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| Rare earth-based hydrogen storage alloys —Test method for measurement of kinetic properties of hydrogenation dehydrogenation reaction |

稀土系储氢合金

吸放氢反应动力学性能测试方法

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Foreword

This document is drafted in accordance with the provisions of GB/T1.1-2020 《Guidelines for Standardization Work Part 1: Structure and Drafting Rules for Standardization Documents》.

Please note that some contents of this document may involve patents, and the issuing organization of this document does not undertake the responsibility for identifying patents.

This document is proposed and managed by the National Rare Earth Standardization Technical Committee (SAC/TC229).

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Rare earth-based hydrogen storage alloys —Test method for measurement of kinetic properties of hydrogenation dehydrogenation reaction

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1 Scope

This document specifies the test method for the kinetic performance of hydrogen absorption/desorption reaction of rare earth hydrogen storage alloys.

This document is applicable to the kinetic test of the hydrogen absorption and desorption reaction of rare earth hydrogen storage alloys by volume method (siverts method). Test temperature range: 25°C~300°C, ambient temperature range 23°C±3°C, test pressure range: 0.001MPa~5MPa The test of 5MPa~10MPa rare earth hydrogen storage alloy can refer to this document.

2 Normative references

The contents of the following documents constitute the essential provisions of this document through normative references in the text. Among them, for dated references, only the version corresponding to the date is applicable to this document; for undated references, the latest version (including all amendments) is applicable to this document.

*GB/T 678 Chemical reagent - Ethanol*

*GB/T 3634.2 Hydrogen Part 2: Pure hydrogen, high pure hydrogen and ultrapure hydrogen*

*GB/T 4842 Argon*

*GB/T 4844 Pure helium, high pure helium and ultra pure helium*

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

3 Terms and Definitions

The following terms and definitions apply to this document.

3.1 hydrogen absorption reaction of hydrogen storage alloy

Hydrogen storage alloy reacts with gaseous hydrogen at a certain temperature and forms a metal hydride through phase transformation.

Note: When the hydrogen storage alloy is hydrogenated at a certain temperature, a solid solution α phase is first formed as the hydrogen pressure increases; after the hydrogen solid solution is saturated, a metal hydride phase (β phase) begins to form, and there are two phases of α phase and β phase Theoretically, the hydrogen pressure remains unchanged; after the hydrogen absorption process is completed, a β single phase is formed, and the hydrogen absorption continues, and the pressure increases rapidly.

3.2 hydrogen desorption reaction of hydrogen storage alloy

hydrogen storage alloy in the hydrogen absorption reaction to form a metal hydride, at a certain temperature, the process of releasing gaseous hydrogen through phase transition.

Note: Hydrogen release is the reverse reaction process of hydrogen absorption.

3.3 reaction kinetics performance

At a certain temperature and pressure, the amount of hydrogen absorbed/desorbed per unit time.

 Note: It mainly depends on the surface catalytic activity of the hydrogen storage alloy, the hydrogen diffusion rate in the hydrogen storage alloy, the generation rate of hydrides and the thermal conductivity of the material.

3.4 sample chamber

The chamber used in the samplechamber tester to react the sample with hydrogen.

 NOTE: Separated from other chambers of the tester by the sample valve.

3.5 system

During the hydrogen absorption kinetics test, before the sample valve is opened to allow hydrogen to be filled into the sample chamber to react with the sample, a fixed volume chamber with a certain amount of hydrogen is filled first.

3.6 Initial equilibrium pressure of sample chamber during hydrogen absorption

The pressure in the sample chamber when the system is connected to the sample chamber and the sample is not absorbing hydrogen.

 Note: When testing the hydrogen absorption kinetics of the sample, the initial equilibrium pressure of the sample chamber during the hydrogen absorption process is higher than the hydrogen absorption platform pressure of the sample.

3.7 initial equilibrium pressure in sample chamber during hydrogen desorption

The pressure of the sample chamber when the system is connected to the sample chamber and the sample is not releasing hydrogen.

Note: When testing the hydrogen desorption kinetics of the sample, the initial equilibrium pressure of the sample chamber during the dehydrogenation process is lower than the dehydrogenation platform pressure of the sample.

3.8 initial system pressure

Fill the system with a certain amount of hydrogen pressure before performing the hydrogen absorption kinetic test.

