# INTERNATIONAL STANDARD

# ISO
# 13573

# Corrosion of metals and alloys — Test method for thermal-cycling exposure testing under high-temperature corrosion conditions for metallic materials

*Corrosion des métaux et alliages — Méthode pour essais de corrosion à haute température, avec exposition à des cycles thermiques, sur des matériaux métalliques*

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# 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 13573 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*, Working Group 13, *High Temperature Corrosion*.

# Corrosion of metals and alloys — Test method for thermal-cycling exposure testing under high-temperature corrosion conditions for metallic materials

## 1 Scope

This International Standard describes the methodology for thermal cycling corrosion testing (known as cyclic oxidation testing) of metallic materials in gaseous environments between ambient and elevated temperatures (series of measurements on a single test piece with repeated, regular and controlled temperature cycles). It also may be applicable to other materials with some modifications. Tests with ultra short dwell times in the range of minutes or seconds are outside the scope of this International Standard.

## 2 Normative references

The following referenced documents are indispensable for the application 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.

ANSI B74.12-92, *Specifications for the Size of Abrasive Grain – Grinding Wheels, Polishing and General Industrial Uses*

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

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

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

ASTM E633-00, *Standard Guide for Use of Thermocouples in Creep and Stress Rupture Testing to 1800°F (1000°C) in Air*

FEPA 43-1984 R:1993, *Grit Sizes for Coated Abrasives*

ISO 3611, *Geometrical product specifications (GPS) — Dimensional measuring equipment: Micrometers for external measurements — Design and metrological characteristics*

ISO 6344-3:1998, *Coated abrasives — Grain size analysis — Part 3: Determination of grain size distribution of microgrits P240 to P2500*

ISO 13385-1, *Geometrical product specifications (GPS) — Dimensional measuring equipment — Part 1: Callipers; Design and metrological characteristics*

ISO 26146, *Corrosion of metals and alloys – Method for metallographic examination of samples after exposure to high temperature corrosive environments*

JIS R6001-87, *Bonded abrasive grain sizes*

## 3 Terms and definitions

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

**3.1**
**scale**
surface film and corrosion products produced on the surface of the test piece by high temperature corrosion

**3.2**
**adherent scale**
scale adhering to the test piece even after cooling

**3.3**
**spalled scale**
scale flaked from the test piece

**3.4**
**delaminated scale**
scale fully or partially detached from the surface but still in contact with the test piece

**3.5**
**gross mass change**
mass change of the test piece after cooling, including collected spalled scale

**3.6**
**net mass change**
mass change of the test piece after cooling, without including the mass of spalled scale

**3.7**
**high temperature corrosion**
corrosion occurring when the temperature is higher than the dew point of aqueous phases of the environment but at least 100 °C

**3.8**
**breakaway**
rapid increase in corrosion rate following a change from protective to non-protective scale growth

**3.9**
**thermal cycle**
sequence of temperatures that is repeated throughout the test. A single thermal cycle consists of the heating phase, the hot dwell time, the cooling time and the cold dwell time

## 4   Test method

### 4.1   Reagents and materials

#### 4.1.1   Test pieces

The test pieces shall have the form of a rectangular plate, a disc or a cylinder with a surface area of 300 mm$^2$ at minimum and a thickness of 1,5 mm at minimum.

If the test pieces cannot be made according to these specifications, the shape and dimensions of the test piece shall be in accordance with the agreement between the parties involved.

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[a] 43-1984 R:1993, *Grit Sizes for Coated Abrasives* ISO 6344-3:1998, *Coated abrasives – Grain size analysis – Part 3: Determination of grain size distribution of microgrits P240 to P2500* | P1200 | 15,3 ± 1,0 | Europe |
| JIS R6001-87, *Bonded abrasive grain sizes* | #1000 | 15,5 ± 1,0 | Japan |
| ANSI B74.12-92, *Specifications for the Size of Abrasive Grain – Grinding Wheels, Polishing and General Industrial Uses* | 600 | 16,0 | America |
| [a]   Federation of European Producers of abrasives | | | |

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

The surface of the test pieces shall not be deformed by marking, stamping or notching. Identification of the test pieces shall be solely on the basis of recording the relative position within the test chamber, however, holes for the test piece support (Figure 5) and or reference marking are permissible.

Where holes are used for the test piece support, they shall be drilled prior to final finishing or application of coatings. These have to 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 and ISO 13385-1.

The test pieces shall be dried after degreasing by ultrasonic cleaning using iso-propanol 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.

The mass of the test pieces shall be determined prior to exposure. At least two measurements shall be made for each test piece. The difference between the measurements shall not exceed 0,05 mg.

It is recommend that duplicate test pieces are used each time.

### 4.1.2   Gas supply for closed system operation

The gas supply system shall be capable of supplying the test gases at a constant rate to the test piece chamber.

When a humidifying regulator is used, it shall be capable of adjusting to the desired humidity. Deionized water of a conductivity less than 1 μS cm$^{-1}$ shall be used, unless otherwise specified.

The space between the humidifying regulator and the test piece chamber shall be kept above the dew point in order to avoid condensation.

The gas flow shall be monitored by a gas flow meter. The flow meter shall be located as close as practicable to the inlet of the test piece chamber except where a humidifying regulator is used, in which case it shall be located upstream to the humidifier.

For testing in air, a specific humidity (mass fraction of water in air) of ~20 g/kg is recommended. This corresponds to a relative humidity of 100 % at 25 °C (dew point) and is easy to obtain by bubbling through a water bath of 25 °C.

If any other humidity is employed, it shall be agreed between the parties concerned.

In the case that the gas is humidified the water vapor content shall be measured.  For example, this can be achieved by the use of a hygrometer before the test piece chamber or by measuring the amount of

water after condensation of the exhaust gases or by measuring the water consumption of the humidifier over the course of the experiment.

The formation of condensed phases from the test gas during the cooling cycle shall be avoided. This may be achieved by turning off the humidification or by switching to an inert gas.

## 4.2   Test apparatus

### 4.2.1   Design of apparatus

The apparatus shall be comprised of a set-up that will transition the test pieces between hot and cold environments in a controllable and reproducible manner. Ideally, the heating device should be equipped with a testing portion capable of separating the test piece from outside air (this assembly is referred to as a closed system) unless this is impracticable for the tests planned. When applicable, a humidifying regulator should be used to continuously supply the gas kept at a constant humidity which should be monitored with a hygrometer. The gas supply shall be controlled by a gas flow meter. A facility to accelerate cooling may also be included. Examples of basic designs are shown in Figures 1 and 2.

The heating device shall be constructed such that the test piece chamber is isolated from the external environment. It shall be ensured that a continuous gas flow within the prescribed range passes over the test pieces.

The test piece chamber shall not be composed of a material that reacts with the test atmosphere during the test to a degree that it changes the composition of the atmosphere.

If a closed system with a test piece chamber cannot be used, then the tests may be performed in an open system with laboratory air. In this case the humidity of the air shall be recorded and the laboratories should be kept free from temperature changes and influences from weather conditions, as far as possible. Ideally, however, closed systems should be used.

The furnace shall be characterized at the exposure temperature prior to the testing to determine the length of the isothermal zone inside the furnace. A common method is by the use of an independent moveable thermocouple.

The time-dependent temperature response during the thermal cycling at a position at, or near to, the test piece shall be recorded prior to the testing in order to allow definition of the parameters of a thermal cycle, according to 4.3.3. This can be achieved by using dummy test pieces and appropriate thermometry.

