Determination of Silicon in High-Silicon Electrical Steel by ICP-AES with On-line Sample Electrolytic Dissolution

Michihiro AIMOTO,^{*†} Hiroyuki KONDO,^{*} and Akihiro ONO^{**}

**Advanced Technology Research Laboratories, Nippon Steel Corp.,
20-1 Shintomi, Futtsu, Chiba 293-8511, Japan*

***The Japan Society for Analytical Chemistry, Gotanda Sanhatsu No. 305,
1-26-2 Nishi-gotanda, Shinagawa, Tokyo 141-0031, Japan*

A flow-injection procedure combining electrolytic sample decomposition and inductively coupled plasma atomic emission spectrometry (ICP-AES) is proposed in order to rapidly determine the content of silicon in high-silicon electrical steel. This system is characterized by sample decomposition through electrolysis directly coupled to ICP-AES. A steel sample is dissolved by electrolysis using a 6 mol L⁻¹ HCl solution as an electrolyte with a flow rate of 5 mL min⁻¹; the electrolyte containing a dissolved sample is subsequently introduced into ICP-AES *via* a nebulizer. The effects of the electrolysis current and the temperature on the decomposition of the sample were studied. Samples were electrolyzed under the condition of a 1.5 A constant current, at room temperature (25°C) to avoid the hydrolysis of silicon to precipitate. Comparing the analytical results of steel samples obtained by this analytical system with those obtained by the gravimetric method, determined values agreed well quantitatively. The RSD of silicon at approximately 3% was 0.3% (*n* = 6).

(Received September 10, 2007; Accepted October 24, 2007; Published December 10, 2007)

Introduction

High-silicon electrical steel, which typically contains 3 wt% silicon, performs effectively as a magnetic and electric energy converter for high-frequency applications, and is used for transformers, dynamos, motor cores and coils. It is an indispensable material in modern life, which provides electricity for our industrial society, such as power generators, and is necessary for industrial machines and transportation equipment. High-silicon electrical steel is also widely used as small-to-medium sized transformers and electric household appliances in the consumer-product sector, as well as hybrid automobile motors in the transport sector. Moreover, further expansions of the markets and applications are expected with the realization of a hydrogen-based society in the near future.

The silicon content in high-silicon electrical steel affects the magnetic properties.¹ When magnetic flux passes through the transformer core of an electric apparatus, energy loss, called iron loss, occurs. The silicon content in the steel is one of the parameters concerning iron loss. Generally, as the silicon content in steel increases, the iron loss decreases. However, an increase in the silicon content deteriorates the ductility of the material, and makes it easy to crack when processing the form and shape of the material. Controlling the silicon content in steel is quite important in the steelmaking process, because it greatly affects its properties.

The silicon content in high-silicon electrical steel is analyzed by spark optical emission spectrometry (Spark-OES) at steel production sites. As for Spark-OES, the passage of an electric

spark from an electrode to a solid sample causes elemental emission *via* atomization to form excited-state atoms and ions, and each element identified and quantified by spectrometric observation. This method is widely used in steelmaking industries due to its rapid analysis time (a few minutes, no need to decompose samples by hot acid) and inherent accuracy. These spectrometers are used for many aspects of the steel processing production cycle, and the quality control of semi-finished and finished products. However, the surface structure and the condition of the samples are typically not controlled quantitatively, and the inhomogeneous spark emission occurs by a sample with a specific surface, structure like elemental segregations, grain boundaries and inclusions. Hence, the significance of the surface structure affects the analytical results for the elements. Because some kinds of high-silicon electrical steel generally have a coarse-grained structure, which leads to inhomogeneous spark emission, variations of the analytical results possibly cause erroneous steelmaking processing. It is necessary to reuse any substandard products by scrap processing, which increases the production cost and scrap reheating energy, in the cases that erroneous analytical results are obtained and reported for process control.

The chemical analysis method for the determination of silicon in high-silicon electrical steel is the gravimetric method.² This analytical method is precisely and reliably applicable to high-silicon electrical steel samples. However, this technique requires time-consuming sample preparation, which includes sample powdering, weighing and decomposition, which is difficult to carry out as well. Hence, we have to develop a new analytical method that is as rapid as the Spark-OES method, and as rigorous as the chemical analysis method for steelmaking process control.

