Weight-based Synthesized Standards Preparation for Correction-free Calibration in X-ray Fluorescence Determination of Tungsten in High-speed Steel

Kenichi NAKAYAMA† and Kazuaki WAGATSUMA

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan

This paper suggests a correction-free calibration method in wavelength dispersive X-ray fluorescence analysis in order to determine tungsten as a major alloyed element in high-speed steels accurately. Matrix effects on fluorescent X-ray intensity of tungsten Lα line were minimized by borate fusion, and the total amount of tungsten in the glassy matrix could be quantified. Glass bead specimens were prepared with 10 to 12 mg of the steel sample and 4.0 g of lithium tetraborate as a flux agent. Without untraceable X-ray intensity correction, a linear calibration curve was obtained by measuring synthesized calibration standards prepared by using standard solutions. As compared with fundamental parameter calculations, the present method gave more accurate results of tungsten in certified reference materials of high-speed steel.

Keywords X-ray fluorescence analysis, high-speed steel, acid decomposition, glass bead, borate fusion, standard solution, weight-based synthesized calibration standard

(Received March 16, 2015; Accepted April 20, 2015; Published August 10, 2015)

Introduction

X-ray fluorescence analysis has often been used for various non-destructive measurements: routine analyses based on the solid reference materials, semi-quantitative screening analyses, and direct measurements in the field. Fluorescent X-rays are affected by the co-existing elements and the physical properties of a specimen (e.g., surface smoothness, geometrical structure including layer and surrounding, and particle-size distribution). The former effect yielding X-ray absorption or enhancement is generally corrected by theoretical calculations, whereas the latter effect is usually overcome by sample preparation. Traceable quantification in X-ray fluorescence analysis might be difficult because of a lack of applicable standards and/or inaccurate corrections without analytical traceability.

Preparation of glass beads (borate fusion method) has been applied for routine quantitative X-ray fluorescence analysis. Several oxidized samples such as iron ore, cement, ceramics, and natural rocks† are suitable for borate fusion. On the other hand, reductive materials containing metals and organic materials should be prepared by pre-oxidizing the sample or fusing it under an inert atmosphere. This is because a platinum crucible used as a fusion vessel would be damaged. On the basis of borate fusion, a homogenous specimen can be prepared to obtain precise results and synthesized standards contribute to reliable calibration for various elemental matrices. A pulverized sample is fused with an alkali flux like lithium tetraborate, lithium metaborate, and these lithium borate mixtures of various proportions, and the fusion is carried out by using a crucible of platinum-alloy containing gold and/or rhodium. Concentration-based glass beads have been usually produced. Because the glass bead comprises a light-element matrix of lithium, boron, and oxygen, X-ray absorption and enhancement effects might be minimized. In a similar procedure, glassy-body specimens containing oxidized analytes and other elements can be also obtained. Therefore, the sample preparation using glass beads possibly reduces X-ray intensity variations depending on the physical structure of samples.

Chemical analysis of tungsten in steel samples generally requires a time-consuming and difficult procedure for the decomposition. Oxidized tungsten compounds, which may be produced in the decomposition by acids, might easily precipitate when preparing the aqueous solution, especially at high concentrations. On the other hand, the tungsten precipitate contains other elements like vanadium, chromium and molybdenum. Therefore, it is rather difficult to determine tungsten by using both the wet chemical analysis and the gravimetric analysis. The present work suggests an improved X-ray fluorescence procedure, as an alternative to such conventional methods, which can be applied to the high-concentration tungsten of high-speed steel.

Whereas steel analyses with X-ray fluorescence spectrometry has been routinely used on the basis of direct measurements with theoretical calculations, a few reports have presented X-ray fluorescence analysis accompanying sample dissolution. Narita et al. determined sub-mass% of sulfur in low-alloy steel by using X-ray fluorescence analysis with borate fusion. The low-alloy steel was decomposed with nitric acid and hydrochloric acid, and then precipitated barium sulfate was fused. For the direct decomposition and borate fusion in a platinum vessel, a high-speed steel specimen was treated by using a chlorine-free acid mixture of hydrofluoric acid with nitric acid. This is
because a platinum vessel is damaged by chlorine and nitrosyl chloride generated by mixing nitric acid with hydrochloric acid. Sieber et al. analyzed low-alloy steel on the basis of borate fusion with an acid decomposition. Satto et al. assayed titanium-alloy in a similar way. Their fusion methods used a platinum dish as a mold. A problem of these methods was that the fusing product could not be transferred completely to the mold; therefore, the quantification had to be conducted based on the concentration of each analyte element.