The temperature regulating device shall be capable of guaranteeing that the temperature of the test piece is kept within the permissible range given in Table 2. The temperature of the furnace may vary or fluctuate due to movement of the furnace (less pronounced when the test piece supports are moved). The control system used shall ensure that the desired temperature inside the furnace is reached rapidly without being exceeded.
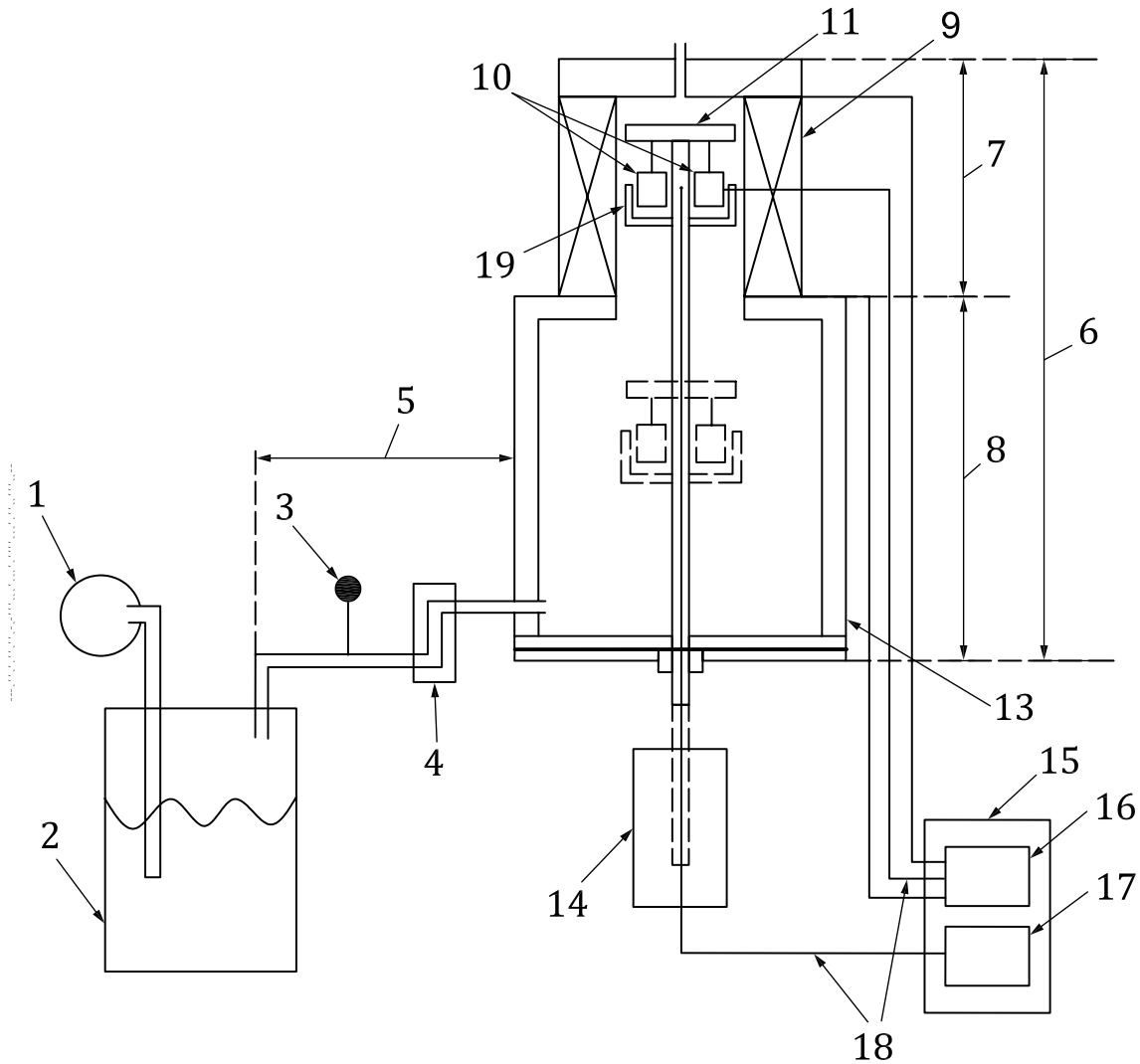
The heating device thermocouples for temperature control shall be as follows: The material for thermocouple shall fully withstand the test temperature. Moreover, the diameter of wire is recommended to be as small as possible, within the limit where the thermoelectric power does not change in service.
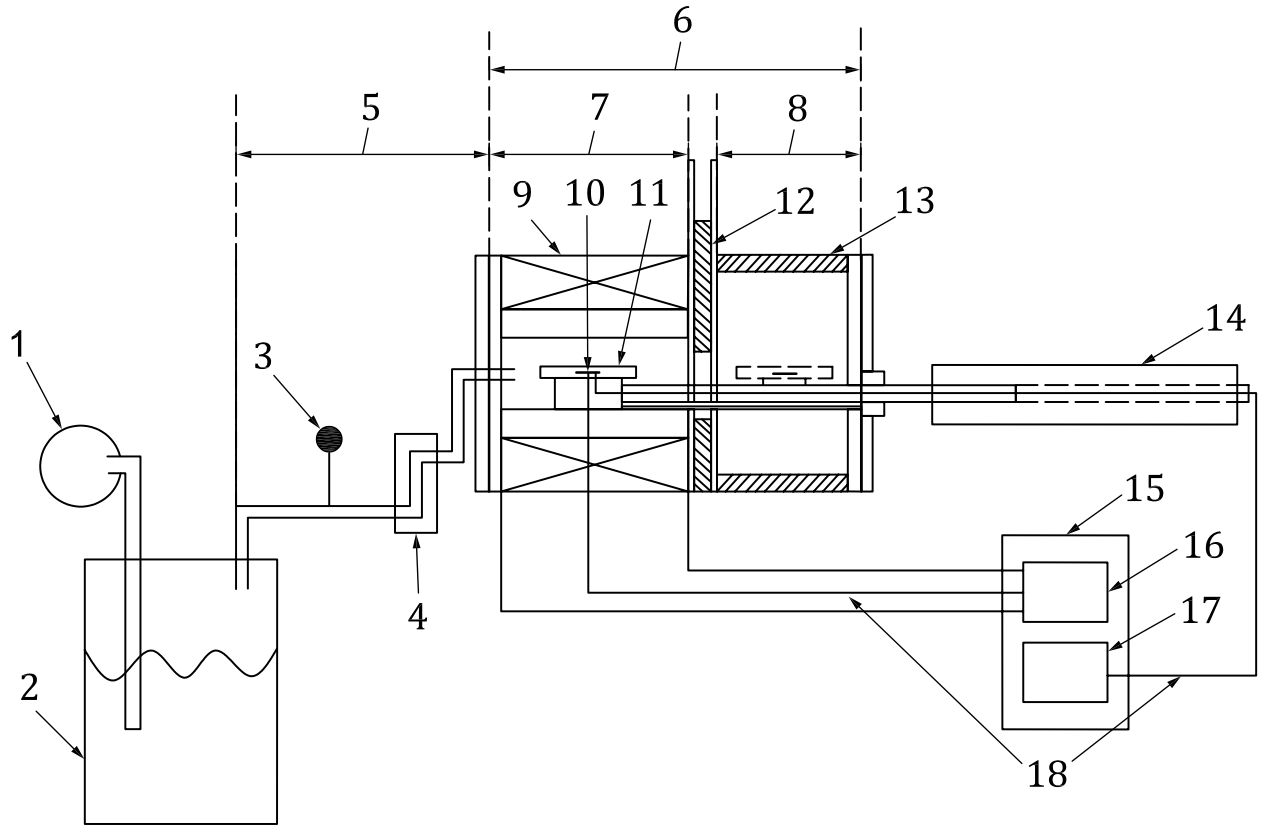
a)

