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Methods for chemical analysis of silicon**-**based composite rare earth ferroalloy and RE**-**Mg ferrosilicon alloy

Part 1: Determination of total rare earth and fifteen rare earth elements contents

*（English Translation）*

稀土硅铁合金及镁硅铁合金化学分析方法

第1部分：稀土总量、十五个稀土元素含量的测定

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Foreword

SAC/TC 229 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritative.

This standard is drafted in accordance with the rules given in the GB/T 1.1—2020 *Directives for standardization—Part 1: Rules for the structure and drafting of standardizing documents*.

This document is Part 1 of GB/T 16477 *(Methods for chemical analysis of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy), GB/T 16477* consists of the following 5 parts under the general title:

*——Part 1:* *Determination of total rare earth and fifteen rare earth elements contents*;

*——Part 2:* *Determination of calcium, magnesium and manganese contents-Inductively coupled plasma atomic emission spectrometry*;

*——Part 3:* *Determination of magnesia content-Inductively coupled plasma atomic emission spectrometry*;

*——Part 4:* *Determination of silicon content;*

*——Part 5:* *Determination of titanium content-Inductively coupled plasma atomic emission spectrometry*.

This standard replaces the GB/T 16477.1-2010 *(Chemical analysis methods of rare earth ferrosilicon alloy and rare earth ferrosilicon magnesium alloy: part 1 Determination of total rare earth content)* in whole*.*

In addition to some structural adjustment and editorial revises, the following technical deviations have been made with respect to the GB/T 16477.1-2010:

a) Changed the determination range of the total rare earth content in method 1 from 0.50% - 6.00% to 0.50% - 10.00% (see clause 1, and clause 1 in version 2010);

b) Changed the determination range of the total rare earth content in method 2 from 2.00% - 42.00% to 10.00% - 40.00% (see clause 1, and clause 10 in version 2010);

c) Added the determination range of fifteen rare earth elements content in methods 1 and 2 (see clause 1);

d) Added "normative reference documents" (see clause 2);

e) Added "Terms and definitions" (see clause 3);

f) Changed the sample weighing of method 1 (see 4.5.1, and 6.1 in version 2010);

g) Changed the preparation way of analytical test solutionn in method 1 (see 4.5.4, and 6.4 in version 2010);

h) Changed some recommended analytical lines (see 4.6.1, 5.6.1, and 6.6.1 in version 2010);

i) Added the calculation formula of fifteen rare earth elements content in method 1 (see 4.7.1);

j) Changed the calculation formula of the total rare earth content in method 1 (see 4.7.2, and clause 7 in version 2010);

k) Changed the sample weighing of method 2 (see 5.5.1, and 14.1 in version 2010);

l) Changed the preparation way of analytical test solution in method 2 (see 5.5.4, and 14.3 in version 2010);

m) Changed the calculation formulas of the total rare earth content in method 2 (see 5.7.1, and clause 15 in version 2010);

n) Added the calculation formula of fifteen rare earth elements content in method 2 (see 5.7.2);

o) Changed "Precision" (see 4.8,5.8, clause 8 and 16 in version 2010);

p) Deleted "Quality assurance and control" (see clause 17 in version 2010).

Attention is drawn to the possibility that some of the elements of this standard may be the subject of patent rights. The issuing body of this document shall not be held responsible for identifying any or all such patent rights.

This standard was proposed and prepared by the SAC/TC 229（*China Rare Earth Standardization Technical Committee*）.

The previous editions of this document are as follows:

——The first edition was issued in 1996 as GB/T 16477.1—1996；

——The first revision was issued in 2010;

——This is the second revised edition.

Introduction

Silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy are important rare earth alloy products. The rare earths in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy products play a role in refining, desulfurizing, and neutralizing harmful impurities with low melting points. Silicon-based composite rare earth ferroalloy has been widely used in the iron and steel industry, it is the basic material for the production of nodularizing agent, vermicularizing agent and inoculant. It is mainly used to remove harmful impurity elements (O, S, N, As, etc.) in iron and steel smelting, and used as additives and alloying agents in the production of iron and steel. RE-Mg ferrosilicon alloy is a good inoculant, creeping agent and modifier, it has strong deoxidation and desulfurization effects. Chemical composition is an important assessment indicator for rare earth ferroalloy products. Scientific and accurate standards for chemical composition analysis methods can enhance the consistency of data between different laboratories by clarifying the scope of application, standardizing reagents and materials, test equipment and procedures, and providing precision data after repeated tests and verifications. It provides rigorous and standardized technical means for quality inspection of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy products, and is conducive to promoting the production and trade of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy products.

This series of standards GB/T 16477 (*Methods for chemical analysis of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy*) consists of 5 parts.

*——Part 1:* *Determination of total rare earth and fifteen rare earth elements contents*;

*——Part 2:* *Determination of calcium, magnesium and manganese contents-Inductively coupled plasma atomic emission spectrometry*;

*——Part 3:* *Determination of magnesia content-Inductively coupled plasma atomic emission spectrometry*;

*——Part 4:* *Determination of silicon content;*

*——Part 5:* *Determination of titanium content-Inductively coupled plasma atomic emission spectrometry*.

The total rare earth content and the content of related rare earth elements in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy products must comply with product standards during transactions. The product standards for silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy were revised in 2023, and its various technical indicators have undergone new changes. On the basis of Ce-group and Y-group rare earth-contained ferrosilicon alloy and ferrosilicon magnesium alloy, La-group has been added. In view of this, it is indeed necessary to revise GB/T 16477.1-2010 to ensure that the standard adapts to industry changes and market needs.

This document adds product testing for Y-group rare earth-contained ferrosilicon alloy and ferrosilicon magnesium alloy, and separately tests the content of fifteen rare earth elements, which is more in line with the industry's actual needs for product testing. This document further improves the applicability of the standard and is of great significance in improving the quality of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy products, promoting their production, trade and expanding application demand.

Methods for chemical analysis of silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy—

Part 1：Determination of total rare earth and fifteen rare earth elements contents

WARNING—Personnel using this document should be familiar with practical experience in routine laboratory work. This document does not identify all possible security issues. Users should have certain professional knowledge or skills and be fully aware that improper operation may cause gas leakage, current leakage, fire or other serious consequences.

1.　Scope

This document specifies the methods for determination of total rare earth and fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy.

This document is applicable to the determination of total rare earth and fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy, including inductively coupled plasma atomic emission spectrometry (Method 1) and EDTA titration method(Method 2). The determination range of method 1 is shown in Table 1. The measurement range of method 2 is shown in Table 2.

Table 1: Determination range of method 1

|  |  |  |  |
| --- | --- | --- | --- |
| Determination of elements | Mass fraction% | Determination of elements | Mass fraction% |
| La | 0.030～10.00 | Dy | 0.030～0.50 |
| Ce | 0.030～10.00 | Ho | 0.030～0.50 |
| Pr | 0.030～0.50 | Er | 0.030～0.50 |
| Nd | 0.030～0.50 | Tm | 0.030～0.50 |
| Sm | 0.030～0.50 | Yb | 0.030～0.50 |
| Eu | 0.030～0.50 | Lu | 0.030～0.50 |
| Gd | 0.030～0.50 | Y | 0.030～10.00 |
| Tb | 0.030～0.50 | Total rare earth | 0.50～10.00 |

Table 2: Determination range of method 2

|  |  |  |  |
| --- | --- | --- | --- |
| Determination of elements | Mass fraction% | Determination of elements | Mass fraction% |
| La | 0.050～40.00 | Dy | 0.050～2.00 |
| Ce | 0.050～40.00 | Ho | 0.050～2.00 |
| Pr | 0.050～2.00 | Er | 0.050～2.00 |
| Nd | 0.050～2.00 | Tm | 0.050～2.00 |
| Sm | 0.050～2.00 | Yb | 0.050～2.00 |
| Eu | 0.050～2.00 | Lu | 0.050～2.00 |
| Gd | 0.050～2.00 | Y | 0.050～40.00 |
| Tb | 0.050～2.00 | Total rare earth | 10.00～40.00 |

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute indispensable provisions of this document. For dated references, only the dated edition is applicable to this document. For undated references, the latest edition of the normative document (including any amendments) applies.