In the present work, high-speed steel samples were directly decomposed in a platinum crucible using hydrofluoric acid and nitric acid, in which a small amount of steel samples (around 11 mg) were weighed and the resulting solution with/without any precipitate was melted with much larger amounts of lithium tetraborate (4.0 g). Because the reaction was completed in the platinum crucible, the calibration could be carried out using the total amounts of added analytes. A set of synthesized standard glass beads was available for X-ray fluorescence calibration by using the corresponding standard solutions. Because of little matrix effect caused by a large extent of dilution with the flux compound, no matrix correction was required.

Experimental

Apparatus
A wavelength-dispersive X-ray fluorescence spectrometer was used: ZSX Primus II (Rigaku Corp., Tokyo, Japan). The X-ray tube of rhodium target was operated at 50 kV and 60 mA. The measuring diameter was set to be 30 mm. Tungsten Lα X-ray diffracted by lithium fluoride (200) was detected with a scintillation counter. X-ray fluorescence spectra of calibration standards were obtained by using the following conditions: 0.010 degrees of the step width and 10 s of the counting time without smoothing calculations. Net intensity of tungsten Lα fluorescent X-rays was calculated by 3-points measurements for 20 s counting per position: 43.000 degree of peak-top position, and 42.300 and 44.000 degrees of two background positions. Background intensity was estimated by a linear approximation. By using a least-squares method, the calibration and determination calculations were based on a calibration curve resulting from regression of the net intensity of tungsten Lα fluorescent X-rays on the amount of tungsten added in a calibration standard. The software equipped with the instrument was not used for the present calibration.

Sample preparation
Around 11 mg of high-speed steel specimen was weighed and placed in a 95% platinum-5% gold-alloy crucible (capacity: 22 cm³; depth: 20 mm, and inner base diameter: 35 mm). The specimen was dissolved in 100 mm³ of 50 mass% hydrofluoric acid (HF) and 100 mm³ of 70 mass% nitric acid (HNO₃) diluted with the same volume of distilled water. The crucible was heated with a hotplate (about 400 K) for about 30 s and then 4.0 g of lithium tetraborate (Li₂B₄O₇; Spectromelt A10; Merck KGaA, Darmstadt, Germany) was added as an alkali flux. Lithium chloride (LiCl) as a releasing agent was added to the flux mixture by pipetting an aqueous solution: 20 mg of LiCl by 88 mm³ addition. The mixture was fused with a Meker burner by the following steps: (1) pre-heating to vaporization of acids with no platinum lid for 2 to 3 min, (2) the first heating with the lid for about 7 min, (3) the first mixing to homogenization, (4) the second heating to re-rise temperature of the melt for about 5 min, (5) the second mixing, and (6) the third heating to better vitrification without the lid for about 1 min. When the third heating was omitted, some of the specimens could not be vitrified completely because of borate crystal generation from cooled melt. After the last heating, the crucible was left for 1 to 2 min, and then cooled by air-flow of a hair dryer. The resulting glass bead specimen was easily released from the crucible.

Synthesized standards
Fifty mg cm⁻³ of iron standard solution for adding the matrix content in calibration standards was prepared: 2.5 g of pure iron was dissolved in 20 cm³ of 70 mass% HNO₃ diluted with the same volume of distilled water and diluted to 50.0 cm³ with distilled water. Ten mg cm⁻³ of tungsten standard solution for adding an analyte was prepared: 0.45 g of sodium tetraoxotangstate(IV) dihydrate (Na₂WO₄·2H₂O) was dissolved in 25.0 cm³ of distilled water. A set of six glass beads containing matrix iron and analyte tungsten was used for X-ray fluorescence calibration. The prepared calibration standards had the following amounts: (1) 11.0 mg of Fe without W, (2) 10.5 mg of Fe with 0.50 mg of W, (3) 10.0 mg of Fe with 1.00 mg of W, (4) 9.50 mg of Fe with 1.50 mg of W, (5) 9.00 mg of Fe with 2.00 mg of W, and (6) 8.50 mg of Fe and 2.50 mg of W. Metal standard solutions were pipetted with two variable-micropipettes of 20 to 200 mm³ and 200 to 1000 mm³ in the Pt-Au crucible containing 4.0 g of Li₃B₂O₅ and 20 mg of LiCl. Glass beads of the standards were made in the same manner as high-speed steel sample. Using these standards, up to 22 mass% of tungsten in high-speed steel could be quantified.

