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Corrosion of metals and alloys — Electrochemical test methods for high-temperature corrosion testing of metallic materials in molten salts

Corrosion des métaux et alliages — Méthodes d'essais électrochimiques de corrosion à haute température de matériaux métalliques dans des sels fondus

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

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Introduction

Corrosion of metals and alloys in high-temperature molten salts is generally an electrochemical phenomenon. Therefore, the corrosion resistance and corrosion mechanism can be evaluated via a variety of electrochemical techniques. This document describes the apparatus and procedures for electrochemical measurements in high temperature molten salts. The closely related guidelines for potentiostatic and potentiodynamic polarization measurement in aqueous solutions are described in ISO 17475.

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Corrosion of metals and alloys — Electrochemical test methods for high-temperature corrosion testing of metallic materials in molten salts

1 Scope

This document describes the general procedure for electrochemical measurements in high-temperature molten salts using potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS), and describes the experimental apparatus.

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.

ISO 8044, *Corrosion of metals and alloys — Vocabulary*

ASTM E220, *Standard method for calibration of thermocouples by comparison techniques*

ASTM E230, *Standard temperature-electromotive forces tables for standardized thermocouples*

ASTM E1350, *Standard test method for testing sheathed thermocouples prior to, during and after installation*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8044 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/

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4 Apparatus

4.1 General

The test apparatus should consist of a heating unit, gas feeding unit, electrochemical measurement unit and electrochemical cell. A basic design of a closed, vertical, apparatus is shown in Figure 1.

4.2 Heating unit or furnace

4.2.1 The apparatus shall be composed of a heating unit or furnace that heats all the test pieces at a uniform temperature. The heating unit shall be equipped with a testing section capable of isolating the test pieces from outside air.

4.2.2 The temperature distribution of the heating unit shall be characterized at the exposure temperature prior to testing to determine the width of the isothermal zone by the use of a

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calibrated movable thermocouple. The heating unit or furnace shall maintain the temperature of the electrochemical cell within the permissible range given in Table 1.

4.2.3 Calibration of thermocouples shall be performed in accordance with ASTM E220, ASTM E230 and ASTM E1350. A representative thermocouple taken from a batch of wire can be calibrated. Thermocouples shall be recalibrated annually or at the beginning and the end of each test, if there is uncertainty about the thermocouple stability.

Table 1 — 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

4.3 Gas feeding unit

4.3.1 The gas supply system shall be capable of supplying test gases at a constant flow rate to the test piece chamber described in Figure 1. The gas flow shall be monitored by a gas flow meter.

4.3.2 When a humidifying regulator is used, it shall be capable of adjusting to the desired humidity. The gas line between the humidifying regulator and test chamber shall be kept above the dew point in order to avoid condensation. In the case that the gas is humidified, the water vapour content shall be measured. This can be achieved by, for example, the use of a hygrometer before the test 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 test.

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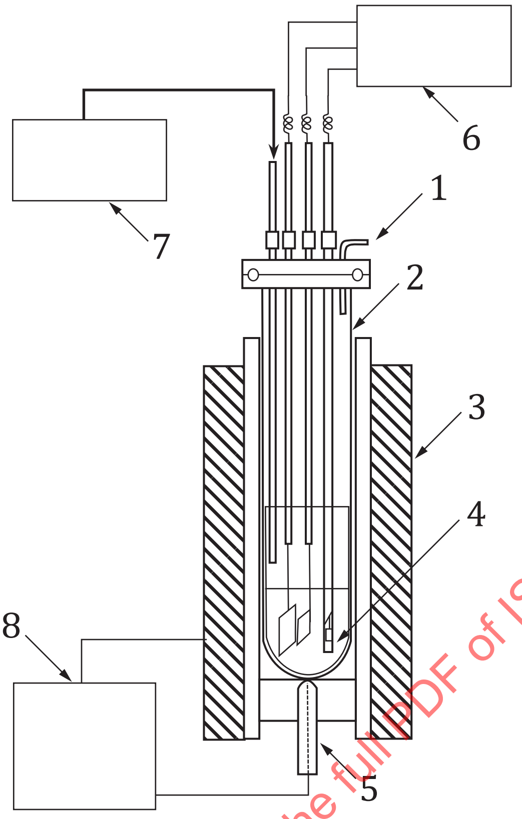

