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Study on the Determination Method of Elemental Silicon and Silicon Dioxide in Calcium-Aluminum-Silicon Alloy

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Abstract: Aiming at the problem that elemental silicon (Si) and silicon dioxide (SiO_2) coexist in calcium--aluminum-silicon alloy and are difficult to directly distinguish and determine, a combined determination scheme of "dilute alkali-weight method+molybdenum blue spectrophotometry" is proposed. Elemental silicon is dissolved by dilute sodium hydroxide solution, while silicon dioxide is insoluble in dilute alkali, and then the two are separated by filtration; the filtrate is acidified, and elemental silicon is determined by weight method+molybdenum blue spectrophotometry; the residue is treated by alkali fusion and acidification, and silicon dioxide is determined again by weight method+molybdenum blue spectrophotometry. the experimental results show that the standard addition recoveries of elemental silicon and silicon dioxide by this method are 99.56%~100.40% and 99.61%~100.08% respectively, and the relative standard deviations (RSD) are all less than 1.40%. It can effectively avoid the interference of aluminum and calcium elements in the matrix, and realize the accurate separation and quantification of the two forms of silicon.

Keywords: Silicon–Aluminum–Calcium Alloy; Elemental Silicon; Silicon Dioxide; Dilute-Alkali Separation; Gravimetry–Molybdenum Blue Spectrophotometry.

1. Introduction

Silicon–aluminum–calcium (Si–Al–Ca) alloys are important composite deoxidizers in iron and steel metallurgy. Their deoxidation efficiency is directly related to the content of elemental silicon, whereas silicon dioxide, as an inert impurity, deteriorates the metallurgical performance of the alloy. Therefore, accurate determination of silicon in these two forms is crucial for alloy quality control.

At present, the determination of total silicon in Si–Al–Ca alloys mainly relies on the potassium fluorosilicate titration method and the perchloric acid dehydration gravimetric method. However, these methods can only quantify total silicon and cannot distinguish between elemental silicon and silicon dioxide. Some studies have attempted to dissolve elemental silicon using dilute acids; nevertheless, dilute acids can readily dissolve silicon–aluminum compounds in the alloy, leading to overestimated results. In contrast, concentrated alkali may cause the slow dissolution of silicon dioxide (forming silicates), resulting in incomplete separation. In this study, dilute alkali was selected as a selective solvent for elemental silicon. Combined with alkali fusion and hydrofluoric acid treatment of the residue, elemental silicon and silicon dioxide were determined using gravimetry coupled with the molybdenum blue spectrophotometric method.

2. Experimental Section

2.1 Experimental Principle

Separation and determination of elemental silicon: Elemental silicon reacts with dilute sodium hydroxide and is converted into soluble silicates, whereas silicon dioxide remains insoluble. the filtrate is acidified, and polyethylene oxide is added to flocculate silicic acid. the precipitate is then filtered, ashed, and ignited, followed by hydrofluoric acid treatment of the residue. the mass difference before and after hydrofluoric acid treatment is taken as the primary gravimetric amount of SiO_2. Subsequently, the remaining residue is volatilized by fusion with a mixed flux and leached with dilute acid. the SiO_2 in the leachate is determined by the molybdenum blue spectrophotometric method; the sum of the two measurements gives the total amount of SiO_2 corresponding to elemental silicon converted to SiO_2. Finally, this value is converted to the elemental silicon content.

Separation and determination of silicon dioxide:

After separation of the alkali-insoluble fraction, the residue is fused with a mixed flux. Polyethylene oxide is added to the filtrate to flocculate and precipitate silicic acid, which is then filtered, ashed, and ignited, followed by hydrofluoric acid treatment of the residue. the mass difference before and after hydrofluoric acid treatment is taken as the primary gravimetric amount of SiO_2. the remaining residue is further volatilized by fusion with a mixed flux and leached with dilute acid. the SiO_2 in the leachate is determined by the molybdenum blue spectrophotometric method; the sum of the two measurements corresponds to the SiO_2 content.

2.2 Principal Reagents and Instruments

2.2.1 Reagents

2.1.1 sodium hydroxide solution:50g/L.

2.1.2 hydrochloric acid:ρ=1.19g/mL.

2.1.3 polyethylene oxide solution:1.0g/L, valid for two weeks.

2.1.4 silver nitrate solution:10g/L.

2.1.5 sulfuric acid:ρ=1.42g/mL.

2.1.6 hydrofluoric acid:ρ=1.15g/mL.

2.1.7 Mixed flux: two parts anhydrous sodium carbonate and one part boric acid, finely ground and thoroughly mixed.

2.1.8 Hydrochloric acid (1+1).

2.1.9 Hydrochloric acid (1+4).

2.1.10 Hydrochloric acid (1+14).

2.1.11 Ammonium molybdate solution:60 g/L.

2.1.12 Oxalic acid–sulfuric acid mixed acid: Weigh 35 g of oxalic acid and dissolve it in 1000 mL of sulfuric acid (1+8).