Results and Discussion

Preparation of glass beads
A specimen of high-speed steel could be rapidly decomposed with the mixed acid of HF and HNO₃. In this work, the decomposition time of the analyzed steels was around 1 min in general. All glass beads containing the steel or metal standard solutions were successfully prepared. Light blue to green glass beads of steel were obtained; this might be because cobalt and chromium coexist. On the other hand, glass beads of calibration standards were light brown because of iron. The fusion process was time-consuming in the present analysis, but X-ray fluorescence measurements could begin within 30 min after weighing the steel sample.

Correction-free calibration
The conventional glass bead method has employed concentration-based standards. An oxide sample can be easily pulverized and weighed to be constant with sub-milligrams, but it is difficult to weigh steel pieces in the same order of amount. Therefore, a matrix correction free calibration with varying sampling was applied in the present quantification. Figure 1 shows tungsten Lα X-ray fluorescence spectra of calibration standards. The obtained spectra generally showed a constant level of background scattering X-rays which was principally determined by mass absorption coefficients of the calibration standards. The present method had a merit benefited from the high dilution effect; the specimen matrixes would have little effect on the absorption of fluorescent X-rays. In the present preparation, 10 to 12 mg of the steel sample was weighed (Table 1).

A calibration curve of tungsten showed good linearity as shown in Fig. 2. Limitation of quantification ability based on the calibration curve should be influenced by the calibration range. In this work, lower use-limit of calibration curve (LUC) were defined by the following equation: LUC = (3Ib) [(ΣI) –
\[ I_{\text{calc},i} = \frac{b}{(m - 2)^{1/2}} I_i \] where \( b \) is the slope of a calibration curve, \( I_i \) is the measured X-ray fluorescence intensity of \( i \)th calibration standard, \( I_{\text{calc},i} \) is the calculated X-ray fluorescence intensity of \( i \)th calibration standard estimated from the calibration curve obtained, and \( m \) is the number of calibration standards. The LUC was estimated to be 0.065 mg, suggesting that the present calibration curve could be used for 0.6 mass% of tungsten in 11 mg of the high-speed steel. On the other hand, conventional lower limit of detection (LLD) was 0.004 mg: \[ \text{LLD} = 3 \frac{s_{\text{blank}}}{b} \] where \( s_{\text{blank}} \) is the standard deviation of 10-times measurements of a calibration standard containing 11.0 mg of iron without tungsten. This suggested that the present measurement would be used for 0.04 mass% of tungsten in 11 mg of the steel sample, but the obtained calibration curve was inapplicable to such low content of tungsten.

**Validation**

The present preparation was applied to obtain the tungsten content in certified reference materials (CRM) of high-speed steels: Japanese Steel Standard (JSS) 607-9, 609-10, 610-10, and 611-11 issued by the Japanese Iron and Steel Federation, Tokyo, Japan. Two glass beads containing each CRM were prepared and measured once. Analytical results and weighed values are listed in Table 1. In spite of variable sampling weights from 10.68 to 12.28 mg, the results were agreed well with the certified values.

A dilution factor (DF) is generally defined by the following equation: \[ \text{DF} = \frac{w_{\text{flux}}}{w_{\text{sample}}} \] where \( w_{\text{flux}} \) is the weight of a flux and \( w_{\text{sample}} \) is the weight of a sample. The range of DF in the present preparation was 327 to 376. Such a large DF was out of the values (DF > 100) recommended by the software of our instrument for correction calculation using fundamental parameters; however, it was worth a comparison with the present calibration method. It could be expected that larger extents of dilution would minimize the matrix effect on the absorption of fluorescent X-rays, which was rather desirable in our calibration method.

As indicated in Table 1, fundamental parameter calculations (using 100 of DF) led to erroneous results of tungsten. A probable reason for the errors is that the exact content of iron, which is needed as a fundamental parameter in the calculation, is not guaranteed in the steel reference materials employed in this study. The iron contents do not suffer from the problem regarding matrix compositions to the range as follows; 69.6 and 69.6 mass% for 607-9, 77.0 and 77.5 mass% for 609-10, 69.3 and 69.7 mass% for 610-10, and 81.8 and 81.5 mass% for 611-11. Such inaccurate estimations of iron would lead to the erroneous results of tungsten that is usually the second or third major component in high-speed steels. On the contrary, our quantification method was based on the measurement of calibration standards.

