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Role of graphite in isotopic analysis of boron in metal boron alloys by Positive-Thermal Ionization Mass Spectrometry (P-TIMS)

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ABSTRACT

Isotopic composition of boron in alloy samples was determined by Positive-Thermal Ionization Mass Spectrometry (P-TIMS) using $Rb_2BO_2^+$. The titanium based boron alloy sample was treated with nitric acid to bring it to slurry form which was fused with rubidium carbonate on the high purity Rhenium filament for the formation of borate. Control of pH was found necessary to be necessary for both the formation of alkali borate compound as well as for obtaining good yield $Rb_2BO_2^+$. Alkaline conditions were required for the formation of rubidium borate during fusion though neutral pH favored formation of $Rb_2BO_2^+$ ions in the ion source. The sample loading procedure was suitably modified to obtain good ion intensities for $Rb_2BO_2^+$ for high precision analysis. Steady ion beam was obtained when graphite was loaded on the filament after fusion of alloy carbonate mixture contrary to the reverse procedure that is normally followed. Sequence of graphite addition on the filament plays an important role in the formation of $Rb_2BO_2^+$ ions. The paper gives the details of the investigations carried out.

1. Introduction

Boron and its compounds boric acid, boron carbide, rare-earth and refractory metal borides find extensive applications in the nuclear industry as neutron sensors, human and instrument shielding against neutrons, nuclear/neutron poison, control/shutoff rods and in nuclear material storage, due to their high neutron absorption cross section. Appropriate treatment methods are required for the isotopic analysis of boron by TIMS in different types of samples. Boron by Positive Thermal Ionization Mass Spectrometry (PTIMS) is analyzed by employing polyatomic ions in the form $M_2BO_2^+$ (M = Na, Rb, Cs) [1–5]. Though the alkali borate compounds are formed by reaction of a solution of boron with alkali carbonate, the actual formation and intensity of $M_2BO_2^+$ obtained depends on a number of parameters such as B/M mole ratio, the sample and treatment and sample loading procedures, the pH of the solution containing boron etc. Samples of boric acid or boric oxide are dissolved in water and treated with alkali carbonate (B/M ratio ~ 2) prior to analysis by TIMS. Boron containing solutions which are acidic either due to treatment or separation procedures used require addition of mannitol during evaporation to prevent loss of boron [6]. Chemically inert powders like boron carbide or metal borides need to be fused with alkali carbonates to obtain $M_2BO_2^+$ [4]. The present study focuses on the treatment procedures for titanium based sintered borides. Like boron carbide, refractory metal borides have an attractive combination of properties such as low density, high melting point and hardness, chemical inertness and excellent thermal and electrical characteristics making them potential materials for many advanced applications [7]. Isotopic analysis of boron is required to assess the performance of the material. Time of flight LIMS [8] or SIMS [9] though non-destructive cannot match the precision of TIMS. For sintered alloys, there is a need for dissolution or disintegration of sample by acid digestion or any other appropriate methodology. This leaves the fragmented sample in the acidic medium and the slurry may not fuse with alkali carbonate to form the alkali borate unless adequate amount of carbonate is added. Since the alloy dissolves in alkaline medium, this property is expected to aid fusion. Large amount of alkali (M/B mole ratio > 4) suppresses ion yield of the $M_2BO_2^+$ ions in TIMS restricting the amount of alkali carbonate that can be used for fusion. Thus for sintered metal base alloys of boron three problems need be addressed: (1) appropriate methods of dissolution, (2) formation of alkali borate, and (3) obtaining good yield of positive ions of $M_2BO_2^+$ for analysis by TIMS. During studies reported previously from our laboratory, fusion of the alloys with alkali carbonates during loading of the mixture on the filament was found to give erratic

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signals in TIMS. Small intensity signals required the analysis to be carried out at higher temperatures resulting in poor precision due to ion source fractionation. The internal normalization method was developed in our laboratory to improve the precision in $^{10}B/^{11}B$ isotope ratio [10]. Stable and high intensity ion beam with high signal/noise ratio can further improve the precision of the data. Subsequently graphite was used during the sample loading procedure as graphite is known to enhance ion current of $M_2BO_2^+$ ions [2,3]. The normal procedure is to deposit the graphite on filament, drop deposit the borate solution on wet graphite and heat the filament to 1.4 A for 5 min [3]. However for analysis of boron alloy, it was observed that deposition of graphite on filament prior to alloy carbonate mixture and subsequent heating of the filament to red hot for fusion did not yield good signal. Consistent and stable signal was obtained when graphite was deposited on the cold filament after fusion of alloy with carbonate. Initially both sodium and rubidium carbonates were used for fusion of the disintegrated alloy for the formation of borate ions in the ion source. However, data acquisition was conducted using $Rb_2BO_2^+$ due to better precision expected at higher mass. $Cs_2BO_2^+$ method was not used as simultaneous collection of the ions at mass 308 and 309 is not possible due to restriction in cup movement for multicollection in our TIMS machine. The present study gives details of the experimental investigations carried out and attempts to seek explanations to the various observations.