ICP-AES has precise, rapid and multi-elemental analysis

[†] To whom correspondence should be addressed.
E-mail: aimoto.michihiro@nsc.co.jp

capability. However, solid samples, like steels, require sample powdering, weighing and acid decomposition. Contamination that occurs during manual procedures of sample-preparation is a concern. Moreover, in the case of the decomposition of high-silicon electrical steel by hot acid, much of the silicon in the acid solution is hydrolyzed into insoluble silicon and forms precipitation, rendering not only silicon, but also makes the measurements of other elements difficult. This hydrolysis effect can possibly cause erroneous analytical results as a consequence of interference of the analytical procedure.

An electrolytic sample decomposition method, where a conductive solution is used to carry charge, and a current is also applied between a metal sample and the electrodes, is proposed³⁻¹⁶ to avoid sample-preparation procedures. Electrolytic sampling of the metal does not occur in a discrete spot compared to the Spark-OES method. Those examined trace and major elements, like chromium, nickel, manganese and silicon contents for alloys such as stainless-steel using ICP-AES as a detector of elements.³⁻⁷ This method is also used as sample-preparation for inductively coupled plasma mass spectrometry^{8,9} or atomic absorption spectrometry.^{10,11} Similarly, we have developed a rapid, precise and quantitative analysis method by electrolytic sample decomposition ICP-AES measurements, and have applied it for silicon, manganese, nickel, copper, aluminum, titanium, chromium, sulfur, and phosphorus determination in low-carbon steel.¹²⁻¹⁴ We also applied electrolytic decomposition of the sample for stripping voltammetry.¹⁵ However, there are presently no studies about the hydrolysis of silicon when electrolysis and quantitative silicon analysis of high-silicon electrical steel are used, except for our previous studies.^{12,16}

In this study, the effect of the electrolytic conditions and the temperature of the electrolytic decomposition of the sample were examined when an electrolytic sample decomposition ICP-AES system was applied to the quantitative analysis of silicon in high-silicon electrical steel.

Experimental

Analytical apparatus

The experimental system was described in our previous study.¹² Our electrolysis unit was handmade of PTFE block. A graphite bar was used as the cathode. Solid samples acted as the anode and electrolyzed and decomposed into electrolyte flow. The sample and holder were sealed using an o-ring and a PTFE holder grid so as not to leak the electrolyte. The gap size of the sample and the graphite bar was 1 mm. The surface and the volume of the electrolysis cell were $\phi 10$ mm and 80 μL , respectively.

HCl of 6 mol L⁻¹ concentration as an electrolyte was carried out continuously by a peristaltic pump through an electrolysis flow cell. The sample was placed into the electrolysis unit, and was electrolyzed as a working electrode fixed by pressing using an air cylinder. Subsequently, the electrolyte, which contained decomposed ions from part of the sample, was soaked up by the nebulizer from a gas-liquid separator, and introduced continuously into the plasma torch of ICP-AES. ICP-AES used in this study was of the SPS1700VR sequential type, SII NanoTechnology Inc., equipped with a quartz spray chamber torch and a concentric nebulizer. The analytical conditions of ICP-AES are given in Table 1. After the sample was placed onto the electrolysis unit, an automatic sequence proceeded under personal-computer control without any human intervention.

Table 1 Analytical condition of ICP-AES

Element (analytical line, nm)	Si (250.69), Fe (259.94)
RF power/kW	1.20
Ar carrier gas pressure/kg cm ⁻²	1.0
Ar plasma gas flow rate/L min ⁻¹	16.0
Data integration duration	65 to 85 s after starting electrolysis

Reagents

Deionized water treated by a Milli-Q system was used for preparing all solutions. The HCl used was of analytical reagent grade from Showa Chemicals Co. Ltd., Japan. A silicon standard solution from Wako Pure Chemical Industries Co. Ltd., Japan, was used for silicon calibration. The pure iron of a JSS (Japanese Iron and Steel certified reference materials) 001-3 standard sample from the Iron and Steel Institute of Japan, which hardly contains silicon, was used as the iron matrix for the calibration standard solution.