**b)**

**Key**

| | | | |
|---|---|---|---|
| 1 | Blower | 11 | Test piece support |
| 2 | Humidifying regulator (electronic type) | 12 | Shielding plate (movable type) |
| 3 | Hygrometer | 13 | Cooling chamber |
| 4 | Air flow meter | 14 | Test piece carrier |
| 5 | Heating zone with ribbon heater | 15 | Temperature regulating device |
| 6 | Testing portion | 16 | Power control device |
| 7 | Heating zone | 17 | Measuring instrument |
| 8 | Cooling zone | 18 | Thermocouples |
| 9 | Heating furnace | 19 | Crucible |
| 10 | Test piece | | |

**Figure 1 — Basic design of a closed horizontal (a) and a vertical (b) apparatus,
examples for setups with movable test piece support**

a)
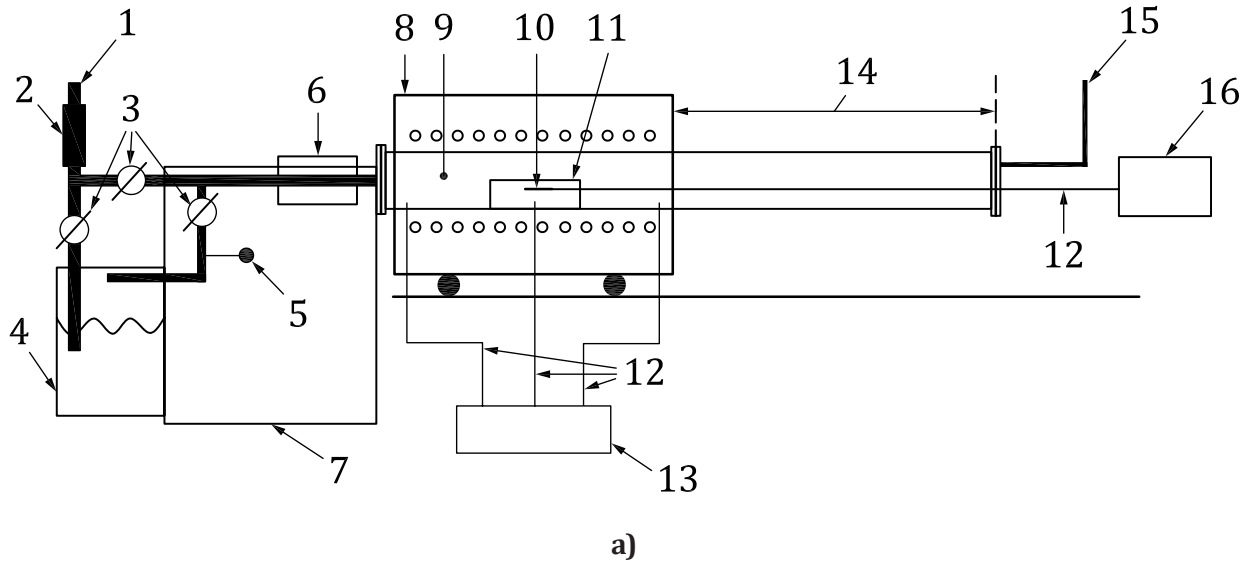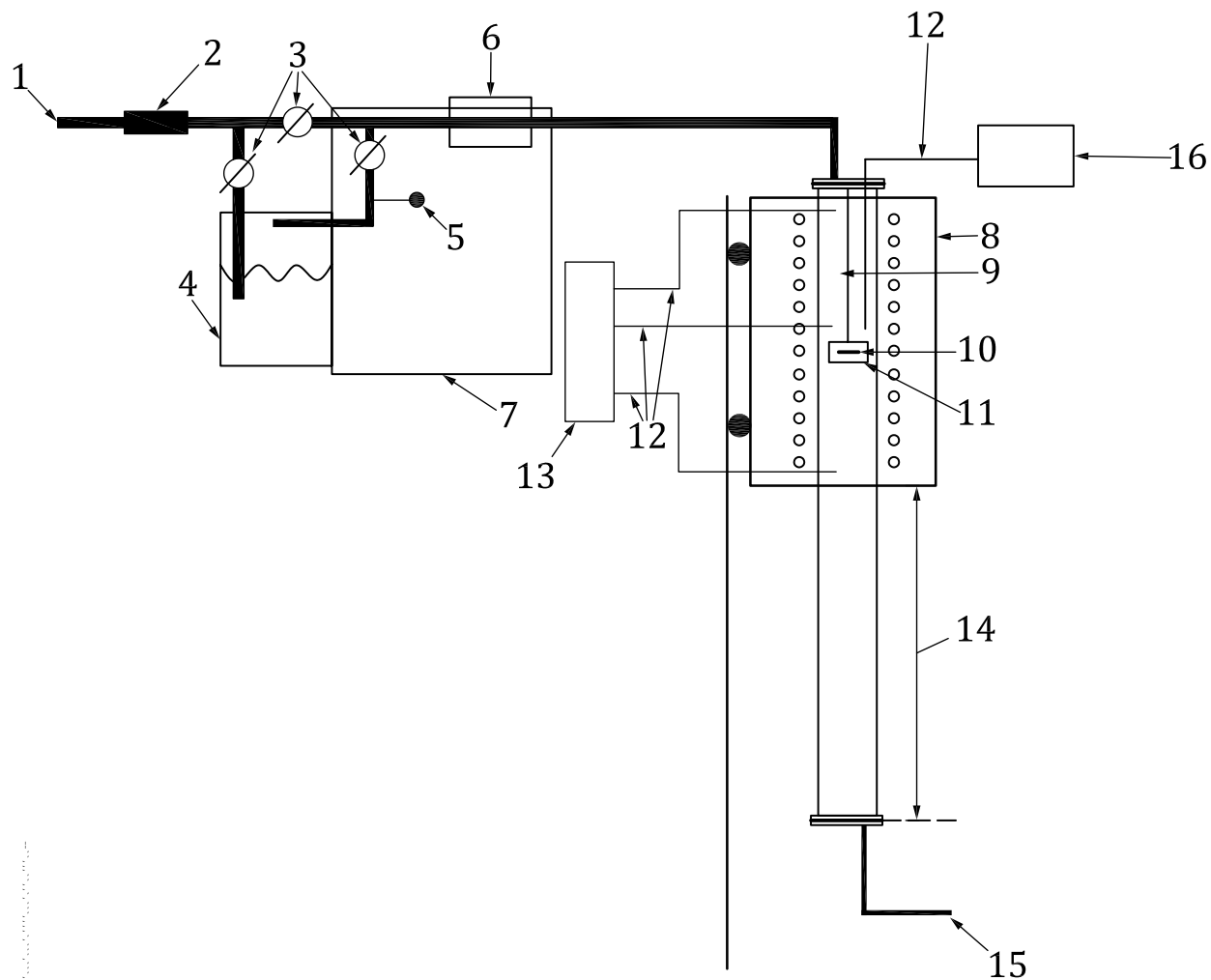
**b)**

**Key**

| | | | |
|---|---|---|---|
| 1 | Gas supply | 9 | Test piece chamber |
| 2 | Gas flow meter | 10 | Test piece |
| 3 | Valves | 11 | Test piece support |
| 4 | Humidifying regulator (electronic type) | 12 | Thermocouples |
| 5 | Hygrometer | 13 | Power/Temperature control device |
| 6 | Heating device containing catalyst for non-equilibrium gas mixtures | 14 | Direction of furnace movement |
| 7 | Heating zone with ribbon heater | 15 | Gas exhaust |
| 8 | Heater | 16 | Measuring instrument |

**Figure 2 — Basic design of a closed horizontal (a) and a vertical (b) apparatus, examples for setups with movable furnace**

**Table 2 — Permissible tolerance of temperature of test pieces**

| Temperature range, °C | ≤ 300 | 300 to 600 | 600 to 800 | 800 to 1 000 | 1 000 to 1 200 | > 1 200 |
|---|---|---|---|---|---|---|
| Temperature tolerance, °C | ±2 | ±3 | ±4 | ±5 | ±7 | By agreement |

### 4.2.2 Temperature monitoring

The temperature shall be measured by a suitable device, according to ASTM E633-00. Thermocouples of type S (Pt – 10 % Rh/Pt) or type R (Pt – 13 % Rh/Pt) are preferred for the temperature range: room temperature up to 1 700 °C. A thermocouple should be positioned close to the test piece surface and shall be calibrated according to the following paragraph. If, however, the environment does not allow the use of such thermocouples in this way, the test piece temperature has to be deduced from the furnace calibration using dummy test pieces and appropriate thermometry in an inert environment.

