**ANALYSIS OF TANTALUM METAL FOR TRACE
AMOUNTS OF NIOBIUM BY ENERGY-DISPERSIVE
X-RAY FLUORESCENCE SPECTROMETRY**

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ANALYSIS OF TANTALUM METAL FOR TRACE AMOUNTS OF NIOBIUM BY ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

Abstract

A nondestructive method is described for quantitatively measuring trace amounts (0-500 ppm) of niobium in tantalum-niobium alloy sheets, turnings, and fabricated parts. The method, which

makes use of an energy-dispersive x-ray spectrometer to compare the sample to be analyzed against known standard samples, can detect niobium levels as low as 10 ppm.

Introduction

Our need was to measure trace concentrations of niobium in tantalum-niobium alloy accurately, nondestructively, and fairly rapidly. X-ray fluorescence is the ideal method. We chose to use our energy-dispersive spectrometer rather than our wavelength instrument because its large sample chamber can accommodate the *diversity of sizes and shapes of the pieces* of material to be analyzed, and because the primary and fluorescent beams are easily filtered.

The energy-dispersive spectrometer and its operating characteristics are described in UCRL-75108.¹

The spectrometric analysis depends on comparing x-ray fluorescence measurements made on the Ta-Nb material to be

analyzed with the same measurements made on Ta-Nb reference samples whose Nb content is precisely known. We made our own reference samples out of disks punched from Ta-Nb sheet containing various trace concentrations of Nb. To determine the Nb content of the reference samples we first used the spectrometer to obtain a primary calibration curve which showed the spectrometer's response to various accurately prepared solutions of Ta with different concentrations of Nb. Solutions made from the same sheets as the reference samples were then run to determine their Nb content by comparing the spectrometer response with the primary calibration curve. The reference sample disks were also analyzed for Nb content by neutron activation analysis, and the results were very close to those obtained from the x-ray fluorescence measurements.

Once the reference samples had been established we were able to put our

¹Richard W. Ryon, Determination of Trace Impurities in Boron Carbide by Energy Dispersive X-Ray Fluorescence Spectrometry, I. Lawrence Livermore Laboratory Rept. UCRL-75108 Preprint (1974).

analysis technique into operation. The procedure is simply to take a sample that is to be analyzed and run it in the x-ray spectrometer, then run the reference

samples to obtain a calibration curve with which to determine the Nb concentration in the sample being analyzed.

Standardization

To determine the Nb content of the reference sample disks, we first prepared primary solution standards from high-purity tantalum and niobium metal. A stock solution of Nb was prepared by dissolving 0.1000 g of Nb shot with HF solution in a Teflon* beaker and then

diluting to 100.0 ml with 10% HF. Samples of Ta turnings weighing 1.0000, 0.9999, 0.9998, 0.9997, 0.9995, 0.9993, and 0.9990 g respectively were dissolved in HF-HNO₃ solution in Teflon beakers. Aliquots of the Nb stock solution containing 0, 100, 200, 300, 500, 700, and 1000 µg Nb were added to the respective Ta solutions, which gave for each 1.0000 g total of metal ions. Each sample was then made up to 25.00 ml with 10% HF solution. These solutions were used to prepare the

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

Fig. 1. Primary calibration curve obtained with the standard solutions of Ta-Nb. This curve was used to determine the Nb concentration in the reference sample disks.

Fig. 2. Calibration curve obtained with the reference sample disks, used to convert Nb K α counts per second in a sample being analyzed to ppm of Nb.

primary calibration curve in Fig. 1 by x-ray fluorescence (XRF) as described below. (Note: The intercept was 49.7 ppm Nb due to the trace amount of niobium in the stock tantalum. This has been corrected for in the Figure.)

The Ta-Nb alloys from which the disks were punched were dissolved in HF-HNO₃ solution and diluted with 10% HF to give solutions containing 1.0000 g metal per 25.00 ml. The Nb content of each of these solutions was determined by comparing the Nb K α peak intensity with the solution primary calibration curve previously prepared.

Three of the four disks were subsequently analyzed by neutron activation analysis (NAA) using 15-MeV neutrons for excitation and gamma spectroscopy for measurement.* The XRF and NAA values agree remarkably well (Fig. 2), having a correlation coefficient r greater than 0.99.

After they were polished with 5- μ m alumina, the disks served as standards for all subsequent analyses. The calibration curve obtained with the disks is given in Fig. 2.

*Analyses performed by D. Nethaway and M. Coops of the LLL Radiochemistry Division.

X-Ray Fluorescence Procedure

A tungsten x-ray tube operating at 35 kV and 30 mA is used to excite the niobium characteristic spectrum. The primary beam is filtered with 0.020-in. (0.05-cm) tin foil to reduce the bremsstrahlung which would otherwise add to the spectrum background and thereby lower the measurement precision.

The fluorescent radiation is filtered with 0.020-in. aluminum foil to attenuate the Ta L-radiation. This is necessary because there are double photon peaks which result from incomplete pulse pileup rejection in the amplifier. These peaks fall in the same spectral region as the Nb K-radiation. If the fluorescent beam is unfiltered, the double photon peaks are so intense that trace analysis is impossible.

5.00-ml aliquots of the solutions to be measured were pipetted into 1-in.-diam (2.5-cm) plastic Spex cups which were then covered with 0.00025-in. (64- μ m) Mylar film. The Ta L β peak from each solution

is used to normalize all measurements. This procedure reduces the experimental scatter of data due to voltage, current, and specimen differences. The Nb K α peak is integrated over a range of 0.32 keV (17 channels) with a straight-line background subtraction. The results for the standard solutions are shown in Fig. 1. The concentration of Nb in the disks was determined by comparing the Nb K α intensity from their respective solutions with the standard solution curve.

The Ta-Nb alloy disks themselves were then measured by x-ray fluorescence using the same procedure as above in order to determine a working curve. The results are given in Fig. 2. When the data are normalized to 38.00 cps (counts/sec) for the Ta L β peak (0.32 keV wide), the sensitivity for Nb K α is 0.0159 cps/ppm. This calibration factor is checked each day that analyses are run.

Applications

The minimum detectable level of niobium in tantalum is 10 ppm for a half-hour counting time using the method described above. (Both the detectable level and the measurement error decrease with the square root of the time spent counting.)

We have analyzed about 40 specimens to date. These include turnings, machined parts, tensile strength specimens, and

rolled sheets. Concentrations observed fall in the range 0-500 ppm. As an example of the precision obtained, both a machined part and the turnings from that part were analyzed. The results were:

Part: 390 $\pm$ 9 ppm

Turnings: 412 $\pm$ 27 ppm

The indicated error range is 3σ based on counting statistics = $3(\text{peak plus background counts})^{1/2}$.