Key

1	gas exhaust
2	test piece chamber
3	heating unit or furnace
4	electrochemical cell
5	thermocouple
6	electrochemical measurement unit
7	gas feeding unit
8	power/temperature control device

Figure 1 — Schematic illustration of the entire electrochemical measurement unit for a high-temperature molten salt

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4.4 Electrochemical measurement unit

4.4.1 The potentiostat should be capable of controlling the electrode potential in the test to within ±1 mV of a preset value. A scanning potentiostat is used for potentiodynamic measurements. For such measurements, the potentiostat shall be capable of automatically scanning the potential at a constant rate between preset potentials. For the EIS measurement, a potentiostat equipped with an electrochemical impedance measurement unit is used.

4.4.2 The electrode potential-measuring instrument should have a high input impedance in the order of 10^{11} Ω to 10^{14} Ω, to minimize current drawn from the system during measurement. The sensitivity and accuracy of the instrument should be sufficient to detect a change of 1,0 mV.

4.4.3 An appropriate current-measuring instrument with maximum error of 0,5 % is used.

4.5 Electrochemical cell

4.5.1 A three-electrode system consisting of a working electrode (the metal to be polarized), a reference electrode for measuring the electrode potential and a counter (auxiliary) electrode shall be used. The test cell should incorporate inlet and outlet gas ports and a port for insertion of a temperature-measuring device. For the EIS measurement, a two-electrode system consisting of two identical working electrodes may be used instead. Examples of the three-electrode and two-electrode cells are shown in Figure 2 a) and b), respectively.

4.5.2 The test chamber shall not be composed of materials that react significantly with the gas environment or the corrosive substance during the test. If a reaction is unavoidable, the reaction shall be small enough to neglect a change in composition of the atmosphere. The crucibles used to hold the molten salt should not react with salt; for example, a high-purity alumina crucible shall be used for a sulfate or chloride bath.

4.5.3 The working electrode is prepared from the test material of interest, usually in the form of a rod or sheet. The working electrode surface, except the test area, shall be protected by an insulating coating that does not react with the test salt and gas. The area immersed below the molten salt/gas interface shall be considered as the effective electrode surface area, if an appropriate insulating coating is not identified. In order to minimize the influence of the electrochemical reaction that occurs at the three-phase gas/electrode/molten salt interface, a flag-shaped working electrode is recommended. The flag-shaped electrode can be manufactured by punching or wire electric discharge machining. An example of the flag-shaped electrode is shown in Figure 3. The level of the molten salt should not drop below the upper edge of the 'flag' section of the sample. The final finishing of the surface of the test pieces shall be performed with abrasives with a mean particle diameter of approximately 15 µm. This can be achieved by the use of abrasives according to Table 2. If another surface finish is required by the parties involved, the surface finish condition shall be agreed and described. After ultrasonic degreasing in an appropriate solvent, such as isopropanol or ethanol, the test pieces shall be dried in hot air.

Table 2 — Designation and mean diameter of particles for suitable coated abrasives

Standard	Designation	Mean diameter µm
FEPA[a] 43-1 and FEPA 43-2 ISO 6344 series	P1200	15,3 ± 1,0
JIS R 6001-1	#1000	15,6 ± 1,0
ANSI B74.12	600	16,0

[a] Federation of European Producers of Abrasives

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4.5.4 The reference electrode may be inserted directly into the molten salt. The type of reference electrode used will depend on the application, e.g. molten salt and temperature. An example of the reference electrode for molten chlorides, molten sulfates and molten carbonates is given in Annex B.

4.5.5 The counter electrode should be sufficiently corrosion resistant in the test environment. If the reaction at the counter electrode is likely to influence the measurement, the counter electrode shall be separated in a compartment. Pt, Au or carbon may be used as a counter electrode.

