Rapid Borate Fusion Pre-treatment for ICP-AES Determination of Tungsten in High-speed Steel

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This paper suggests a rapid decomposition and dissolution method for stable solution preparation in inductively coupled plasma atomic emission spectrometry when tungsten in a high-speed steel is quantified. The steel sample was decomposed with a mixture of hydrofluoric and nitric acid, and then the resulting solution was fused with lithium tetraborate. The vitrified borate was able to dissolve in nitric acid containing tartaric acid to prepare the final sample solutions. This pre-treatment method has a superior feature: borate could effectively prevent tungsten hydrolysis in the prepared solution. The standard for quantification could be prepared in a similar procedure using metal standard solutions. The present method enabled more rapid and accurate determination of tungsten in certified reference materials of high-speed steel compared to the conventional dissolution procedure.

KEY WORDS: inductively coupled plasma atomic emission spectrometry; acid decomposition; alkali fusion; tungsten determination; high-speed steel.

1. Introduction

High-speed steel is frequently used as a cutting tool material. The most important property for this type of steel is that it needs to have excellent abrasion and heating resistances. Tungsten (and molybdenum) is a typical alloying element to yield these resistances of high-speed steel; therefore the content of tungsten needs to be accurately determined to control the performance of the final steel products as well as to save the resource of tungsten as an expensive and rare metal. A high-speed steel contains up to 19 mass% of tungsten, and then analysts may be faced with the difficulties in tungsten gravimetric analysis. Great difficulty may be experienced in tungsten gravimetric analysis. Because of generated fine tungsten precipitates, the tungsten analyte might be lost on vessel transfer and filtration. Furthermore, such precipitates often contain other elements such as vanadium, chromium, and molybdenum which are the alloyed elements in steel materials. On the other hand, analysts may be faced with another difficulty in tungsten wet analysis. This is because tungsten frequently precipitates in a prepared solution. For steel wet analysis, several kinds of steel are generally decomposed with a mixture of nitric acid and hydrochloric acid, but tungsten will precipitate in such mixed acid solution. A sufficient fuming with sulfuric and phosphoric acids or adding of hydrofluoric acid would be taken in the tungsten-contained steel solution. Polyphosphoric complex ions or fluoride ions could be complexing agents against tungsten. For example, the Japanese Industrial Standards (JIS) determines an analytical method of tungsten in a steel sample based on the solution preparation using sulfuric and phosphoric acids for inductively coupled plasma atomic emission spectrometry (ICP-AES). However, this ICP-AES method is inapplicable when tungsten content is more than 10 mass% in a steel sample, whereas several commercial high-speed steels may contain 19 mass% of tungsten, meaning that the JIS document may be incomplete for the tungsten analysis of steels. High content tungsten will be determined by using above-mentioned gravimetric analysis according to the JIS analyses of steel. The goal of this study is to suggest a rapid sample preparation, instead of the JIS method, for high-alloyed steels containing a large amount of tungsten.

In ICP-AES—one of the most employed analytical method, sulfuric and phosphoric acids cause a little uncertainty on analytical results. For example, a high viscosity of sulfuric acid solution may lead to erroneous results. This is because a difference of the solution viscosity governs the sampling rate introduced into the ICP-AES instrument. Even if the internal standard method would be applied, it may give us an inaccurate analytical result. In addition, the fuming process must be time-consuming, and the extra fuming might lead to precipitation. Borosilicate glassware—one of the most used, which is popularly employed in volumetric vessel, will be readily corroded in a presence of hydrofluoric acid; however, the other vessels such as polypropylene volumetric pipette might be inferior to the borosilicate one in precision.