GB/T 6379.2 *Accuracy(trueness and precision)of measurement methods and results--Part 2:Basic method for the determination of repeatability and reproducibility of a standard measurement method*

GB/T 6682 *Water for analytical laboratory use - Specification and test methods*

GB/T 8170 *Rules of rounding off for numerical values & expression and judgement of limiting values*

JJG 768 *Verification Regulation of Emission Spectrometer*

3 Terms and definitions

This document does not require any specific terms or definitions.

4.　Method 1:Inductively coupled plasma atomic emission spectrometry.

4.1　 Method summary

After the test portion is decomposed by nitric acid and hydrofluoric acid, the rare earths are precipitated and separated from iron, add perchloric acid to smoke and hydrochloric acid to decompose the rare earth fluoride. Add ammonia to precipitate rare earths to separate magnesium, calcium and other impurity elements. The mass concentration of fifteen rare earth elements are directly determined with an inductively coupled plasma atomic emission spectrometer in dilute hydrochloric acid medium, and the sum of the mass fractions of fifteen rare earth elements are the total rare earth content.

4.2　Reagents or materials

Unless otherwise stated, only reagents confirmed to be of analytical grade or above and secondary water complying with GB/T 6682 are used in the analysis. Liquid reagents are stored in plastic bottles, and certified standard solutions are preferred.

4.2.1　 Lanthanum oxide *w*(REO) ≥ 99.5%, *w*(La2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.2　 Cerium oxide *w*(REO) ≥ 99.5%, *w*(CeO2/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.3　 Praseodymium oxide *w*(REO) ≥ 99.5%, *w*(Pr6O11/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.4　 Neodymium oxide *w*(REO) ≥ 99.5%, *w*(Nd2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.5　 Samarium Oxide *w*(REO) ≥ 99.5%, *w*(Sm2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.6　 Europium oxide *w*(REO) ≥ 99.5%, *w*(Eu2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.7　 Gadolinium Oxide *w*(REO) ≥ 99.5%, *w*(Gd2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.8　 Terbium oxide *w*(REO) ≥ 99.5%, *w*(Tb4O7/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.9　 Dysprosium Oxide *w*(REO) ≥ 99.5%, *w*(Dy2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.10　 Holmium oxide *w*(REO) ≥ 99.5%, *w*(Ho2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.11　 Erbium Oxide *w*(REO) ≥ 99.5%, *w*(Er2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.12　 Thulium oxide *w*(REO) ≥ 99.5%, *w*(Tm2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.13　 Ytterbium oxide *w*(REO) ≥ 99.5%, *w*(Yb2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.14　 Lutetium Oxide *w*(REO) ≥ 99.5%, *w*(Lu2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.15　 Yttrium oxide *w*(REO) ≥ 99.5%, *w*(Y2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

4.2.16　 Hydrogen peroxide [*w*(H2O2) ≥ 30%].

4.2.17　 Nitric acid (ρ=1.42 g/mL).

4.2.18　 Hydrofluoric acid (ρ = 1.15 g/mL).

4.2.19　 Perchloric acid (ρ = 1.66 g/mL).

4.2.20　 Ammonia (ρ = 0.90 g/mL).

4.2.21　 Nitric acid, diluted （1+1）.

4.2.22　 Hydrochloric acid, diluted （1+1）.

4.2.23　 Hydrofluoric acid wash solution: 100 mL of water contains 2 mL of hydrofluoric acid (4.2.18).

4.2.24　 Ammonium chloride-ammonia wash solution: 100 mL of water contains 2 g of ammonium chloride and 2 mL of ammonia (4.2.20).

4.2.25　 Hydrochloric acid wash solution: 100 mL of water contains 4 mL of hydrochloric acid (4.2.22).

4.2.26　 Lanthanum standard stock solution, Dissolve 0.234 6 g of lanthanum oxide （4.2.1） in 10 mL of hydrochloric acid （4.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of lanthanum.

4.2.27　 Cerium standard stock solution, Dissolve 0.245 7 g of cerium oxide （4.2.2） in 20 mL of nitric acid （4.2.21）and a small amount of hydrogen peroxide (4.2.16) into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of cerium.

4.2.28　 Praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution， Dissolve 0.241 6 g of praseodymium oxide (4.2.3), 0.233 3 g of neodymium oxide (4.2.4), 0.231 9 g of samarium oxide (4.2.5), 0.231 6 g of europium oxide (4.2.6), 0.230 5 g of Gadolinium oxide, (4.2.7), 0.235 3 g of terbium oxide (4.2.8), 0.229 6 g of dysprosium oxide (4.2.9), 0.229 1 g of holmium oxide (4.2.10), 0.228 7 g of erbium oxide (4.2.11) , 0.228 4 g of thulium oxide (4.2.12), 0.227 8 g of ytterbium oxide (4.2.13), 0.227 5 g lutetium oxide of (4.2.14) in 60 mL of nitric acid （4.2.21） into a 200 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg each of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

4.2.29　 Yttrium standard stock solution， Dissolve 0.254 0 g of yttrium oxide （4.2.15） in 10 mL of hydrochloric acid （4.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of yttrium.

4.2.30　 Standard stock solution for blank test, Transfer 2.00 mL of lanthanum standard stock solution (4.2.26), 2.00 mL of cerium standard stock solution (4.2.27), 2.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28), 2.00 mL of yttrium standard stock solution (4.2.29) and 10 mL of hydrochloric acid （4.2.22） into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 10.00 μg of fifteen individual rare earth.

4.2.31　 Standard stock solution I, Dissolve 1.154 0 g of lanthanum oxide （4.2.1） in 10 mL of hydrochloric acid （4.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of cerium standard stock solution (4.2.27), 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) and 2.00 mL of yttrium standard stock solution (4.2.29) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.32　 Standard stock solution II, Dissolve 1.208 8 g of cerium oxide （4.2.2） in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of lanthanum standard stock solution (4.2.26), 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) and 2.00 mL of yttrium standard stock solution (4.2.29) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.33　 Standard stock solution III, Dissolve 1.249 7 g of yttrium oxide (4.2.15) in 10 mL of hydrochloric acid （4.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of lanthanum standard stock solution (4.2.26), 2.00 mL of cerium standard stock solution (4.2.27), and 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. The individual rare earth content is shown in Table 3.

4.2.34　 Standard stock solution IV, Dissolve 0.851 4 g of lanthanum oxide (4.2.1), 0.184 3 g of cerium oxide (4.2.2), 0.184 3 g of yttrium oxide (4.2.15) in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.35　 Standard stock solution V, Dissolve 0.527 8 g of lanthanum oxide (4.2.1), 0.061 5 g of cerium oxide (4.2.2), 0.558 9 g of yttrium oxide (4.2.15) in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 5.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.36　 Standard stock solution VI, Dissolve 0.058 7 g of lanthanum oxide (4.2.1), 1.041 5 g of yttrium oxide (4.2.15) in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 10.00 mL of cerium standard stock solution (4.2.27), 10.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.37　 Standard stock solution VII, Dissolve 0.859 9 g of cerium oxide (4.2.2), 0.063 5 g of yttrium oxide (4.2.15) in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 10.00 mL of lanthanum standard stock solution (4.2.26), 20.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

4.2.38　 Standard stock solution VIII, Dissolve 0.117 3 g of lanthanum oxide (4.2.1), 0.503 7 g of cerium oxide (4.2.2) in 10 mL of nitric acid （4.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 25.00 mL of cerium standard stock solution (4.2.27), 40.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (4.2.28), and 10.00 mL of yttrium standard stock solution (4.2.29) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 3.

