INTERNATIONAL STANDARD

ISO 4215

First edition
2022-09

Corrosion of metals and alloys — Test method for high-temperature corrosion testing of metallic materials by thermogravimetry under isothermal or cyclic conditions

Corrosion des métaux et alliages — Méthode d'essai de corrosion à haute température des matériaux métalliques par thermogravimétrie en conditions isothermes ou cycliques

Reference number
ISO 4215:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 156, *Corrosion of metal and alloys*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Oxidation and corrosion tests at high temperature on metallic materials are often performed according to the isothermal or to the cyclic exposure methods specified in ISO 21608[6] and ISO 13573[5] respectively. These methods rely on measuring the mass change at the end of the exposure. An alternative approach is to employ a thermogravimetric method which enables a continuous monitoring and recording of mass as a function of time under isothermal or cyclic operation.

Under isothermal exposure the thermogravimetric analysis allows the measurement of mass gain due to oxidation or corrosion and of mass loss due to volatilization. The corresponding kinetics can be assessed thereby distinguishing between mass gain due to oxidation or mass loss due to volatilization. Moreover, it allows the detection of a mass change due to the loss of a part of the oxide scale during the high temperature dwell or during cooling. Re-oxidations subsequent to the formation of cracks in the oxide scale can also be detected.

Under thermal cycling conditions the mass change of the sample can be measured as well. The corresponding kinetics can be assessed thereby distinguishing between mass gain due to oxidation and mass loss due to spalling. The occurrence of breakaway oxidation can be also precisely identified and the test is fully automated without the need to take the samples out of the corrosive atmosphere for mass measurements.

The main areas of application are the following:

— the test method describes the general conditions of analysis for materials such as pure metals and metallic alloys using thermogravimetric techniques;

— the thermogravimetric test can be used in the isothermal mode (mass variation versus time at a given temperature) or in the cyclic mode (mass variation versus time according to defined thermal cycles).

Corrosion of metals and alloys — Test method for high-temperature corrosion testing of metallic materials by thermogravimetry under isothermal or cyclic conditions

1 Scope

This document specifies the thermogravimetric method (continuous measurement) for isothermal and cyclic exposure of metals and metallic alloys at high temperature under corrosive conditions.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ASTM E3-01,*Standard Practice for Preparation of Metallographic Specimens*

ASTM E220-02, *Standard Test Method For Calibration Of Thermocouples By Comparison Techniques*

ASTM E230-03, *Standard Specification and Temperature-Electromotive Force (EMF) Tables for Standardized Thermocouples*

ASTM E407-07e1, *Standard Practice for Microetching Metals and Alloys*

ASTM E1350-97,*Standard Test Methods for Testing Sheathed Thermocouples Prior to, During, and After Installation*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

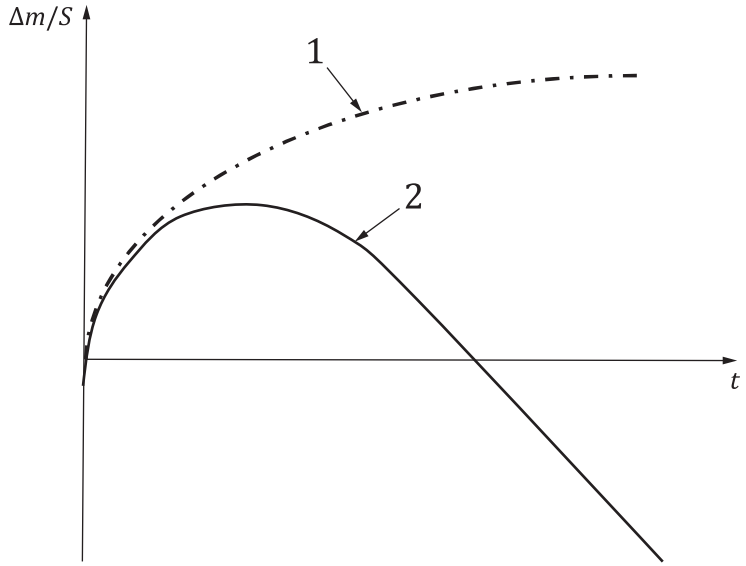
— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
thermogravimetry
TG
technique in which the mass of a *test piece* (3.4) is measured with respect to temperature or time, the test piece being heated according to a given temperature program

3.2
thermogravimetry curve
TG curve
curve obtained by plotting the mass of the test piece divided by its surface area as the ordinate (Y axis) and the elapsed time *t* as the abscissa (X axis)

Note 1 to entry: See Figure 1.