2. Experimental

2.1. Sample treatment method

About 40 mg of starting material in pellet form containing 30% boron was taken for digestion with concentrated nitric acid. For irradiated samples lead shielding was used during the sample treatment procedure as it was found to give a contact dose of about 40 mR. In view of the moderate solubility of titanium boride in concentrated nitric acid, this acid was used for disintegration of the pellet. The sample was treated repeatedly with 0.5 mL of HNO_3 for complete fragmentation of pellet as a mandatory step for representative sampling. This required a total volume of 3 mL acid. This was followed by evaporation of the acid under an infrared lamp and subsequently repeated addition and evaporation using Millipore water to reduce the acidity to allow fusion with Rb_2CO_3 or Na_2CO_3. 5–15 μL of the sample was pipetted out onto a Teflon sheet and mixed with different amounts of Rb_2CO_3/Na_2CO_3 to give B/M mole ratios of 5–0.5. The pH of these solution mixtures was tested with pH paper which gave an estimate of the alkalinity. A portion of this mixture containing about 5 μg of B was fused on the high purity Re filament by heating to red hot. This homogenizes the two phases allowing the reaction of the molten alloy with alkali carbonate to form alkali borate. Unirradiated TiB_2 powder which could be directly fused with carbonate was also analyzed. NIST standard SRM-951 with B/Rb mole ratio 5–0.5 were also analyzed with and without graphite.

2.2. Sample loading technique

During the initial experiments it was observed that the ion yield for the alloy samples during TIMS analyses were inconsistent. The loading conditions followed could not ascertain sufficient ion current for analysis. Different loading techniques investigated were: (A) mixing of disintegrated sample with different amounts of Rb_2CO_3/Na_2CO_3 solution and fusing the mixture on the filament by heating the filament to red hot, (B) fusion of sample carbonate mixture on the Re filament with prior coating of 100 μg of graphite slurry in 50% ethanol, and (C) fusion of the fragmented sample

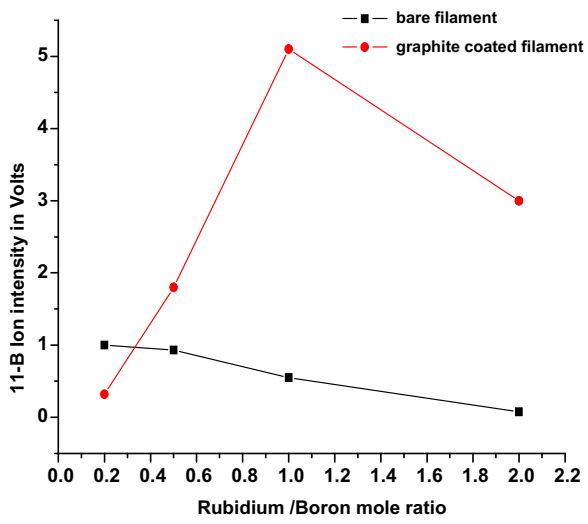

Fig. 1. Ion intensity of $Rb_2BO_2^+$ obtained for NIST SRM 951 with different Rb/B mole ratio.

mixture on the filament and deposition of graphite slurry on the filament at ambient temperature followed by heating to 1.4 A. For NIST standard SRM-951 the normal loading conditions were followed which consisted of loading the boron containing sample on graphite coated filament heated to 1.4 A for 5 min. The isotopic analysis was carried out by employing TIMS (Isoprobe-T, Micromass UK) with 9 Faraday cups. The ion currents at masses 88 and 89 corresponding to $^{23}Na_2{}^{10}B^{16}O_2^+$ and $^{23}Na_2{}^{11}B^{16}O_2^+$ and at masses 212 and 213 corresponding to $^{85}Rb_2{}^{10}B^{16}O_2^+$ and $^{85}Rb_2{}^{11}B^{16}O_2^+$ were monitored during TIMS analysis as $Na_2BO_2^+$ and $Rb_2BO_2^+$, respectively. Data were collected for 5 blocks with each block of 12 scans.

3. Results and discussion

Ion intensities of $Rb_2BO_2^+$ obtained from 1 μg standard SRM 951 with different Rb/B mole ratios loaded on the bare Rhenium filament and graphite coated filament are shown in Fig. 1. The borate was prepared by mixing an aliquot of the solution of rubidium carbonate with boric acid. It can be seen that graphite is required to enhance the ion current when Rb/B mole ratio is 0.5 or higher and the pH is more than 9. Undissolved solid sample (e.g., disintegrated metal alloy of boron) in powder form can be analyzed after fusion with alkali carbonate achieved by heating the filament to red hot. The actual amount of boride fused and unreacted reactants remaining is difficult to estimate unlike in standard solutions of boric acid. The alkali/boron mole ratio in the fused sample is also not definite. The details of the observations for the alloy sample under different loading conditions using rubidium carbonate are summarized in Table 1. As is observed from rows 2, 3 and 7, both alkaline and acidic fusion mixtures result in poor ion yield. This is expected as fusion to form rubidium borates is negligible under acidic conditions, and alkaline conditions does not favor formation $Rb_2BO_2^+$ ions. The signal improves moderately (row 4) when the alkaline sample mixture is fused on the filament along with graphite (procedure B). However if graphite is deposited on the filament at ambient temperature, after fusion of alkaline mixture, and reheated to 1.4 A, high ion current is obtained (rows 5, 8 and 9). Graphite enhances the ion intensity provided it is loaded on the filament following the fusion of alloy and carbonate. Fusion of alloy in presence of graphite causes interference in the fusion process. This can be attributed to additional reactions taking place simultaneously or in succession which can lead to inconsistency in ion production. For example