Table 3: Each of individual rare earth content in standard stock solutions I to VIII

 In ug/mL

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| number | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb |
| Ⅰ | 492 0 | 10 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅱ | 10 | 492 0 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅲ | 10 | 10 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅳ | 363 0 | 750 | 10 | 10 | 10 | 10 | 10 | 10 |
| Ⅴ | 225 0 | 250 | 25 | 25 | 25 | 25 | 25 | 25 |
| Ⅵ | 250 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| Ⅶ | 50 | 350 0 | 100 | 100 | 100 | 100 | 100 | 100 |
| Ⅷ | 500 | 205 0 | 200 | 200 | 200 | 200 | 200 | 200 |
| number | Dy | Ho | Er | Tm | Yb | Lu | Y | — |
| Ⅰ | 5 | 5 | 5 | 5 | 5 | 5 | 10 | — |
| Ⅱ | 5 | 5 | 5 | 5 | 5 | 5 | 10 | — |
| Ⅲ | 5 | 5 | 5 | 5 | 5 | 5 | 492 0 | — |
| Ⅳ | 10 | 10 | 10 | 10 | 10 | 10 | 500 | — |
| Ⅴ | 25 | 25 | 25 | 25 | 25 | 25 | 220 0 | — |
| Ⅵ | 50 | 50 | 50 | 50 | 50 | 50 | 410 0 | — |
| Ⅶ | 100 | 100 | 100 | 100 | 100 | 100 | 250 | — |
| Ⅷ | 200 | 200 | 200 | 200 | 200 | 200 | 50 | — |

4.2.38　 Argon, φ(Ar)>99.99%.

4.3　Apparatus

4.3.1　 Inductively coupled plasma atomic emission spectrometer. Under the best working conditions of the apparatus, any apparatus that meets the following indicators can be used:

——Resolution is less than 0.006 nm, wavelength range is 160 nm ～ 500 nm;

——Shall be in accordance with verification regulation of emission spectrometer and technical indicators required in JJG 768.

4.3.2　 The recommended analysis lines for each element are shown in Table 4.

Table 4: Analysis lines

 In nm

|  |  |  |  |
| --- | --- | --- | --- |
| Determination of elements | Analysis lines | Determination of elements | Analysis lines |
| La | 408.671、398.852 | Dy | 353.170 |
| Ce | 418.660、446.021 | Ho | 345.600 |
| Pr | 405.654、422.532 | Er | 369.265 |
| Nd | 410.946 | Tm | 313.125 |
| Sm | 359.259 | Yb | 328.937 |
| Eu | 381.965 | Lu | 261.542 |
| Gd | 310.050 | Y | 377.433 |
| Tb | 350.914 | — | — |

4.4　 Sample

The alloy sample are made into powder sample and passed through a 0.125 mm sieve.

4.5　 Procedure

4.5.1　 Test portion

Weigh out the sample (4.4) according to Table 5, accurate to 0.000 1 g.

Table 5: Weighing amount of sample

|  |  |  |  |
| --- | --- | --- | --- |
| Mass fraction% | Test portion g | Constant volumemL | Volume of hydrochloric acid（4.2.22）mL |
| 0.50～1.00 | 1.00 | 100 | 10 |
| >1.00～2.00 | 0.50 | 100 | 10 |
| >2.00～4.00 | 0.25 | 100 | 10 |
| >4.00～8.00 | 0.25 | 200 | 20 |
| >8.00～10.00 | 0.25 | 250 | 25 |

4.5.2　 Parallel determination

Carry out two tests in parallel.

4.5.3　 Blank test

Carry out a blank test along with the test portion(4.5.1).

4.5.4　 Preparation of analytical test solution

4.5.4.1　 Put the test portion (4.5.1) in a 200 mL polytetrafluoroethylene beaker, slowly add 5 mL of nitric acid (4.2.17), 5 mL of hydrofluoric acid (4.2.18), and 0.5 mL of hydrogen peroxide ( 4.2.16). Purge the cup wall with about 10 mL of water and heating it at 130 °C to 190 °C for 30 minutes, then add 5 mL of nitric acid (4.2.17), 5 mL of hydrofluoric acid (4.2.18), and 0.5 mL of hydrogen peroxide (4.2.16). After heating for 30 minutes, take down, add 5 mL of hydrofluoric acid (4.2.18) and continue heating 30 minutes. Add 15 mL of hydrofluoric acid (4.2.18) and about 30 mL water and boil it, then keep it warm in a water bath at 80°C to 90 °C for 60 minutes. Remove and cool slightly, filter in a plastic funnel with slow quantitative filter paper, wash the beaker 3 or 4 times and the filter paper 8 or 10 times with hydrofluoric acid washing solution (4.2.23).

4.5.4.2　 Put the filter paper and precipitate into a 300 mL beaker, add 20 mL of nitric acid (4.2.17), 5 mL of perchloric acid (4.2.19), cover with a watch glass, then heat to destroy the filter paper and dissolve the precipitate. Evaporate with thick smoke until the solution evaporates to a volume of about 2 mL to 3 mL, take it out and cool slightly. Add 5 mL of hydrochloric acid (4.2.22), 2 drops of hydrogen peroxide (4.2.16), and heat until complete dissolution, then add about 50 mL water and heat until nearly boiling. Add ammonia water (4.2.20) dropwise while stirring until precipitation just appears, then slowly add 0.1 mL of hydrogen peroxide (4.2.16) and 20 mL of ammonia water (4.2.20) while stirring. Use a small amount of water to rinse beaker wall and bring to a boil. Remove and filter with medium-speed quantitative filter paper while it is hot, wash the beaker 2 to 3 times with ammonium chloride-ammonia washing solution (4.2.24), and precipitate 6 to 7 times.

4.5.4.3　 Collect the filtrate in a beaker, wash the precipitate in the beaker with hot hydrochloric acid (4.2.22), wash the beaker and filter paper with hydrochloric acid washing solution (4.2.25) until there is no yellow color, and steam the solution until it is almost dry. Add hydrochloric acid (4.2.22) according to Table 5, transfer to the corresponding volumetric flask when cooling to room temperature, dilute to volume with water and mix well, wait for testing.

4.5.5　 Preparation of series standard solutions

4.5.5.1　 Preparation of series standard solutions for blank test

Transfer 0 mL, 1.00 mL, 5.00 mL and 10.00 mL of the standard stock solution for blank test (4.2.30) into four 100 mL of volumetric flasks respectively, add 10 mL hydrochloric acid (4.2.22) and dilute to volume with water and mix well. The concentration of series standard solutions for blank test are as follows: 0 μg/mL, 0.10 μg/mL, 0.50 μg/mL, and 1.00 μg/mL.

4.5.5.2　 Preparation of series standard solutions for analytical test

Transfer 2.00 mL each of standard stock solutions I to VIII (4.2.31 ～ 4.2.38) into eight 100 mL of volumetric flasks, add 10 mL of hydrochloric acid (4.2.22) respectively, dilute to volume with water and mix well. The concentration of series standard solutions are shown in Table 6. According to the main rare earth element of the sample, six standard points are selected as series standard solutions.