Calibration of thermocouples shall be performed in accordance with ASTM E220-02, ASTM E230-03, or ASTM E1350-97. A representative thermocouple taken from the batch of wire may be calibrated.

It is recommended that thermocouples are recalibrated annually or at the beginning and the end of each experiment, if there is uncertainty about thermocouple stability.

The thermocouple shall be capable of confirming the temperature of the test piece to be within the range given in Table 2. It has to be on a defined, fixed place as close to the test pieces as possible.

Thermocouple sheaths shall be used to protect the thermocouple wires. The thermocouple sheaths shall fully withstand the test temperature and environment.

## 4.3 Procedure

### 4.3.1 Support of test pieces

The test pieces shall be supported, according to the following principles:

The test piece shall be supported by a material that does not react at the test temperature. Contact between the test piece and support shall be minimized.

The support of the test piece to be used shall be designed to be able to collect the scale, even if it flakes during testing or during cooling after finishing the test.

When testing multiple test pieces simultaneously, each test piece shall be inserted into an individual test piece support in order to enable the collection of all scale, including the scale spalled from each test piece.

The support design shall ensure that no major faces of the test pieces are shielded from the test atmosphere.

Examples of suitable test piece supports and basic layout of test piece arrangement are shown in Figures 3 to 5.

Where the possibilty of the depletion of active species in the test atmosphere is a concern, the exchange of the test atmosphere can be improved by the use of holes or slots in the bottom area of the side walls of the test piece support.

When only net mass change data are required, multiple test pieces may be inserted in a single test piece support.
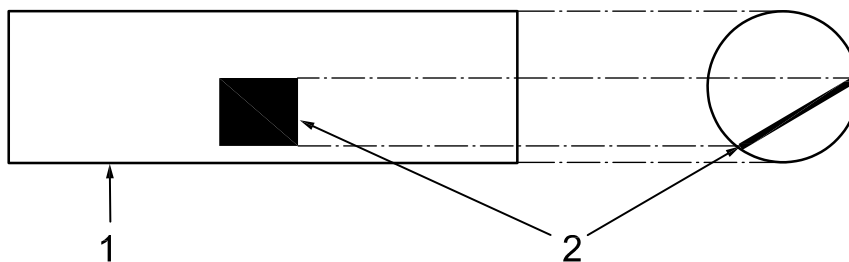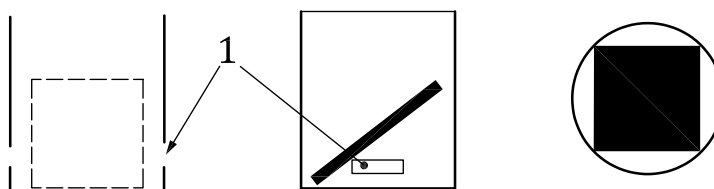
**Key**

1    High purity alumina tube for supporting test piece
2    Test piece

NOTE    left = side view; right = cross sectional view

**Figure 3 — Test piece support and basic layout of test piece arrangement — tube design**
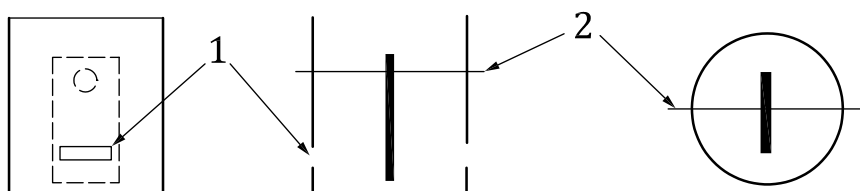(this type of support is not suitable for rapid heating and cooling)



**Key**

1    holes

NOTE    left = side view; centre = cross sectional view; right = top view

**Figure 4 — Test piece support and basic layout of test piece arrangement — round crucible**



**Key**

1    holes
2    alumina rod

NOTE    left = side view; centre = cross sectional view; right = top view

**Figure 5 — Test piece support and basic layout of test piece arrangement — rod supported design**

### 4.3.2    Test environment

The gas flow shall be high enough to ensure that no significant depletion of reaction species will occur. At the same time, the gas flow shall be slow enough to allow the gas mixture to preheat and, in some applications, to reach equilibrium. The flow rate of the test gas shall be sufficient to ensure complete replacement of the test gas within the test chamber at least three times an hour.

For testing in air in closed systems, the humidity should be controlled, as specified in 4.1.2.

For testing in air in open systems, it should be noted that the humidity of laboratory air varies significantly depending on the location of the laboratory and local weather conditions. It must be recognized that these variations may affect test results significantly. In this case, the humidity of the laboratory air shall be recorded during the test.

For testing in other environments, the humidity should be specified and measured.

### 4.3.3 Definition of a thermal cycle

A thermal cycle consists of: the heating phase, the hot dwell time, the cooling time, and the cold dwell time. An example for a hot dwell temperature of $T_{dwell} = 1\,000\,°C$ is given in Figure 6. The four phases of a temperature cycle are defined in the following paragraphs.
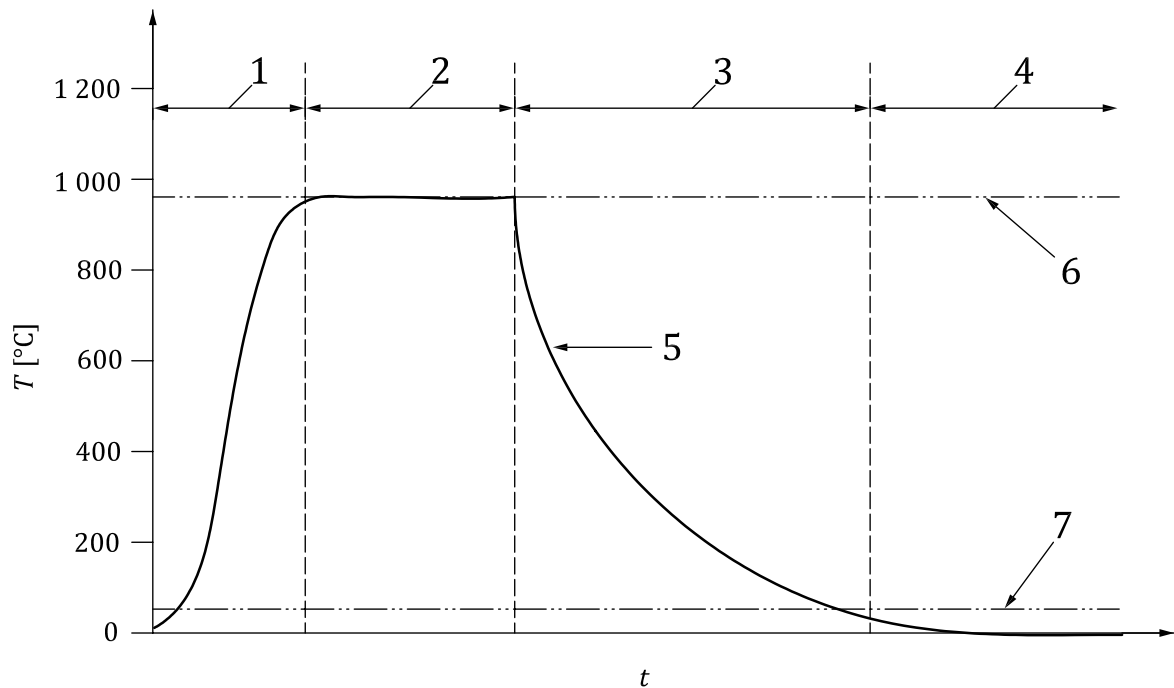