Authors have been developed a rapid X-ray fluorescence quantification of tungsten in a high-speed steel. In the present paper, a similar preparation method was applicable to wet tungsten analysis based on the ICP-AES. Lithium tetraborate has been often used for a decomposition agent in ICP quantification. Awaji et al. applied the borate fusion to inductivelycoupled plasma mass spectrometry (ICP-MS) of trace elements in granitic rocks. Ogdárd et al. directly measured lithium tetraborate fused disks for laser abration ICP-MS of natural rocks. The other alkali fusion was also used; for instance, Danzaki and Wagatsuma conducted sodium carbonate fusion for ICP-AES determination of silicon in silicon carbide. A high-speed steel can be completely decomposed by using acid dissolution with a mixture of hydrofluoric acid and nitric acid and alkali fusion with lithium tetraborate, resulting in a sample form of borate glass which can be easily dissolved only with nitric acid. On the other hand, a fuming procedure with sulfuric acid and phosphoric acid has been frequently employed for tungsten wet analysis; however, this process is time-consuming. Sometimes, hydrogen peroxide is used as a complexing agent, but oxygen bubbles in the resulting solution may prevent a stable introduction of sample solution to an ICP-AES instrument. Additionally, hydrofluoric acid can be added for stable tungsten solution preparation, but the hydrofluoric acid solution needs difficult operations because of its glass corrosion.

In the present work, nitric-acid-based solutions containing tungsten of high-speed steel were obtained with no tungsten precipitate. High-speed steel was decomposed with hydrofluoric acid and nitric acid, and the resulting solution was fused with lithium tetraborate in a platinum-gold alloy crucible. The vitrified borate-glass was dissolved with nitric acid with a coexistence of tartaric acid. In the similar manner, standard solutions for calibration were prepared, where lithium tetraborate added to standard solutions of iron and tungsten was fused in the crucible, and finally the vitrified glass was dissolved. Tungsten did not precipitate from the nitric acid solution containing the borate and tartaric acid.
This is because the dissolved borate would act as a complexing agent. With the present method, the solution preparation for tungsten ICP-AES determination of the high-speed steel was able to be carried out for about one and a half hours.

2. Experimental

2.1. Apparatus

An inductively coupled plasma atomic emission spectrometer was used, IRIS-AP HR Advantage Floor mount DUO (Thermo Fisher Scientific Inc., Waltham, USA; Thermo Jarrell Ash, Franklin, USA) was employed. A 27.12-MHz radio-frequency generator was operated at 1.15 kW. The following flow-conditions of argon gas were used in line with gas-flow parameters recommended in this system: 15 dm³ min⁻¹ of coolant gas, 0.5 dm³ min⁻¹ of auxiliary gas, and 1.9 × 10⁸ Pa (28 pound-force per square inch) of nebulizer gas. Solutions were introduced with a glass concentric nebulizer and a cyclone spay chamber. The rate of a peristaltic pump was 130 rounds per minute. By observing the plasma axially, the intensities of all emission lines were accumulated for 10 s (wavelength shorter than 275 nm) or 5 s (wavelength longer than 275 nm) on a charge injection device (CID) detector. The mean value of triplicate measurements was used for analytical calculations. By using a least-squares method, the calibration and determination calculations were based on a calibration curve resulting from regression of the emission intensity ratio of analyte/yttrium on the amount of analyte added in a calibrating solution. The software equipped with the instrument was not used for the present calibration. Measured emission lines were 309.911 and 311.071 nm of vanadium; 206.149 and 266.602 nm of chromium; 224.306 and 371.030 nm of yttrium as an internal standard; 202.030, 203.844, 204.598, 204.963, and 207.911 nm of molybdenum; and 202.998, 203.844, 204.598, 204.963, 207.911, 209.860, 220.448 nm of tungsten.

