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Corrosion of Metals and Alloys - Test Method for Thermal-cycling Exposure Oxidation Testing under High-temperature Corrosion Conditions for Metallic Materials

金属和合金的腐蚀 金属材料在高温腐蚀条件下的热循环暴露氧化试验方法

(ISO 13573:2012, MOD)

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1 Scope

This Standard stipulates the equipment, gas supply, samples, test process, calculation and analysis of mass change, post-test sample evaluation and test report of isothermal exposure oxidation testing of metallic materials under high-temperature corrosion conditions.

This Standard is applicable to test method for thermal-cycling corrosion testing (namely, cyclic oxidation test) of metallic materials from the ambient temperature to high-temperature gas environment (each sample shall receive a series of repeated, regular and controlled temperature cycles). After proper adjustments are made, the test method may also be adopted in the testing of other materials.

This Standard is not applicable to testing that adopts extremely short holding time (a few minutes or a few seconds).

2 Normative References

The following documents are indispensable to the application of this document. In terms of references with a specified date, only versions with a specified date are applicable to this document. In terms of references without a specified date, the latest version (including all the modifications) is applicable to this document.

GB/T 1598 *Platinum - 10% Rhodium/Platinum Thermocouple Wires - Platinum - 13% Rhodium/Platinum Thermocouple Wires - Platinum - 30% Rhodium/Platinum - 6% Rhodium Thermocouple Wires*

GB/T 9258.3 *Coated Abrasives - Grain Size Analysis - Part 3: Determination of Grain Size Distribution of Micro-grits P240 to P2500* (GB/T 9258.3-2017, ISO 6344-3:2013, IDT)

GB/T 13298 *Inspection Methods of Microstructure for Metals*

GB/T 16701 *Methods for Measuring the Thermoelectric Force of Noble Metal and Base Metal Thermocouple Wires*

4---humidity regulator (electronic);

5---hygrometer;

6---heating device with non-equilibrium gas mixture catalyst;

7---heating zone with heating belt;

8---heating device;

9---sample chamber;

10---sample;

11---sample holder;

12---thermocouple;

13---power/temperature control device;

14---moving direction of heating stove;

15---gas emission;

16---measurement device.

Figure 2 (continued from previous page)

4.1.2 In the design of the heating device, the isolation of the sample chamber from the external environment shall be guaranteed.

4.1.3 It shall be guaranteed that flow that passes through the sample is continuous and within the stipulated range.

4.1.4 The sample chamber shall not adopt any materials that would react with the test environment during the testing process and lead to changes of the composition of the test environment.

4.1.5 If the sealed test system with sample chamber cannot be used, it is also allowable to conduct the test under the atmospheric environment in the laboratory. Atmospheric humidity shall be recorded; try to maintain at a constant temperature and be free from the effect of weather conditions in the laboratory.

4.1.6 Before the test, examine the heating stove at the exposure temperature of the test; determine the dimensions of the uniform temperature zone in the heating stove. Generally speaking, the method of independent activity thermocouple shall be adopted.

4.1.7 The temperature regulating device shall be able to guarantee that sample temperature maintains within the allowable deviation range that is stipulated in Table

4.2.5 Thermocouple wire shall adopt thermowell for protection. Thermowell shall be able to be used at the test temperature and under the test environment.

5 Gas Supply of Sealed System

5.1 Gas supply system shall be able to steadily provide gas for testing at a constant rate to the sample chamber.

5.2 Gas flow meter shall be adopted to monitor the gas flow. Flow meter shall be placed near the entrance of the sample chamber. However, when humidity regulator is used, flow meter shall be placed at the upstream of the humidifier.

5.3 When humidity regulator is used, humidity regulator shall be able to adjust humidity to an expected value. Unless it is otherwise stipulated, deionized water, whose conductivity is lower than 1 μS/cm shall be used. In order to prevent from condensation, the temperature of the space between the humidity regulator and the sample chamber shall be maintained above the dew point.

5.4 After gas is humidified, water vapor content shall be tested. Testing methods include: use a hygrometer to measure in front of sample chamber, or, measure water content after the condensation of the discharged gas, or, measure the amount of water consumption in the humidifier during the test.

5.5 When the test is conducted in the air, it is recommended to adopt 20 g/kg specific humidity ratio (namely, mass fraction of water content in the air). This specific humidity ratio is the relative humidity 100% at 25 °C (dew point), which can be easily obtained through bubbling in water bath at 25 °C. If other humidity values are adopted, the consent of various relevant parties shall be obtained.