**Key**

| | | | |
|---|---|---|---|
| $t$ | Time | 4 | Cold dwell time ($T < 50\,°C$) |
| $T$ | Temperature | 5 | Temperature curve |
| 1 | Heating time | 6 | $T = 0{,}97 \cdot T_{dwell} = 0{,}97 \cdot 1\,273\,K = 1\,235\,K = 962\,°C$ |
| 2 | Hot dwell time ($T > 0{,}97 \cdot T_{dwell}$) | 7 | $T = 50\,°C = 323\,K$ |
| 3 | Cooling time | | |

**Figure 6 — Definition of a thermal cycle with a hot dwell temperature of 1 000 °C**

The heating time starts when the test pieces are heated (e.g. by entering the furnace) and ends with the beginning of the hot dwell time.

The hot dwell time starts when the actual temperature exceeds 97 % of the desired hot dwell temperature, $T_{dwell}$ (measured in K). Extensive numerical calculations and comparison between hypothetical and real temperature cycles have shown that only those times of the temperature cycle contribute to oxidation of the test pieces where the temperature is close to the hot dwell temperature [3]. The hot dwell time ends upon removal from the furnace.

The cooling time starts when the heating of the test piece is stopped (e.g. by the removal of the test piece from the furnace) and ends when the actual test piece temperature falls below 50 °C.

The cold dwell time starts after the test pieces have cooled below 50 °C and ends when the test pieces are heated again.

### 4.3.4 Types and dwell times of thermal cycles

#### 4.3.4.1 Typical types of thermal cycles

Two general types of thermal cycles are typical for industrial applications:

**Thermal cycling with long dwell time** aims to simulate conditions in large-scale industrial facilities encountered in applications such as power generation plants, waste incineration or chemical industry. In these applications, the metallic components are designed for extremely long term operation, e.g. for typically up to 100 000 h. Thermal cycling of materials occurs due to planned plant shutdowns e.g. for regular maintenance or due to unplanned shutdowns as a result of offset conditions. Therefore, the time intervals between various thermal cycles are relatively long and the number of cycles is, related to the long operation time of the components, relatively small, i.e. typically around 50 cycles.

**Thermal cycling with short dwell time** is typically experienced in applications such as industrial gas turbines, jet engines, automotive parts, heat treatment facilities etc. The intervals between start and shutdown of the facilities are generally much shorter than in applications with long dwell times. Also, the design life and/or the time until complete overhaul/repair (typically 3 000 to 30 000 h) are shorter and, depending on the specific practical application, the number of cycles is much higher than in the cases above.

#### 4.3.4.2 Heating and cooling times

Heating and cooling rates may affect the results significantly and are determined by the detailed features of the experimental facilities. Controlling parameters include the thermal mass of the system, the transfer mechanism, and the presence or otherwise absence of forced cooling. It is recommended that heating times should not exceed 30 min while cooling times should not be longer than 60 min.

#### 4.3.4.3 Standard test parameters for long dwell time testing

The definition of 4.3.3 for a thermal cycle shall be applied to long dwell time testing. For practical reasons, it is useful to stay within a 24 h operation rhythm. Therefore, experiments shall be performed with a 20 h hot dwell time and a 4 h period which includes the cooling time, the cold dwell time, and the heating time. The heating and cooling times, according to 4.3.3, shall be reported.

#### 4.3.4.4 Standard test parameters for short dwell time testing

The definition of 4.3.3 for a thermal cycle shall be applied to short dwell time testing. The hot dwell time shall be 1 h, the cold dwell time shall be 15 min. Heating and cooling times, according to 4.3.3, shall be reported. For weighing procedures for mass determinations, the cold dwell time may be extended but shall be kept as short as possible.

#### 4.3.4.5 Other dwell times

Dwell times that differ from the standard in 4.3.4.3 and 4.3.4.4 are allowed under exceptional circumstances if agreed between the parties concerned.

### 4.3.5 Testing duration

The testing duration shall be at least 300 h of accumulated hot dwell time to allow a significant oxidation of the test pieces. For more reliable results it is, however, recommended to extend the accumulated hot dwell time to at least 1 000 h.

Figure 7 shows three different types of oxidation behaviour giving an indication of minimum testing duration. Testing is usually terminated when protective behaviour is no longer found for the materials.
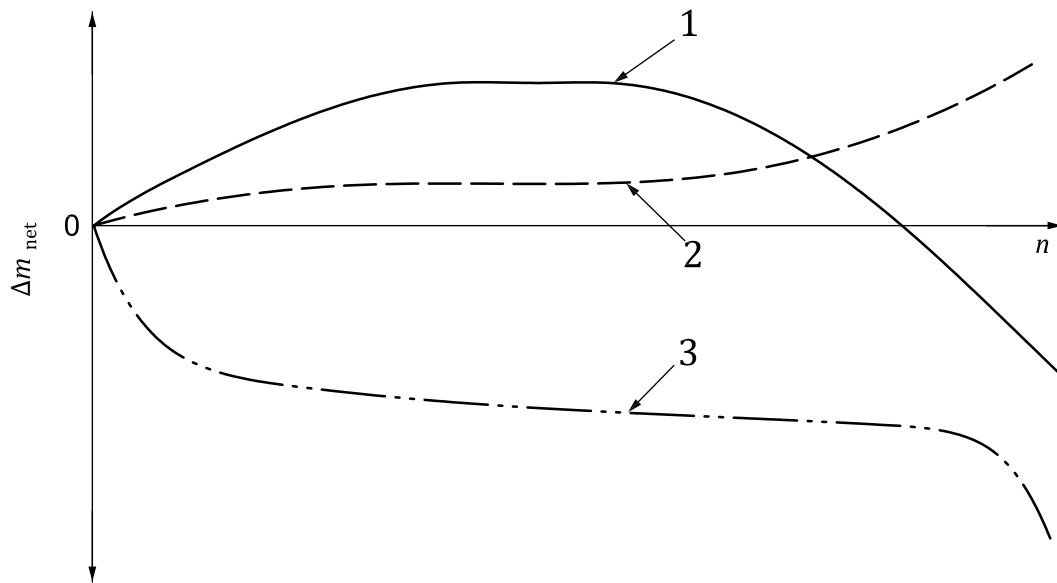


**Key**

$n$       number of cycles

$\Delta m_{net}$    net mass change according to Formula (3)

1       Spalling after initial protective period

2       Breakaway oxidation after initial protective period

3       Spallation from the start of testing

**Figure 7 — Different types of oxidation behaviour during thermal cycling**

## 4.4 Determination of mass change

### 4.4.1 Principle

In order to define oxidation kinetics, determination of the mass change has to be performed. It is recommended to use duplicate test pieces for each material. When handling specimens, the use of tweezers is recommended. Test pieces shall never be touched with the hands to eliminate any contamination (grease, salts). Care has to be taken when using gloves as the contamination with the separating agent of the gloves leads to falsification in mass determination. If repeated measurements are not consistent, the temperature and humidity of the weighing environment has to be controlled.

### 4.4.2 Measurements prior to testing

New test piece supports shall be baked in air to remove volatile compounds from production. The recommended baking conditions are at least 24 h at a temperature of 1 000 °C. If water adsorption is suspected to have occurred, used test piece supports shall be dried at significantly above 100 °C.

