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LA-5672

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Reporting Date: July 1974

Issued: October 1974

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Nitride Nitrogen in Boron Carbide**

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R. E. Perrin*

A. Zerwekh

W. H. Ashley

*Present address: Teledyne Isotopes, Westwood, NJ 07675.

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7408-ENG. 56

**Work supported by U.S. Atomic Energy Commission's Division of
Reactor Research and Development.**

**Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00 Microfiche \$1.45**

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SEALED-TUBE DISSOLUTION METHOD FOR
DETERMINATION OF NITRIDE NITROGEN IN BORON CARBIDE

by

R. E. Perrin, A. Zerwekh, and W. H. Ashley

ABSTRACT

Nitride nitrogen in B_4C is determined by dissolving the sample in 14M H_2SO_4 in a sealed fused-silica tube, distilling the nitrogen as ammonia from alkaline solution, and titrating the ammonium hydroxide in the distillation receiver with standardized acid. The Winkler distillation and the titration are proven operations that are directly applicable to the analysis of the B_4C solution. Recovery of nitrogen from B_4C was difficult and time-consuming by the usual caustic-fusion and leach methods, but it was simplified by substituting the technique of high-temperature dissolution in 14M H_2SO_4 . With the sealed-tube method, analysis of six prepared mixtures of BN and B_4C gave a mean recovery of 99.9% nitrogen, with a standard deviation of 0.94%. Fourteen portions of B_4C production material gave a mean nitrogen value of 917 ppm, with a standard deviation of ± 30 ppm. Twelve analyses of the same material by the caustic-fusion method gave a mean nitrogen content of 928 ppm, with a standard deviation of ± 84 ppm. The sealed-tube method for determining nitrogen is highly selective; none of the impurities found in B_4C interfere.

I. INTRODUCTION

As part of a joint program between Los Alamos Scientific Laboratory (LASL) and the Hanford Engineering Development Laboratory (HEDL), methods were developed or improved for the chemical characterization of B_4C to be used as the absorber material in the control rods of the Fast Flux Test Facility (FFTF) reactor. One goal of the program was to improve the method for determining nitride nitrogen in the carbide. In conventional methods, the sample is fused with caustic and an inert gas is used to sweep the nitrogen into an HCl scrubber. The scrubber solution is made alkaline, and the ammonia is redistilled to remove caustic carried over from the fusion apparatus. The amount of ammonia is determined by

either a colorimetric measurement using Nessler's reagent or a titrimetric determination using either 0.01M or 0.1M HCl and a special indicator.

The caustic-fusion technique requires the careful attention of a highly experienced analyst to attain complete dissolution of the carbide without loss of nitride nitrogen. Dissolution requires about 2 h per sample per analyst. Experience with a variety of B_4C samples has shown a wide material-to-material difference in dissolution rates, with some samples stubbornly resisting complete dissolution.

A sealed-tube technique had been used successfully at LASL for the dissolution of many refractory materials, including carbides and nitrides,¹ and was evaluated for

use in dissolution of B_4C materials. Cosgrove and Shears² used the technique for BN, obtaining complete dissolution with 14M H_2SO_4 at 320°C, and Keele³ successfully dissolved BN with 6M H_2SO_4 plus $KClO_4$ at 300°C. Our evaluation showed that the sealed-tube method was very satisfactory for dissolving B_4C , and the technique was incorporated into our method for determination of nitride nitrogen.

II. EXPERIMENTAL

A. Effect of H_2SO_4 Molarity

For the sealed-tube method, the first variable studied was H_2SO_4 molarity. Using one batch of B_4C (100-mesh size), 100-mg portions were subjected to 16-h reactions at 350°C with 7 ml of H_2SO_4 in five molarities ranging from 9M to 16M. Complete dissolution was obtained only with 14M H_2SO_4 . Combinations of H_2SO_4 and $HClO_4$ were then evaluated using the same quantities and strengths of H_2SO_4 plus 0.1 and 2 ml of 12M $HClO_4$. The 0.1-ml quantity of $HClO_4$ had no effect on the dissolution rate. All five strengths of H_2SO_4 with 2-ml of 12M $HClO_4$ did result in complete dissolution, but excessive gas generation caused explosions when the tubes were opened. Immersion of the tubes in liquid nitrogen before opening did not significantly reduce the force of the explosions, consequently the use of $HClO_4$ was not investigated further.