Calculations of quantity for electrolyzed sample

In this study, electrolysis was performed at a constant current. The electrolyzed sample quantity could be calculated using Faraday's law of electrolysis. If electric current was loaded at 1.5 A constant current for 1 min duration, and totally used for the electrolysis of iron, supposing that the iron matrix electrolyzed to ion as Fe²⁺, 26 mg of iron should theoretically be dissolved. When the flow rate of electrolyte was 5 mL min⁻¹, 5.2 mg mL⁻¹ (0.52%) of iron should have been electrolyzed and dissolved in the electrolyte. Due to those calculations, it might be unnecessary to weigh the sample for calibration and quantitative analysis of the content in the sample.

Results and Discussion

Calibration

To obtain a calibration curve for Si determination, from the blank to 200 $\mu\text{g mL}^{-1}$ solutions with iron for matrix matching were prepared. Silicon standard solutions were prepared by diluting a 1000 $\mu\text{g mL}^{-1}$ standard solution by 6 mol L⁻¹ HCl. Iron that co-existed in the solutions was prepared by dissolving the pure iron sample by 6 mol L⁻¹ HCl, and added to the solutions, depending on the iron content in the electrolyte, which differed according to the electrolysis conditions.

A linear relationship between the signal intensity and the silicon concentration was obtained up to a signal intensity of 200 $\mu\text{g mL}^{-1}$ by standard solutions. The background equivalent concentration (BEC) was 4 $\mu\text{g mL}^{-1}$ with the absence of an iron matrix in the solutions. However, BEC increased to 22 $\mu\text{g mL}^{-1}$ in the presence of 0.52% iron in solution. The reason for the increase of the background should be attributed to the matrix interference of iron; 22 $\mu\text{g mL}^{-1}$ of BEC was equivalent to 0.44% in the solid steel sample.

Effect of loaded current for electrolysis

Previous work¹²⁻¹⁶ in our laboratory has shown that electrolysis can be successfully used for the rapid decomposition of general steel samples. In this study, we investigated the effect of a loaded current from 0 to 2.0 A for the electrolysis of high-silicon electrical steel. The electrolyte was used at a flow rate of 5 mL min⁻¹. The sample used was a high-silicon electrical steel sample that contained proximately 3 wt% silicon and polished with the aluminum paper in a grinder before analysis.

Fig. 1 Relationship between the loaded current for electrolysis and the content of iron (a) and silicon (b) in electrolyte.

Fig. 2 Relationship between the time after starting electrolysis and the content of iron (a) and silicon (b) in the electrolyte. A, Current loaded; B, non-current-loaded (electrolyte flow only).

The relationship between the loaded current for electrolysis and the contents of iron and silicon in electrolyte is presented in Fig. 1. The loaded current from 0 to 1.5 A, and the signal intensities of both iron and silicon were proportional to the loaded current. However, the electrolyzed content of the sample declined over 1.5 A, possibly because of electrolytic interference by insulation caused by the large generation of electrolytic gas, which consisted of hydrogen in the flow cell. Using our flow cell and the flow rate condition mentioned above, the suitable current was indicated to be 1.5 A (current density of approximately 1.9 A/cm²) for steel sample electrolysis with this system.

Analytical responses

The relationship between the time after starting electrolysis and the content of iron and silicon in the electrolyte at room temperature 25°C is shown in Fig. 2. The sample used was 3 wt% silicon steel, and the loaded current was 1.5 A. Because of the soaking and replacing time of the solution in the nebulizer and the spray chamber of ICP-AES, the signal was observed from 20 s after starting electrolysis, and became constant at 60 s, one sample could be analyzed within 90 s using this system. The iron content in the electrolyte was about 0.52% at that time, the same as calculated with electric quantity of the constant current. Iron that decomposed by HCl electrolyte without electrolysis was in trace amounts. Therefore, the steel sample was thought to be dominantly electrolyzed by the current.