2.2. Sample Preparation

About 11 mg of high-speed steel was placed in a platinum-gold crucible, which is usually used to prepare fused borate glass beads in XRF analysis. The steel was dissolved with an acid mixture: 100 mm³ of 50 mass% hydrofluoric acid and 100 mm³ of 70 mass% of nitric acid diluted with the same volume of distilled water. After adding the acid mixture, the crucible was left for about 30 second, heated on a hotplate (400 K) about 30 s for complete decomposition, and then the solution was slightly concentrated (but no dryness). Weighed 0.40 g of lithium tetraborate was added to the crucible and it was heated with a Meker burner. Borate fusion was carried out by the following steps: (1) pre-heating to vaporization of acids with no platinum lid for 1 to 2 min, (2) the first heating with the lid for about 3 min, (3) agitating to collect melted drops on the bottom of the crucible, (4) the second heating with the lid for about 1 min. The resulting melted mixture was left for about 1 min, and then cooled by air-flow of a hair dryer. The vitrified borate was dissolved with nitric acid solution: 4.0 cm³ of 70 mass% nitric acid diluted with the same volume of distilled water, 2.0 cm³ of 0.2 g cm⁻³ of tartaric acid, and 4.0 cm³ of distilled water. The resulting solution was placed in 100 cm³ of a volumetric flask. Additional reagents were added in the flask: 16 cm³ of 70 mass% nitric acid diluted with the same volume of distilled water, and 3 cm³ of 0.2 g cm⁻³ of tartaric acid. Finally, yttrium as an internal standard was added: 10 cm³ of 50 μg cm⁻³ yttrium solution. Then, the final solution had generally a similar composition as follows: sample of about 11 mg high-speed steel, internal standard of 0.50 mg yttrium, mineral acid containing about 10 cm³ of 70 mass% nitric acid, an complexing agent of 1.0 g tartaric acid, and a remaining flux agent of 0.40 g lithium tetraborate.

2.3. Calibrating Standards

Ten mg cm⁻³ of tungsten standard solution was prepared. By using a poly (tetrafluoroethylene) beaker, 0.25 g of pure tungsten was dissolved in aqueous solution containing 1.0 cm³ of 50 mass% hydrofluoric acid and a few droplets of nitric acid. And then, the resulting solution was diluted with distilled water in 25.0 cm³ of a polypropylene volumetric flask. For addition of matrix content, 50 mg cm⁻³ of iron standard solution was used. Additionally, 5.0 mg cm⁻³ of vanadium, 4.0 mg cm⁻³ of chromium, and 4.0 mg cm⁻³ of molybdenum standard solutions were prepared. A set of six borate-glass standards was prepared: (1) 11.0 mg of iron without tungsten, (2) 10.5 mg of iron and 0.50 mg of tungsten, (3) 10.0 mg of iron and 1.00 mg of tungsten, (4) 9.50 mg of iron and 1.50 mg of tungsten, (5) 9.00 mg of iron and 2.00 mg of tungsten, and (6) 8.50 mg of iron and 2.50 mg of tungsten. By using two variable micropipettes for 20 to 200 mm³ and 200 to 1000 mm³, tungsten and iron standard solutions were added to 0.40 g of lithium tetraborate in the platinum-gold crucible. The vitrified borate mixtures and their nitric acid solution samples were obtained by using the same fusing process as high-speed steel specimen.

3. Results and Discussion

3.1. Solution Preparation

High-speed steels were rapidly decomposed for about 1 min. The borate fusion in the present preparation was for within 10 min. This is much faster than the borate fusion process generally employed for X-ray fluorescence (XRF) method for about 20 min. This is because lithium tetraborate used as the flux agent is reduced by a factor of one-tenth: 0.40 g for the present fusion and 4.00 g for the XRF glass bead specimen. The present preparation, as well as our XRF preparation, was carried out without appreciable damage of the platinum crucible. This might be because small amount of steel with about 36-times amount of borate flux in the crucible was fired at relatively low temperature with a burner. Despite the smaller dilution factor, the borate mixture was successfully vitrified. In this study, a large bottom crucible having about 35 mm in diameter was used, but smaller bottom crucible (for example, 12.5 mm in diameter) might be preferable to fuse 0.40 g of the flux.

No precipitates were observed during the working solutions in preparation of high-speed steel and calibrating standards. This is because the remaining borate might act as an effective complexing agent like tartaric acid or phosphoric acid. Despite the small amount of 11 mg steel sample, precipitate was observed in nitric-acid solution without tartaric acid. The addition of tartaric acid was essential for the present preparation. On the other hand, tungsten precipitated in synthetic nitric-acid solution containing only tartaric acid as the complexing agent. Accordingly, no precipitates might be due to the combined action of borate and tartaric acid ions. In several previous reports, a mixture of sulfuric acid and phosphoric acid has been applied for tungsten wet analysis, where the water content is often vaporized and the concentrated acid is fumed well. And then, aqueous dilution of the resulting solution is time-consuming because of the exothermic process. The present nitric-acid-based solution was able to be obtained for about one and a half hours.

