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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

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Foreword

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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:

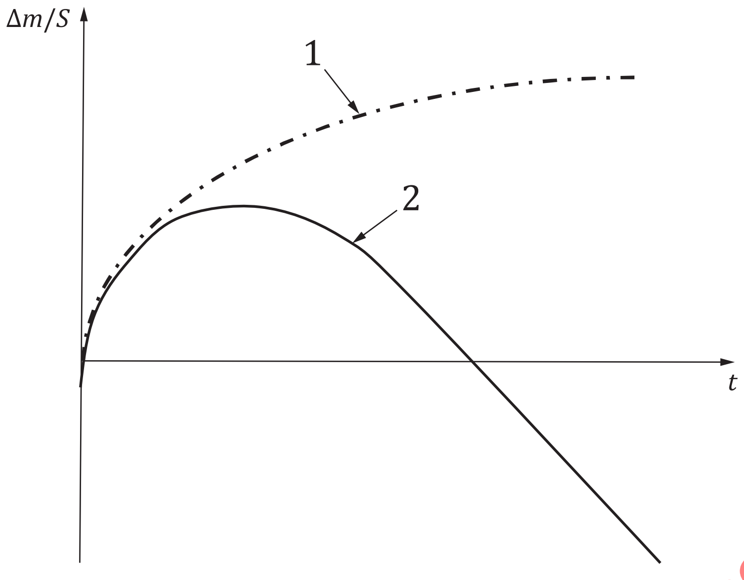
— ISO Online browsing platform: available at https://www.iso.org/obp

— 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

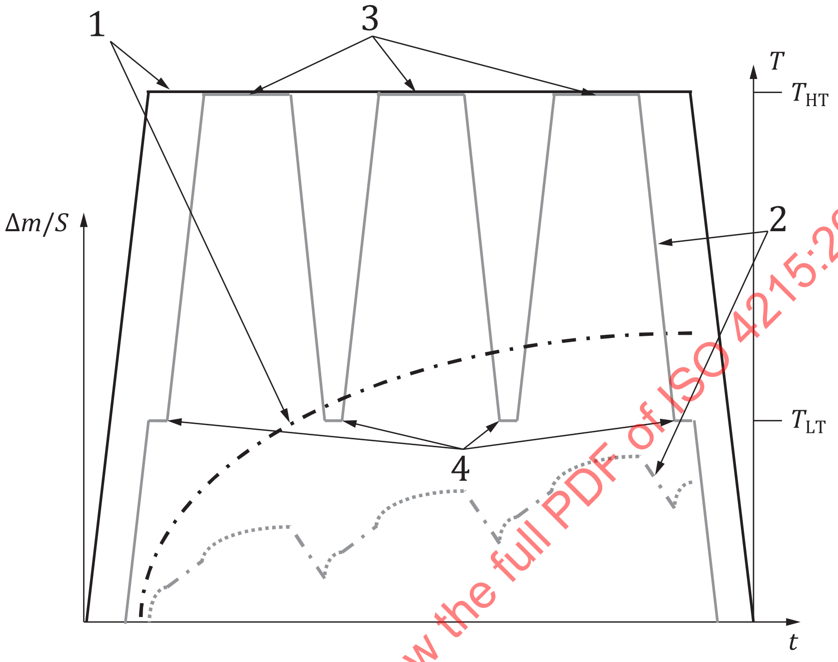
4 Test method

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
Δ*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.