2.1.13 Ammonium ferrous sulfate solution:60 g/L.

2.1.14 Silicon dioxide standard stock solution: 1.00 mL contains 50 μg/mL SiO_2.

2.2.2 Instruments

2.2.1 Electronic analytical balance: readability 0.1 mg.

2.2.2 Programmable muffle furnace: temperature controllable to 1000 °C ± 5 °C.

2.2.3 Platinum crucible:30–40 mL.

2.2.4 Spectrophotometer.

2.2.3 Experimental Procedure

2.2.3.1 Sample Preparation

Accurately weigh 0.200 g of the sample (to 0.0001 g) into a 250 mL plastic beaker. Add 40 mL of dilute sodium hydroxide solution, cover with a watch glass, and digest in a 100 °C water bath for 1 h. Filter through a medium-speed quantitative filter paper, and rinse the filter paper and residue with hot water until neutral. Retain the residue and the filter paper; transfer the residue to a platinum crucible and ash at low temperature (for determination of SiO_2 in the sample).

2.2.3.2 Determination of Elemental Silicon

2.3.2.1 Acidify the filtrate with 15 mL of hydrochloric acid and evaporate to complete dryness on an electric hot plate. Remove and allow to cool, then add 10 mL of hydrochloric acid and 10 mL of polyethylene oxide solution. Rinse the inner wall of the beaker with hot water, stir thoroughly, and rinse the beaker wall and glass rod again with hot water. Maintain at low temperature for 10 min to ensure complete dissolution of soluble salts, and filter through a slow-speed quantitative filter paper. Collect the filtrate in a 250 mL volumetric flask, and wash the precipitate with hot water until chloride ions are no longer detected (checked with silver nitrate solution).

2.3.2.2 Transfer the precipitate to a platinum crucible. After low-temperature ashing, ignite in a high-temperature furnace at 1000 °C for 1 h. Remove and weigh. Repeat the ignition and weighing until constant mass is obtained (m1). Moisten the ignited precipitate with a small amount of water, add 2 drops of sulfuric acid and 5 mL of hydrofluoric acid, and evaporate at low temperature until sulfuric acid fumes appear. Remove and allow to cool slightly, then add 3 mL of hydrofluoric acid and continue evaporation until sulfuric acid fumes are completely expelled. Subsequently, ignite at 1000 °C for 30 min, remove, and weigh. Repeat until constant mass is obtained (m2).

2.3.2.3 Add approximately 1 g of the mixed flux to the ignited platinum crucible and fuse at 1000 °C for 5 min. Remove, cool, and leach with 5 mL of hydrochloric acid (1+1). Combine the leachate into the volumetric flask containing the original filtrate (V).

2.3.2.4 Pipette 10.00 mL (V1) of the test solution into a 100 mL volumetric flask. Add 8 mL of anhydrous ethanol and 8 mL of hydrochloric acid (1+14), dilute with water to approximately 50 mL, and add 5 mL of ammonium molybdate solution. Allow to stand at room temperature for 20 min, then add 20 mL of the oxalic acid–sulfuric acid mixed acid and stand for 1 min. Add 5 mL of ammonium ferrous sulfate solution, dilute to volume with water, and mix well. Measure the absorbance at 680 nm using a spectrophotometer with a 10 mm cuvette, using the blank solution as the reference. Determine the corresponding amount of SiO_2 (m3) from the calibration curve.

2.2.3.3 Determination of Silicon Dioxide

2.3.3.1 Transfer the filter paper and residue obtained after digestion with sodium hydroxide solution and filtration into a platinum crucible. Ash, then add approximately 1 g of the mixed flux and fuse in a high-temperature furnace at 1000 °C for 10 min. Remove and allow to cool.

2.3.3.2 Leach the fused melt by heating with 100 mL of hydrochloric acid (1+4). Heat at low temperature and evaporate to complete dryness. After cooling, add 10 mL of hydrochloric acid and 10 mL of polyethylene oxide solution. Rinse the inner wall of the beaker with hot water, stir thoroughly, then rinse the beaker wall and glass rod again with hot water. Maintain at low temperature for 10 min to ensure complete dissolution of soluble salts, and filter through a slow-speed quantitative filter paper. Collect the filtrate in a 250 mL volumetric flask, and wash the precipitate with hot water until chloride ions are no longer detected (checked with silver nitrate solution). Thereafter, proceed according to Sections 2.3. 2.2–2.3. 2.4.

2.2.3.4 Preparation of Working Calibration Curve

Pipette 0, 1.00, 2.00, 4.00, 6.00, 8.00, and 10.00 mL aliquots of the SiO_2 standard solution into separate 100 mL volumetric flasks, and then proceed according to Section 2.3. 2.4. Measure the absorbance with the reagent blank as the reference and construct the working (calibration) curve.

2.2.3.5 Result Calculation

2.3.5.1 Calculation of Elemental Silicon

$$Si(\%) = \frac{\mathrm{m}_1 - m_2 + m_3 \times V/V_1}{m} \times 0.4674 \times 100$$

2.3.5.2 Calculation of Silicon Dioxide

$$SiO_2(\%) = \frac{\mathrm{m}_1 - m_2 + m_3 \times V/V_1}{m} \times 100$$

Where:

m -- Sample mass, unit (g);

0.4674—Conversion factor between silicon dioxide and elemental silicon.

