eliminated by the use of extraction replicas. For radioactive specimens there are a number of additional advantages of using extractions. The amount of radioactivity is drastically reduced which reduces the detector dead-time and also minimizes extraneous x-rays produced by K-capture decay processes or self-fluorescence.

The author is with the Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

In the following sections three examples of the analysis of second phase particles are described and illustrate the improvement obtained by the use of extraction replicas for qualitative analysis, quantitative analysis, and analysis of radioactive specimens.

Aged type 321 stainless steel

Analytical electron microscopy was used to characterize the precipitate phases present in type 321 stainless steel after 17 years of service at ~600°C. Four precipitate phases were identified.[1,2] Large particles of Fe-Cr sigma phase and titanium carbosulfide ($Ti_4C_2S_2$) were present along with a high concentration of ~25nm diameter Ti-rich MC particles and a much lower concentration of ribbon-shaped precipitates. The long dimension of these ribbon-shaped precipitates was often > 1μm and was aligned along $\langle 001 \rangle_\gamma$. One of the other dimensions was < 1nm and the third dimension was ~20nm, resulting in an elongated plate-like precipitate on $\{110\}_\gamma$. Conventional selected area diffraction (SAD) and microdiffraction techniques showed that the phase had an hexagonal structure with unit cell dimensions a_0=0.608 nm and c_0=0.364 nm, and also that the orientation relationship between the precipitate (p) and the austenite matrix (γ) was $(0001)_p \parallel (001)_\gamma$ and $(1\bar{2}10)_p \parallel (110)_\gamma$. The elemental composition of the phase was determined by x-ray microanalysis of isolated precipitates on carbon extraction replicas. A JEM 120CX equipped with a Kevex 5100 system was used. Particular care was taken to select precipitates without Ti-rich MC particles in close association. An example of an analysed precipitate is arrowed in Fig. 1(a) and the energy dispersive x-ray spectrum is shown in Fig. 1(b). The average composition in at. % of five different precipitates was 29.9Ti, 25.7Fe, 15.4Ni, 12.5P, 12.6As, and 3.9Cr. In thin-foil specimens the contribution from the matrix masked that from the precipitate to the extent that no P or As were detected. The compositional information together with the crystallographic information from electron diffraction allowed the precipitate to be identified as a complex phosphide-arsenide with a structure similar to Fe_2P and $(Fe,Cr)_2As$.[3]

X-ray microanalysis of the small Ti-rich MC particles[4] also present on the extraction replicas provided a more reliable indication of the elements present (see Fig. 2) than analysis performed on thin-foil specimens. The analyses were made with a Philips EM400T equipped with a field emission gun. It has been suggested that the presence of Cr, Fe and Ni indicates that some thin matrix layer remains on the extracted particles.[5] However the Cr/Fe and Fe/Ni ratios are far from those of the matrix and evidence suggests that the Cr, Fe and Ni are in solution in the carbide.

Aluminum Ion Implanted with Molybdenum

The microstructures of aluminum ion-implanted with molybdenum and subjected to various heat treatments are being investigated for correlation with near surface properties such as corrosion. Specimens with peak concentrations of ~4.4 and 11 at. % Mo within the ~50nm thick implanted region have been annealed at temperatures of 425 to 600°C to produce precipitate phases.[6,7] For Al-4.4 at. % Mo annealed at >550°C the precipitates form a pseudo-lamellar structure with precipitate dimensions >100nm. X-ray microanalysis of precipitates in backthinned foils indicated a composition of Al - 6.7 ± 0.5 at. % Mo. Since the aluminum content is over-emphasized by the presence of an Al_2O_3 surface film (identified by EELS) and by contributions from the matrix as a result of beam spreading and secondary fluorescence, x-ray microanalysis was repeated on carbon extraction replicas [Fig. 3(a)]. The replicas were made by evaporation of ~200nm of carbon onto the implanted surface, followed by electropolishing in a solution of 2 vol.% HCl in methanol at a current density of 2.8A/cm^2. Beryllium support grids were used. The indicated composition of the precipitates increased to 8.3 ± 1.2 at. % Mo [Fig. 3(b)] which is consistent with the composition of $Al_{12}Mo$, the precipitate predicted from the Al-Mo phase diagram. A positive identification of the precipitates as $Al_{12}Mo$ was obtained from

crystallographic information obtained by convergent beam electron diffraction (CBED). Simmilar results were obtained for annealed Al - 11 at. % Mo in which the $Al_{12}Mo$ precipitates formed a continuous film.