The 14M H_2SO_4 was evaluated for the dissolution of 100-mg samples of seven different B_4C materials at 350°C. Two samples dissolved completely after 16 h, four required 40 h, and one required 72 h. The cause of the differing dissolution rates is unknown.

B. Effect of Mesh Size

Samples from the same seven B_4C materials were ground to 200- and 270-mesh particle size, and subjected to 14M H_2SO_4 at 350°C. The dissolution rate of samples ground to pass a 200-mesh screen increased significantly over that for the 100-mesh

size of samples described in Sec. II.A. Six of the batches dissolved completely after a 16-h heating period. The batch that had previously required 72 h to dissolve completely at 100-mesh size dissolved in 48 h at the 200-mesh size. Further reduction to 270-mesh size did not increase the dissolution rate significantly.

C. Effect of Reaction Temperature

The dissolution-resistant B_4C batch discussed in Sec. II.B and a batch of another B_4C (70-mesh) that required more than a 5-day dissolution time at 350°C in 14M H_2SO_4 were used to determine the dissolution rates as a function of reaction temperature. Samples of this B_4C (100-mg, 200-mesh) were reacted with 7 ml of 14M H_2SO_4 at 400 and 500°C. One batch completely dissolved in 16 h at 400°C; the second batch took 72 h at this temperature. At 500°C, both batches dissolved within 16 h. At the higher temperature, the amount of powdered dry ice used to pressurize the steel shell must be reduced from 50 to 25 g,⁴ otherwise the copper gasket flows and the steel shell is vented. The rate of tube failure at 500°C is about 5%, but the steel shell contains the pressure. After the intact tubes are cooled, the pressure is essentially ambient. Since adjusting the time and temperature to 16 h and 500°C, only one sample has failed to dissolve completely. This sample was dissolved by returning it to the furnace for an additional 8 h.

Most batches of B_4C need not be reduced to powder for dissolution when a 500°C temperature is used. The sample that did not dissolve after 5 days at 350°C did dissolve after 16 h at 500°C, even in its original 70-mesh particle size. Additional experiments indicate that many samples can be dissolved in chunks at 500°C.

D. Comparison of Sealed-Tube and Caustic-Fusion Methods

Samples from three batches of ground B_4C pellet material were analyzed for nitrogen by the sealed-tube and the

caustic-fusion methods (see Table I). No significant differences in mean values were observed, but there were obvious differences in operational ease. In every case the precision of the sealed-tube method was better.

TABLE I
NITROGEN RECOVERY FROM B₂C PELLET MATERIAL

Batch No.	Nitrogen (ppm)	
	Sealed-Tube Method	Caustic-Fusion Method
1	803, 781, 815, 777 876, 780, 736 Mean and SD: 795 ± 43	789, 914, 680, 818, 880, 864, 985 875 ± 64
2	1794, 1824, 1724, 1830 Mean and SD: 1793 ± 49	1688, 1882, 1772, 1824 1791 ± 82
3	3813, 3817, 4090, 3925 Mean and SD: 3911 ± 130	3914, 3618, 3988, 3761 3820 ± 165

A sample from Batch 2 did not dissolve completely after 16 h in the sealed tube, so it was returned to the furnace until it did dissolve. Another sample from Batch 2 did not dissolve completely in the standard caustic-fusion heating pattern, a fact discovered during comparison of results from 50- and 100-mg portions of sample, where the nitrogen recovery from 50-mg portions was always higher. Adjustment of the caustic-fusion heating pattern allowed complete recovery of nitrogen from both sample sizes, but such adjustment involves extra work and decreases the number of samples that may be run during a day.

With the sealed-tube dissolution method, eight determinations can be made in a day, but the rate could be doubled by the addition of another furnace and four more steel shells at a cost of approximately \$600. Four caustic-fusion analyses can be made in a day, but an increase to eight would require another induction furnace and associated fusion apparatus costing about \$2000.

III. RECOMMENDED PROCEDURE FOR SEALED-TUBE METHOD

A. Apparatus

Balance, analytical, capable of weighing to 0.1 mg.

Beakers, tall-form, 400-ml, Pyrex.

Buret, precision, 5-ml, for standard acid.