3. Results and Discussion

3.1 Optimization of Dilute Alkali Separation Conditions

3.1.1 Selection of Sodium Hydroxide Concentration

With a fixed sample mass of 0.2000 g and a reaction time of 60 min, the dissolution of elemental silicon was investigated at different sodium hydroxide concentrations (20, 30, 50, 70, and 100 g/L). the results showed that (i) at concentrations below 30 g/L, elemental silicon dissolved slowly, with dissolution rates below 90%; (ii) at 50 g/L, the dissolution reached 99.9% and no appreciable dissolution of silica was observed; and (iii) at concentrations above 70 g/L, partial dissolution of silica occurred, leading to unsuccessful separation. Therefore, a 50 g/L sodium hydroxide solution was selected as the separation reagent.

3.1.2 Reaction Time Optimization

With the sample mass fixed at 0.2000 g and the sodium hydroxide concentration set to 50 g/L, the effect of reaction time (20, 40, 60, and 90 min) on the dissolution of elemental silicon was investigated. the results indicated that when the reaction time was shorter than 40 min, the dissolution rate of elemental silicon was approximately 95.0%. At 60 min, the dissolution rate stabilized at above 99.9%. Extending the reaction time to 90 min did not further improve dissolution (remaining at 99.9%); however, it increased the dissolution of aluminum and calcium, resulting in the formation of $Al(OH)_3$ and $Ca(OH)_2$ precipitates that interfered with subsequent filtration. Therefore, a reaction time of 60 min was selected.

3.2 Interference Test

Interference of the major matrix elements Al and Ca on silicon determination in Si–Al–Ca alloys: Different concentrations of Al^{3+} (0–400 μg/mL) and Ca^{2+} (0–300 μg/mL) were added to a silicon standard solution (50 μg/mL), and the absorbance was measured according to the experimental procedure. the results showed that when $Al^{3+} \leqslant 400$ μg/mL and $Ca^{2+} \leqslant 300$ μg/mL, the recovery of silicon ranged from 97.8% to 102.2%, indicating that the matrix elements exert no significant interference on the molybdenum blue spectrophotometric method and that no additional masking agent is required..

3.3 Validation Tests

3.3.1 Preparation of Homemade Standard Samples

High-purity silicon powder, high-purity aluminum powder, and analytical-grade calcium carbonate were dried at 105 °C for 30 min. After cooling, three standard samples were prepared by weighing the high-purity silicon powder, high-purity aluminum powder, and calcium carbonate according to the target component ratios (Si/Al/Ca). the mixtures were ground (particle size < 0.074 mm), homogenized thoroughly, and sealed for subsequent use.

3.3.2 Uniformity and Accuracy

Six replicate determinations were performed for each of the three self-prepared Si–Al–Ca standard samples (B1–B3). the results are shown in Table 1.

Table 1. Homogeneity and Accuracy

Sample ID	Self-prepared value	Analytical result		
	Si(%)	Si(%)	RE(%)	RSD(%)
B1	20.00	20.03	0.15	0.97
B2	45.00	45.14	0.31	1.13
B3	70.00	70.11	0.16	1.13

As shown in Table 1, the relative errors (RE) of the self-prepared Si–Al–Ca standard samples were all below 0.40%, and the relative standard deviations (RSDs) were all below 1.20%, meeting the analytical requirements.

3.3.3 Precision and Spiked Recovery

Six replicate determinations were performed for each of the four Si–Al–Ca samples (S1–S4), and spike-recovery tests were conducted using high-purity silicon powder and high-purity silicon dioxide. the results are shown in Table 2.

Table 2. Precision and Spike-Recovery Results

Sample ID	Si(%)	RSD(%)	Si spike recovery (%)	SiO_2(%)	RSD(%)	SiO_2 spike recovery(%)
S1	43.63	1.20	99.72	2.91	1.16	99.61
S2	22.13	0.98	100.40	44.99	0.95	100.08
S3	18.91	1.29	99.56	48.10	1.31	99.83
S4	25.00	1.05	99.88	42.68	1.10	99.75

As shown in Table 1, the RSDs of this method were all below 1.40%, and the spike recoveries ranged from 99.56% to 100.08%, meeting the requirements for precision and accuracy in industrial analysis.

4. Conclusion

The proposed method—selective dissolution with dilute alkali combined with gravimetry and molybdenum blue spectrophotometry—enables effective separation and determination of elemental silicon and silicon dioxide in Si–Al–Ca alloys, thereby overcoming the limitation of conventional methods that cannot differentiate between silicon species;

The optimum conditions were 50 g/L sodium hydroxide solution and a 60 min digestion reaction. Under these conditions, the separation efficiency was high, matrix interference was minimal, and both precision and accuracy met the analytical requirements;

The method does not require expensive instrumentation and features low reagent cost and ease of operation, making it a preferred analytical approach for routine quality control in Si–Al–Ca alloy manufacturing enterprises and steel plants.

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