It is sometimes difficult to handle tungsten standard solution for analytical use. Sulfuric acid and phosphoric acid based solution has a high viscosity (density) when it is introduced to an emission spectrometer, which may lead to a large variation in the sensitivity. Therefore, the prepared
Table 1. Analytical results (in mass%) of tungsten and its coprecipitation elements of vanadium, chromium and molybdenum in certified reference materials of high-speed steel issued by the Japanese Iron and Steel Federation.

| Sample | Specimen number | Tungsten | Vanadium | Chromium | Molybdenum |
|--------|----------------|----------|----------|----------|------------|
|        | Present method* | Certified value | Present method* | Certified value | Present method* | Certified value | Present method* | Certified value |
| 607-9  | #1             | 17.46 ± 0.03 | 17.29     | 0.92     | 0.90       | 3.95       | 4.00       | 0.283       | 0.278       |
|        | #2             | 17.65 ± 0.04 |           | 0.93     | 3.98       |           |           | 0.278       |             |
| 609-10 | #1             | 6.15 ± 0.03  | 6.11      | 1.95     | 1.92       | 3.98       | 4.02       | 4.83        | 4.85        |
|        | #2             | 6.20 ± 0.03  |           |           | 1.97       |           |           | 4.92        |             |
| 610-10 | #1             | 9.02 ± 0.07  | 9.03      | 3.30     | 3.25       | 3.95       | 3.99       | 3.00        | 3.07        |
|        | #2             | 9.10 ± 0.08  |           | 3.35     |           | 3.99       |           | 3.08        |             |
| 611-11 | #1             | 6.14 ± 0.04  | 6.10      | 2.16     | 2.14       | 4.08       | 4.06       | 4.96        | 4.91        |
|        | #2             | 6.14 ± 0.03  |           | 2.19     |           | 4.09       |           | 4.96        |             |

*: mean value with standard deviation of measured five emission lines.

3.2. Calibration

The calibrating standard solution was prepared by mixing metal standard solution. The precise volume of the standard solution containing an analyte could be directly added to synthesize calibrating standard solutions. In the present preparation, a glassy solid containing an analyte was able to be prepared, and then dissolved for every measurement. This prepared borate glass containing an analyte can be stored in a similar manner as a borate glass bead for XRF analysis.

Five emission lines of tungsten were measured: 202.998, 204.963, 207.911, 209.860, and 220.448 nm. Calibration curves of these lines were successfully obtained. The lower limit of detection (LLD) is \( s_{\text{blank}} / b \), where \( s_{\text{blank}} \) is the standard deviation of 10-times measurements in a calibrating solution containing 11.0 mg of iron without tungsten and \( b \) is the slope of a calibration curve. The LLD of the most sensitive emission line (207.911 nm) was 0.001 mg, suggesting that the present measurement could be applied for 0.01 mass% or less of tungsten.

3.3. Validation

Certified reference materials (CRM) of high-speed steels were assayed by using the present method: 607-9, 609-10, 610-10, and 611-11 of Japanese Steel Standard (JSS) issued by Japanese Iron and Steel Federation, Tokyo, Japan. Two solutions of each CRM were prepared and measured once. Analytical results of tungsten by using the present ICP-AES agreed well with the certified value as showed in Table 1.

Table 1 contains analytical values of vanadium, chromium, and molybdenum, indicating that these coprecipitation elements together with tungsten can be successfully determined. These results suggested that accurate quantification was carried out by the present preparation.

4. Conclusion

Tungsten in a high-speed steel was determined in inductively coupled plasma atomic emission spectrometry by using a combined sample pre-treatment technique, comprising acid decomposition, alkali fusion, and dissolution with nitric acid. As the quantification standard, storable borate-glass containing tungsten was able to be prepared by adding metal standard solutions. The nitric acid solution containing no precipitates was rapidly and easily prepared for the high-speed steel containing more than 10 mass% of tungsten.

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