Calibration Method for Determination of Nitrogen Content in Steel by Thermo-Conductimetry after Fusion in the Current of an Inert Gas

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A calibration method for determining the nitrogen content in steel by a thermo-conductimetric method after fusion in the current of an inert gas is proposed. In this calibration method, a pure chemical substance whose nitrogen content can be calculated based on its molecular weight is used as a calibrant. The nitrogen recovery and thermostability of 9 chemical substances in the fusion procedure were investigated; it was found that potassium nitrate is the most suitable as a calibrant. The results of analysis of 9 steel samples of certified reference materials demonstrate that the proposed calibration method is applicable to determination of nitrogen contents between 0.001% and 0.5%.

Keywords Calibration method, nitrogen determination, steel, thermo-conductimetry, potassium nitrate

In steel, nitrogen readily forms metal nitrides or metal carbonitrides combined with aluminum, boron, silicon, titanium, vanadium or zirconium present as impurities. The mechanical and metallurgical properties of steels are influenced by the nitrogen content or the forms of nitrides. Generally, as the nitrogen content increases, the tensile strength increases and the total elongation decreases. The nitrogen content in low-alloy steel is typically 0.003 - 0.006%. Very low nitrogen levels of 0.002% or less may be desirable in thin-sheet steel. In stainless steel alloying 15 - 30% chromium, 0.02 - 0.03% nitrogen is contained.1

The determination of nitrogen in steel has usually been carried out by wet chemical methods or instrumental methods.2 Such wet chemical methods as titrimetric or spectrophotometric method after distillation2 are used as the standard method for the nitrogen determination. In general, however, these methods require much labor, skill and time.

In order to satisfy the needs for rapid and easy determinations, instrumental methods, such as a thermo-conductimetric method after fusion in the current of an inert gas, have been developed and are widely used in the metal industry. In these methods, certified reference materials (CRMs) of steel containing a known amount of nitrogen are generally used for calibrations. The nitrogen contents in those CRMs are usually determined by the wet chemical analysis method. Therefore, a pure chemical substance whose nitrogen content can be calculated based on its molecular weight is preferable as a calibrant in the instrumental method, if this is feasible.

The present paper describes a new calibration method which uses a pure chemical substance as a calibrant for determining the nitrogen content by a thermo-conductimetric method after fusion in the current of an inert gas.

Experimental

Chemical substances

Table 1 lists nine chemical substances, i.e. six kinds of inorganic compounds including two metal nitrides3 and three kinds of organic compounds. They were investigated concerning the nitrogen recovery and thermostability in a fusion procedure in the current of an inert gas. As inorganic compounds, potassium nitrate (KNO₃) was investigated on behalf of nitrates, and ammonium sulfate ((NH₄)₂SO₄), ammonium oxalate ((NH₄)₂C₂O₄·H₂O) and ammonium tungstate ((NH₄)₁₀W₁₂O₄₁·5H₂O) were selected as ammonium salts. As metal nitrides, chromium nitride (Cr₂N) and niobium nitride (NbN) were selected since the formation of nitrogen compounds is similar to formation in steel. As organic compounds, N,N'-o-(1,2-phenylene)bismaleimide (C₁₄H₈N₂O₄) and 1-hexadecylpyridinium chloride (C₂₁H₃₁Cl·H₂O) were chosen since they could be weighed directly, and urea (H₂NCONH₂) was selected as a substance which could be dissolved in water.

Apparatus

A Horiba-EMGA650 oxygen/nitrogen analyzer was used to determine the nitrogen evolved from the chemical
substances and steel samples.

An ANELVA AGS-7000 mass spectrometer was used to detect and identify the gases which evolved from chemical substances in the fusion procedure.

**Preparation for a calibrant**

Cr2N, NbN, (NH4)6W12O41·5H2O, C14H8N204 and C21H38C1N·H2O, which could be weighed directly, or which could not be dissolved in water, were prepared by weighing directly. Quantities of each substance corresponding to 100, 200 and 400 µg of nitrogen were weighed in nickel capsules (6 mm~X 12.5 mm) using a microbalance (Mettler M5SA). KNO3, (NH4)2SO4, (NH4)2C204 · H2O and H2NCONH2 were prepared by dissolving in water. Each substance was prepared to nitrogen contents of 1, 2 and 4 g/l, and 100 µl of the each solution was transferred into nickel capsules. The solution was dried at 90° C for 2 h in a drying oven and cooled in a desiccator.