Distillation apparatus (see Fig. 1).

Flasks, Erlenmeyer, 250-ml, Pyrex, with ground-glass stoppers.

Furnace, capable of 500°C, with minimum interior dimensions 100 mm by 100 mm by 410 mm.

Mortar, Plattner, tool steel, hardened.

Probe, weighing and transfer (see Fig. 2).

Shell, steel, with cap (see Fig. 3).

Sieve, 200-mesh, U.S. Standard Sieve Series.

Stirrer, magnetic.

Torch, hand, for oxygen and natural gas.

Tubes, clear fused-silica, 12-mm o.d. by 2-mm wall by 380 mm long, sealed at one end.

B. Reagents

Boric acid, reagent grade, saturated solution.

Hydrochloric acid, 0.01N. Compare with NaOH solution that is standardized with SRM 84 potassium acid phthalate.

Fig. 1. Distillation assembly for the determination of nitrogen.

14. Place the fused-silica tube in a container of powdered dry ice to a depth of 25 mm above the surface of the solution. Freeze for 15 min.

15. For each tube, prepare a glass-stoppered 250-ml Erlenmeyer flask containing 50 ml of water and 2 ml of 30% H_2O_2 .

CAUTION: Steps 16 and 17 should be performed behind a safety shield. Lightweight leather gloves should be worn.

16. Score the fused-silica tube around at least one-third of the tube circumference at about 75 mm above the surface of the frozen sample.

17. Wrap the tube in gauze and break it at the score mark.

18. Invert both sections of the tube into the Erlenmeyer flask, and allow the tubes to warm to room temperature with the open ends submerged in the liquid.

19. Rinse the tubes thoroughly with distilled water.

20. Stopper the flask and shake well to assure contact of all SO_2 with the solution.

21. Add 60 g of NaOH pellets, 300 ml of water, and 6 or 8 ceramic boiling chips to each distillation flask. (Potassium sulfate is relatively insoluble, so NaOH is preferred. If KOH is used, it will be necessary to recharge the boiling flask after only two distillations.)

22. With the cooling water off, boil the solution through the condenser for 10 min, turn on the cooling water, and continue the distillation until the solution volume is reduced to 150 ml.

23. Cool the flask to 15°C and add a blank solution containing 7 ml of 14M H_2SO_4 and 2 ml of 30% H_2O_2 in 150 ml of water.

24. Distill 150 ml of this solution into a 400-ml tall-form beaker containing 10 ml of water, 1 ml of saturated boric acid solution, and 3 drops of mixed indicator.

25. Chill the distillation flask to 15°C and transfer the sample solution to it

with sufficient water to bring the total volume in the distillation flask to 300 ml. (If the caustic solution is not chilled before addition of the dissolved sample, there will be some spattering of the caustic, and high results will occur. Redistillation of the ammonia solution will give the correct value.)

26. Distill the sample in the same manner as the blank.

27. Titrate both samples and blank with 0.01N HCl until the indicator changes to a steel gray color.

28. Calculate the nitrogen content of the samples as follows:

$$\text{ppm N} = \frac{(A - B)N \times 14.008 \times 10^3}{W}$$

where A = milliliters of standard HCl for the sample,

B = milliliters of standard acid for the blank,

N = normality of the standard HCl, and

W = weight of sample in grams.

IV. RELIABILITY

In the absence of certified reference materials, the accuracy of the sealed-tube method was evaluated by the analysis of six prepared mixtures of BN and B_4C . The mean recovery of nitrogen was 99.9% with a standard deviation of 0.94%.

To test the precision of the method, a B_4C production material was well characterized as to metallic impurities, boron, total carbon, and soluble carbon content. Fourteen portions of this material were analyzed by the sealed-tube-dissolution-titration method. A mean nitrogen value of 917 ppm was obtained, with a standard deviation of ± 30 ppm. Twelve analyses of the same material by the caustic-fusion method gave a mean nitrogen content of 928 ppm with a standard deviation of ± 84 ppm.

The sealed-tube method is highly selective, and interfering substances in B_4C have not been found. The possible difficulties caused by SO_2 are eliminated by addition of H_2O_2 .

ACKNOWLEDGMENT

We thank G. R. Waterbury for his helpful suggestions in this work.

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