5.6 In the cooling stage, prevent test gas from generating condensed phase. It may be implemented by turning off the humidifier or switching into inert gas.

6 Samples

6.1 The shape of samples shall be plate, disc or cylinder. Surface area shall be not less than 300 mm^2; thickness shall be not less than 1.5 mm. If the above-mentioned requirements cannot be satisfied, the shape and the dimensions of samples shall comply with the requirements in the agreement reached among the various relevant parties.

6.2 The surface of samples shall be mechanically polished, so as to guarantee that the layer that would affect machining is eliminated. The final polishing of the surface of samples shall adopt polishing materials, whose average particle diameter is around 15 μm; P1200 polishing materials that comply with the requirements in GB/T 9258.3 may be used. If it is requested by relevant parties to adopt other surface polishing methods, in the time period when the temperature approaches the heating holding temperature.

c) Cooling time: the time from the stopping of heating (for example, taking sample out of the heating furnace) to the time that the actual temperature of the sample decreases to below 50 °C;

d) Cooling holding time: the time from the moment when the actual temperature is lower than 50 °C to the re-heating of the sample.

7.4 Thermal Cycle Type and Holding Time

7.4.1 Thermal cycle type

There are two typical types of thermal cycle in industrial application:

a) Long-term thermal cycle: it is used to simulate the service of large-scale industrial equipment in practical application, for example, power plant, waste incineration or chemical industry. In the above-mentioned application, metal components are designed to have an extremely long service life, for example, generally over 100,000 h. Planned factory shutdown (for example, routine maintenance) or accidental shutdown caused by abnormal situations would all lead to thermal cycle of materials. Therefore, in comparison with the long service life of components, the time interval of different thermal cycles is relatively long; the number of cycles is relatively small (generally around 50 times).

b) Short-term thermal cycle: typical application of short-term thermal cycle includes: industrial gas turbines, jet engines, automotive parts and thermal treatment equipment, etc. In comparison with long-term application, the time interval between equipment turning-on and turning-off is generally much shorter. Meanwhile, the designed service life and (or) the time needed for thorough overhauling/maintenance (generally, 3,000 h ~ 30,000 h) is even shorter (depend on specific situation of practical application); the number of cycles is larger.

7.4.2 Heating and cooling time

The heating and cooling rate will affect the test result to a very large extent, and it depends on the detail features of test equipment. Controlling factors include: system thermal mass, transmission mechanism, and whether or not there is strong cold. The recommended heating time does not exceed 30 min; the recommended cooling time does not exceed 60 min.

7.4.3 Standard test parameters of long-term test

When the thermal cycle defined in 7.3 is used in long-term thermal cycle test, in

1---spalling after primitive protective stage;

2---oxidation breakaway after primitive protective stage;

3---spalling since the starting of the test.

Figure 7 -- Different Types of Oxidation Behaviors in Thermal Cycle

8 Calculation of Mass Change

8.1 General Rules

In order to define oxidation kinetics, mass change needs to be determined. It is recommended that each type of material shall adopt backup samples. When samples are being processed, tweezers are recommended. Do not touch the samples with bare hands, so that contamination (grease and salt) can be avoided. Be cautious when using gloves, because the contamination caused by isolates on the gloves would lead to errors in mass determination. If repeated tests are inconsistent, the temperature and the humidity of the weighing environment shall be recorded.

8.2 Weighing before Test

8.2.1 Newly used sample holder shall be dried in the air, so as to eliminate volatile chemicals brought during the production process. It is recommended to dry it at 1,000 °C for at least 24 h. If already-used sample might manifest phenomena of water absorption, it shall be dried at the temperature of much higher than 1,000 °C.

8.2.2 Before exposure, measure the mass of the sample [($m_T(t_0)$), see Figure 8]. Each sample shall at least be respectively tested twice; the accuracy shall be not lower than 0.02 mg. The maximum difference among the measurement results shall not exceed ± 0.05 mg.

8.2.3 Before exposure, measure the mass of sample holder [($m_s(t_0)$), see Figure 8]. Each sample holder shall at least be respectively tested twice. When the mass of sample holder is lower than 20 g, the accuracy shall be not lower than 0.02 mg; the maximum different among the measurement results shall not exceed 0.05 mg. When the mass of sample holder is not less than 20 g, the accuracy shall be not lower than 0.1 mg; the maximum difference among the measurement results shall not exceed 0.3 mg. When mass change data is merely needed, the mass of sample holder may not be measured.