Table 6: Each rare earth concentration of series standard solutions

 In μg/mL

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| standard sequence | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb |
| 1 | 98.4 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 2 | 0.2 | 98.4 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 4 | 72.6 | 15 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 5 | 45 | 5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 6 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 7 | 1 | 70 | 2 | 2 | 2 | 2 | 2 | 2 |
| 8 | 10 | 41 | 4 | 4 | 4 | 4 | 4 | 4 |
| standard sequence | Dy | Ho | Er | Tm | Yb | Lu | Y | — |
| 1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | — |
| 2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | — |
| 3 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 98.4 | — |
| 4 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 10 | — |
| 5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 44 | — |
| 6 | 1 | 1 | 1 | 1 | 1 | 1 | 82 | — |
| 7 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | — |
| 8 | 4 | 4 | 4 | 4 | 4 | 4 | 1 | — |

4.6　 Determination

4.6.1　 Drawing of standard curve for analytical tests

After the inductively coupled plasma emission spectrometer is running stably, determin the emission intensity of each rare earth element in the series standard solutions (4.5.5.2) in sequence under the selected apparatus working conditions, and use the apparatus software to draw a standard working curve. The correlation coefficient of the standard curve of each element should be great than 0.999.

4.6.2　 Determination of analytical test solution

After the standard curve meets the determination requirements, determine the emission intensity of each rare earth element in the analytical test solution (4.5.4) immediately. The apparatus processes the data automatically that based on the standard curve(4.6.1), calculates and outputs the mass concentration of each rare earth element in the analytical test solution.

4.6.3　 Drawing of standard curve for blank test

After the inductively coupled plasma emission spectrometer is running stably, determin the emission intensity of each rare earth element in the series standard solutions for blank test (4.5.5.1) in sequence under the selected apparatus working conditions, and use the apparatus software to draw a standard working curve. The correlation coefficient of the standard curve of each element should be above 0.999, otherwise it needs to be re-standardized or the standard solution needs to be prepared again for standardization.

4.6.4　 Determination of blank test solution

After the standard curve of the blank test (4.6.3) meets the determination requirements, determine the emission intensity of each rare earth element in the blank test solution (4.5.3) immediately. The apparatus processes the data automatically that based on the standard curve (4.6.3), calculates and outputs the mass concentration of each rare earth element in the blank test solution.

4.7　 Test data processing

4.7.1　 Test data processing of fifteen rare earth elements content

The content of fifteen rare earth elements is expressed as mass fraction (*w*x), calculated according to formula (1):

……………………………………（1）

Where:

*ρ1*——Mass concentration of individual rare earth in the analysis test solution, which is obtained from the standard curve,, in micrograms per milliliter （μg/mL）;

*ρ0*——Mass concentration of individual rare earth in the blank test solution, which is obtained from the standard curve, in micrograms per milliliter （μg/mL）;

*V2*——Volume of the test solution, in mililiter （mL）;

*V0*——Total volume of the test solution, in mililiter （mL）;

*m1*——Mass of the test portion, in grams （g）;

*V1*——Dispensed volume of the test portion, in mililiter （mL）.

When the absolute difference between two parallel determination results is not greater than the corresponding repeatability limit in Table 8, the average value shall be taken as the determination result. When the result is less than 1.00%, the calculation result shall retain two significant figures. When the result is greater than or equal to 1.00%, the calculation results are kept to two decimal places, and numerical rounding is performed in accordance with the provisions of GB/T 8170.

4.7.2　 Test data processing of total rare earth

Total rare earth are expressed as mass fraction (*w*RE), calculated according to formula (2):

……………………………………………（2）

When the absolute difference between two parallel determination results is not greater than the corresponding repeatability limit in Table 7, the average value shall be taken as the determination result. When the result is less than 1.00%, the calculation result shall retain two significant figures. When the result is greater than or equal to 1.00%, The calculation results are kept to two decimal places, and numerical rounding is performed in accordance with the provisions of GB/T 8170.

4.8　 Precision

4.8.1　 Raw precision data and statistics

The precision data were counted in 2023 by eight laboratories conducting collaborative tests on 11 different levels of samples of the total rare earth and the fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy. Each laboratory independently determined each level of the total rare earth and fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy 11 times under repeatability conditions. The test data is statistically analyzed according to GB/T 6379.2.

4.8.2　 Repeatability

The absolute difference of the determined values obtained from two independent determinations under the repeatability conditions， is not greater than the repeatability limits (*r*), which is in the range of the following average values in Table 7 and Table 8. The cases that the absolute difference is greater than the repeatability limits (*r*) are less than 5%. The repeatability limit (*r*) is calculated by linear interpolation or epitaxy method on the basis of the data listed in Table 7 and Table 8.

Table 7: Repeatability limit for total rare earth content (Method 1)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Mass fraction/% | 0.50 | 1.00 | 1.04 | 2.11 | 5.39 | 9.37 |
| Repeatability limit（*r*）/% | 0.02 | 0.04 | 0.05 | 0.08 | 0.10 | 0.12 |
| Matrix | Y | Y | La | Ce | Ce | Ce |
| Note：The repeatability limit (*r*) is 2.8×S*r*, and S*r* is the standard deviation of the repeatability limit. |

Table 8: Repeatability limit for fifteen rare earth elements content (Method 1)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Determination of elements | Mass fraction% | Repeatability limit*（r）*% | Determination of elements | Mass fraction % | Repeatability limit*（r）*% |
| Y | 0.48 | 0.03 | Tb | 0.040 | 0.003 |
| 0.83 | 0.03 | 0.12 | 0.02 |
| 8.46 | 0.10 | 0.40 | 0.02 |
| La | 0.20 | 0.02 | Dy | 0.041 | 0.003 |
| 1.42 | 0.05 | 0.12 | 0.02 |
| 8.21 | 0.12 | 0.41 | 0.02 |
| Ce | 0.35 | 0.03 | Ho | 0.044 | 0.003 |
| 3.13 | 0.07 | 0.12 | 0.02 |
| 7.12 | 0.07 | 0.41 | 0.02 |
| Pr | 0.043 | 0.003 | Er | 0.043 | 0.003 |
| 0.13 | 0.02 | 0.12 | 0.02 |
| 0.42 | 0.03 | 0.41 | 0.02 |
| Nd | 0.046 | 0.003 | Tm | 0.041 | 0.002 |
| 0.13 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.03 | 0.40 | 0.03 |
| Sm | 0.041 | 0.003 | Yb | 0.041 | 0.003 |
| 0.12 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.02 | 0.40 | 0.02 |
| Eu | 0.041 | 0.003 | Lu | 0.041 | 0.003 |
| 0.12 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.02 | 0.42 | 0.03 |
| Gd | 0.041 | 0.003 | **-** |
| 0.12 | 0.02 |
| 0.41 | 0.02 |
| Note：The repeatability limit (*r*) is 2.8×S*r*, and S*r* is the standard deviation of the repeatability limit. |

4.8.3　 Reproducibility

The absolute difference of the determined values obtained from two independent determinations under the reproducibility conditions， is not greater than the reproducibility limits (*R*), which is in the range of the following average values in Table 9 and Table 10. The cases that the absolute difference is greater than the reproducibility limits (*R*) are less than 5%. The reproducibility limit (*R*) is calculated by linear interpolation or epitaxy method on the basis of the data listed in Table 9 and Table 10.

