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A rapid method for determining boron in metallic alloys

Boron is an important alloying element in a number of commercial alloys. Small quantities of boron (< 0.1 wt%), when added to low alloy steels and cast irons, improve their mechanical properties, while large quantities of boron (> 1.0 wt%), when added to transition metal alloys with Ni, Fe, Co, etc., produce wear resistant hard facing alloys and promote the formation of amorphous alloys under certain processing conditions. Determination of boron concentration in these alloys by conventional analytical techniques, such as wet chemistry, atomic absorption and emission spectroscopy, is extremely difficult and time-consuming [1]. The problems are primarily associated with the slow rate of dissolution of boron-containing materials in chemical solutions which is required for these techniques. Very low solid solubility of boron in transition metals promotes the formation of stable boride phases in these alloys which are often responsible for the improved properties. These phases are highly stable and often remain as an undissolved residue in the solution, reducing the accuracy of the concentration analysis.

A method is reported herein for the non-destructive rapid determination of boron in metallic alloys. The method primarily employs

neutron activation analysis and can be used in alloys where the oxygen concentration is relatively low. A typical analysis consists of irradiating the boron-containing samples with high-energy neutron particles (14.5 MeV), a procedure which produces radioactive isotopes as reaction products. The characteristic emissions from these radioactive isotopes in the form of gamma- or beta-rays are then measured to obtain the chemical composition both qualitatively and quantitatively.

Selection of a specific energy band of radioactivity from the activated alloy, free from interference from other alloying constituents, is required for accurate compositional analysis. Table I gives the nuclear reactions of elements with 14.5 MeV neutrons which are of particular interest in the present investigation. The nominal composition of the boron containing alloys used in this study is given in Table II.

When boron is activated with 14.5 MeV neutrons, two measurable isotopes of ^8Li and ^{11}Be with half-lives, τ , of 0.84 and 13.5 sec, respectively, are produced. The measurement of activity from the ^8Li isotope is extremely difficult since it requires specialized *in situ* counting equipment. Moreover, although the measurement of the ^{11}Be isotope activity can be easily achieved, its measurement at 2.1 MeV is not very sensitive and is subject to severe spectral interference from 1.78 MeV gamma rays arising from the ^{28}Al

TABLE I Nuclear properties of elements of interest to this work

Element	Nuclear reaction	Half life, τ (sec)	Gamma-ray energy (MeV)	Abundance (%)	Cross-section (mb)
B	$^{11}\text{B}(n, p)^{11}\text{Be}$	13.6	2.12, 4 (6–8 β^-)	80.2	3.3
	$^{11}\text{B}(n, \alpha)^8\text{Li}$	0.85	β^-	80.2	15
Ni	$^{60}\text{Ni}(n, p)^{60}\text{Co}$	600	0.059	26.1	150
Si	$^{28}\text{Si}(n, p)^{28}\text{Al}$	138	1.78	92.2	240
O	$^{16}\text{O}(n, p)^{16}\text{N}$	7.1	6–7	99.8	42
Fe	$^{56}\text{Fe}(n, p)^{56}\text{Mn}$	9×10^3	0.84	91.7	114

reaction product isotope of silicon, which is also present in the alloys. It can be seen from Table I that boron also decays with the emission of beta activity in the 6–9 MeV energy band, and displays no interference from other alloying elements, with the exception of oxygen. As discussed later, small quantities of oxygen in the alloy will not affect the boron analysis using this technique. Hence, the beta activity in the 6–8 MeV energy band is utilized in this study.

The neutrons of 14.5 MeV energy are produced in a Kaman Nuclear Model A-710 neutron generator by the deuterium–tritium (d–t) reaction. The generator operates with a mixture of tritium and deuterium to continuously replenish the tritium target housed in a sealed tube. A 150 kV power supply is used to accelerate deuterium ions to produce 10^{10} neutrons sec^{-1} upon striking a tritium target. Target cooling is accomplished with a circulating freon cooling system which provides maximum operating stability and tube life. The radioactive emissions (e.g. beta rays) from the samples after irradiation in the neutron generator, are measured by scintillation spectrometry. The scintillation detector is composed of two NaI (Tl) crystals coupled to a Canberra Model 80 multichannel analyser. The radioactive emission from the sample is measured indirectly by measuring the charge current produced by interaction of the beta emitting activity with the detector

TABLE II Nominal chemical composition of Ni–B alloys

Alloy designation	Nominal composition			
	Ni (wt%)	Si (wt%)	Fe (wt%)	B (wt%)
A	Balance	4.5	0.3	2.9
B	Balance	0.6	1.8	16.5

crystals. Corrections are made for analyser dead-time, neutron flux variation and the background contribution.