Coated cavities in neutron-irradiated aluminum[8]

Commercial purity 1100 grade aluminum was irradiated at ~328°K to neutron fluences of 1.4 X 10^{27} n/m^2 (E>0.1 MeV) and 2.3 X 10^{27} n/m^2 (E<0.025 eV). About 5.3 at. % Si was created by the reaction $^{27}Al(n,\gamma)^{28}Al$ followed by β decay to ^{28}Si. Crystalline silicon precipitates and coated cavities were observed [see Fig. 4(a)]. Defects marked A and B are coated cavities clinging to the surface of the foil. The cavities marked B have "collapsed". X-ray microanalysis of the 4 to 11 nm thick amorphous shells on free-standing cavities at the edge of the foil showed Al, Si, Mn and Cu K x-rays and a high background [Fig 4(b)]. When the high voltage of the AEM was turned off the Al and Si peaks disappeared and the Cu x-ray intensity decreased [Fig. 4(c)]. The Mn and some of the Cu K x rays are believed to be due to x rays from the decay by internal conversion (K-capture) of the nuclides ^{65}Zn and ^{55}Fe in the alloy. With the specimen in the microscope extra Cu x-ray emission occurs from fluorescence of the copper specimen holder.

In order to reduce the background radiation from the radioactive specimen and at the same time minimize secondary fluorescence of the matrix, carbon extraction replicas were produced [Fig. 5(a)]. X-ray microanalysis confirmed that both the precipitates and cavity coatings [Fig. 5(b)] were silicon.

Conclusions

Reliable procedures for the preparation of extraction replicas can be developed. In general, the methods are no more complex than techniques for the preparation of thin foils. Compositions determined by x-ray microanalysis of extracted precipitates are usually more accurate than equivalent measurements from thin-foil specimens. Of course, complimentary examination of thin-foil specimens is still necessary to obtain a complete phase identification .

References

1. J.M. Leitnaker and J. Bentley, Met. Trans. 8A (1977) 1605-1613.

2. J. Bentley and J.M.Leitnaker, "Stable phases in aged type 321 stainless steel", in The Metal Science of Stainless Steel, E.W. Collings and H.W. King, eds., The Metallurgical Society of AIME: Warrendale, PA, 1979, 70-91.

3. L. Hollan, Ann. Chim. 1 (1966) 437-448

4. R.W. Carpenter and J. Bentley, "On the performance of a field emission gun TEM/STEM", SEM/1977 I, 153-160 and 126.

5. D.B. Williams, private communication.

6. L.D. Stephenson et al., "Analytical electron microscopy of aluminum ion-implanted with molybdenum" in 41st Ann. Proc. EMSA, G.W. Bailey, ed., San Francisco Press, San Francisco, CA, 1983, 262-263.

7. J. Bentley et al., "Second phase formation in aluminum annealed after ion-implanation with molybdenum", in Ion Implantation and Ion Beam Processing of Materials, G.K. Hubler et al., eds., North Holland: New York, 1984, 151-156.

8. K. Farrell, J. Bentley and D.N. Braski, Scripta Met. 11 (1977) 243-248.

Figure captions

FIG. 1.--Carbon extraction replica of type 321 stainless steel aged 17 years at ~600°C. (a) Bright-field micrograph showing rod-shaped complex phosphide-arsenide precipitates and small Ti-rich MC particles. (b) Energy-dispersive x-ray spectrum of the precipitate arrowed in (a).

FIG. 2.--Isolated MC-type carbide precipitate on carbon extraction replica of type 321 stainless steel aged 17 years at ~600°C. (a) Bright-field image. (b) Energy-dispersive x-ray spectrum. Analysis time 100 s; vertical scale = 1000 counts/channel.

