ANALYTICAL APPLICATIONS OF ELECTRON OPTICAL INSTRUMENTATION

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operated for the U. S. ATOMIC ENERGY COMMISSION
by UNION CARBIDE CORPORATION-NUCLEAR DIVISION
under Contract W-7405-eng-26

August 28, 1972

THIS PREPRINT WAS PREPARED FOR SUBMISSION TO
Sixteenth Conference on Analytical Chemistry
in Nuclear Technology, Sponsored by ORNL,
Gatlinburg, Tenn., Oct. 24-26, 1972

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The Y-12 Plant electron optical capabilities include: transmission electron microscopy (TEM), scanning electron microscopy (SEM), and electron probe microanalysis. These capabilities have proved most valuable in material characterizations, particularly microchemical analysis of small specimens or the microstructure of larger specimens.

This instrumentation contains some unique capabilities such as the TEM's ability to study morphological detail of very small areas with its resolution of $< 10 \text{ \AA}$. Selected area electron diffraction patterns can yield chemical and crystallographic features of an object area in a thin foil and be identified with the image observed directly in the TEM. The SEM, with its minimal sample preparation, great depth of field, and 200 - 300 $\text{\AA}$ resolution is an essential tool in our microanalytical laboratory. Ceramics and metals, as well as organic materials, are quickly analyzed for high resolution surface detail, failure modes, and surface morphology. The microchemical application of our SEM has been greatly improved by the addition of an energy-dispersive X-ray spectrometer for qualitative and semi-quantitative chemical analysis of all elements from fluorine to uranium. The electron probe has an almost unique capability in that it can analyze cubic micron size volumes of material for all elements from beryllium to uranium qualitatively and, in most cases, quantitatively. I should like to describe briefly some examples of recent studies which demonstrate the microanalytical application and capability of these disciplines.

Uranium-0.5 weight percent titanium, alpha phase, martensitic uranium alloy, shows large increases in strength due to precipitation of U_2Ti on aging at moderate temperatures. Rapid precipitation of this planar precipitate occurred on aging at temperatures greater than $400^{\circ}C$. From photomicrographs like the one in Figure 1 (SLIDE 1), it was possible to correlate crystallographic data with microstructure utilizing stereographic techniques. Analysis showed the $\{10\bar{1}0\}_{U_2Ti} \parallel \{010\}_{\alpha-U}$ and $[0001]_{U_2Ti} \parallel [100]_{\alpha-U}$.

Reactor beads composed of uranium-loaded (> 50 wt.%) pyrolytic carbon-coated cation exchange resin beads, heat-treated to $3000^{\circ}C$, were ion thinned and examined by TEM. A transmission micrograph from a typical bead is shown in (SLIDE 2). The microstructure illustrates a random distribution of fine particles in a matrix of low-density microporous carbon. Measurements made on the micrograph indicate that individual particles ranged in size from 75 A to 150 A. Selected area diffraction and dark field microscopy showed the particles to exhibit a pattern similar to an ordered UC-US solid solution phase reported by X-ray studies.

As a result of the Y-12 Plant's work on the Rover Nuclear Propulsion Program, a need arose for quantitative electron microprobe analysis of both the metal and carbon in metal carbides. Due to the non-stoichiometric nature of these materials, it was first necessary to obtain reference materials with well-established chemical analyses which were homogeneous on the micrometer scale. Several NbC_x and ZrC_x materials were prepared at the Y-12 Plant by vapor deposition and subjected to extensive chemical

and microprobe examinations. The majority of these materials were as homogeneous as our microprobe precision of ± 0.2 weight percent could measure. The results of the chemical analysis and the corresponding trends in composition for the chemical and electron microprobe results are listed in (SLIDE 3). From these results, it is obvious that these materials constitute well-characterized reference materials.

A SEM fractographic study of uranium-7.5 wt.% niobium-2.5 wt.% zirconium alloy was undertaken to better understand this relatively new material. Tensile specimens from properly heat-treated and aged-alloys fracture predominately in the dimple rupture mode as shown in (SLIDE 4A). Second-phase precipitates resembling those found in some maraging steels are frequently observed in the pits and sides of the dimples (SLIDE 4B, 4C). Energy-dispersive analysis of these small inclusions has indicated they are zirconium rich, possibly zirconium nitride (SLIDE 5).

Test specimens, stressed by bending in moist air and under water, have exhibited mixed modes of fracture with a predominance of intergranular fracture at the initiation site (SLIDE 6). The failure time of coupons stressed in water or moist air is generally measured in thousands of hours; the presence of chloride ions drastically reduces failure time.

As a result of these studies, characteristic fracture modes have been identified for two types of stress corrosion in this alloy: a transgranular, quasi-cleavage type in air and an intergranular mode in moisture.

These are but a few examples which demonstrate the microanalytical capabilities of electron optical instrumentation. As the requirements of material properties at the Y-12 Plant become more and more stringent, analytical instrumentation will play an ever increasing role in their characterization.

ACKNOWLEDGEMENT

The following acknowledgements belong to members of the Y-12 Plant who made valuable contributions to this presentation:

R. K. Bennett for his SEM fractography study of 0-7.5 Nb-2.5 Zr alloy.

D. H. Johnson and A. M. Ammons for their TEM study of U-0.5Ti alloy.

F. W. Postma for his assistance in the electron microprobe analysis of metal carbides.

SLIDE 1

SLIDE 2

Batch	Material	Metal w/o $\pm$ *			Carbon w/o $\pm$ *	
		Chemical	Microprobe		Chemical	Microprobe
V	NBC _x	88.66 $\pm$ 0.20	88.69 $\pm$ 0.19		11.20 $\pm$ 0.06	11.20 $\pm$ 0.15
W**		88.76 $\pm$ 0.11	88.76 $\pm$ 0.11		11.14 $\pm$ 0.06	11.14 $\pm$ 0.09
X		89.10 $\pm$ 0.11	89.23 $\pm$ 0.18		10.83 $\pm$ 0.06	10.83 $\pm$ 0.15
A	ZrC _x	88.36 $\pm$ 0.25	88.23 $\pm$ 0.08		11.27 $\pm$ 0.06	11.47 $\pm$ 0.09
B		88.41 $\pm$ 0.20	88.45 $\pm$ 0.11		11.31 $\pm$ 0.07	11.30 $\pm$ 0.13
C**		88.51 $\pm$ 0.11	88.51 $\pm$ 0.04		11.35 $\pm$ 0.11	11.35 $\pm$ 0.09

*Confidence interval (95%) of the mean

**"Reference" for Microprobe

Y-12 METAL CARBIDE REFERENCE MATERIALS

SLIDE 3

-A-

-B-

DIMPLE RUPTURE FRACTURE IN DUCTILE URANIUM -
7.5% Nb - 2.5% Zr ALLOY (HEAT TREATED AT 800° C,
WATER QUENCHED, AND AGED FOR ONE HOUR AT
150° C)

A - PREDOMINANTLY DIMPLE RUPTURE
B - AREA WITH HIGH CONCENTRATION
OF INCLUSIONS
C - DETAIL OF INCLUSIONS

SLIDE 4

**X-RAY SPECTRA OF THE TWO AREAS MARKED IN THE
ABOVE MICROGRAPH (U-7.5NB-2.5 ZR)**

-A-

-B-

GRAIN FORMATIONS OBSERVED IN THE INTER-
GRANULAR FRACTURES

A - DEEP CRACKS BETWEEN GRAINS
B - AREA LEADING INTO QUASI CLEAVAGE
C - INTERMITTENT QUASI CLEAVAGE

SLIDE 6