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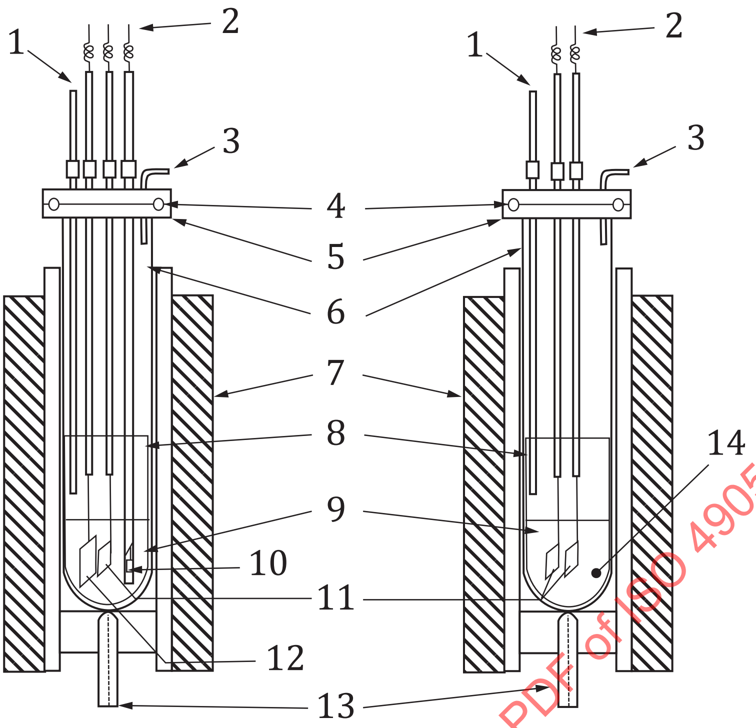

a) Three-electrode system for polarization and EIS measurements **b) Two-electrode system for EIS measurements**

Key

1	gas inlet
2	lead wire
3	gas exhaust
4	O-ring
5	stainless steel flange
6	silica tube
7	heating unit or furnace
8	high-purity alumina crucible
9	molten salt
10	RE: reference electrode
11	WE: working electrode
12	CE: counter electrode
13	thermocouple
14	electrochemical cell

Figure 2 — Schematic diagram of the electrochemical cell for a high-temperature molten salt system

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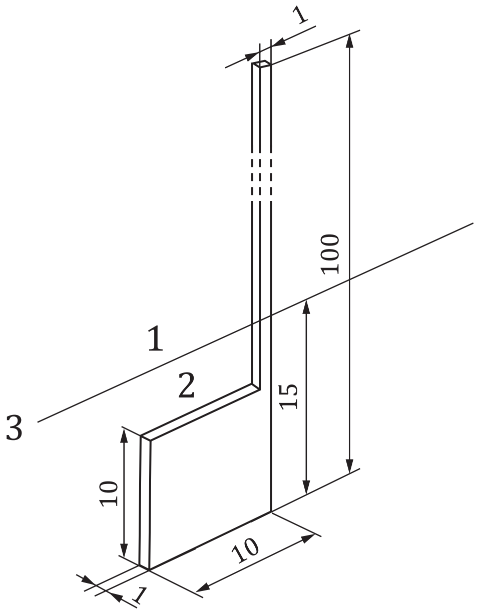
Dimensions in millimetres



Key

1	gas phase
2	molten salt
3	gas/molten salt interface

Figure 3 — Flag-shaped working electrode example

4.6 Molten salt

4.6.1 The type of molten salt to be used in the test shall be selected in accordance with the environment for which the test is intended. Table A.1 lists examples of chemical compositions and test temperatures for selected molten salts.

4.6.2 The molten salt shall be prepared by mixing reagent-grade chemicals. The salt should be dried well before use. The prepared substance shall be mixed well to ensure it is homogeneous.

WARNING — When working with hazardous molten salts, all necessary safety precautions shall be taken.

4.7 Test atmosphere

The test gas should be selected in accordance with the salt used. Examples are shown in Annex A.

5 Procedure

5.1 Preparation and placement of the electrochemical cell

The electrochemical cell shall be set in a heating furnace and an inert gas shall flow through the system whilst heating the specimen to the required test temperature. The specimen shall be set in the upper location (low-temperature zone) during heating. The inert gas shall be replaced with the test gas before the expected melting. The gas flow rate shall be determined within a range that does not affect the measurement results. Once the test temperature is reached and the salt is completely molten, the electrodes shall be lowered into the molten salt. The electrodes shall be immersed at a constant depth. After immersion over a specified period, the measurement shall be started.