4 Method Summary

Under the required test temperature, make hydrogen gas contact with the constant temperature metal sample in a sample chamber with a certain volume, calculate the hydrogen absorption amount according to the change of gas pressure during the pressure balance process, and the rate of change of hydrogen absorption with time was recorded to obtain the hydrogen absorption kinetics. At the required test temperature, connect the hydrogen-absorbed saturated sample to the system to discharge hydrogen, calculate the hydrogen release amount according to the change of gas pressure during the pressure balance process, and record the change rate of hydrogen release amount with time to obtain the hydrogen release kinetic performance .

5 reagents

Unless otherwise stated, only reagents confirmed to be of analytical grade were used in the analysis.

5.1 Hydrogen: GB/T3634.2, high-purity hydrogen, volume fraction ≥99.999%.

5.2 Helium: GB/T4844, high-purity helium, volume fraction ≥ 99.999%.

5.3 Argon: GB/T4842, volume fraction ≥ 99.99%.

5.4 Anhydrous ethanol: GB/T678.

6 Instruments and equipment

6.1 Balance

The division value is not greater than 0.0001g.

6.2 Pressure-composition isotherm (PCI) tester

test pressure accuracy: ±0.04%.

Temperature control accuracy: ±0.1°C.

Sample chamber volume: 6cm3±1.5cm3, the recommended ratio of system volume to sample chamber volume is 8.5:1~15.0:1.

The structure of the pressure-composition isotherm (PCI) tester is shown in Figure 1:

**hydrogen storage vessel**

**System**

**Sample** **chamber**

* **low-pressure gauge**
* **Low pressure valve**

**Master valve**

**Switching valve**

* **Hydrogen valve**

**Outside**

* **Heating furnace**
* **High-pressure gauge**
* **Vacuum valve**
* **Vacuum pump**

**Sample valve**

**circulating water**

**air release valve**

**Outdoor air**

Fig. 1 Structure diagram of PCI tester

6.3 Test sieve

50 mesh, aperture 0.282mm.

7 samples

The rare earth hydrogen storage alloy is crushed and passed through a 50-mesh test sieve (6.3) to obtain a hydrogen storage alloy sample with a particle size of ≤0.282mm.

8 test steps

8.1 Sample

Clean the sample chamber with absolute ethanol (5.4) and dry it. Weigh 1.000g±0.200g of the sample (7) into the sample chamber, tighten the sample chamber, and set it aside.

8.2 Parallel test

Weigh two samples (8.1) for parallel determination.

8.3 Equipment air tightness testing

Connect the sample chamber to the system, then fill the tester with hydrogen (5.1) [helium (5.2) or argon (5.3)] with the maximum pressure allowed by the equipment, and confirm that the tester has no gas leakage (leakage rate ≤ 1×10 -9g•s-1).

8.4 Determination of sample chamber volume

8.4.1 Depressurize the sample chamber and the system, and stabilize the sample chamber at the required test temperature.

8.4.2 Evacuate the sample chamber and system to no higher than 0.001MPa and the reading will not change, record the pressure Pr1 of the sample chamber.

8.4.3 Close the sample valve, slowly fill the system with [helium (5.2) or argon (5.3)], increase the system pressure by 0.1 MPa, record the system pressure Pd1; open the sample valve, record the sample chamber after stabilization Pressure Pr2.

8.4.4 Repeat 8.3.3 for 5 ~7 times to obtain Pri (i= 1,2,3,......) Pdi (i= 1,2,......) . Sample chamber volume V2 is calculated according to Formula (1) :

……………………………………………（1）

In the formula

*P*d——System pressure, in Mpa;

*P*ri——Sample chamber pressure , in mpa;

*V*1——System volume, in cubic centimeters(cm3).

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

8.5 Sample activation

8.5.1 Vacuumize the sample chamber and system to no higher than 0.001MPa, then raise the temperature of the sample chamber to 150°C, continue vacuuming for 30 minutes, and then lower the temperature of the sample chamber to 40°C.

8.5.2 Close the sample valve, fill the system with hydrogen to 6MPa, open the sample valve to fully react the sample with hydrogen, and stop hydrogen absorption if the pressure change per minute is less than 0.001MPa.

8.5.3 Close the sample valve, evacuate the system to no higher than 0.001MPa, then open the sample valve to release hydrogen from the sample, and stop the hydrogen release if the pressure change per minute is less than 0.001MPa.