Each capsule and 0.5 g of pure iron (Japanese Iron and Steel CRMs, JSS002-3; N=0.0005%) were placed in a graphite crucible (12 mm4X 18 mm), and fused in the current of an inert gas.

**Procedure of the analytical method**

The prepared chemical substance or a steel sample weighed about 0.5 - 1.0 g was placed in a crucible and heated at about 2500° C for 30 s in a current of helium gas (800 ml/min). Nitrogen and hydrogen in the sample were extracted as N2 and H2. Oxygen was reacted with a graphite crucible and CO evolved. CO and H2 were oxidized by copper oxide, forming CO2 and H2O, respectively. These gases were removed with soda-asbestos and magnesium perchlorate, only N2 was carried to the thermal conductivity detector.

The calibration curve was obtained by determining the nitrogen content in 6 kinds of Japanese Iron and Steel CRMs containing a nitrogen content of between 0.0038% and 0.0465% (JSS061-4, JSS368-3, JSS603-7, JSS609-8, JSS650-7, JSS651-10).

The determination of the nitrogen content was carried out after correcting the crucible and capsule blank values.

**Results and Discussion**

**Nitrogen recovery in the fusion procedure**

Figures 1 – 3 show the amount of nitrogen evolved from chemical substances in the fusion procedure. It was found that KNO3, Cr2N and H2NCONH2 have good linearity and agreement between theoretical and experimental values. The nitrogen recovery of these substances was higher than 97%. However, Cr2N is not suitable as a calibrant, since weighing a very small amount of the substance is not practicable.

The nitrogen recovery from NbN and C14H8N204 was about 93%. (NH4)2SO4 and (NH4)2C204 · H2O showed low recovery, because nitrogen escaped during the drying process in the preparation. On the other hand, the nitrogen recovery from (NH4)6W12O41·5H2O and C21H38C1N·H2O exceeded 100%. It is considered that nitrogen compounds were derived by thermal decom-

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**Table 1 Pure chemical substances investigated**

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Formula</th>
<th>Nitrogen content, %</th>
<th>mp/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium nitrate</td>
<td>KNO3</td>
<td>13.85</td>
<td>339</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH4)2SO4</td>
<td>21.19</td>
<td>280</td>
</tr>
<tr>
<td>Ammonium oxalate</td>
<td>(NH4)2C2O4·H2O</td>
<td>19.70</td>
<td>133</td>
</tr>
<tr>
<td>Ammonium tungstate</td>
<td>(NH4)2W12O41·5H2O</td>
<td>4.47</td>
<td>—</td>
</tr>
<tr>
<td>Chromium nitride</td>
<td>Cr2N</td>
<td>11.86</td>
<td>1650</td>
</tr>
<tr>
<td>Niobium nitride</td>
<td>NbN</td>
<td>13.10</td>
<td>2573</td>
</tr>
<tr>
<td>N,N'-o-(1,2-phenylene)bismaleimide</td>
<td></td>
<td>10.44</td>
<td>245</td>
</tr>
<tr>
<td>1-Hexadecylpyridinium chloride</td>
<td></td>
<td>3.91</td>
<td>85</td>
</tr>
<tr>
<td>Urea</td>
<td>H2NCONH2</td>
<td>46.62</td>
<td>133</td>
</tr>
</tbody>
</table>

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Fig. 1 Recovery of nitrogen from inorganic compounds.
Identification of the gases evolved

In order to identify the gases which evolved from chemical substances, the gases evolved in the fusion were carried to a mass spectrometer directly and analyzed. The mass spectra obtained from KNO$_3$ and C$_{21}$H$_{38}$ClN•H$_2$O are shown in Figs. 4 and 5, respectively. From KNO$_3$, N$_2$ and N$^+$ were detected. Other forms of nitrogen, such as nitrogen compounds, were not detected. CO$_2$ and H$_2$O were derived from impurities in the helium carrier gas, since these gases were detected in the blank analysis. The same experiments were carried out using H$_2$NCONH$_2$, (NH$_4$)$_2$SO$_4$ and (NH$_4$)$_2$C$_2$O$_4$; it was confirmed that only N$_2$ and N$^+$ were detected as nitrogen. On the other hand, it was found that many compounds above 40 of mass number were detected from C$_{21}$H$_{38}$ClN•H$_2$O. The nitrogen recovery thus exceeded 100%, because these products were detected with N$_2$ at the detector.

