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THE DEVELOPMENT AND FABRICATION OF A BORON ABSORPTION TUBE FOR SPECTROGRAPHIC ANALYSIS

by

J. T. Dusek

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ANL-7164
Instruments (TID-4500)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CFSH PRICES

H.C. \$ 1.00; MN. 50

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March 1966

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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THE DEVELOPMENT AND FABRICATION OF A BORON ABSORPTION TUBE FOR SPECTROGRAPHIC ANALYSIS

by

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ABSTRACT

Techniques were developed for fabricating thin-walled boron tubes for use as hollow-cathode discharge tubes in special spectrographic applications. The most successful specimens made contained 10 w/o of tungsten. Some data are presented on composition of the boron specimens and the high-temperature interactions that occurred during specimen sintering.

INTRODUCTION

Water-cooled, hollow-cathode discharge tubes fabricated from various materials have been used in several spectrographic analyses. Tubes made of uranium alloys have been used in the unirradiated condition to determine alloy constituents.¹ Tubes made of either lithium hydroxide or uranium alloys have been used as emission and absorption sources to determine the amount of the lithium-6 and -7 (Ref. 2) or the uranium-235 and -238 isotopes.³ This technique might be applicable in determining the amounts of boron isotopes, B^{10} and B^{11} , present in a sample.

A search of the literature revealed that no information was available on the fabrication of thin-walled tubes of boron. This work was undertaken to study the parameters involved in sintering boron, and to develop techniques for producing thin-walled tubes. The finished tubes were to be used in the apparatus, and the operating results have been reported by Goleb.⁴

EXPERIMENTAL DEVELOPMENT

Studies involving the sintering of boron were made with natural amorphous boron.* Pellets were pressed under a pressure of 700 kg/cm² and were sintered in vacuo and in argon atmosphere at temperatures from 1400 to 2000°C. The sintering studies were made with the use of tungsten

*A. D. McKay, Inc.

setter plates to support the boron pellets. Considerable reaction occurred between the boron and tungsten at 2000°C, and thoria setter plates were substituted for the tungsten. A moderate reaction was observed between the boron pellets and thoria; however, this reaction did not cause deformation of the boron pellets.

The reaction between the boron pellets and tungsten at 2000°C suggested a liquid-phase sintering as a means of increasing the densification of the boron pellets, and to improve the sintered strength of the boron. Tungsten powder was added, and the sintering characteristics of these mixtures were studied.

Thin-walled tubes were fabricated by using a modified slip-casting technique. Slip casting entails the preparation of a slurry composed of particulate material suspended in a liquid media. This slurry is poured into a plaster mold, which absorbs the liquid and leaves a wall of solid material on the surface of the plaster mold.

The amorphous boron powder was screened through a 325-mesh sieve to crush or remove all agglomerates. A casting slurry was prepared by mixing this boron powder with a 1 w/o ammonium alginate water solution. A ratio of 1.5 g of boron powder to 1 cc of the alginate solution produced a satisfactory slurry. This slurry was charged to a 1.27-cm-diam plaster mold, fitted with a 0.794-cm-diam brass rod. The brass rod served as the core of the boron tube. The filled mold was vibrated, to improve densification of the boron piece. The time used to cast and vibrate the mold was 1 hr. After the boron tube was cast, the brass core was extracted, and the plaster mold containing the cast boron cylinder was dried at 80°C for 10 min. This drying time was sufficient to cause the boron tube to shrink away from the plaster mold and facilitate its removal. The cast boron tube was then dried at 80°C, packed in thoria, and sintered in vacuo at 2000°C. This procedure was also used to form tubes containing mixtures of boron and tungsten. When these materials were fabricated, the boron and tungsten powders were mixed in a ball mill and then stirred into the ammonium alginate solution to form a slurry.

DISCUSSION AND RESULTS

Pellets pressed from amorphous boron and sintered in an argon atmosphere at temperatures up to 1800°C were found to lack mechanical strength. These pellets were friable and did not sinter under these conditions. At 2000°C the pellets reacted with the tungsten setter plates and crucibles. This reaction was severe and caused complete destruction of the pellets by melting.

Thoria disks were used to avoid the reaction between the boron pellets and the tungsten crucibles. Boron pellets fired in argon at 2000°C developed more strength than pellets sintered at 1800°C. They still, however, lacked sufficient strength to withstand normal handling. No melting reaction was observed between the boron pellets and the thoria setter plates. A bright-red-colored reaction zone was observed where the boron pellet had been in contact with the thoria.

