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Determination of trace boron in steels by prompt gamma-ray activation analysis

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즉발감마선방사화분석법에 의한 철강시료 중의 붕소 측정

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요 약: 철강 중의 미량 붕소는 소재의 기계적, 물리적 특성에 중요한 영향을 준다. 즉발감마선 방사화분석법에 의해 저합금강 시료 중의 미량 붕소를 측정하였다. 시료는 한국표준과학연구원에서 제조한 저합금강 표준물질KRISS 101-01-C21~C26을 이용하였으며, 측정방법의 유효성 확인을 위해 NIST SRM 362, 364, 1761, 1762를 정확도관리용 시료로 사용하였다. NIST SRM 362를 제외하고는 측정 농도가 인증값의 불확도 범위내에서 잘 일치하였다. 불확도는 ISO guideline에 따라 평가하였으며, 포함인자 2를 적용하여 확장불확도를 산출하였다. 붕소 농도 mg/kg수준에서 상대확장불확도는 3%에서 7% 사이였다. 그 결과를 용매추출-유도결합플라스마 방출분광분석결과와 비교하여 제시하였다.

Abstract: A trace amount of boron in steel significantly influences its mechanical and physical properties. A prompt gamma ray activation analysis (PGAA) method is used to measure boron in low alloy steel samples of KRISS 101-01-C21~C26. NIST SRMs of 362, 364, 1761 and 1767 serve as the control standards to validate the measurement method. The measured values of the NIST SRMs are consistent with their certified values within the expected uncertainties, except for that of NIST SRM 362. Experimental uncertainties are evaluated according to the guidelines given by the International Organization for Standardization (ISO). The expanded uncertainties are calculated with a coverage factor of 2, at approximately 95% confidence level. The calculated relative expanded uncertainties of boron mass fractions are between 3% and 7% at the mg/kg level. The results are compared with the results measured by the solvent extraction-inductively coupled optical emission spectrometry (ICP/OES) method.

Key words : Prompt gamma-ray activation analysis, boron, low alloy steel, certified reference material, uncertainty

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1. Introduction

Boron is one of the most important alloys in steels. A minute quantity of boron is added to unalloyed or low alloyed steels to enhance their hardness. Boron forms boron nitride in steel, which increases the strength and hardness of the steel. However, a high concentration of boron makes a steel remarkably brittle and causes serious deterioration.[1,2] Therefore, a reliable analytical method is necessary to control trace amounts of boron at the mg/kg level in steels.

There are some analytical methods which can be used to measure boron in steels, such as inductively coupled plasma optical emission spectrometry (ICP/OES),[3,4] inductively coupled plasma mass spectrometry (ICP/MS),[5,6] isotope dilution inductively coupled plasma mass spectrometry (ID-ICP/MS)[7] and high-performance liquid chromatography (HPLC).[8] However, these methods are not very sensitive to boron and have serious non-spectral interference and matrix effects. Furthermore, they require a pre-concentration and matrix separation process, which sometimes causes contamination and/or loss of analyte. A prompt gamma-ray activation analysis (PGAA) method offers an excellent alternative which is sensitive to boron.[9-11] It has no evaporation loss or contamination issues because it is non-destructive. PGAA has been used to measure trace levels of boron in various samples: geological materials,[13,14] food and biological samples,[15] minerals,[16] refractory alloys,[16] glasses,[9] etc.

Korea Research Institute of Standards and Science (KRISS) prepared six low alloy steel samples as candidates for certified reference materials (CRM), which are now in the process of certification. The boron mass fractions of these materials are currently being measured using the solvent extraction-ICP/OES method. This paper describes the PGAA procedures performed to determine the boron mass fraction of the materials, and the results are compared with those values measured using solvent extraction-ICP-OES. Every attempt has been made to optimize and assess the accuracy of measurements by the PGAA procedures.

2. Experimental

2.1. Sample preparation

Six low alloy steel certified reference material (CRM) candidate materials, KRISS 101-010-C21~C26, were prepared in the form of small chips. They were characterized for 15 elements (C, Mn, P, S, Si, Cu, Ni, Cr, V, Mo, W, Co, Ti, Al and B) using ID-ICP/MS, ICP/OES, gravimetry, infrared absorption method and neutron activation analysis (NAA) methods. It is estimated that the mass fraction range of boron in these samples ranges from 7 mg/kg to 90 mg/kg based on the solvent extraction-ICP/OES measurement.