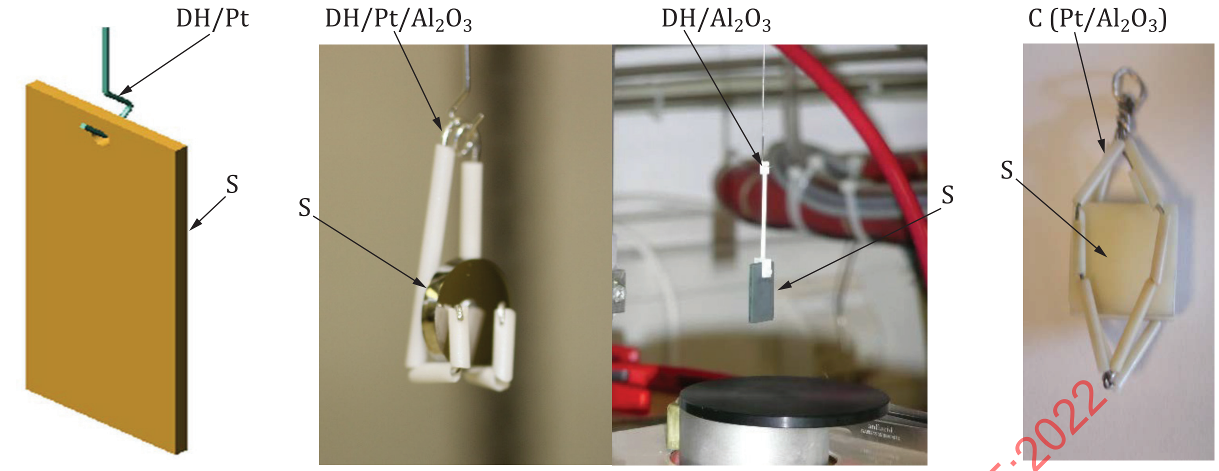
Where holes are used for test piece support they shall be drilled prior to final finishing or application of coatings. These must be taken into account when calculating the surface area.

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

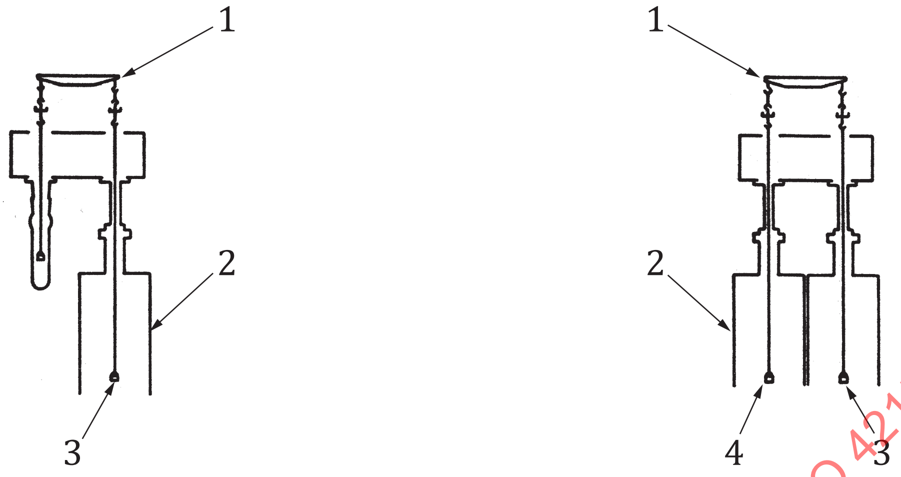
5.1 Thermobalance

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 the two furnaces to be equal. With such a device, as the buoyancy effect is identical in both furnaces, the TG curve does not show a significant deviation.



Key

1	balance beam
2	furnace
3	sample
4	inert reference

Figure 4 — Thermobalance with one furnace (left) and symmetrical thermobalance with two furnaces (right)

5.2 Furnace

The furnace shall be able to achieve controlled heating and cooling cycles. The furnace shall be characterized at the exposure temperature prior to the testing to determine the length of the isothermal zone inside the furnace. This can be achieved using an independent moveable thermocouple.

The temperature shall be controlled such that the temperature of the test piece is kept within the permissible range given in Table 2.

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

5.3 Temperature probe

The temperature shall be measured by a suitable device. Thermocouples of type K (Ni/Cr - NiAl) up to 800 °C, type S (10 %Rh/Pt – Pt) and type R (Pt/13 %Rh – Pt) up to 1 100 °C or type B (Pt/30 %Rh – Pt/6 %Rh) above 1 100 °C are preferred. The thermocouple shall be capable of confirming the temperature of the test piece to be within the range given in Table 2.

A thermocouple should be positioned close to the test piece surface and shall be calibrated according to 6.2. According to the commercial thermobalances, the thermocouple to be used can be the control temperature thermocouple or a thermocouple attached to the TG rod.

The type of thermocouple used shall be noted and included in the test report. The temperature probe shall be resistant to the oxidizing or corrosive atmosphere in dry or humid conditions. Thermocouple sheaths shall be used to protect the thermocouple wires. The thermocouple sheaths shall withstand fully the test temperature and environment.