Table 9: Reproducibility limit for total rare earth content (Method 1)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Mass fraction/% | 0.50 | 1.00 | 1.04 | 2.11 | 5.39 | 9.37 |
| Reproducibility limit（*R*）/% | 0.05 | 0.04 | 0.09 | 0.15 | 0.17 | 0.27 |
| Matrix | Y | Y | La | Ce | Ce | Ce |
| Note：The Reproducibility limit (*R*) is 2.8×S*R*, and S*R* is the standard deviation of the Reproducibility limit. |

Table 10: Reproducibility limit for fifteen rare earth elements content (Method 1)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Determination of elements | Mass fraction % | Reproducibility limit*（R）*% | Determination of elements | Mass fraction % | Reproducibility limit*（R）*% |
| Y | 0.48 | 0.03 | Tb | 0.040 | 0.003 |
| 0.83 | 0.04 | 0.12 | 0.02 |
| 8.46 | 0.12 | 0.40 | 0.04 |
| La | 0.20 | 0.02 | Dy | 0.041 | 0.004 |
| 1.42 | 0.06 | 0.12 | 0.02 |
| 8.21 | 0.14 | 0.41 | 0.03 |
| Ce | 0.35 | 0.09 | Ho | 0.044 | 0.006 |
| 3.13 | 0.11 | 0.12 | 0.02 |
| 7.12 | 0.17 | 0.41 | 0.03 |
| Pr | 0.043 | 0.009 | Er | 0.043 | 0.004 |
| 0.13 | 0.02 | 0.12 | 0.02 |
| 0.42 | 0.04 | 0.41 | 0.04 |
| Nd | 0.046 | 0.006 | Tm | 0.041 | 0.005 |
| 0.13 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.05 | 0.40 | 0.04 |
| Sm | 0.041 | 0.005 | Yb | 0.041 | 0.004 |
| 0.12 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.04 | 0.40 | 0.04 |
| Eu | 0.041 | 0.005 | Lu | 0.041 | 0.004 |
| 0.12 | 0.02 | 0.12 | 0.02 |
| 0.40 | 0.03 | 0.42 | 0.04 |
| Gd | 0.041 | 0.003 | **-** |
| 0.12 | 0.02 |
| 0.41 | 0.05 |
| Note：The Reproducibility limit (*R*) is 2.8×S*R*, and S*R* is the standard deviation of the Reproducibility limit. |

5.　Method 2: EDTA titration method.

5.1　 Method summary

After the test portion is decomposed by nitric acid and hydrofluoric acid, the rare earth and thorium are precipitated and separated from iron in the form of fluoride. Add nitric acid , perchloric acid to destroy the filter paper and then extracted with hydrochloric acid, adjust the pH value to 5.5, precipitate thorium with hexamethylenetetramine. Add ascorbic acid to reduce cerium, iron, add acetylacetone to mask titanium, aluminum and other elements. Then use xylenol orange as an indicator to titrate the total rare earth content with EDTA standard solution. The total rare earth multiplied by the relative content of fifteen rare earth elements to obtain the absolute content of fifteen rare earth elements.

5.2　Reagents or materials

Unless otherwise stated, only reagents confirmed to be of analytical grade or above and secondary water complying with GB/T 6682 are used in the analysis.

5.2.1　 Lanthanum oxide *w*(REO) ≥ 99.5%, *w*(La2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.2　 Cerium oxide *w*(REO) ≥ 99.5%, *w*(CeO2/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.3　 Praseodymium oxide *w*(REO) ≥ 99.5%, *w*(Pr6O11/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.4　 Neodymium oxide *w*(REO) ≥ 99.5%, *w*(Nd2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.5　 Samarium Oxide *w*(REO) ≥ 99.5%, *w*(Sm2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.6　 Europium oxide *w*(REO) ≥ 99.5%, *w*(Eu2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.7　 Gadolinium Oxide *w*(REO) ≥ 99.5%, *w*(Gd2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.8　 Terbium oxide *w*(REO) ≥ 99.5%, *w*(Tb4O7/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.9　 Dysprosium Oxide *w*(REO) ≥ 99.5%, *w*(Dy2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.10　 Holmium oxide *w*(REO) ≥ 99.5%, *w*(Ho2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.11　 Erbium Oxide *w*(REO) ≥ 99.5%, *w*(Er2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.12　 Thulium oxide *w*(REO) ≥ 99.5%, *w*(Tm2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.13　 Ytterbium oxide *w*(REO) ≥ 99.5%, *w*(Yb2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.14　 Lutetium Oxide *w*(REO) ≥ 99.5%, *w*(Lu2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.15　 Yttrium oxide *w*(REO) ≥ 99.5%, *w*(Y2O3/REO) ≥ 99.99%, ignited at 950°C for 1 hour and then cool to room temperature in a desiccator.

5.2.16　 Ascorbic acid.

5.2.17　 Nitric acid (ρ = 1.42 g/mL).

5.2.18　 Hydrofluoric acid (ρ = 1.15 g/mL).

5.2.19　 Perchloric acid (ρ = 1.66 g/mL).

5.2.20　 Hydrogen peroxide [*w*(H2O2) ≥ 30%].

5.2.21　 Hydrochloric acid, diluted （1+1）.

5.2.22　 Nitric acid, diluted （1+1）.

5.2.23　 Ammonia, diluted （1+1）.

5.2.24　 Mixed acid wash solution: Add 5 mL each of nitric acid (5.2.17) and hydrofluoric acid (5.2.18) to 100 mL of solution, and store in a plastic bottle.

5.2.25　 Hexamethylenetetramine solution (ρ=200 g/L).

5.2.26　 Acetylacetone solution（1+19）.

5.2.27　 Bromocresol green indicator solution (0.2%): Dissolve 0.2 g of bromocresol green indicator in 6 mL of NaOH solution (0.05 mol/L), and dilute to 100 mL with water.

5.2.28　 Xylenol Orange Indicator Solution (0.1%).

5.2.29　 Dissolve 2.000 0 g of metallic zinc [*ω*(Zn) > 99.9%] with 10 mL of hydrochloric acid （5.2.21）and 10 mL of water into a 250 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask, then dilute to volume with 5 mL 0f hydrochloric acid (5.2.21) and water, mix well. 1 mL of this solution contains 1 mg of zinc.

5.2.30　 Disodium ethylenediaminetetraacetate (EDTA) standard titration solution [c（EDTA ≈ 0.015 mol/L].

　a）Preparation: Dissolve 11.2 g of disodium ethylenediaminetetraacetate (EDTA) in a small amount of water into a 250 mL beaker, transfer to a 200 0 mL volumetric flask, then dilute to volume with water and mix well.

　b）Calibration: Transfer 20.00 mL of zinc standard solution (5.2.29) into a 250 mL Erlenmeyer flask with 50 mL of water, adjust the pH of the solution to 5.5 with hydrochloric acid (5.2.21) or ammonia (5.2.23). Add 5 mL of hexamethylenetetramine (5.2.25) and 2 drops of xylenol orange indicator solution (5.2.28), then titrate with EDTA standard titration solution (5.2.30) until the solution changes from purple to bright yellow, which is the end point. Calibrate three times in parallel, and take the average value when the difference in the volume of the consumed EDTA standard titration solution (5.2.30) does not exceed 0.10 mL.

The concentration (c) of EDTA standard titration solution (5.2.30) is calculated according to formula (3), in moles per liter (mol/L):

………………………………………………………（3）

Where:

*ρ2*——Mass concentration of zinc standard solution (5.2.29), in grams per liter（g/L）;

*V3*——Pipette volume of zinc standard solution (5.2.29), in mililiter（mL）;

*V4*——Volume of EDTA standard solution (5.2.30) consumed for titration of zinc, in mililiter（mL）;

*M1*——Mass of the test portion，in grams（g）.