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5.2 Test environment with flowing reactive gas

5.2.1 If a flowing reactive gas is used, the composition of the test gas shall be chosen in a way that it keeps the corrosive activity of the molten salt stable.

5.2.2 The flow rate of the test gas shall be sufficiently high so as to fill the test chamber at least three times in 1 h. This is to ensure that the corrosion rate is not determined by the supply of the reactants.

5.2.3 The flowing gas shall be preheated to reach equilibrium in the gas phase. An appropriate catalyst shall be used, if necessary.

5.3 Electrochemical measurement

5.3.1 Record the open-circuit potential with time after immersion. The period of exposure at open-circuit prior to polarization and EIS measurement will depend on the purpose of the test. In some applications, it can be useful to allow the open-circuit potential to approach a constant value. Otherwise, a constant period (e.g. 1 h) should be allowed. Depending on the salt melt, quantity and test chamber dimension, the required time to stabilize the salt at a temperature and gas composition may vary strongly, thus an appropriate cell size should be considered.

5.3.2 Commence the potential scan in either an anodic or a cathodic direction, beginning at the open-circuit potential or any other potential, depending on the purpose of the test, and record the current variation with time. A series of typical polarization curves of Ni-base alloys in mixed molten salts of chlorides and sulfates at 873 K are shown in Figure 4. The polarization indicates that the corrosion resistance increases in order of Alloy 214 < Alloy 600 < Alloy 625.

NOTE The choice of potential scan rate depends on the purpose of the test.

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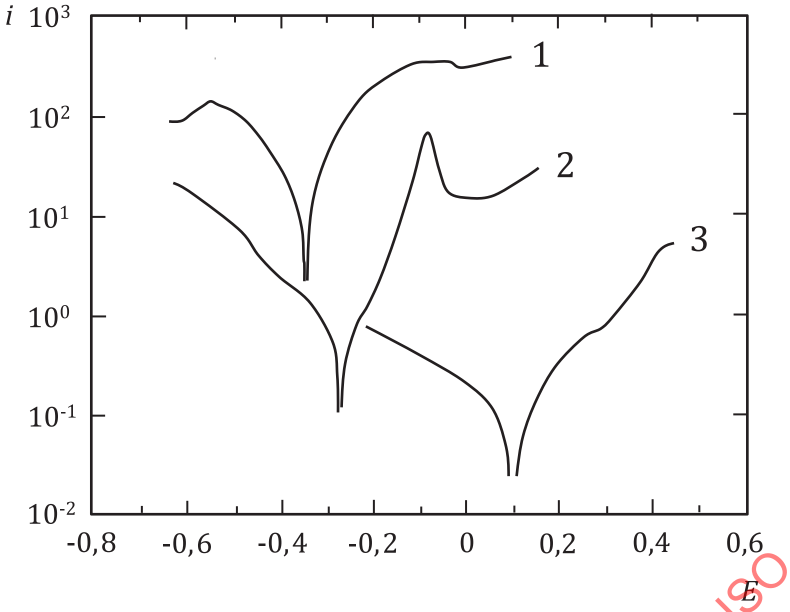

Key

i	current density, expressed in A/m^2
E	potential, expressed in V vs. Ag/Ag+ potential (0,1 mole fraction)
1	Alloy 214
2	Alloy 600
3	Alloy 625

NOTE In 25 mol%NaCl - 25 mol%KCl - 16,6 %Na_2SO_4 - 16,6 %K_2SO_4 - 16,6 %$ZnSO_4$.

Figure 4 — Polarization curves of Ni-base alloys under air containing (10 % H_2O + 10 000 ppm HCl) at 873 K recorded at potential scan rate of 1 mVs^{-1}

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5.3.3 AC voltage (or AC current) with a small amplitude in a wide frequency range is applied between the working electrode and counter electrode for the three-electrode system, and between two-working electrodes for the two-electrode system. The amplitude of the applied voltage should be as small as possible from linearity between current density and voltage. The EIS measurement should be conducted at the open-circuit potential to evaluate the corrosion resistance of materials in molten salts under immersion conditions. On the basis of the current (or voltage) response, record the absolute value of the impedance and phase shift so that a Bode diagram can be plotted, and record the real part and imaginary part of impedance for construction of the Nyquist diagram. Both plots are described in ISO 17474. As an example, the Bode diagram of Ni-base alloys measured in mixed molten salts of chlorides and sulfates at 873 K are shown in Figure 5. The Bode diagram indicates the corrosion resistance of Alloy 625 is higher than that of Alloy 214 in this melt.