8.5.4 Raise the temperature of the sample chamber to 150°C, continue vacuuming for 30 minutes, and then lower the temperature of the sample chamber to 40°C to complete the primary activation of the sample.

Note: Generally, it is considered that the change of the maximum hydrogen absorption capacity for 3 consecutive times is ≤0.05%, and the sample can be considered to be fully activated. The temperature, pressure and times of activation depend on the characteristics of the sample to ensure that the sample is fully activated.

8.6 Hydrogen absorption kinetics test

8.6.1 Stabilize the sample chamber at the required test temperature.

8.6.2 Vacuum the sample chamber and system to no higher than 0.001MPa.

8.6.3 The initial pressure P1 of the system is calculated according to the formula (2):

 ……………………………………………（2）

In the formula

*P*2——The initial equilibrium pressure of the sample chamber during the hydrogen absorption process, in megapascals (MPa);

*V*1——System volume, in cubic centimeters (cm3);

*V*2——The volume of the sample chamber, in cubic centimeters (cm3).

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

8.6.4 Open the sample valve, the hydrogen reacts with the sample, the instrument automatically records the change of pressure with time, and draws the change curve of hydrogen absorption and time. Hydrogen absorption Wa is calculated according to formula (3):

……………………………………（3）

In the formula

*P*2——The initial equilibrium pressure of the sample chamber during hydrogen absorption, in megapascals (MPa);

*P*3——The pressure of the sample chamber after hydrogen absorption, in megapascals (MPa);

*V*1——System volume, in cubic meters Centimeter (cm3);

*V*2——The volume of the sample chamber, in cubic centimeter (cm3);

$M\_{H\_{2}}$——The molar mass of hydrogen, in grams per mole (g/mol)

*m*——Sample volume, in grams (g);

*R*——Molar gas constant, take 8.314, the unit is Joule per mole Kelvin [J/(mol K)];

*T*——Molar gas constant, take 8.314, the unit is Joule per mole Kelvin [J/(mol K)];

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T 8170.

8.6.5 Close the sample valve after the test.

8.7 Hydrogen desorption kinetics test

8.7.1 After the hydrogen absorption is completed, stabilize the sample chamber at the required test temperature, and record the pressure P3 of the sample chamber after hydrogen absorption.

8.7.2 The initial equilibrium pressure P4 of the sample chamber during hydrogen desorption is according to formula (4) calculate:

  ………………………………………………（4）

In the formula:

*P*3——The pressure of the sample chamber after hydrogen absorption, in megapascals (MPa);

*V*2——The volume of the sample chamber, in cubic centimeters (cm3);

*V*1——System volume, in cubic centimeters (cm3);

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

If the initial equilibrium pressure P4 of the sample chamber during dehydrogenation is lower than the dehydrogenation platform pressure of the sample, perform operations after 8.7.3; if the initial equilibrium pressure P4 of the sample chamber during dehydrogenation is higher than the dehydrogenation platform pressure of the sample, the suction After reducing the pressure P3 of the sample chamber after hydrogen, recalculate the initial equilibrium pressure P4 of the sample chamber during the dehydrogenation process until it is lower than the dehydrogenation plateau pressure of the sample, then perform operations after 8.7.3.

8.7.3 Vacuumize the system to no higher than 0.001MPa.

8.7.4 Open the sample valve to connect the sample chamber with the system, the sample starts to release hydrogen, record the change of pressure with time, and draw the change curve of hydrogen release amount and time. The amount of hydrogen released Wd is calculated according to the formula (5):

 ………………………………………(5)

In the formula:

*P*4——The initial equilibrium pressure of the sample chamber during dehydrogenation, in megapascals (MPa);

*P*5——The pressure of the sample chamber after hydrogen depletion, in megapascals (MPa);

*V*1——System volume, in cubic meters Centimeter (cm3);

*V*2——The volume of the sample chamber, in cubic centimeter (cm3);

$M\_{H\_{2}}$——The molar mass of hydrogen, in grams per mole (g/mol);

*m*——Sample volume, in grams (g);

*R*——Molar gas constant, 8.314, in joules per mole Kelvin [J/(mol K)];

*T*——Hydrogen desorption reaction temperature, in Kelvin (K);