Effect of the sample electrolysis temperature

In the case of sample decomposition by hot acid, much silicon in the sample might be hydrolyzed into precipitates in an acid solution. For the gravimetric method, it was necessary to use HF, one of the strongest and most corrosive acids known to human exposure and difficult to handle, to dissolve the sample.

Fig. 3 Effect of the electrolysis temperature on the content of iron in the electrolyte. A, Current loaded; B, non-current-loaded (electrolyte flow only); C, difference of A and B.

Fig. 4 Effect of the electrolysis temperature on the content of silicon in the electrolyte. A, Current loaded; B, non-current-loaded (electrolyte flow only); C, difference of A and B.

However using this method by electrolysis, no precipitation occurred in the decomposition of the sample. We estimated that the hydrolysis reaction of silicon depended upon the temperature of the sample decomposition. Therefore, we examined the effect of the working temperature with sample heating.

To heat the sample, an infrared lamp was set at the center of the sample fixing cylinder.^{14,16} The sample temperature was controlled by a thermo-controller with monitoring by a thermoelectric couple. The sample used was 3 wt% silicon content steel. The sample was initially heated by a lamp up to an arbitrary temperature, and was then electrolyzed at a constant current of 1.5 A. The results of current-loaded (line A), non-current-loaded (HCl decomposition, line B), and the difference of A and B (thought to be only electrolyzed content, line C) are shown in Figs. 3 and 4.

In the case of iron, Fig. 3, the content was slightly increased (line A) with increasing sample temperature, under the effect of HCl decomposition (line B). From 25 to 50°C, since line C was almost constant, electrolysis might be stable at in those temperatures. However, over 80°C the decline of iron content was observed due to silicon hydrolysis mentioned in next paragraph.

For silicon (Fig. 4) there was a slight decline of the silicon content observed in lines A and B during analysis at temperatures ranging from 25 to 50°C. Then silicon in the electrolytic solution was hydrolyzed into white-colored precipitates, as visibly recognized and analytical signals rapidly became lower at the temperatures over 60°C. At 90°C signal intensity of silicon decreased to $67.2 \mu\text{g mL}^{-1}$, less than half of that at 25°C, $155.9 \mu\text{g mL}^{-1}$. Over 90°C, many precipitates of the silicon hydrolysis reaction were formed at the electrolysis cell and tubes, which blocked the flow of the electrolyte, making analysis impossible. Those results indicated that for a sample containing 3 wt% silicon, the intensive reaction of silicon hydrolysis occurred above 60°C for the sample temperature, and increased with an elevation of the working temperature.

Most of the silicon in high-silicon electrical steel could be solved in an iron matrix, and silicon was considered to be electrolyzed into the electrolyte with the iron matrix. Condensation and gelatinization reactions of generated silicic acid might have occurred above 60°C, which resulted in the precipitates. It was supposed that silicic acid was generated in the electrolyte for this hydrolysis reaction. By the examination mentioned above, a suitable working temperature was indicated as 25°C for steel sample electrolysis so as to avoid the effect of uncontrollable acid decomposition of iron and the precipitation of silicic acid.

Determination of silicon in high-silicon electrical steel samples

Considering those studies, we applied this method to several kinds of high-silicon electrical steel samples. The samples were decomposed by electrolysis at 25°C and a constant current of 1.5 A. The sample surface used for the analysis was cleaned in acetone by an ultrasonic cleaner before analysis. For the quantitative analysis of silicon in steel samples, the silicon content and the iron content in solution were measured by ICP-AES at the same time, and the silicon content was normalized by the iron content.

Figure 5 shows the quantitative results of samples obtained from molten steel in the steel-refining process, using a gravimetric method defined by ISO439 and the proposed method. When comparing the analytical results obtained with the above method with those obtained with the gravimetric method, the quantitatively determined values agreed well. The relative standard deviation of silicon at 3.05 wt% is approximately 0.3% ($n = 6$). The quantitative results of plate-shaped samples taken from the treated steel sheet products are shown in Fig. 6. From 0.5 to 5.1 wt%, the results of both methods generally agreed well, tending to obtain slightly higher values of the proposed method than those of the gravimetric method, due to the surface concentration gradient of silicon caused during production.