Key

t	time
$\Delta m/S$	mass change by surface area
n	number of cycles
1	net mass gain
2	net mass loss

Figure 1 — Two examples of TG curve with a net mass gain or a net mass loss after an initial mass gain (NMC versus time or versus number of cycles)

3.3
sample
small part or fraction of a material coming from a series of products, designed to represent the whole amount

3.4
test piece
full product or unique fraction, taken from the sample and used for the test

3.5
buoyancy effect
apparent variation of the sample mass, related to the pressure effect on its volume in a given atmosphere

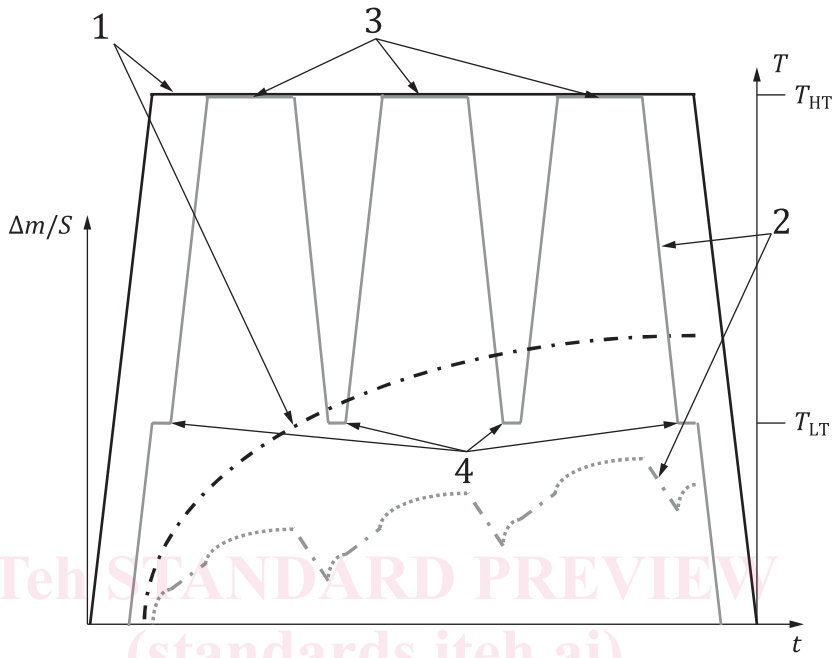
4 Test method

4.1 Principle

The test piece is heated at a constant and controlled heating rate (at least 60 °C/min, deviations from this and the reasons shall be reported in the test report) up to an elevated temperature T_{HT} in a controlled gaseous environment (inert, reducing, oxidative, or corrosive -dry or humid- atmosphere). If the reaction between the test piece and the atmosphere can be fully prevented during the heating (oxidation of pure metals with low stability oxides such as Cu, Ni, or Co), it is possible to use an inert gas during heating prior to the introduction of the reacting gas when the temperature T_{HT} is reached. In all other cases, the atmosphere is established before the heating of the sample.

For an isothermal test, the temperature T_{HT} is maintained constant during the test duration (see Figure 2).

In cyclic mode the temperature is first increased to a temperature T_{LT} at a constant heating rate. T_{LT} is maintained constant during a time to be defined (cold dwell). The temperature is then increased at a given heating rate (≥60 °C/min, deviations from this and the reasons shall be reported in the test report) to the temperature T_{HT} and maintained constant during a time to be defined (hot dwell). The final stage is a cooling from T_{HT} to T_{LT} with a controlled initial cooling rate at least equal to 60 °C/min. The temperature cycle can be repeated a number of times to be defined (see Figure 2).



Key

t	time
$\Delta m/S$	mass change by surface area
T	temperature
1	isothermal mode
2	cyclic mode
3	hot dwells
4	cold dwells

Figure 2 — Temperature and net mass change as a function of time during a thermogravimetric test in isothermal or cyclic mode

At the end of either procedure the test piece is cooled down to room temperature and the mass variation of the test piece is measured versus time t during the duration of the test and recorded as a TG curve.

4.2 Test pieces

The test pieces are in solid form and may be of different geometries: sheets, films, rectangular cuboid, cylinders and discs. The dimensions of the test piece shall be restricted to a value less than the diameter of the furnace used for the test, thus avoiding contact with the walls of the furnace.

The test pieces shall be finished by machining so that the strata affected by cutting do not remain.

The final finishing of the surface of the test pieces shall be performed with abrasives with mean particle diameter of approximately 15 µm. This can be achieved by the use of abrasives according to Table 1.

If another surface finish is required by the parties involved, the surface finish condition shall be described.

Table 1 — Designation and mean diameter of particles of coated abrasives according to regional standards

Standard	Designation	Mean diameter µm	Region
FEPA 43-1984 R:1993[9] ISO 6344-3[2]	P1200	15,3 ± 1,0	Europe
JIS R6001-87[7]	#1000	15,5 ± 1,0	Japan
ANSI B74.12-92[8]	600	16,0	America

Sharp edges of test pieces can give anomalous behaviour. These shall be slightly rounded during the final stages of test piece preparation.

The surface of the test pieces shall not be deformed by marking, stamping or notching. However, holes for either test piece support or reference marking, or both, are permissible.