5.2.31　 Lanthanum standard stock solution， Dissolve 0.234 6 g of lanthanum oxide （5.2.1） in 10 mL of hydrochloric acid （5.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of lanthanum.

5.2.32　 Cerium standard stock solution， Dissolve 0.245 7 g of cerium oxide （5.2.2） in 20 mL of nitric acid （5.2.22）and a small amount of hydrogen peroxide (5.2.20) into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of cerium.

5.2.33　 Praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution， Dissolve 0.241 6 g of praseodymium oxide (5.2.3), 0.233 3 g of neodymium oxide (5.2.4), 0.231 9 g of samarium oxide (5.2.5), 0.231 6 g of europium oxide (5.2.6), 0.230 5 g of Gadolinium oxide, (5.2.7), 0.235 3 g of terbium oxide (5.2.8), 0.229 6 g of dysprosium oxide (5.2.9), 0.229 1 g of holmium oxide (5.2.10), 0.228 7 g of erbium oxide (5.2.11) , 0.228 4 g of thulium oxide (5.2.12), 0.227 8 g of ytterbium oxide (5.2.13), 0.227 5 g lutetium oxide of (5.2.14) in 60 mL of nitric acid （5.2.22） into a 200 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg each of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

5.2.34　 Yttrium standard stock solution， Dissolve 0.254 0 g of yttrium oxide （5.2.15） in 10 mL of hydrochloric acid （5.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, then dilute to volume with water and mix well. 1 mL of this solution contains 1 mg of yttrium.

5.2.35　 Standard stock solution for blank test, Transfer 2.00 mL of lanthanum standard stock solution (5.2.31), 2.00 mL of cerium standard stock solution (5.2.32), 2.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33), 2.00 mL of yttrium standard stock solution (5.2.34) and 10 mL of hydrochloric acid （5.2.21） into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 10.00 μg of fifteen individual rare earth.

5.2.36　 Standard stock solution I, Dissolve 1.154 0 g of lanthanum oxide （5.2.1） in 10 mL of hydrochloric acid （5.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of cerium standard stock solution (5.2.32), 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) and 2.00 mL of yttrium standard stock solution (5.2.34) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.37　 Standard stock solution II, Dissolve 1.208 8 g of cerium oxide （5.2.2） in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of lanthanum standard stock solution (5.2.31), 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) and 2.00 mL of yttrium standard stock solution (5.2.34) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.38　 Standard stock solution III, Dissolve 1.249 7 g of yttrium oxide (5.2.15) in 10 mL of hydrochloric acid （5.2.21） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of lanthanum standard stock solution (5.2.31), 2.00 mL of cerium standard stock solution (5.2.32), and 1.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. The individual rare earth content is shown in Table 11.

5.2.39　 Standard stock solution IV, Dissolve 0.851 4 g of lanthanum oxide (5.2.1), 0.184 3 g of cerium oxide (5.2.2), 0.184 3 g of yttrium oxide (5.2.15) in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 2.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.40　 Standard stock solution V, Dissolve 0.527 8 g of lanthanum oxide (5.2.1), 0.061 5 g of cerium oxide (5.2.2), 0.558 9 g of yttrium oxide (5.2.15) in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 5.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.41　 Standard stock solution VI, Dissolve 0.058 7 g of lanthanum oxide (5.2.1), 1.041 5 g of yttrium oxide (5.2.15) in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 10.00 mL of cerium standard stock solution (5.2.32), 10.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.42　 Standard stock solution VII, Dissolve 0.859 9 g of cerium oxide (5.2.2), 0.063 5 g of yttrium oxide (5.2.15) in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 10.00 mL of lanthanum standard stock solution (5.2.31), 20.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

5.2.43　 Standard stock solution VIII, Dissolve 0.117 3 g of lanthanum oxide (5.2.1), 0.503 7 g of cerium oxide (5.2.2) in 10 mL of nitric acid （5.2.22） into a 100 mL beaker while heating gently until complete dissolution, transfer to a 200 mL volumetric flask after cooling, transfer 25.00 mL of cerium standard stock solution (5.2.32), 40.00 mL of praseodymium-neodymium-samarium-europium-gadolinium-terbium-dysprosium-holmium-erbium-thulium-ytterbium-lutetium standard stock solution (5.2.33), and 10.00 mL of yttrium standard stock solution (5.2.34) into a 200 mL volumetric flask, then dilute to volume with water and mix well. 1 mL of this solution contains 5 mg of rare earth. Each of individual rare earth content is shown in Table 11.

Table 11: Each of individual rare earth content in standard stock solutions I to VIII

 In ug/mL

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| number | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb |
| Ⅰ | 492 0 | 10 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅱ | 10 | 492 0 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅲ | 10 | 10 | 5 | 5 | 5 | 5 | 5 | 5 |
| Ⅳ | 363 0 | 750 | 10 | 10 | 10 | 10 | 10 | 10 |
| Ⅴ | 225 0 | 250 | 25 | 25 | 25 | 25 | 25 | 25 |
| Ⅵ | 250 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| Ⅶ | 50 | 350 0 | 100 | 100 | 100 | 100 | 100 | 100 |
| Ⅷ | 500 | 205 0 | 200 | 200 | 200 | 200 | 200 | 200 |
| number | Dy | Ho | Er | Tm | Yb | Lu | Y | — |
| Ⅰ | 5 | 5 | 5 | 5 | 5 | 5 | 10 | — |
| Ⅱ | 5 | 5 | 5 | 5 | 5 | 5 | 10 | — |
| Ⅲ | 5 | 5 | 5 | 5 | 5 | 5 | 492 0 | — |
| Ⅳ | 10 | 10 | 10 | 10 | 10 | 10 | 500 | — |
| Ⅴ | 25 | 25 | 25 | 25 | 25 | 25 | 220 0 | — |
| Ⅵ | 50 | 50 | 50 | 50 | 50 | 50 | 410 0 | — |
| Ⅶ | 100 | 100 | 100 | 100 | 100 | 100 | 250 | — |
| Ⅷ | 200 | 200 | 200 | 200 | 200 | 200 | 50 | — |

5.2.44　 Argon, φ(Ar)>99.99%.

5.3　Apparatus

5.3.1　 Inductively coupled plasma atomic emission spectrometer. Under the best working conditions of the apparatus, any apparatus that meets the following indicators can be used:

——Resolution is less than 0.006 nm, wavelength range is 160 nm ～ 500 nm;

——Shall be in accordance with verefication regulation of emission spectrometer and technical indicators required in JJG 768.

5.3.2　 The recommended analysis lines for each element are shown in Table 12.

Table 12: Analysis lines

 In nm

|  |  |  |  |
| --- | --- | --- | --- |
| Determination of elements | Analysis lines | Determination of elements | Analysis lines |
| La | 408.671、398.852 | Dy | 353.170 |
| Ce | 418.660、446.021 | Ho | 345.600 |
| Pr | 405.654、422.532 | Er | 369.265 |
| Nd | 410.946 | Tm | 313.125 |
| Sm | 359.259 | Yb | 328.937 |
| Eu | 381.965 | Lu | 261.542 |
| Gd | 310.050 | Y | 377.433 |
| Tb | 350.914 | — | — |

5.4　 Sample

The alloy sample are made into powder sample and passed through a 0.125 mm sieve.

5.5　 Procedure

5.5.1　 Test portion

Weigh out the sample (5.4) according to Table 13, accurate to 0.000 1 g.

Table 13: Weighing amount of sample

|  |  |
| --- | --- |
| Mass fraction of total rare earth content% | Test portiong |
| 10.00～20.00 | 0.50 |
| >20.00～40.00 | 0.25 |

5.5.2　 Parallel test

Carry out two tests in parallel.