Effect of the heating condition

The effect of the heating conditions in the fusion procedure on the nitrogen recovery and the patterns of gases evolved from KNO$_3$ and H$_2$NCONH$_2$ were
investigated. Figure 6 shows the nitrogen recovery from both substances under different heating conditions; the normal condition (A) of fusion for 30 s after pre-heating, and condition (B) involved 30 s of waiting after pre-heating and then slow heating for 120 s. KNO₃ showed approximately 100% of nitrogen recovery under both conditions. On the other hand, the nitrogen recovery from H₂NCONH₂ was only about 60% under condition (B) because of the evolution of nitrogen compounds during the waiting period or slow heating.

Figure 7 shows the patterns of nitrogen and oxygen evolved from KNO₃. Under heating condition (A), nitrogen and oxygen were evolved at about the same time. On the other hand, nitrogen was evolved at about 800°C followed by oxygen evolution at about 1500°C under heating condition (B). The reason is considered to be that N₂ and CO were evolved at the same time in the following reaction under condition (A):

\[
2\text{KNO}_3 + 5\text{C(crucible)} = \text{K}_2\text{O} + \text{N}_2 + 5\text{CO}
\] (at 2500°C).

However, under condition (B), N₂ was evolved by thermal decomposition of KNO₃ at about 800°C, and at the same time, K₂CO₃ was generated by reacting with the graphite crucible. At about 1500°C, K₂CO₃ was decomposed, and oxygen evolved as CO.

Figure 8 shows the patterns of gases which evolved from H₂NCONH₂. Under heating condition (A), nitrogen and oxygen were evolved at about the same time. On the other hand, several peaks of the nitrogen and oxygen were detected under condition (B). This shows that several nitrogen compounds, such as NH₂CONHCONH₂ and organic compounds, were generated in the fusion procedure. It is well known that the melting temperature of H₂NCONH₂ is 133°C, and that NH₂CONHCONH₂ is generated at about 160°C.

**The calibration curves**

Based on these results, KNO₃ was found to be the most suitable as a calibrant. The established calibration method is shown in Fig. 9. The calibration curves obtained by this method are shown in Fig. 10. As shown in this figure, the calibration curves gave good linearity in the range of nitrogen content between 0.0005% and 0.5%.
Determination of the nitrogen content in steels

Using these calibration curves, the nitrogen contents in 9 steel samples of CRMs were determined. Table 2 shows the certified values determined by the titrimetric method and experimental values. The values of the nitrogen content found by the proposed method show good agreement with the certified values at between 0.0007% and 0.415% nitrogen content.

International cooperative test

Based on the study described in this paper, Japan proposed a calibration method using KNO₃ in a committee meeting of ISO/TC17/SC1. The proposal was adopted in a working draft of ISO/TC17/SC1/WG27. The precision of this method was then evaluated by international cooperative tests at 10 laboratories. Each laboratory carried out three determinations for each of the CRMs listed in Table 2. Two of the three determinations were carried out under conditions that were as constant as possible, with the determination being performed during a short interval of time by one operator. The third determination was carried out on a different day by the same operator using the same apparatus, but with a new calibration.

Figure 11 shows the precision curves obtained by the international cooperative test. The repeatability ($r$) and the reproducibility ($R_w$) refer to determinations performed within one day and different days, respectively, in one laboratory. $R$ represents the reproducibility in different laboratories. In this figure, the value of precision shows a value that is 2.8-times of the standard deviation defined in ISO 5725. It was found that the lower limit of the determination of the proposed method
was 0.001% nitrogen content, because the RSD of R was about 20% at that content.

References


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