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

8.7.5 After the test, vacuumize the sample chamber and system to no higher than 0.001MPa.

8.7.6 Close the sample valve after the test.

8.8 Test results

8.8.1 Hydrogen absorption kinetic performance results.

The hydrogen absorption rate Ra between 60% of the maximum hydrogen absorption capacity and 90% of the maximum

 ……………………………………………（6）

In the formula:

*W*a0.6 ——The hydrogen discharge amount of 60% of the maximum hydrogen discharge amount, read from the hydrogen discharge amount versus time change curve (8.6.4), and the unit is mass fraction (%);

*W*a0.9 ——The hydrogen discharge amount of 90% of the maximum hydrogen discharge amount, read from the hydrogen discharge amount versus time curve (8.6.4), and the unit is mass fraction (%);

*t*a0.6——The time to reach 60% of the maximum hydrogen discharge, read from the hydrogen discharge versus time curve (8.6.4), in seconds (s);

*t*a0.9——The time to reach 90% of the maximum hydrogen discharge, read from the hydrogen discharge versus time curve (8.6.4), in seconds (s).

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

8.8.2 The hydrogen absorption rate Rd between 60% of the maximum hydrogen absorption capacity and 90% of the maximum

……………………………………………（7）

In the formula：

*W*d0.6——The hydrogen discharge amount of 60% of the maximum hydrogen discharge amount, read from the hydrogen discharge amount versus time change curve (8.7.4), and the unit is mass fraction (%);

*W*d0.9——The hydrogen discharge amount of 90% of the maximum hydrogen discharge amount, read from the hydrogen discharge amount versus time curve (8.7.4), and the unit is mass fraction (%);

*t*d0.6——The time to reach 60% of the maximum hydrogen discharge, read from the hydrogen discharge versus time curve (8.7.4), in seconds (s);

*t*d0.9——The time to reach 90% of the maximum hydrogen discharge, read from the hydrogen discharge versus time curve (8.7.4), in seconds (s).

The results retain two significant figures, and the rounding off of values shall be carried out in accordance with the provisions of GB/T8170.

9 precision

9.1 Repeatability

The difference between the measured values of two independent test results obtained under repeatability conditions does not exceed the repeatability limit (r), and the case of exceeding the repeatability limit (r) does not exceed 5%, the repeatability limit (r) is obtained in accordance with the provisions of GB/T6379.2 using the data measured at the test temperature in Table 1.

Tab1 repeatability limit

|  |  |  |  |
| --- | --- | --- | --- |
| Kinetic performance | Platform pressure rangeMPa | Test temperature℃ | Repeatability limit（*r*）%•s-1 |
| Absorption rate *R*a | 1~5  | 40 | 0.002 |
| 0.1~1 | 40 | 0.001 |
| 0.01~0.1 | 150 | 0.009  |
| 0.001~0.01 | 200 | 0.004 |
| Dehydrogenation rate *R*d | 1~5  | 40 | 0.001 |
| 0.1~1 | 40 | 0.001 |
| 0.01~0.1 | 150 | 0.002 |
| 0.001~0.01 | 200 | 0.001 |

9.2 Reproducibility

The difference between two independent test results obtained under reproducible conditions does not exceed the reproducibility limit (R), and the case of exceeding the reproducibility limit (R) does not exceed 5%, the reproducibility limit (R) is obtained in accordance with the provisions of GB/T 6379.2 using the data measured at the test temperature in Table 2.

 Tab2 Reproducibility limit

|  |  |  |  |
| --- | --- | --- | --- |
| Kinetic performance | Platform pressure rangeMPa | Test temperature℃ | Reproducibility limit （*R*）%•s-1 |
| Absorption rate *R*a | 1~5  | 40 | 0.003  |
| 0.1~1 | 40 | 0.002  |
| 0.01~0.1 | 150 | 0.017  |
| 0.001~0.01 | 200 | 0.011 |
| Dehydrogenation rate *R*d | 1~5  | 40 | 0.003  |
| 0.1~1 | 40 | 0.001 |
| 0.01~0.1 | 150 | 0.002 |
| 0.001~0.01 | 200 | 0.001 |

10 Test report

The test report should include the following:

a) The document number;

b) Necessary instructions for identifying the sample;

c) Testing time;

d) Measurement results;

e) Operations not specified in this document;

f) Any circumstances that may affect the results.