5.4 Data acquisition device

A data acquisition device is required in order to achieve the automatic acquisition of either the mass of the test piece and of the temperature or time, or both, and graphically represent the mass variation versus temperature or time. It shall have a sufficient acquisition rate to enable accurate monitoring of the TG curve. It is recommended that it should be able to record at least 1 000 data points over the test duration.

5.5 Test piece holder

The test piece holder is attached to the balance and located in the furnace. The test piece can also be directly hung to the balance in order to have the whole surface in contact with the reactive atmosphere (see Figure 3). The test piece holder shall be made of a material that does not react with the given atmosphere or the material under investigation in the whole temperature range defined for the test.

5.6 Reactive gas and gas flow

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

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 and not to cause errors in weighting.

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. This can be achieved by, for example, 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.

WARNING — Before any use of reactive gases, it is required to check that the thermobalance is suitable for this type of measurement with particular regard the safety of the operators and that there is no risk of corrosion or degradation of parts of the instrument, especially metallic parts (thermocouple, balance, and furnace).

5.7 Protection of the thermobalance

If an inert gas is used to protect the metallic parts of the balance during the test, ensure that the atmosphere surrounding the sample is not modified.

6 Calibration

6.1 Mass calibration

Calibration of the balance shall be performed using standard masses over an appropriate range without gas flow in the thermobalance (in order to prevent either any buoyancy or convection effects, or both). Calibration shall be performed at least once a year or whenever significant changes have occurred to the equipment.

6.2 Thermocouple calibration

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.

Thermocouples shall be recalibrated annually or at the beginning and the end of each experiment if there is uncertainty about thermocouple stability.

7 Procedure

7.1 General

The test method shall be adapted to the instrument and to the experimental conditions. Two modes are described: the test in isothermal mode and the test in cyclic mode.

A preliminary test (called blank test) shall be run using a test piece of identical volume (preferably with the same dimensions) made of an inert material (with respects to the reactive atmosphere), at the same temperature, heating rate and with the same gas flow rate as used for the test itself in order to measure the apparent mass variation due to either buoyancy or convection effects, or both.

7.2 Isothermal test

a) The mass of the test pieces shall be determined prior to exposure. 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.

b) Install the test piece in the holder (if used) or hang the test piece to the balance suspension.

c) Close the furnace.

d) As an option, it is recommended to apply a primary vacuum in the furnace before to fill the furnace with the chosen corrosive gas.

e) Zero the balance.

f) Set the gas flow rate (decided as described in 5.6), start the gas circulation and let the system adjust itself. Wait that no mass change occurs anymore (mass variation amplitude lower than 0,1 % of the final total mass change).

g) Define the temperature profile to be run. The program must include the initial and final temperatures, the temperature scanning rates between the two temperatures, and the duration of the isothermal level (hot dwell time) at the final temperature.

h) Start the program and start the recording of the temperature and of the thermogravimetric curve (see Figure 2).

i) Weigh the test piece at room temperature without gas flow, in the same conditions as in e).

j) Remove the test piece from the thermobalance and weigh it in the same conditions as in a).

7.3 Cyclic test

Run the operations defined in 7.2 a), b), c), d), e) and f).

In order to prepare the temperature cycle to run in the cyclic mode, the program shall include the T_{HT} and T_{LT} temperatures, the temperature scanning rates (heating and cooling for the cycle), the level durations Δt_{HT} , Δt_{LT} respectively at T_{HT} and T_{LT}, and the number of cycles to be run.

Two modes are available:

- Mode 1: Start with a cold dwell time at T_{LT} (see Figure 2).
- Mode 2: Start with a hot dwell time at T_{HT}.

Choose the frequency of acquisition with the program in order to record at least two specific data points at each cycle: the mass at the beginning of the high temperature dwell, $m(t_i)$, and the mass at the end of the high temperature dwell $m(t_i + \Delta t_{\mathrm{HT}})$.

Run the operations defined in 7.2 f) to h).

8 Expression of results — Graphical presentation

Present the obtained thermogravimetric data as a curve giving $\Delta m/S$ where S is the initial test piece surface area versus time, including the temperature profile used for the test.

NOTE The curve of the derivative of $\Delta m/S$ versus time can be added to the plot.