The mass of the test pieces shall be determined prior to exposure ($m_T(t_0)$, Figure 8). At least two individual measurements shall be made for each test piece with a precision of 0,02 mg. The maximum difference between the measurements shall not exceed ± 0,05 mg.

The mass of the test piece supports shall be determined prior to exposure ($m_S(t_0)$, Figure 8). At least two individual measurements shall be made for each test piece support. Where the test piece support has a mass of less than 20 g, the precision shall be 0,02 mg. The maximum difference between the measurements shall not exceed ± 0,05 mg. For test piece supports of higher mass the precision shall be 0,1 mg. The maximum difference between the measurements shall not exceed ± 0,3 mg in this case.

When only net mass change data are required, mass determination of the test piece support is not required.

### 4.4.3 Intermediate and final mass change determination

After removing from the furnace, the test piece support containing the test pieces shall be settled in the weighing room for 15 min to allow the test pieces to acclimatize. The test pieces shall not be descaled. However, loosely adherent or delaminated oxide scale shall be removed by gently tapping the test piece on the inside of the test piece support to ensure that the spalled scale is collected. All spalled scale shall be retained in the test piece support upon re-insertion into the furnace for continued exposure.

In the case that hygroscopic corrosion products have been formed, test pieces should be weighed as soon as possible or shall be stored in a desiccator, after removal from the furnace, until immediately before weighing.

If significant formation of volatile species occurs, this will interfere with the mass determination. An indication for the formation of volatile species is deposition of liquid or solid products at the cooler parts of the furnace.

For each mass change determination (at intermediate stages and final stage), the mass of the test piece support (containing one test piece and spalled scale), the test piece support (including spalled scale) and the mass of the test piece (including adherent scale) shall be determined as shown in Figure 8. Three individual measurements shall be made for each test piece support containing one test piece, each test piece support and each test piece with a precision of 0,02 mg for each measurement. The standard deviation for each set of measurements shall not exceed 0,05 mg.

Care shall be taken during mass measurements to avoid spallation of oxide scale caused by mechanical contacts with tweezers etc. A test piece support with a rod support design, as shown in Figure 5, circumvents the problem and allows the determination of mass changes without direct contact of the tweezers with the test piece, as shown in Figures 9 and 10.



$$m_{ST} \qquad m_S \qquad m_T$$

**Key**
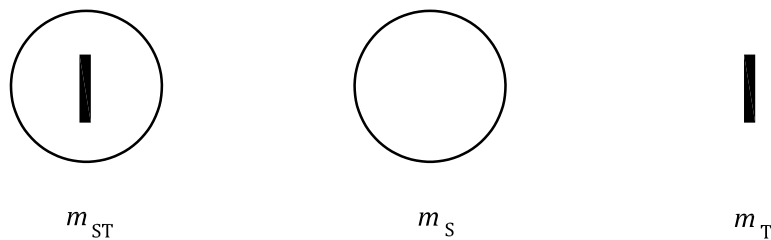
$m_{ST}$     mass of test piece support with test piece

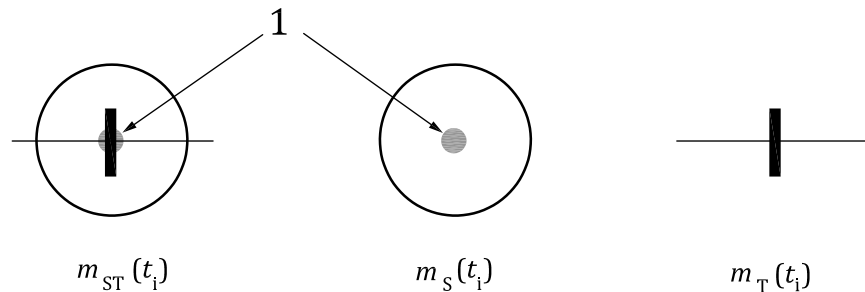$m_S$      mass of test piece support

$m_T$      mass of test piece

**Figure 8 — Mass determination – variant I**

**Key**
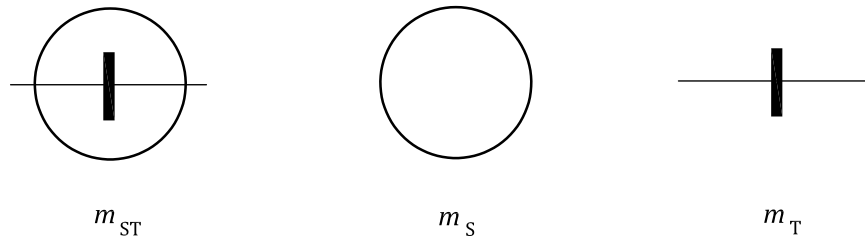
$m_{ST}$    mass of test piece support with test piece held by alumina rod
$m_S$    mass of test piece support
$m_T$    mass of test piece with rod

**Figure 9 — Mass determination – variant II**
(test piece can be removed by holding the rod with tweezers)



**Key**

$m_{ST}(t_i)$    mass of test piece support with test piece held by e.g. alumina rod at $t_i$
$m_S(t_i)$    mass of test piece support including spall at $t_i$
$m_T(t_i)$    mass of test piece with rod at $t_i$
1    spalled oxide

**Figure 10 — Mass determination variant II**
(in which spallation has occurred)

Gross mass change $\Delta m_{gross}$ as defined in 3.5 is determined according to Formula (1):

$$\Delta m_{gross}(t_n) = m_{ST}(t_n) - m_{ST}(t_0)$$

(1)

where

$\Delta m_{gross}(t_n)$    is the gross mass change at time $t_n$ (mg),

$m_{ST}(t_n)$    is the mass of test piece support and test piece at time $t_n$ (mg),

$m_{ST}(t_0)$    is the mass of test piece support and test piece prior to the test (mg).

The mass of spalled oxide $\Delta m_{spall}$ is determined according to Formula (2):

$$\Delta m_{spall}(t_n) = m_S(t_n) - m_S(t_0)$$

(2)

where

$\Delta m_{spall}(t_n)$      is the mass change of spalled material at time $t_n$ (mg),

$m_S(t_n)$      is the mass of test piece support at time $t_n$ (mg),

$m_S(t_0)$      is the mass of test piece support prior to the test (mg).

$m_{ST}(t_n)$      is the mass of test piece support and test piece including spall at time $t_n$ (mg).

Net mass change $\Delta m_{net}$ as defined in 3.6 is determined according to Formula (3):

$$\Delta m_{net}(t_n) = m_T(t_n) - m_T(t_0)$$

<div align="right">(3)</div>

where

$\Delta m_{net}(t_n)$      is the net mass change at time $t_n$ (mg),

$m_T(t_n)$      is the mass of test piece at time $t_n$ (mg),

$m_T(t_0)$      is the mass of test piece prior to the test (mg),

or when a rod supported design, as shown in Figure 7, is used by Formula (4):

$$\Delta m_{net}(t_n) = \Delta m_{gross}(t_n) - \Delta m_{spall}(t_1)$$

<div align="right">(4)</div>

where

$\Delta m_{net}(t_n)$      is the net mass change at time $t_n$ (mg),

$\Delta m_{gross}(t_n)$      is the gross mass change at time $t_n$ (mg),

$\Delta m_{spall}(t_n)$      is the mass of spalled material at time $t_n$ (mg).

### 4.4.4    Frequency of mass change determination

For long dwell time testing, mass change measurements shall be made once each working day for the initial part of the test, measurements may be made less frequently as the test progresses.

In short dwell time testing, the extension of the cold dwell phase due to the mass change measurements must be taken into account. Therefore the number of mass change measurements shall be small enough to minimize these possible influences but high enough to obtain meaningful mass change curves. Mass change measurements on a daily basis have proven to be practicable.