NOTE The choice of amplitude and frequency range of the applied AC voltage depends on the purpose of the test. For example, an amplitude of 10 mV and a frequency range of 10 kHz to 10 mHz (or 1 mHz) can be useful for determining general trends and for comparing materials.

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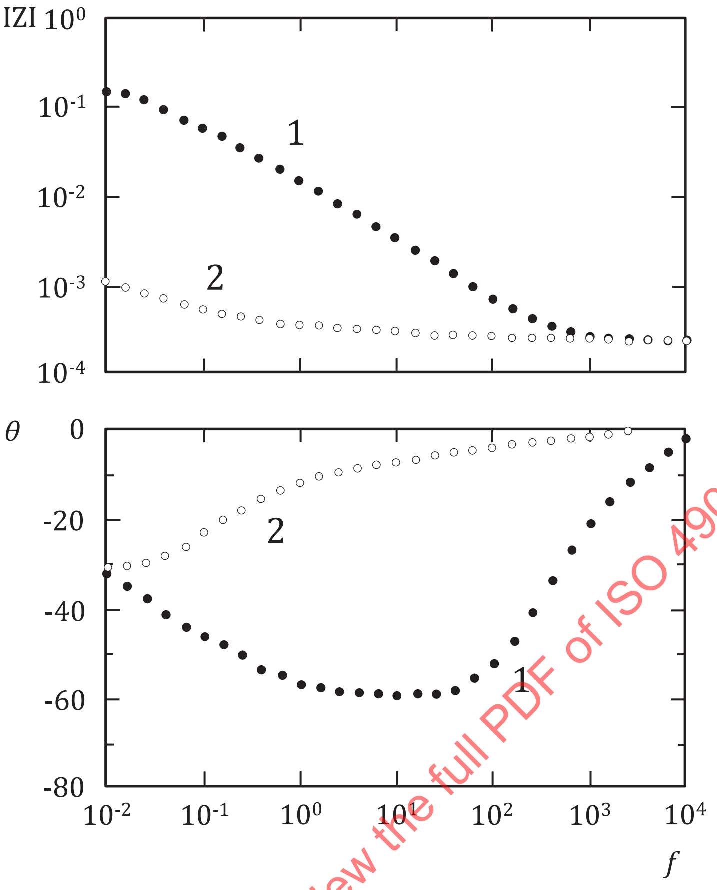

Key

IZI impedance, expressed in ohm square meter

θ phase shift, expressed in degree

f frequency, expressed in hertz

1 Alloy 625

2 Alloy 214

NOTE In 25 mol%NaCl - 25 mol%KCl -16,6 %Na_2SO_4 - 16,6 %K_2SO_4 - 16,6 %$ZnSO_4$.

Figure 5 — Bode diagram of Ni base alloys measured under air containing (10 %H_2O + 10 000 ppm HCl) at 873 K

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6 Test report

6.1 General

The test report shall include the following information which is common for both potentiodynamic polarization and EIS measurements:

a) reference to this document, i.e. ISO 4905;

b) full description of the test material from which the specimens were taken: chemical composition, heat treatment, type of the material, etc.

c) method of manufacturing the specimens and details of the surface preparation;

d) molten salt composition, volume and temperature;

e) composition and flow rate of the test gas;

f) volume of test chamber;

g) measured dimensions and calculated area of the specimen exposed to the test solution;

h) description of cell and electrodes used;

i) time required to check stability and the time of immersion prior to polarization or EIS measurement.

In addition to the above items, the report shall contain the technique-dependent information, as given in 6.2 and 6.3.

6.2 Reports with potentiodynamic polarization measurements

a) open-circuit potential and whether it was steady, and the end potential;

b) potential scan rate;

c) plot of applied current density versus applied potential, including an indication of any correction for solution potential drop and its method of evaluation.

6.3 Reports with EIS measurements

a) amplitude and frequency range of AC voltage;

b) impedance plot in Nyquist diagram and/or Bode diagram (ISO 17474);

c) record the state in which the test was conducted.

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