Additional boron pellets were set on thoria disks and sintered in vacuo at 2000°C. These pellets were moderately strong and dense. The red-colored reaction zone, however, was again observed. Samples of the red-colored material were collected, and X-ray powder diffraction patterns indicated that the material was thorium hexaboride (ThB_6).

During these experiments, a pellet of boron spalled and portions of the pellet came in contact with the tungsten crucibles. When this happened, a melting reaction occurred between the boron and the tungsten with the apparent formation of a volatile species. The remaining portion of the boron pellet became hard and dense and had a metallic appearance. Spectrochemical analyses indicated that the boron contained about 8 to 12 w/o tungsten. An X-ray diffraction pattern of the tungsten-contaminated boron yielded the data shown in Table I. This pattern did not correspond to any boron-tungsten compound in the ASTM file. Similarities of this pattern to that of the compound MoB_2 suggested that the compound may be WB_2 .

TABLE I. X-ray Diffraction Data on Tungsten-Boron Phase

Intensity*	d Spacing (observed), Å	Intensity*	d Spacing (observed), Å
VS	3.67	W	1.54
M	3.16	W	1.50
S	2.60	M	1.35
M	2.12	W	1.32
VS	2.01	W	1.30
M	1.64	W	1.23
W	1.58	M	1.20

*VS = very strong M = moderate
 S = strong W = weak

To eliminate the reaction between the boron pellets and the tungsten crucibles, a thoria coating was applied to the crucible side walls. Pellets of pressed boron were sintered at 2000°C in vacuo. These pellets did not have the metallic appearance of the boron pellets in which tungsten contamination had occurred. These pellets also did not develop the sintered strength of pellets that contained tungsten. X-ray diffraction analyses

indicated that there was no boron-tungsten phase, and spectrochemical analyses revealed that these pellets contained only approximately 0.2 w/o tungsten.

The low sintered densities of the boron pellets, which were developed at 1800°C, and the reaction between boron and tungsten, which was observed at 2000°C, indicate a critical sintering temperature. A mixture of 10 w/o tungsten 90 w/o boron was made, since the boron pellets that were contaminated with tungsten contained about 8 to 12 w/o of the metal. This mixture was melted with use of a modified Mendenhall-wedge technique, and the melting point was found to be 2015°C. From this the optimum sintering temperature of a boron-tungsten mixture was estimated to be between 1950 and 2000°C.

The addition of 10 w/o tungsten to the boron improved the sintered density and strength of the pellets. The effect of the tungsten on the analyses of the boron isotopes was unknown. For this reason, tubes were made from boron as well as from the boron-10 w/o tungsten mixture. These tubes were sintered at 2000°C to achieve as high a density as possible. A photograph of one of the tubes is shown in Fig. 1 and data on tubes fabricated are shown in Table II. Tubes produced from natural boron, in which no tungsten was added, had sufficient strength for use in the boron analyses. They, however, were only moderately strong and were not of high density. X-ray diffraction analyses revealed that the only phase present was boron. Tubes fabricated from natural boron in which 10 w/o tungsten was added had good strength and relatively high density. X-ray diffraction analysis of these tubes showed that they contained both boron and a boron-tungsten compound. Tubes fabricated from boron enriched in the B^{10} isotope and 10 w/o tungsten sintered to moderately high strength and were fairly dense. X-ray analysis showed these tubes to contain boron and a boron-tungsten phase.

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Fig. 1

Boron Tube with
8 to 12% Tungsten

TABLE II. Data on Boron Tubes

Tube No.	Boron Type	Tungsten Content, %	Dimensions, cm			Density, g/cc	Phases Found by X-ray Diffraction	Tube Condition
			Length	OD	Wall Thickness			
1	Natural	8-12	5.3	2.2	0.2	1.949	Boron and tungsten-boron phase.	Dense and strong.
2	Natural	0.2	5.4	2.2	0.2		Boron	Moderately dense and strong.
3	Enriched B^{10}	10	4.9	2.2	0.2	1.397	Boron and tungsten-boron phase.	Moderately dense and strong.

The use of these boron tubes for the determination of the boron isotopes B^{10} and B^{11} , by atomic absorption spectrophotometric techniques, indicated that a small amount of tungsten did not interfere with

the absorption measurements.⁴ In fact, the tungsten addition improved the performance in the spectrographic-analysis application. This improvement was attributed to the higher electrical conductivity of the tubes containing tungsten, as compared to those fabricated from boron alone.

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