



Wet chemical method for determination of free carbon content in boron carbide

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ABSTRACT

A wet chemical method has been developed for the estimation of free carbon in boron carbide. A chromic-sulfuric acid mixture is used to selectively oxidize the free carbon to carbon dioxide which is precipitated as barium carbonate in a known excess of barium hydroxide solution. The free carbon content is then calculated from the barium hydroxide consumed.

KEYWORDS: Control rod, boron carbide, free carbon

1. INTRODUCTION

Boron carbide is being used in many industries in recent years as it possesses a combination of suitable properties, such as high melting point, high hardness, low density, high Young's modulus, and shear modulus [1–5]. It is also chemically inert to mineral acids, alkalis, and highly resistant to oxidation and corrosion. [8,9]. It is used as an abrasive for polishing and lapping, in the manufacture of wear resistant parts, ceramic armors and metal matrix composites for sporting equipment [9, 10]. It also finds use as an excellent control rod and radiation shielding material in the nuclear industry due to the high neutron absorption cross-section of ^{10}B [11].

Boron carbide can be prepared from various boron compounds such as boric acid, boric oxide, borax, decaborane, as well as by the direct combination of its elemental constituents [1,6-7,12-14]. The carbothermic reduction of boric anhydride by carbon in an electric arc furnace is the most commonly employed commercial method for the production of boron carbide [15]. However, this process involves loss of boron due to evaporation of the volatile oxides of boron leaving behind free carbon as impurity. Presence of free carbon in boron carbide affects its performance for example as a control rod material in nuclear fast reactors. It can also lead to carburization of the clad and make it brittle. Hence, it is necessary to know the free carbon content in boron carbide.

Single phase boron carbide has a wide composition range (9 - 20 at. % C) [16]. The determination of total carbon content does not imply knowledge of the free carbon content. Hence there is a need to develop a method to determine the free carbon content in boron carbide. X-ray methods [17] are time consuming and non-specific; they do not differentiate graphite from hexagonal boron nitride, a frequent impurity in B_4C . Moreover, only graphitic carbon can be determined by the X-ray method; any carbon in non-graphite form goes undetected. Makerenko [18] suggested a technique based on the oxidation of boron carbide using oxygen combustion in the presence of free carbon. However, Schwetz and Hassler [19] opine that the oxygen combustion methods are not suited for B_4C since free carbon and B_4C oxidize simultaneously at the same rate. Nazarchuk and Mekhanoshina [20] carried out an extensive study on the methods of removal of free carbon and suggested that the best oxidizing mixture for the removal of free carbon from boron carbide is the one containing sulfuric, nitric and perchloric acids with potassium dichromate. However, this acid mixture oxidizes not only the free carbon but also the boron carbide to some extent. The procedure suggested by ASTM [21] uses a chromic-sulfuric acid oxidation for 1h and detection of the evolved gases directly using a low-pressure method. The low-pressure method suffers from selectivity problems – any gaseous/vapour species apart from CO_2 also gets included and leads to over estimation. Also, its suitability for estimating higher contents of free carbon is limited by the size of the manometer. Chandramouli [22] suggested a chromic-sulfuric acid leaching method which involves measuring the total carbon content before and after leaching. However, this is a very time consuming method and the results may not be accurate for small

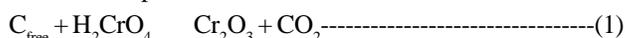
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quantities of free carbon since it is obtained by a difference of two large numbers. The present work is an attempt to develop a simple, efficient, specific and reliable method to estimate the free carbon content in boron carbide. It involves chromic-sulfuric acid leaching of the sample followed by selective absorption of the carbon dioxide evolved in a known excess of barium hydroxide.

2. Principle

Wet chemical methods for removing free carbon are based on the difference between the oxidation properties of boron carbide and free carbon. In this study, a chromic-sulfuric acid mixture is used to selectively oxidize the free carbon present as impurity to carbon dioxide. The carbide phase remains unreacted as a black residue.



The carbon dioxide thus formed is collected in a known excess of an aqueous solution of barium hydroxide as barium carbonate precipitate.



3. EXPERIMENTAL

3.1 Reagents and chemicals

Boron carbide was procured from M/s. Orion Chem Pvt Ltd, Mumbai, India (Source 1), M/s. OPCIL, Mumbai, India (Source 2), and M/s. Bhukanwala, Mumbai, India (Source 3). 98% pure barium hydroxide was procured from M/s. Sarabhai M Chemicals Pvt. Ltd., Gujarat, India. GR grade potassium hydrogen phthalate and AR grade sodium dichromate were procured from M/s. Merck India. AR grade oxalic acid was procured from M/s. Hi Pure fine chem Industries, Chennai, India. Phenolphthalein was procured from M/s. Merck India.