FIG. 3.--Aluminum ion-implanted with molybdenum to a peak concentration of ~4.4 at. % Mo and annealed at 550°C for 100 min. (a) Bright-field image of $Al_{12}Mo$ precipitates on carbon extraction replica. (b) Energy-dispersive x-ray spectrum from extracted precipitate.

FIG. 4.--(a) Coated cavities and silicon precipitates in 1100 grade aluminum neutron-irradiated at ~328 K. (b) Energy-dispersive x-ray spectrum from coated cavity projecting over edge of electropolished thin foil. (c) X-ray spectrum obtained with accelerating voltage turned off.

FIG. 5.--(a) Carbon extraction replica of 1100 grade aluminum neutron-irradiated at ~328 K showing silicon precipitates and coated cavities. (b) Energy-dispersive x-ray spectrum from cavity coating.

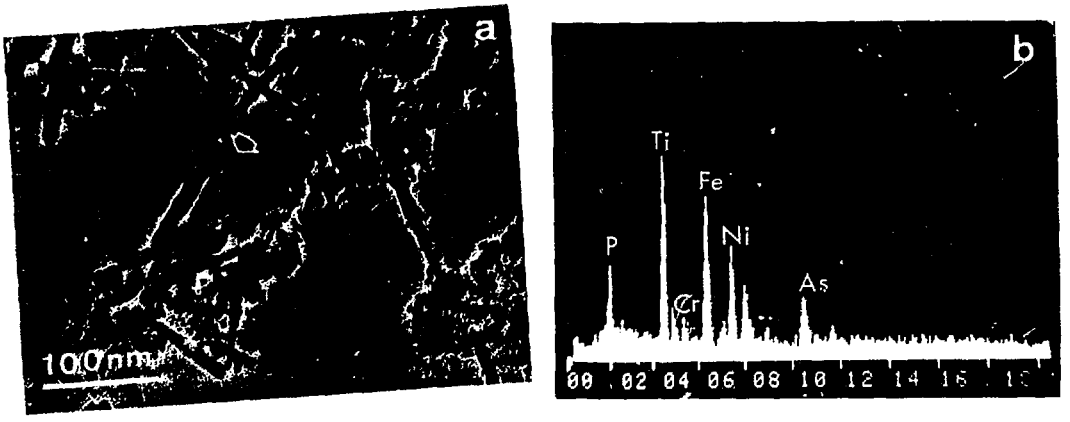

Fig 1

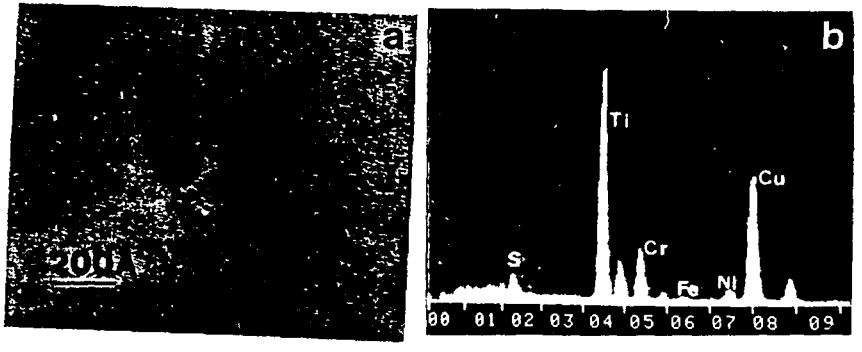

Fig 2

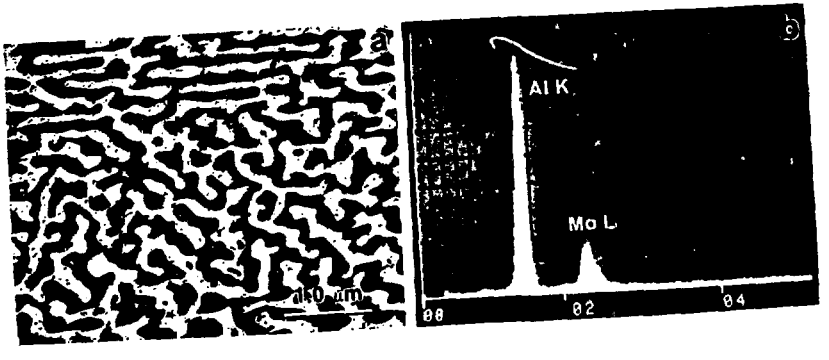

Fig 3

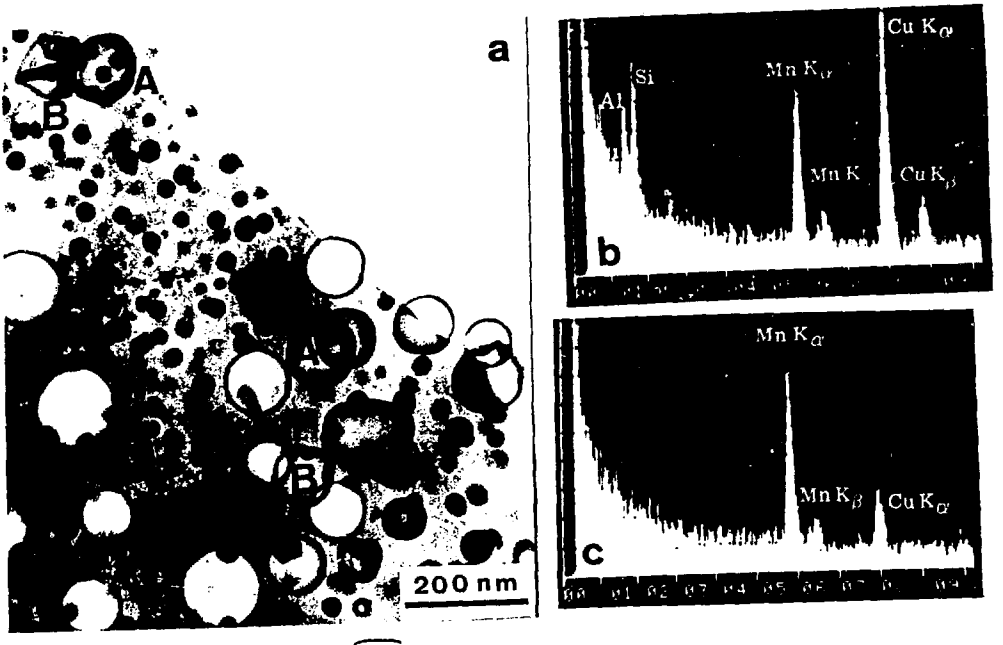
a
A
B
A
B
200 nm
Al
Si
Mn Kα
Mn K
Cu Kα
Cu Kβ
b
Mn Kα
Mn Kβ
Cu Kα
c

Fig 4

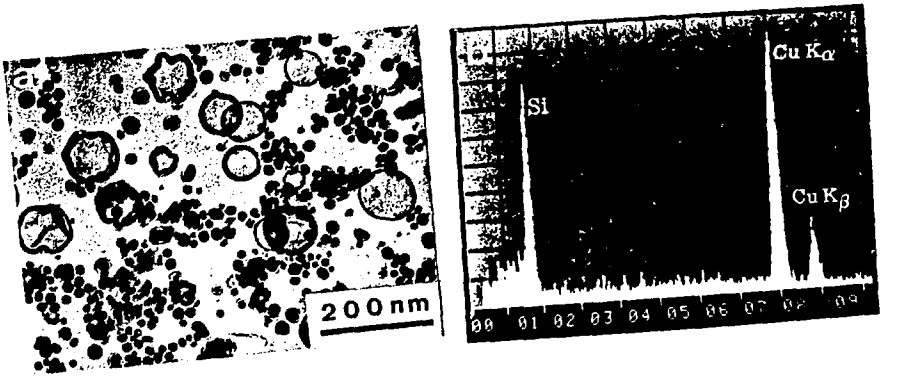
200nm
Si
Cu Kα
Cu Kβ

Fig 5