It is recommended to document the macroscopic appearance of the test piece surface by macro photographs.

### 4.5    Analysis of mass change

Net mass change of test pieces shall be plotted versus time, as shown in Figure 11. According to common use in high temperature oxidation testing, the mass change is usually described mathematically by Formula (5). The values for the oxidation rate constant $k$, the exponent of the growth law $n$, the protective oxide growth time $t_{protective}$, and the corresponding number of cycles $N_{protective}$, shall be reported. Determination of these values is described in the following paragraphs.
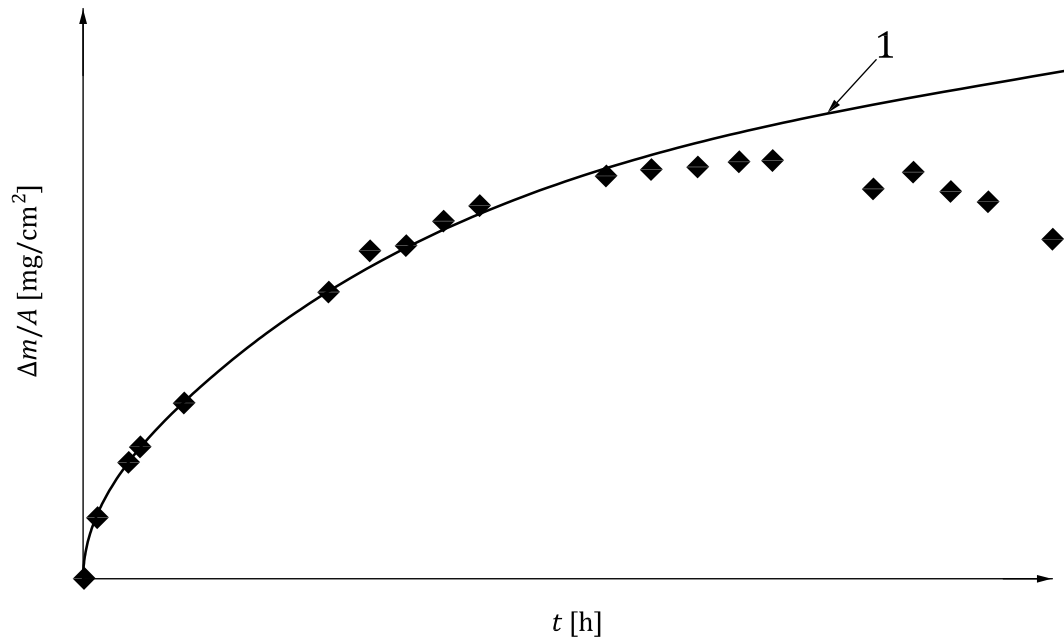
**Key**

$t$     time

◆     Experimental data

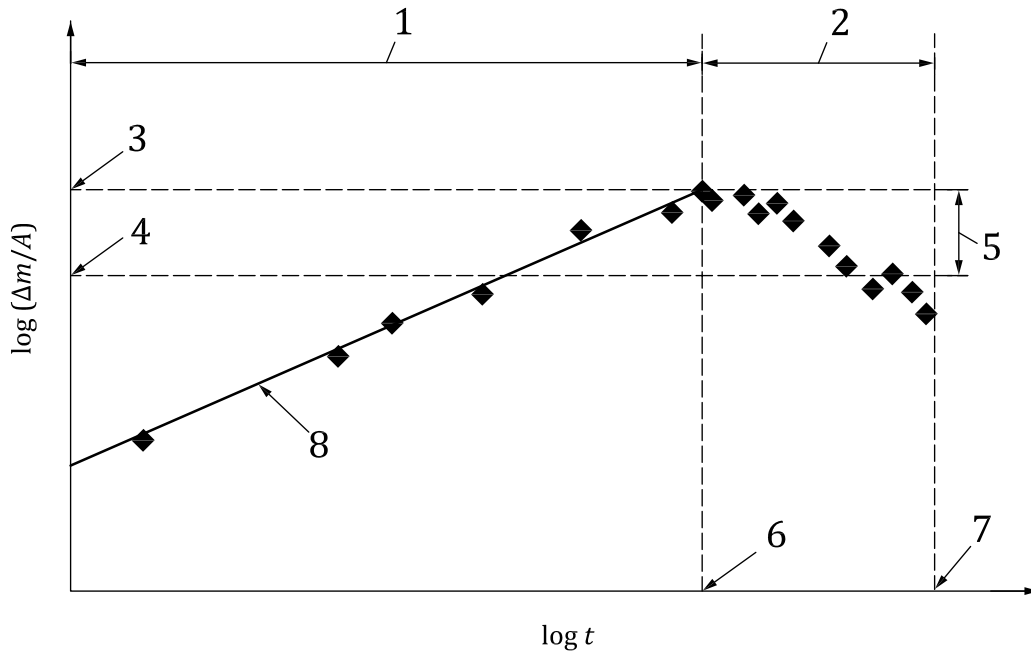1     Fit to experimental data

**Figure 11 — Net mass change as a function of time**

The double logarithmic plot (log net mass change versus log time) may reveal a change in the mechanism of oxidation behaviour (spallation, breakaway oxidation) by a change of the slope. As long as protective oxide growth takes place, it can be described mathematically by Formula (5).

$$\left(\frac{\Delta m_{\text{net}}}{A}\right)^{n} = kt \quad \rightarrow \quad \frac{\Delta m_{\text{net}}}{A} = k^{\frac{1}{n}} t^{\frac{1}{n}} \quad \rightarrow \quad \log\left(\frac{\Delta m_{\text{net}}}{A}\right) = \log\left(k^{\frac{1}{n}} t^{\frac{1}{n}}\right) = \frac{1}{n}(\log k + \log t) \tag{5}$$

A change in the mechanism (spallation, breakaway oxidation) becomes apparent by a change of the slope in the double logarithmic plot. The point at which this occurs can normally be identified by visual inspection and determines the end of the linear part of the curve.

Analysis of the linear part of the curve by linear regression yields the slope b = 1/$n$ and the y-axis intercept, as shown in Figure 12.

**Key**

| | | | |
|---|---|---|---|
| ♦ | Experimental data | 5 | $\log (\Delta m/A)_{protective}$ - $\log (\Delta m/A)_{300\ h}$ |
| 1 | Linear range | 6 | $\log t_{protective}$ |
| 2 | $t_{300\ h}$ - $t_{protective}$ | 7 | $\log t_{300\ h}$ |
| 3 | $\log (\Delta m/A)_{protective}$ | 8 | Fit to experimental data |
| 4 | $\log (\Delta m/A)_{300\ h}$ | | |

**Figure 12 — Double logarithmic plot of mass change vs. time**

From the y-axis intercept the oxidation rate constant $k$, for the linear region, shall be calculated as given in Formula (6)

$$a = \log k^{\frac{1}{n}} \quad \rightarrow \quad a = \frac{1}{n} \log k \quad \rightarrow \quad k = 10^{a \cdot n} \tag{6}$$

For a stricter mathematical determination of $k$, $n$ and the protective oxide growth time $t_{protective}$ an iterative procedure shall be applied. Firstly, a best fit line shall be drawn through the data points in the "linear range" using the functionality of simple spreadsheet calculations. The correlation coefficient defined by Formula (7) shall be maximized by including or excluding data points near to the point where the data points leave the linearity area.

$$\rho_{\log t, \log \Delta m/A} = \frac{\text{cov}\left(\log t, \log \frac{\Delta m}{A}\right)}{\sigma_{\log t} \cdot \sigma_{\log \Delta m/A}} \tag{7}$$

with the standard deviations $\sigma_{\log \Delta m/A}$ and $\sigma_{\log t}$ and the covariance $\text{cov}\left(\log t, \log \frac{\Delta m}{A}\right)$ between two data sets defined by Formula (8).

$$\text{cov}(x,y) = \frac{1}{n} \sum_{j=1}^{n} (x_i - \mu_x)(y_i - \mu_y) \tag{8}$$

The data points included in the calculation of the correlation coefficients shall be used to finally calculate $k$ and $n$. The latest data point included in the linear regression shall be reported as $t_{protective}$ (protective oxide growth time).