3.2 Apparatus

A schematic of the experimental assembly is shown in Fig. 1. The sample is taken in a round bottom flask fitted with a lid that has an inlet and outlet for a carrier gas (argon) and a thistle funnel with a stopcock for addition of chromic acid. The flow rate of the argon gas is controlled by a needle valve. The round bottom flask is placed in a heating mantle and the temperature is maintained at 373K. Carbon dioxide evolved in the reaction is carried by the flowing argon to a burette filled with barium hydroxide solution where it is absorbed. The remaining gas is passed through a bubbler to prevent any back reaction.

3.3 Procedure

Chromic acid solution was prepared by adding 18M H₂SO₄ with continuous stirring to a saturated aqueous solution of sodium dichromate in water. This solution was cooled and stored in a dark glass

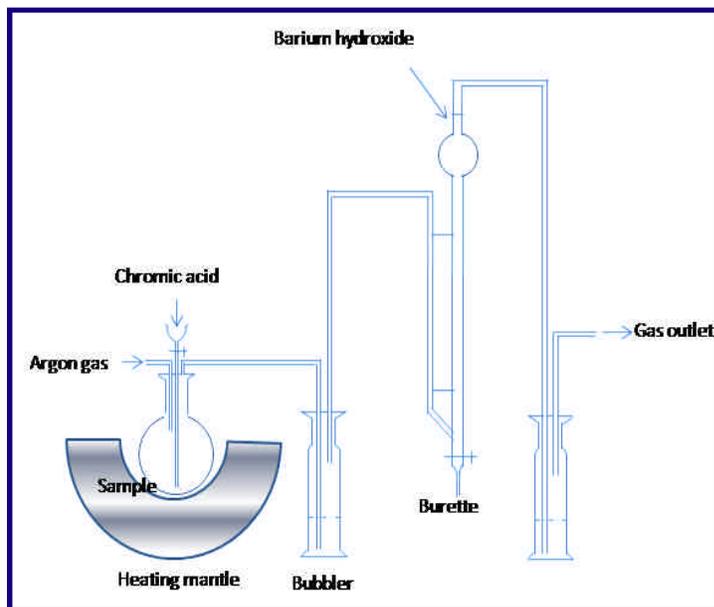


Fig.1. Schematic of the experimental assembly

container. A saturated solution of barium hydroxide was prepared by filtering a boiled and cooled aqueous solution. This was standardized against standard potassium hydrogen phthalate (KHP) solution prepared by dissolving accurately weighed KHP in double distilled water. The indicator used was phenolphthalein.

Powders of graphite and the boron carbide obtained from M/s OPCIL were sieved in an electromagnetic sieve shaker supplied by M/s. Electrolab, Mumbai, India and the powders in the 250-300 μ range were mixed to prepare samples of boron carbide containing 1, 3 and 5 wt % free carbon. Finer particle sizes are known to aid the oxidation reaction. However, particle sizes were restricted to 250-350 μ to avoid any carbide phase oxidation as suggested by Schwetz and Hassler [19]. The bulk density and specific surface area (measured using instrument supplied by M/s. Quantachrome, USA) of the powders were measured to be 2.00 g/cc and 2.11 m²/g respectively.

The sample (~30mg) is taken in a round bottom (RB) flask. Argon gas is used to flush out any carbon dioxide present in the RB flask and provides an inert cover from atmospheric carbon dioxide. After about 10 minutes, barium hydroxide solution and chromic acid are added into the burette and RB flask respectively in that order, and the reaction is allowed for 30 minutes. Chromic acid oxidizes the free carbon alone to carbon dioxide [21]. The carbon dioxide thus evolved is carried by argon through a distilled water bubbler to the barium hydroxide solution where it is collected as barium carbonate. The bubbler solution is made slightly acidic to prevent any dissolution of

carbon dioxide. The excess barium hydroxide solution is titrated against standard potassium hydrogen phthalate using phenolphthalein indicator. The method was validated using oxalic acid solution as standard, prepared by dissolving accurately weighed oxalic acid in double distilled water.

To cross verify the results obtained by the above method, the samples were analyzed for total carbon content before and after acid leaching by an Eltra CS 800 analyzer [22]. The acid leached samples were washed with double distilled water and dried under an infra red lamp in preparation for estimation using CS 800. The difference between the two values gives the free carbon content.