Those results showed that the proposed method is sufficiently accurate for practical use. This analytical system should be expected to replace the conventional Spark-OES and gravimetric methods because it took only 90 s, as rapid as the Spark-OES method, and much faster than the gravimetric method, which took over 1 h. The results of the proposed method should be more accurate than those of Spark-OES, which might be concerned with the occurrence of sectional spark emission.

Conclusions

A high-silicon electrical steel sample was directly dissolved by electrolysis using a flow cell at 25°C, and a solution containing dissolved ions was introduced into ICP-AES continuously.

Fig. 5 Relationship between the results of the conventional gravimetric method and the proposed method (molten steel samples).

Fig. 6 Relationship between the results of the conventional gravimetric method and the proposed method (steel sheet samples).

Using this system, the silicon content can be easily, rapidly and precisely analyzed. No significant differences exist between the results of the proposed method and those obtained by the conventional method. All manual sample-preparation procedures associated with conventional chemical analysis are eliminated, and no human intervention is required. This method is available for the quality control of the steelmaking process, and can be extended to the quantitative analysis of other elements in ferrous or non-ferrous alloys.

Acknowledgements

The authors gratefully appreciate Prof. Kazuaki Wagatsuma, Tohoku University, Dr. Koichi Chiba, National Institute of Advanced Industrial Science and Technology, Japan, Dr. Maki Sato, Toho Catalyst Co., Ltd., Dr. Katsuyuki Yanagihara, Nippon Steel Corp. and Mr. Takeshi Uemura for their valuable suggestions concerning this research.

References

1. J. H. Yu, J. S. Shin, J. S. Bae, Z.-H. Lee, T. D. Lee, H. M. Lee, and E. J. Lavernia, *Mater. Sci. Eng., A*, **2001**, 307(1–2), 29.

2. ISO 439, "Steel and Iron—Determination of Total Silicon Content—Gravimetric Method", **1994**.
 3. I. G. Souza, H. F. Bergamin, F. J. Krug, J. A. Nobrega, P. V. Oliveira, B. F. Reis, and M. F. Gine, *Anal. Chim. Acta*, **1991**, 245, 211.
 4. D. Yuan, X. Wang, P. Yang, and B. Huang, *Anal. Chim. Acta*, **1991**, 251, 187.
 5. O. N. Grebneva and N. M. Kuz'min, *J. Anal. Chem.*, **1998**, 53, 398.
 6. K. Ogle and S. Weber, *J. Electrochem. Soc.*, **2000**, 147, 1770.
 7. A. P. G. Gervasio, B. F. Reis, M. F. Gine, and H. Bergamin, *Quim. Nova*, **2000**, 23, 482.
 8. A. P. Packer, A. P. G. Gervasio, C. E. S. Miranda, B. F. Reis, A. A. Menegario, and M. F. Gine, *Anal. Chim. Acta*, **2003**, 485, 145.
 9. D. Goltz, M. Boileau, and G. Reinfelds, *Spectrochim. Acta*, **2003**, 58, 1325.
 10. J. B. B. Silva, M. B. O. Giacomelli, I. G. Souza, and A. J. Gurtius, *Talanta*, **1998**, 47, 1191.
 11. D. Yuan, X. Wang, P. Yang, and B. Huang, *Anal. Chim. Acta*, **1991**, 243, 65.
 12. H. Kondo, A. Ono, T. Uemura, and T. Minami, *Bunseki Kagaku*, **1996**, 45, 8777.
 13. H. Kondo, M. Aimoto, A. Ono, and K. Chiba, *Anal. Chim. Acta*, **1999**, 394, 293.
 14. M. Aimoto, H. Kondo, and A. Ono, *Tetsu to Hagane*, **2007**, 93, 100.
 15. T. Tanaka, K. Shitan, and H. Kondo, *Bunseki Kagaku*, **2001**, 50, 855.
 16. M. Aimoto, H. Kondo, M. Sato, A. Ono, and T. Uemura, in *Proceedings of the Fifth International Conference on Progress in Analytical Chemistry in the Steel and Metals Industries*, ed. R. Tomellini, **1999**, Luxemburg, 623.
-