The number of cycles, $N_{protective}$, that corresponds to the protective oxide growth time, $t_{protective}$, and which is the last data point in the linear part of the curve shall be reported.

Additionally, the following net mass changes difference shall be reported as given in Formulae (9) and (10), and shown in Figure 13.

$$\Delta m_{net}(t_{300\,h}\text{-}t_{protective}) = \Delta m_{net}(t_{300\,h}) - \Delta m_{net}(t_{protective})$$

(9)

where

$\Delta m_{net}(t_{300\,h})$ is the net mass change of test piece after 300 h (mg),

$\Delta m_{net}(t_{protective})$ is the net mass change of test piece at $t_{protective}$ (mg)

$$\Delta m_{net}(t_{1\,000\,h}\text{-}t_{protective}) = \Delta m_{net}(t_{1\,000\,h}) - \Delta m_{net}(t_{protective})$$

(10)

where

$\Delta m_{net}(t_{1\,000\,h})$ is the net mass change of test piece after 1 000 h (mg),

$\Delta m_{net}(t_{protective})$ is the net mass change of test piece at $t_{protective}$ (mg).

**Key**

$t$     time
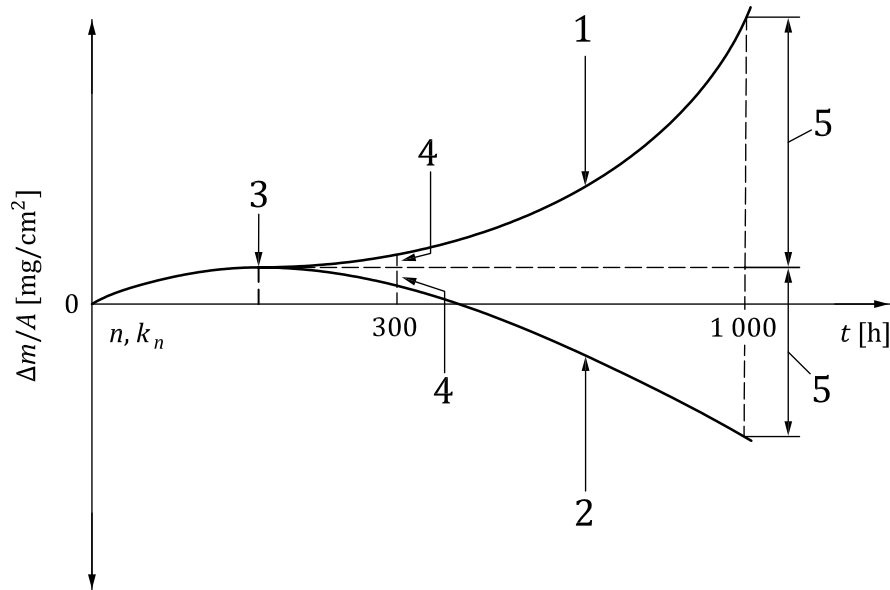1    breakaway behaviour
2    spallation behaviour
3    $t_{\text{protective}}$
4    $\Delta m_{\text{net}}(t_{300\text{ h}}\text{-}t_{\text{protective}})$
5    $\Delta m_{\text{net}}(t_{1\,000\text{ h}}\text{-}t_{\text{protective}})$

**Figure 13 — Net mass change differences $\Delta m_{\text{net}}(t_{300\text{ h}}\text{-}t_{\text{protective}})$ and $\Delta m_{\text{net}}(t_{1000\text{ h}}\text{-}t_{\text{protective}})$ for materials showing spallation behaviour (lower line) and breakaway behaviour (upper line)**

The parameters $k$ and $n$ are both essential descriptors and shall always be quoted together. Ranking in terms of only one of these parameters is not appropriate. Both parameters shall be used to evaluate, interpolate or extrapolate mass change data. If used for extrapolation, it is essential to ensure that no change in mechanism will occur during the extrapolated time period.

NOTE     The parameter $k$ is not equivalent to the parabolic rate constant $k_{\text{p}}$.

## 4.6   Post-test evaluation of test pieces

### 4.6.1   Macroscopic evaluation

The macroscopic appearance of the test piece surface shall be photographed.

### 4.6.2   Observation of surface and cross section of test pieces

Metallographic examination should be made on the surface and cross section. A detailed procedure for quantitative analysis is given in ISO 26146.

## 5   Report

### 5.1   Matters to be described

The following data, where known, shall be included in the report on the test results.

### 5.1.1   Test material

a)   Manufacturer,

b)   Name of material (Manufacturer designation; ASTM, DIN etc.),

c)   Grade or symbol,

d)   Heat number / batch number,

e)   Chemical composition (Analysis technique),

f)   Processing condition,

g)   Heat treatment condition,

h)   Microstructure of the material determined according to ASTM E3-01 and etching according to ASTM E407-07e1.

### 5.1.2   Test piece

a)   Designation of the test piece,

b)   Sampling conditions of the test piece from raw material (Crystallographic orientation, rolling direction etc.),

c)   Dimensions and the surface area of the test piece,

d)   Surface finish condition of the test piece,

e)   Degreasing method of the test piece,

f)   Method of the test piece support,

g)   Initial mass.

### 5.1.3   Testing environments

a)   Test temperature as well as maximum and minimum temperatures during the test, in °C,

b)   Test duration,

c)   Chemical environment including humidity,

d)   Hot dwell time, cold dwell time, heating time, cooling time,

e)   Volume of test chamber,

f)   Volume flow rate of test gas,

g)   Open or closed system, according to 4.2.1,

h)   In the case of the use of open systems, the humidity of the laboratory air.

### 5.1.4   Test results

a)   Plot of net mass change per area in mg cm$^{-2}$ versus time according to 4.5,

b)   Plot of the amount of spalled scale in mg cm$^{-2}$ versus time,

c)   Results of any metallographic investigations performed according to 4.6,

d)   Photograph of appearance after testing,

e)  Photograph of cross section, including the surface layer of the metallographic section of test piece after testing. The chosen magnifications shall clearly show the extent of the total attack in a single micrograph to show the external corrosion product layer thickness,

f)  Oxidation rate $k$, exponent of the growth law $n$, cycles $N_{protective}$, and the accumulated hot dwell time $t_{protective}$ that corresponds to the end of the linear region before the onset of spallation or breakaway oxidation according to 4.5, as well as $\Delta m_{net}(t_{300\ h} - t_{protective})$ and $\Delta m_{net}(t_{1\ 000\ h} - t_{protective})$.

## 5.2  Supplementary note

It is also desirable to describe the following matters in the report on the test results:

a)  Mechanical properties of the initial material,

b)  Microstructure of the initial material and sampling conditions,

c)  Details of the test apparatus.

# Bibliography

[1]    ISO 8044, *Corrosion of metals and alloys – Basic Terms and Definitions*

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[3]    STREHL G., & BORCHARDT G. The effect of heating on the total oxidation time. In "Standardisation of thermal cycling exposure testing: (EFC 53)", Eds. M. Schütze, M. Malessa, Woodhead Publishing, Cambridge,  2007

[4]    JIS Z 2282, Method of Cyclic Oxidation Testing at Elevated Temperatures for Metallic Materials

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