5.5.3　 Blank test

Carry out a blank test along with the test portion(5.5.1).

5.5.4　 Preparation of analytical test solution

5.5.4.1　 Put the test portion (5.5.1) in a 250 mL polytetrafluoroethylene beaker, slowly add 5 mL of nitric acid (5.2.17), 5 mL of hydrofluoric acid (5.2.18), and 0.5 mL of hydrogen peroxide (5.2.20). Purge the cup wall with about 10 mL of water and heating it at 130°C to 190°C for 30 minutes. Add 5 mL of nitric acid (5.2.17), 5 mL of hydrofluoric acid (5.2.18), and 0.5 mL of hydrogen peroxide (5.2.20). After heating for 30 minutes, add 5 mL of hydrofluoric acid (5.2.18) and continue heating 30 minutes. Remove and add water until the volume is 50 mL, stir thoroughly for 1 minute and let stand for 15 minutes. Filter with slow filter paper, wash the beaker 3 times with mixed acid washing solution (5.2.24), and wash the sediment 8 times.

5.5.4.2　 Transfer the precipitate together with the filter paper into 300 mL beaker, add 20 mL of nitric acid (5.2.17), 5 mL of perchloric acid (5.2.19), then heat to destroy the filter paper and dissolve the precipitate. Evaporate and emit thick smoke to a volume of 2 mL～3 mL, remove and cool, then add 2 mL of hydrochloric acid (5.2.21), 20 mL of water and heat to boil. Remove and cool again, transfer to 50 mL volumetric flask, dilute to volume with water and mix well, then dry filter.

5.5.4.3　 Transfer 20.00 mL of test solution (5.5.4.2), add 2 drops of bromocresol green indicator (5.2.27), and add hexamethylenetetramine solution (5.2.25) to adjust the solution from yellow to green with an excess of 2 drop, then heat and boil for 2 minutes to turn the solution from green to blue. Cool to room temperature with running water. Add 0.5 g of ascorbic acid (5.2.16), 10 mL of acetylacetone solution (5.2.26), 5 mL of hexamethylenetetramine solution (5.2.25), and mix well after each addition of reagents. Add 5 drops of xylenol orange indicator solution (5.2.28), and titrate with EDTA standard titration solution (5.2.30) until the solution changes from purple-red to yellow-green, which is the end point.

5.5.4.4　 Transfer 5.00 mL of test solution (5.5.4.2) into 100 mL volumetric flask that with 10 mL of hydrochloric acid (5.2.21), dilute to volume with water and mix well for testing.

5.5.5　 Preparation of series standard solutions

5.5.5.1　 Preparation of series standard solutions for blank test

Transfer 0 mL, 1.00 mL, 5.00 mL and 10.00 mL of the standard stock solution for blank test (5.2.35) into four 100 mL of volumetric flasks respectively, add 10 mL hydrochloric acid (5.2.21) and dilute to volume with water and mix well. The concentration of series standard solutions for blank test are as follows: 0 μg/mL, 0.10 μg/mL, 0.50 μg/mL, and 1.00 μg/mL.

5.5.5.2　 Preparation of series standard solutions for analytical test

Transfer 2.00 mL each of standard stock solutions I to VIII (5.2.36 ～ 5.2.43) into eight 100 mL of volumetric flasks, add 10 mL of hydrochloric acid (5.2.21) respectively, dilute to volume with water and mix well. The concentration of series standard solutions are shown in Table 14. According to the main rare earth element of the sample, six standard points are selected as series standard solutions.

Table 14: Each rare earth concentration of series standard solutions

 In μg/mL

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| standard sequence | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb |
| 1 | 98.4 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 2 | 0.2 | 98.4 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 4 | 72.6 | 15 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 5 | 45 | 5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 6 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 7 | 1 | 70 | 2 | 2 | 2 | 2 | 2 | 2 |
| 8 | 10 | 41 | 4 | 4 | 4 | 4 | 4 | 4 |
| standard sequence | Dy | Ho | Er | Tm | Yb | Lu | Y | — |
| 1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | — |
| 2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | — |
| 3 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 98.4 | — |
| 4 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 10 | — |
| 5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 44 | — |
| 6 | 1 | 1 | 1 | 1 | 1 | 1 | 82 | — |
| 7 | 2 | 2 | 2 | 2 | 2 | 2 | 5 | — |
| 8 | 4 | 4 | 4 | 4 | 4 | 4 | 1 | — |

5.6　 Determination

5.6.1　 Drawing of standard curve for analytical test

After the inductively coupled plasma emission spectrometer is running stably, determine the emission intensity of each rare earth element in the series standard solutions (5.5.5.2) in sequence under the selected apparatus working conditions, and use the apparatus software to draw a standard working curve. The correlation coefficient of the standard curve of each element should be great than 0.999, otherwise it needs to be re-standardized or the standard solution needs to be prepared again for standardization.

5.6.2　 Determination of analytical test solution

After the standard curve meets the determination requirements, determine the emission intensity of each rare earth element in the analytical test solution (5.5.4.4) immediately. The apparatus processes the data automatically that based on the standard curve(5.6.1), calculates and outputs the mass concentration of each rare earth element in the analytical test solution.

5.6.3　 Drawing of standard curve for blank test

After the inductively coupled plasma emission spectrometer is running stably, determine the emission intensity of each rare earth element in the series standard solutions for blank test (5.5.5.1) in sequence under the selected apparatus working conditions, and use the apparatus software to draw a standard working curve. The correlation coefficient of the standard curve of each element should be above 0.999, otherwise it needs to be re-standardized or the standard solution needs to be prepared again for standardization.

5.6.4　 Determination of blank test solution

After the standard curve of the blank test (5.6.3) meets the determination requirements, determine the emission intensity of each rare earth element in the blank test solution (5.5.3) immediately. The apparatus processes the data automatically that based on the standard curve (5.6.3), calculates and outputs the mass concentration of each rare earth element in the blank test solution.

5.7　 Test data processing

5.7.1　 Test data processing of total rare earth content

Total rare earth are expressed as mass fraction (*w*RE), calculated according to formula (4):

……………………………………（4）

Where:

*c*——Concentration of EDTA standard titration solution, in moles per liter（mol/L）;

*V6*——Volume of EDTA standard solution consumed for titration, in mililiter（mL）;

*V5*——Volume of EDTA standard titration solution consumed by blank solution, in mililiter（mL）;

*V7*——Total volume of the test solution, in mililiter （mL）;

*m2*——Mass of the test portion, in grams （g）;

*V8*——Dispensed volume of the test portion, in mililiter （mL）;

*‾M2*——Average molar mass of rare earths in the alloy, in grams per mole (g/mol).

……………………………………（5）

Where:

*mtotal*——Total mass of rare earth metals in the test solution, in grams （g）;

*mtotal*——Total amount of substance with rare earth metals in the test solution, in mole （mol）;

*Mi* ——Molar mass of each rare earth in the test solution, in grams per mole (g/mol);

*i* ——I = 1,2,…，N;

*mi* ——Mass of each rare earth in the test solution, in grams （g）, calculated according to formula (6):

……………………………………（6）

Where:

*ρ4*——Mass concentration of individual rare earth in the analysis test solution, which is obtained from the standard curve, in micrograms per milliliter （μg/mL）;

*ρ3*——Mass concentration of individual rare earth in the blank test solution, which is obtained from the standard curve, in microgram per milliliter （μg/mL）;

*V9*——Volume of the test solution, in mililiter （mL）.