The ninety-five percent confidence interval for the 607-9 was obtained as 17.5 ± 0.4 mass%, whereas the certified value is 17.29 mass%. In addition, one glass bead specimen containing the 607-9 was 10-times quantified as follows: 17.58, 17.65, 17.62, 17.61, 17.65, 17.60, 17.66, 17.60, 17.60, and 17.64 mass%. The repeated counting gave 17.62 ± 0.03 mass% of the content of iron, which is needed as a fundamental parameter in the calculation, is not guaranteed in the steel reference materials employed in this study. The iron contents do not suffer from the problem regarding matrix compositions to the range as follows; 69.6 and 69.6 mass% for 607-9, 77.0 and 77.5 mass% for 609-10, 69.3 and 69.7 mass% for 610-10, and 81.8 and 81.5 mass% for 611-11. Such inaccurate estimations of iron would lead to the erroneous results of tungsten that is usually the second or third major component in high-speed steels. On the contrary, our quantification method was based on the measurement of calibration standards.

The ninety-five percent confidence interval for the 607-9 was obtained as 17.5 ± 0.4 mass%, whereas the certified value is 17.29 mass%. In addition, one glass bead specimen containing the 607-9 was 10-times quantified as follows: 17.58, 17.65, 17.62, 17.61, 17.65, 17.60, 17.66, 17.60, 17.60, and 17.64 mass%. The repeated counting gave 17.62 ± 0.03 mass% of the content of iron, which is needed as a fundamental parameter in the calculation, is not guaranteed in the steel reference materials employed in this study. The iron contents do not suffer from the problem regarding matrix compositions to the range as follows; 69.6 and 69.6 mass% for 607-9, 77.0 and 77.5 mass% for 609-10, 69.3 and 69.7 mass% for 610-10, and 81.8 and 81.5 mass% for 611-11. Such inaccurate estimations of iron would lead to the erroneous results of tungsten that is usually the second or third major component in high-speed steels. On the contrary, our quantification method was based on the measurement of calibration standards.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specimen number</th>
<th>Sample weight/ mg</th>
<th>Using calibration curve</th>
<th>Using fundamental parameter calculation</th>
<th>Certified value, mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>607-9</td>
<td>#1</td>
<td>10.75</td>
<td>17.4</td>
<td>19.7</td>
<td>17.29</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>11.84</td>
<td>17.6</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>609-10</td>
<td>#1</td>
<td>11.44</td>
<td>6.14</td>
<td>7.14</td>
<td>6.11</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>10.95</td>
<td>6.25</td>
<td>7.16</td>
<td>6.16</td>
</tr>
<tr>
<td>610-10</td>
<td>#1</td>
<td>10.68</td>
<td>9.26</td>
<td>10.4</td>
<td>9.03</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>11.34</td>
<td>9.30</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>611-11</td>
<td>#1</td>
<td>12.28</td>
<td>6.10</td>
<td>7.16</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>10.69</td>
<td>6.15</td>
<td>7.02</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1](image1.png) Tungsten Lα X-ray fluorescence spectra of synthesized calibration standards: 0 mg (●), 0.50 mg (○), 1.00 mg (■), 1.50 mg (□), 2.00 mg (▲), and 2.50 mg (★).

![Fig. 2](image2.png) Calibration curve of tungsten added in calibration standard / mg.

**Table 1** Analytical results of tungsten in certified reference materials of high-speed steel issued by the Japanese Iron and Steel Federation.

![Graph](image3.png) X-ray intensity of tungsten Lα line / kcps
mean value and standard deviation. These results suggested that precise quantification was expected by employing the X-ray fluorescence procedures suggested in this study. The present technique might be widely applicable to major alloying elements in titanium-alloy and other alloyed materials, which can be decomposed without hydrochloric acid.

Conclusions

Tungsten content in specimens of high-speed steel was rapidly obtained in X-ray fluorescence analysis by using a combined sample pre-treatment technique; acid decomposition of the solid sample and a preparation of the glass bead. Milligrams-based calibration standard containing tungsten was prepared by using metal standard solution. Without any matrix correction, the linear calibration curve was simply obtained between the fluorescent X-ray intensity of tungsten Lα line and the tungsten content added, thus enabling the tungsten content to be determined more accurately than the correction method using fundamental parameters.

Acknowledgements

The support of this work by the 24th ISIJ Research Promotion Grant is acknowledged with appreciation. The authors express appreciation to the colleagues of Analytical Research Core for Advanced Materials, Institute for Materials Research, Tohoku University, Japan, for helpful suggestions.

References