Approximately 375 mg of sample is taken from each bottle. Samples are weighed and sealed into bags of fluorinated ethylene propylene resin (FEP) film (13 μm thick) into a sample area of approximately 10 ×10 mm^2. Similarly sized samples of two low alloy steel CRMs of SRM 362 and SRM 364 (chip form) are prepared in the same manner as controls. Two additional low alloy steel CRMs of SRM 1761 and SRM 1767 are also prepared as controls. These steels are 1 mm thick, 12.7 mm diameter disks, each weighing approximately 1 g.

Two pellet type calibration standards are prepared for the boron sensitivity calibration. One standard is prepared from a mixture of NIST SRM 951[12] (boric acid), silicon dioxide and graphite.[13,16] The other is prepared from a different mixture of NIST SRM 951 and graphite.

2.2. Irradiation and counting

Neutron irradiation and counting of prompt gamma emissions are performed at the thermal neutron PGAA station at the NIST Center for Neutron Research. Each sample is fully immersed in the central portion of the neutron beam (2 cm in diameter), where the flux of thermal neutron is 3×10^8 cm^{-2} s^{-1} (cadmium ratio >2500). Irradiation times for the steels vary from about 1 hour to 20 hours depending on the boron mass fraction. Variations in the neutron beam fluence rate are monitored by irradiating a titanium foil once each day. The variation is about 0.2% over the course of the analyses.

Table 1. Example of standard uncertainty budget for the determination of boron in KRISS low alloy steel sample 101-01-C23

Parameter	Unit	Type (A/B)	Typical value	Standard uncertainty
Mass fraction of calibration standard, C_c	mg/kg	B	30.00	0.02
Mass of sample, m_x	mg	B	374.9	0.5
Mass of calibration standard, m_c	mg	B	301.2	0.5
Sample counts, N_x		A	116100	410
Calibration standard counts, N_c		A	135200	400
Elapsed time of sample counting, t_x	s	B	13104.0	0.6
Elapsed time of standard counting, t_c	s	B	28224.0	0.6
Ratio of isotopic abundance, R_θ		B	1.00	0.01
Ratio of neutron flux, R_ϕ		B	1.008	0.002
Ratio of neutron cross section, R_σ		B	1	0
Ratio of γ-ray detection efficiency, R_ε		B	1.015	0.001
Background correction, B	mg/kg	B	0.85	0.11
Determined concentration, C_x (mg/kg)			44.6	
Combined standard uncertainty, u_c (mg/kg)			0.5	
Relative standard uncertainty, u_{Rel} (%)			1.2	

The background rate of the boron peak is measured by irradiating an empty Teflon bag as a blank, which is (0.17±0.02) cps. The contribution of silicon dioxide and graphite added to the calibration standard is also checked by irradiating pellets of silicon dioxide and graphite. This indicates a negligible amount of boron compared with that added from the boric acid.

3. Results and Discussion

Doppler broadened[17] boron peaks are observed within an energy range of 466 keV~490 keV. The peak is integrated and the baseline is subtracted by a fixed-window algorithm using a linear baseline. Although the steel samples contain cobalt and nickel, which might cause spectral interference to the boron peak by emitting γ-rays of 484.257 keV and 483.351 keV, respectively, their interference is negligible in this study. This is because the samples have only a few g/kg of cobalt and nickel, and those elements have gamma-ray intensities that are multiple orders of magnitude smaller than that of boron.

The mass fraction of boron in each sample, C_x, is determined from the measurements according to

$$C_x = C_c \times \frac{m_c(N_x/t_x)}{m_x(N_c/t_c)} \times R_\theta R_\sigma R_\phi R_\varepsilon - B \qquad (1)$$

where C_c is the mass fraction of boron in the calibration standard. $m_{x,c}$ are the masses, $t_{x,c}$ are the irradiation times and $N_{x,c}$ are the measured boron peak counts of the sample (x) and calibration standard (s), respectively. R_θ and R_σ are the ratios of isotopic abundances and effective cross sections for the sample and calibration standard, respectively. R_ϕ is the ratio of neutron fluences including self shielding[18] and fluence rate variation. R_ε is the ratio of gamma-ray counting efficiencies including self absorption[19] and pulse pile-up.[20] B is the background correction.