9 Analysis of the mass change

9.1 General

The objective of the analysis is to convert the raw data consisting in mass change versus time (see Clause 8) into oxidation kinetics parameters.

9.2 Isothermal exposure

NOTE Reference can be made to ISO 21608[6] for isothermal testing (discontinuous measurement). Nevertheless, because thermogravimetry allows much more precise measurements with more data points, a specific analysis can be done.

An initial check of the results shall be performed by plotting $\Delta m/S$ where S is the test piece surface area versus time for the high temperature dwell.

If mass loss occurs from the start of the exposure or after a period of mass gain, volatilization of the oxide scale, of the metal, or of the corrosion product should be considered before proceeding further. The occurrence of volatilization should be proven before further analysis of the oxidation kinetics.

For analysis of the kinetics the data are plotted in a log-log plot: $\log(\Delta m/S)$ versus $\log(t)$ for the high temperature dwell. If a linear regression is found between time 0 and time t^*, the parameters (k,n) of the law $\Delta m/S = k \cdot t^n$ can be given as an interpolation between 0 and t^*. The log-log plot is used for interpolation only and before any breakaway or change of slope. The results are expressed as follows:

Between time 0 and t^*, the oxidation kinetics can be interpolated by a power law $\Delta m/S = k \cdot t^n$ with the following values of k, n and t^*.

If no linear fit can be found using the log-log plot, no standard analysis is provided.

For some values of the coefficient "n", a more precise analysis of the kinetics can be provided as follows, and the kinetics parameters found with the following analysis can be used for extrapolations:

Linear kinetics - for a value of “n” close to 1 (between 0,9 and 1,1), a linear regression of $\Delta m/S = f(t)$ is performed and the result is expressed as follows:

Between time 0 and t^*, the oxidation kinetics are linear $\Delta m/S = k_l \cdot t$ with k_l = value expressed in mg/cm^2/s (k_l is called the linear rate constant).

Parabolic kinetics - for a value of “n” close to 0,5 (between 0,35 and 0,65), the user plots the data in a parabolic plot, i.e. $\Delta m/S$ versus-$\sqrt{(t)}$ and applies a linear regression. The result is then expressed as follows:

Between time 0 and t^*, the oxidation kinetics are parabolic $\Delta m/S = \sqrt{(k_p \cdot t)}$ where k_p is the value expressed in mg^2/cm^4/s (k_p is called the parabolic rate constant).

In order to get an improved fit or to perform subsequent extrapolations, the data may be represented in a plot of $\Delta m/S$ -t and the “complete parabolic law” may be fitted, i.e.:

$$t = A + B\,\Delta m/S + C(\Delta m/S)^2$$

between time t_{start} and the end of the experiment. t_{start} is chosen in order to obtain a good quality fit. If a good fit is obtained, the result is expressed as after a transient regime of duration t_{start}, the oxidation kinetics follows a complete parabolic law: $t = A + B\,\Delta m/S + C(\Delta m/S)^2$ with $k_p = 1/C$ expressed in mg^2/cm^4/s (k_p is called the pure parabolic rate constant corresponding to the final stationary state regime of oxidation kinetics).

9.3 Thermal cycling exposure

NOTE Reference can be made to ISO 13573[5] thermocyclic exposure (discontinuous measurement). Nevertheless, because thermogravimetry allows more precise measurements with more data points, and because crucibles are not used, a more specific analysis can be done.

A graph of $\Delta m/S$ where S is the test piece surface area versus time is plotted for the entire duration of thermal cycling.

A net mass change (NMC), Δm_{net}, plot versus time or versus the number of cycles is obtained by keeping only one data point $\Delta m/S$ for each thermal cycle. Because of buoyancy, these data points are taken always at the same temperature. The data point $\Delta m/S$ at the end of each high temperature dwell should be taken. This set of data can be analysed in the same manner as a result of discontinuous measurements using the thermocyclic exposure (discontinuous measurement) method given in ISO 13573[5].

A gross mass gain (GMG), Δm_{gross}, plot versus time or versus the number of cycles is obtained by keeping two data points $\Delta m/S$ for each thermal cycle. Because of buoyancy, these data points are taken always at the same temperature. It is recommended to keep the data point $M_i^{bg} = (\Delta m/S)$ at the beginning of