4. RESULTS AND DISCUSSION

The oxidation of the free carbon could be completed in 30 minutes with a sample size of ~30 mg, particle size ~250µ and temperature about 373K. In order to confirm completion of the reaction, graphite powder was heated in chromic acid medium at 373K. It was observed that after about 20 minutes the carbon sample had completely dissolved with no residue and the chromic acid had turned green. Blank runs were done to confirm that the consumption of barium hydroxide was exclusively due to the carbon dioxide evolved from the sample. Oxalic acid was used as the standard for validation of this method. The results of the standardizations are given in Table 1. As is evident, the recovery of carbon is well in agreement with the theoretical value of 19.06 wt. % carbon. The accuracy of the results is within 0.5wt. % and the precision as given by the standard deviation is 1.6%.

Table 1. Standardization using oxalic acid

Sample	Wt % C
Oxalic acid	18.99
	19.50
	19.42
	18.98
	18.80
Mean	19.14 ± 0.47

Boron carbide samples from different vendors were analyzed for free carbon and the results are shown in Table 2. The free carbon content is observed to be lowest in the sample obtained from Source 2 and highest in that obtained from Source 3. It is also observed that the sample received from Source 3 was inhomogeneous as reflected in the standard deviation. Fig 2 shows the X-ray diffraction patterns of acid leached and unleached samples Source 3. The patterns of both the samples match with the reference pattern given by JCPDS file no 35-0798. The unleached sample shows a peak corresponding to graphite (JCPDS file no 75-2078) whereas there is no such peak in the acid leached sample. This confirms the oxidation of free carbon by sulfochromic acid.

Table 2. Free carbon content in samples from different Vendors (as wt %)

	Source 1	Source 2	Source 3
	0.88	0.38	6.50
	0.84	0.39	6.10
	0.90	0.38	8.80
	0.78	0.37	9.00
	0.85	0.37	8.00
	0.86	0.40	7.90
Mean	0.85 ± 0.04	0.38 ± 0.01	7.70 ± 1.2

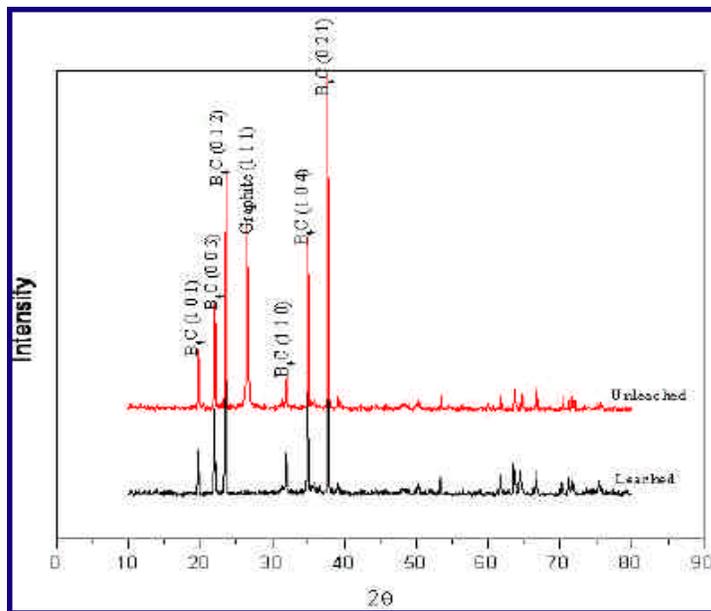


Fig.2. XRD patterns of acid leached and unleached boron carbide samples from Source 3.

The sample with the lowest free carbon content was used to prepare samples containing approx. 1%, 3%, and 5% free carbon. The free carbon content in these samples determined by this method is compared with the values obtained using CS 800 analyzer (Table 3). The results of the analyses are in good agreement with the expected values and the two methods are observed to compare well with each other.

Table 3. Free carbon content in samples with added carbon

Added Carbon	0 wt. %	1 wt. %		3 wt. %		5 wt. %	
		Wet Chemical	CS 800	Wet chemical	CS 800	Wet chemical	CS 800
0.38		1.31	1.47	3.34	3.94	5.64	5.45
0.39		1.40	1.38	3.42	4.11	5.18	5.43
0.38		1.33	1.29	3.70	3.81	5.48	5.74
0.37		1.52	1.37	3.73	3.50	5.18	5.12
0.37		1.34	1.32	3.56	4.07	5.71	5.75
0.40		1.38	1.35	3.22	3.78	5.07	5.94
		1.34	1.41	3.13	3.89	5.56	5.59
		1.31	1.30	3.27	3.99	5.66	5.63
Mean	0.38 ± 0.01	1.37 ± 0.07	1.36 ± 0.06	3.42 ± 0.22	3.89 ± 0.19	5.44 ± 0.25	5.58 ± 0.25

5. CONCLUSION

This method of estimation is simple, fast and economic. It does not require any sophisticated instruments. It can be used even for low levels of free carbon. The chromic sulfuric acid rightly chosen is just oxidizing enough to react with only the free carbon and the reaction is allowed to go to completion. This is seen in the results of the analyses.

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