$m_{ST}(t_n)$---mass of sample holder and sample at (t_n) moment, expressed in (mg);

$m_{ST}(t_0)$---before test, initial mass of sample holder and sample, expressed in (mg).

8.3.7 The mass Δm_{spall} of spalled scale shall be calculated in accordance with Formula (2).

$$\Delta m_{\text{spall}}(t_n)=m_{\text{S}}(t_n)-m_{\text{S}}(t_0) \qquad \cdots\cdots(2)$$

Where,

$\Delta m_{spall}(t_n)$---mass change of spalled scale at (t_n) moment, expressed in (mg);

$m_S(t_n)$---mass of sample holder at (t_n) moment, expressed in (mg);

$m_S(t_0)$---before test, initial mass of sample holder, expressed in (mg).

8.3.8 The mass change Δm_{net} of sample shall be calculated in accordance with Formula (3).

$$\Delta m_{\text{net}}(t_n)=m_{\text{T}}(t_n)-m_{\text{T}}(t_0) \qquad \cdots\cdots(3)$$

Where,

$\Delta m_{net}(t_n)$---mass change of sample at (t_n) moment, expressed in (mg);

$m_T(t_n)$---mass of sample at (t_n) moment, expressed in (mg);

$m_T(t_0)$---before test, initial mass of sample, expressed in (mg).

8.3.9 When rod-support design shown in Figure 5 is adopted, the mass change Δm_{net} of sample shall be calculated in accordance with Formula (4).

$$\Delta m_{\text{net}}(t_n)=\Delta m_{\text{gross}}(t_n)-\Delta m_{\text{spall}}(t_n) \qquad \cdots\cdots(4)$$

Where,

$\Delta m_{net}(t_n)$---mass change of sample at (t_n) moment, expressed in (mg);

$\Delta m_{gross}(t_n)$---gross mass change at (t_n) moment, expressed in (mg);

$\Delta m_{spall}(t_n)$---mass change of spalled scale at (t_n) moment, expressed in (mg).

8.4 Frequency of Determination of Mass Change

8.4.1 In terms of long-term test, in the initial stage of the test, in every workday, measure mass change once. As time goes by, the frequency of measurement may be decreased.

8.4.2 In terms of short-term test, the prolonged cooling holding time caused by the

$$a=\lg k^{\frac{1}{n}}\rightarrow a=\frac{1}{n}\lg k\rightarrow k=10^{a\cdot n} \qquad \cdots\cdots(6)$$

9.5 More rigorous mathematical calculation of (*k*), (*n*) and protective oxide growth time ($t_{protective}$) shall adopt iterative program. Firstly, the simple calculation function of electronic spreadsheet shall be adopted to draw the most suitable fitting straight line within the range of linearity. Points near data points beyond the range of linearity shall be included or eliminated, so that the correlation coefficient defined in Formula (7) can be minimum.

$$\rho_{\lg t,\lg\Delta m/A}=\frac{\operatorname{cov}(\lg t,\lg\Delta m/A)}{\sigma_{\lg t}\cdot\sigma_{\lg\Delta m/A}} \qquad \cdots\cdots(7)$$

9.6 The standard deviation between two groups of data $s_{lg}\Delta m/A$, s_{lgt} and covariance cov(*lgt*, *lgΔm/A*) shall be calculated in accordance with Formula (8).

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

9.7 Data points included in the calculation of correlation coefficient are used in the final calculation of *k* and *n*. The data point that is the last to emerge in linear regression is $t_{protective}$ (protective oxide growth time).

9.8 Number of cycles ($N_{protective}$), which is associated with protective oxide growth time ($t_{protective}$), and the data point at the end of the linear part of the curve shall be written into test report.