When the absolute difference between two parallel determination results is not greater than the corresponding repeatability limit in Table 15, the average value shall be taken as the determination result. When the result is less than 1.00%, the calculation result shall retain two significant figures. When the result is greater than or equal to 1.00%, the calculation results are kept to two decimal places, and numerical rounding is performed in accordance with the provisions of GB/T 8170.

5.7.2　 Test data processing of fifteen rare earth elements content

The content of fifteen rare earth elements is calculated as mass fraction (*w*x), calculated according to formula (7):

………………………………………（7）

Where:

*w(RE)*——Total rare earth content （%）;

*mi*——Mass of each rare earth in the test solution, in grams （g）;

*i*——I = 1,2,…，N.

When the absolute difference between two parallel determination results is not greater than the corresponding repeatability limit in Table 16, the average value shall be taken as the determination result. When the result is less than 1.00%, the calculation result shall retain two significant figures. When the result is greater than or equal to 1.00%, the calculation results are kept to two decimal places, and numerical rounding is performed in accordance with the provisions of GB/T 8170.

5.8　 Precision

5.8.1　 Raw precision data and statistics

The precision data were counted in 2023 by eight laboratories conducting collaborative tests on 11 different levels of samples of the total rare earth and the fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy. Each laboratory independently determined each level of the total rare earth and fifteen rare earth elements contents in silicon-based composite rare earth ferroalloy and RE-Mg ferrosilicon alloy 11 times under repeatability conditions. The test data is statistically analyzed according to GB/T 6379.2.

5.8.2　 Repeatability

The absolute difference of the determined values obtained from two independent determinations under the repeatability conditions， is not greater than the repeatability limits (*r*), which is in the range of the following average values in Table 15 and Table 16. The cases that the absolute difference is greater than the repeatability limits (*r*) are less than 5%. The repeatability limit (*r*) is calculated by linear interpolation or epitaxy method on the basis of the data listed in Table 15 and Table 16.

Table 15: Repeatability limit for total rare earth content (Method 2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Mass fraction/% | 12.45 | 26.79 | 25.99 | 35.95 |
| Repeatability limit（*r*）/% | 0.10 | 0.30 | 0.19 | 0.15 |
| Matrix | Ce | Ce | Y | Y |
| Note：The repeatability limit (*r*) is 2.8×S*r*, and S*r* is the standard deviation of the repeatability limit. |

Table 16: Repeatability limit for fifteen rare earth elements content (Method 2)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Determination of elements | Mass fraction % | Repeatability limit*（r）*% | Determination of elements | Mass fraction % | Repeatability limit*（r）*% |
| Y | 0.052 | 0.002 | Gd | 0.041 | 0.002 |
| 0.39 | 0.01 | 0.40 | 0.01 |
| 1.58 | 0.02 | 1.59 | 0.03 |
| 16.43 | 0.12 | Tb | 0.042 | 0.002 |
| 36.85 | 0.16 | 0.39 | 0.01 |
| La | 0.20 | 0.01 | 1.59 | 0.03 |
| 4.15 | 0.07 | Dy | 0.042 | 0.002 |
| 9.23 | 0.10 | 0.41 | 0.01 |
| 37.19 | 0.12 | 1.61 | 0.02 |
| Ce | 0.34 | 0.02 | Ho | 0.042 | 0.002 |
| 8.05 | 0.07 | 0.39 | 0.02 |
| 17.64 | 0.10 | 1.60 | 0.03 |
| 37.64 | 0.15 | Er | 0.042 | 0.002 |
| Pr | 0.061 | 0.01 | 0.40 | 0.01 |
| 0.43 | 0.02 | 1.60 | 0.03 |
| 1.60 | 0.02 | Tm | 0.042 | 0.002 |
| Nd | 0.045 | 0.002 | 0.39 | 0.01 |
| 0.42 | 0.01 | 1.59 | 0.04 |
| 1.61 | 0.03 | Yb | 0.042 | 0.002 |
| Sm | 0.042 | 0.002 | 0.40 | 0.01 |
| 0.40 | 0.02 | 1.60 | 0.03 |
| 1.58 | 0.03 | Lu | 0.040 | 0.002 |
| Eu | 0.042 | 0.002 | 0.40 | 0.01 |
| 0.40 | 0.02 | 1.60 | 0.04 |
| 1.59 | 0.03 | **-** |
| Note：The repeatability limit (r) is 2.8×Sr, and Sr is the standard deviation of the repeatability limit. |

5.8.3　 Reproducibility

The absolute difference of the determined values obtained from two independent determinations under the reproducibility conditions, is not greater than the reproducibility limits (*R*), which is in the range of the following average values in Table 17 and Table 18. The cases that the absolute difference is greater than the reproducibility limits (*R*) are less than 5%. The reproducibility limit (*R*) is calculated by linear interpolation or epitaxy method on the basis of the data listed in Table 17 and Table 18.

Table 17: Reproducibility limit for total rare earth content (Method 2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Mass fraction/% | 12.45 | 26.79 | 25.99 | 35.95 |
| Repeatability limit（*r*）/% | 0.28 | 0.82 | 0.53 | 0.40 |
| Matrix | Ce | Ce | Y | Y |
| Note：The Reproducibility limit (*R*) is 2.8×S*R*, and S*R* is the standard deviation of the Reproducibility limit. |

Table 18: Reproducibility limit for fifteen rare earth elements content (Method 2)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Determination of elements | Mass fraction % | Repeatability limit*（r）*% | Determination of elements | Mass fraction % | Repeatability limit*（r）*% |
| Y | 0.052 | 0.005 | Gd | 0.041 | 0.005 |
| 0.39 | 0.03 | 0.40 | 0.03 |
| 1.58 | 0.04 | 1.59 | 0.07 |
| 16.43 | 0.33 | Tb | 0.042 | 0.004 |
| 36.85 | 0.45 | 0.39 | 0.03 |
| La | 0.20 | 0.03 | 1.59 | 0.09 |
| 4.15 | 0.20 | Dy | 0.042 | 0.004 |
| 9.23 | 0.34 | 0.41 | 0.03 |
| 37.19 | 0.27 | 1.61 | 0.05 |
| Ce | 0.34 | 0.04 | Ho | 0.042 | 0.004 |
| 8.05 | 0.18 | 0.39 | 0.04 |
| 17.64 | 0.41 | 1.60 | 0.08 |
| 37.64 | 0.29 | Er | 0.042 | 0.005 |
| Pr | 0.061 | 0.007 | 0.40 | 0.03 |
| 0.43 | 0.04 | 1.60 | 0.09 |
| 1.60 | 0.05 | Tm | 0.042 | 0.005 |
| Nd | 0.045 | 0.004 | 0.39 | 0.03 |
| 0.42 | 0.03 | 1.59 | 0.12 |
| 1.61 | 0.07 | Yb | 0.042 | 0.006 |
| Sm | 0.042 | 0.004 | 0.40 | 0.03 |
| 0.40 | 0.03 | 1.60 | 0.09 |
| 1.58 | 0.07 | Lu | 0.040 | 0.004 |
| Eu | 0.042 | 0.004 | 0.40 | 0.03 |
| 0.40 | 0.04 | 1.60 | 0.11 |
| 1.59 | 0.08 | **-** |
| Note：The Reproducibility limit (*R*) is 2.8×S*R*, and S*R* is the standard deviation of the Reproducibility limit.. |

6　Test report

Varify the validity of the method by the certified reference materials or control samples The test report shall provide the following aspects:

——Test subject;

——Document number;

——Analysis results and their expression;

——Differences from basic analysis steps;

——Observed anomalies;

——Test date.