The experimental analysis consists of irradiating the sample material in the neutron generator station followed by measuring the radioactive emission at the counting station. Transfer of samples to and from the neutron generator is accomplished automatically through a pneumatic tube shuttle-system operated by compressed nitrogen gas. The samples of the boron alloys, weighing approximately 4 to 6 g, and the standards were contained individually in polyethylene capsules (of diameter 2.5 cm and length 5 cm) for easy transport of the materials during the analysis. Generally the samples are either in granular or foil form. Boron was determined by irradiating each sample for 30 sec, delaying for 15 sec and counting for 60 sec. The discriminator on the analyser was set to accept those current pulses caused by high-energy beta activity above 4.5 MeV. The concentration of boron in the alloy is determined by comparing the ratio of the activities of the unknown sample to that of the standard.

The concentration of boron measured by a series of analyses on two boron-containing alloys are shown in Table III along with the results obtained by wet chemical analysis. The wet chemical analysis is slow and tedious since the dissolution of the sample by preliminary fusion with sodium hydroxide can take up to two days. Typically, a single analysis by the neutron activation technique takes around five minutes. The results obtained by neutron activation analysis are in excellent agreement with those from the wet chemical analysis.

Since the technique depends upon the counting of all the emissions above 4.5 MeV, the samples

TABLE III Composition boron determined by 14.5 MeV neutron activation

Method	Boron composition (wt%)	
	Alloy A	Alloy B
Neutron Activation		
Run 1	2.4	14.8
Run 2	2.6	14.2
Run 3	2.9	14.7
Run 4	2.2	15.2
Run 5	2.5	15.4
Run 6	2.6	15.6
Average	2.5	15.0
Chemical analysis	2.3	15.2

and the standards must be free from high-energy activities from other alloying elements. Oxygen, as seen from Table I could cause interference since it produces 6–7 MeV gamma rays through a (n, p) reaction. In the present study no evidence of oxygen interference was found in the alloys investigated. The mass spectroscopy analysis of oxygen showed that its presence was less than 20 ppm. However, careful attention should be given in analysing very-fine powdered materials. For example, when powdered boron was used as a standard, the concentrations were lower than those shown in Table III.

Further analysis of this standard by mass spectroscopy showed the presence of significant oxygen, while X-ray diffraction analysis showed the presence of the oxide phase. To support this result, it has been reported that boron can indeed oxidize on standing and this can lead to the formation of boric acid [2]. Further work with the boron powder was discontinued and boron chips and boron carbide were used as standards instead.

It was found that 1 mg of oxygen will produce 2 counts min^{-1} of activity in the 6–7 MeV energy range. From this, it can be estimated that the presence of 1 wt% of oxygen will cause a 5% error in the boron measurement. In pure metallic alloys, the oxygen content seldom exceeds 0.02 wt% due to its very low solid solubility and, hence, should not present any significant problem to the analysis of boron.

In summary, the neutron activation technique provides a unique method for the accurate determination of the boron content in metallic alloys. This method is rapid and non-destructive and needs no prior sample preparation, in contrast to other conventional techniques. This technique can be routinely used to control the boron melt chemistry during the production of alloys on an industrial scale.

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X-ray studies on the thermal expansion of silver thiogallate

In a programme undertaken to obtain detailed information on the temperature variation of the lattice parameters and the coefficients of thermal expansion of some chalcopyrite ternary semiconducting compounds, the results on the thermal

expansion of AgInSe_2 [1] and AgGaSe_2 [2] have been previously reported. Results of a similar study on AgGaS_2 will be presented in this note. Silver thiogallate (AgGaS_2) is isotypic with chalcopyrite and exhibits some interesting physical properties [3, 4]. In a study of this compound, Korczak and Staff [5] measured the linear expansion using a macroscopic method and reported a