Experimental uncertainties are evaluated according to the guidelines given by the International Organization for Standardization (ISO).[21] The uncertainty components and their standard uncertainties for the determination of boron in the KRISS low alloy steel sample 101-01-C23 are listed in *Table* 1. Type A standard uncertainties are evaluated using statistical methods, and the remaining uncertainties are all considered to be Type B. The mass fraction of boron in the calibration standard, C_c, is approximately 30 mg/kg, and the resultant standard uncertainties are 0.02 mg/kg. The standard uncertainty of the sample weight is 0.5 mg. The uncertainty of $N_{x,c}$ is attributed to counting statistics. To reduce the relative uncertainty of $N_{x,c}$, more than 10^5 boron peak counts are collected for each irradiation, and the relative uncertainties of N_x and N_c are approximately 0.04%. The standard

uncertainties of t_x and t_s are estimated based on an assumption of uniform distribution with the least significant digit of 1 s. R_θ is given as the ratio of isotopic abundances of ^{10}B of sample (θ_x) and calibration standard (θ_s), whose standard uncertainty is calculated according to the error propagation law. The value of θ_s is 19.827±0.013% according to the certificate of SRM 951.[12] θ_x is assumed to be the natural isotopic abundance of ^{10}B, which is 19.9 ±0.2%.[23] The standard uncertainty of R_ε is estimated based on an assumption of uniform distribution with the least significant digit of 0.001. The standard uncertainty of R_ϕ is estimated by combining the uncertainty of correction for neutron self absorption and the variation in the neutron fluence rate during the measurement. R_σ is assumed to be 1 and whose uncertainty is ignored. Background correction, B, is calculated from the background rate measurement with a standard uncertainty that is estimated to be 0.11 mg/kg. The combined standard uncertainty is calculated according to the error propagation law.

The measurements are repeated four times for each sample. The determined mass fractions of boron in the steel samples are listed together with those values measured by solvent extraction-ICP/OES in *Table* 2. In the table, the expanded uncertainty of the PGAA results is obtained by multiplying the combined uncertainty with a coverage factor of k=2 at approximately 95% confidence level. The major sources of the uncertainty are the measurement repeatability, the isotopic (^{10}B) abundance of the sample and the background correction. The background correction is not a significant uncertainty source at high mass fractions, but it is more significant at lower mass fractions. The results from the two different methods are consistent within the uncertainties of the solvent extraction ICP/OES results. The expanded uncertainties of the PGAA results are much smaller than those of the ICP/OES results.

Table 2. Comparison of PGAA result and ICP/OES results for the determination of boron in KRISS low alloy steel samples.

Sample No.	PGAA, mg/kg	ICP/OES, mg/kg
101-01-C21	6.7 ± 0.5	7 ± 1
101-01-C22	12.8 ± 0.6	13 ± 4
101-01-C23	45 ± 1	46 ± 5
101-01-C24	44 ± 1	46 ± 9
101-01-C25	92 ± 3	89 ± 8
101-01-C26	27.7 ± 0.9	27 ± 6

Table 3. Determined results of control samples

Sample No.	Measured value, mg/kg	Certified value, mg/kg
SRM 362	30 ± 1	25 ± 1
SRM 364	106 ± 3	106 ± 1
SRM 1761	20.9 ± 0.8	20 ± 1
SRM 1767	10.2 ± 0.6	10 ± 1

The measured results of the control standards, NIST low alloy steel SRMs, are given in *Table* 3. The measured values of all the control standards except NIST SRM 362 are in good agreement with the certified values. The PGAA value of 30 mg/kg measured for SRM 362 is 20% higher than the certified value, but it is closer to R. M. Lindstrom's value of 33.2±0.8 mg/kg (1σ uncertainty) from PGAA measurements of NIST SRM 1262.[22] NIST SRM 1262 and 362 are the same material, but have different appearances. The former was issued in disk form and the later was issued in chip form.

4. Conclusion

Trace amounts of boron in low alloy steel samples were determined by the PGAA method with small relative expanded uncertainties. The results are in good agreement with the certified values of CRMs and those measured by solvent extraction ICP/OES measurement within the expanded uncertainties. The major sources of uncertainty in the PGAA measurement are measurement repeatability, the isotopic abundance of ^{10}B and background correction. However, the uncertainty of the PGAA measurement is much smaller than those of the solvent extraction ICP/OES. This shows that the PGAA method can be used as a certification method for trace amounts of boron in steel samples.

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