9.9 Net mass change (see Figure 13) stipulated in Formula (9) and Formula (10) shall also be written into test report.

$$\Delta m_{\text{net}}(t_{300\text{ h}}-t_{\text{protective}})=\Delta m_{\text{net}}(t_{300\text{ h}})-\Delta m_{\text{net}}(t_{\text{protective}}) \qquad \cdots\cdots(9)$$

Where,

$\Delta m_{net}(t_{300h})$---after 300 h of test, net mass change of sample, expressed in (mg);

$\Delta m_{net}(t_{protective})$---in ($t_{protective}$), net mass change of sample, expressed in (mg).

$$\Delta m_{\text{net}}(t_{1\,000\text{ h}}-t_{\text{protective}})=\Delta m_{\text{net}}(t_{1\,000\text{ h}})-\Delta m_{\text{net}}(t_{\text{protective}}) \qquad \cdots\cdots(10)$$

Where,

$\Delta m_{net}(t_{1000h})$---after 1,000 h of test, net mass change of sample, expressed in (mg);

$\Delta m_{net}(t_{protective})$---in ($t_{protective}$), net mass change of sample, expressed in (mg).

g) Initial mass.

11.1.3 Test environment

Test environment shall include the following content:

a) Test temperature, and the highest and the lowest temperature [expressed in (°C)] during the test process;

b) Test cycle;

c) Chemical environment, including humidity;

d) Heating time, holding time, cooling time, cooling holding time;

e) Volume of test chamber;

f) Volume flow of test gas;

g) Whether it is open system or sealed system (in accordance with 4.1);

h) When open system is adopted, laboratory's atmospheric humidity.

11.1.4 Test result

Test result shall include the following content:

a) The relation chart of gross mass change per unit area, net mass change [expressed in (mg/cm^2)] and time (in accordance with Chapter 9).

b) The relation chart of spalled scale amount [expressed in (mg/cm^2)] and time.

c) Metallographic analysis result obtained in accordance with 10.2.

d) Appearance photos after the test.

e) After the test, sample's cross section photos (including the surface layer of the metallographic part after the test). The selected magnification times shall be able to distinctly display the total damage in one photo, so as to display the thickness of the external corrosion product layer.

f) Oxidation rate (k); growth law index (n); number of cycles ($N_{protective}$); accumulative holding time ($t_{protective}$) (determined in accordance with Chapter 9) that is associated with the end point of the range of linearity before spalling or oxidation breakaway; $\Delta m_{net}(t_{300h} - t_{protective})$; $\Delta m_{net}(t_{1000h} - t_{protective})$.

11.2 Supplementary Requirements

Test report should include the following content that is related with test result:

Appendix B

(Informative)

Technical Differences between This Standard and ISO 13573:2012 and Causes

Table B.1 provides technical differences between this Standard and ISO 13573:2012 and causes for these differences.

Table B.1 -- Technical Differences between This Standard and ISO 13573:2012 and Causes

Chapter No. in This Standard	Technical Differences	Causes
2	In terms of normative references, this Standard makes adjustment with technical differences, so as to get adapted to the technical conditions of China. The adjustment is intensively reflected in Chapter 2 “Normative References”. The specific adjustment is as follows: ---GB/T 1598, GB/T 16701, GB/T 18036 and JJG 141 are used to replace ASTM E633-00, ASTM E220-02, ASTM E230-03, ASTM E1350-97; ---GB/T 13298 is used to replace ASTM E3-01 and ASTM E407-07e1; ---GB/T 9258.3 is used to replace ISO 6344-3.	---GB/T 1598, GB/T 16701, GB/T 18036 and JJG 141 are commonly used standards on thermocouple and verification in China. In order to adapt to the technical conditions of China and enhance the operability of this Standard, GB/T 1598, GB/T 16701, GB/T 18036 and JJG 141 are used to replace ASTM E633-00, ASTM E220-02, ASTM E230-03, ASTM E1350-97; ---GB/T 13298 is a commonly used standard on the preparation and inspection of metallographic samples in China. In order to adapt to the technical conditions of China and enhance the operability of this Standard, GB/T 13298 is used to replace ASTM E3-01 and ASTM E407-07e1; ---GB/T 9258.3-2017 *Coated Abrasives - Grain Size Analysis - Part 3: Determination of Grain Size Distribution of Micro-grits P240 to P2500* (ISO 6344-3:2013, IDT);
6.2	Table 1 is deleted. “P1200 polishing materials that comply with the requirements in GB/T 9258.3 may be used” is added.	When tests are submitted for mechanical approval in China, P1200 polishing materials requested in GB/T 9258.3 are generally used. Meanwhile, it is inconvenient to purchase the polishing materials stipulated in Table 1. In order to enhance the operability of this Standard, Table 1 is deleted; “P1200 polishing materials that comply with the requirements in

------ The End ------