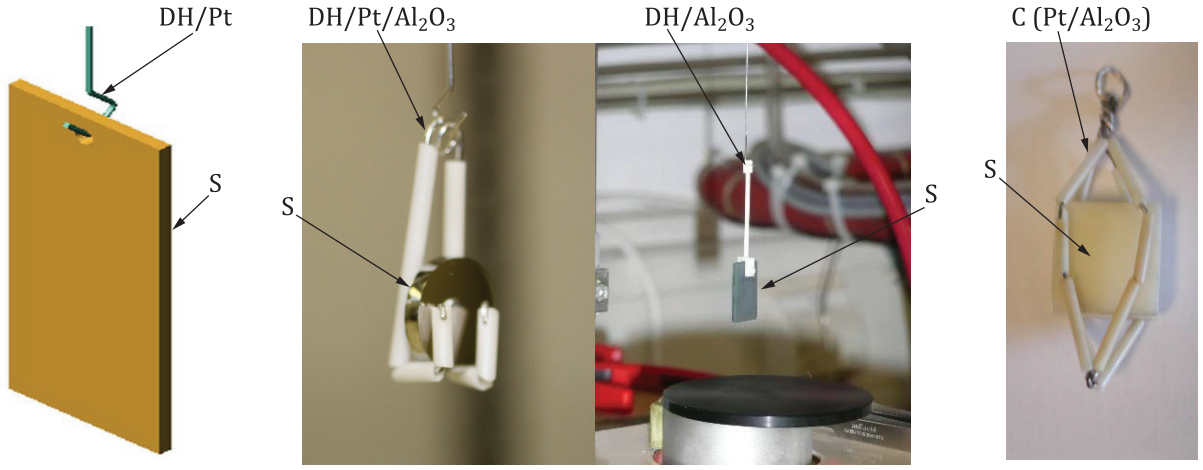
Where holes are used for test piece support they shall be drilled prior to final finishing or application of coatings. These must be taken into account when calculating the surface area.

The dimensions of the test pieces shall be measured prior to exposure at a minimum of three positions for each dimension with a precision of ±0,02 mm by means of the measuring instruments specified in ISO 3611[1] and ISO 13385-1[4].

The test pieces shall be dried after degreasing by ultrasonic cleaning using isopropanol or ethanol.

If it is suspected that specimens may adsorb significant amounts of atmospheric contaminants such as water, it is recommended that the cleaned test pieces are stored in a desiccator prior to weighing and exposure.

A hole is machined in the top part of the test piece to allow it to be suspended from the balance (see Figure 3). Platinum wire, quartz rod or an intermediary alumina piece shall be used to suspend the test piece. When it is not possible to machine a hole in the test piece (e.g. coated test piece), a cradle shall be used to hang the test piece (see Figure 3). If a holder is used, it shall be adapted to the shape and the size of the test piece. It shall not limit the access of the reactive gas to the sample or prevent spalled parts of the sample from falling down.



a) Using a hole drilled in the specimen and a Pt wire to hold the specimen **b) Using a hole drilled in the sample and a platinum/alumina sample holder** **c) Using a hole drilled in the sample and an alumina sample holder** **d) Using a platinum/alumina cradle**

Key

S	sample
DH/Pt	drilled hole and platinum hanging wire
Pt/Al_2O_3	platinum/alumina hanging system
DH/Al_2O_3	drilled hole and alumina hanging road
C (Pt/Al_2O_3)	cradle of platinum wire and alumina

Figure 3 — Test pieces hung to the balance

The vaporization of Pt as a volatile oxide can be significant at temperatures higher than 1 100 °C in oxygen-rich atmospheres. In this case alumina shall be preferred to platinum. Moreover, depending on the specimen materials, the reaction with Pt (e.g. eutectic formation) or Si has to be carefully addressed before thermogravimetry test.

5 Test apparatus

5.1 Thermobalance

The thermobalance shall be able to measure the mass variation with an accuracy equal to 0,1 % of the final total mass variation. For every condition of temperature and gas flow, a blank test shall be performed with an inert sample. The resulting drift of the balance under isothermal conditions shall be at least 100 times less than the instantaneous rate of mass loss or gain over the test period. If this is difficult to achieve, the use of a symmetrical thermobalance (with two symmetrical furnaces) should be considered to decrease the balance drift.

It is recommended to install the thermobalance in a controlled temperature room. Depending on the thermobalance and the accuracy that is required for the measurement, it may be necessary to set up the instrument on a vibration-reduced table.

The thermobalance shall allow a constant flow of gas around the test piece in order to allow a homogeneous interaction on the whole surface of the test piece in the reactive gaseous atmosphere.

Issues with buoyancy and convection effects in the gas flow can be resolved using a symmetrical thermobalance built with two identical furnaces (see Figure 4). In this case the test piece is introduced in the measuring furnace and a reference piece with identical dimensions, but inert in the given temperature range and gas, is introduced to the reference furnace. The gas flow rates are adjusted in