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Two-electrode method using acetic acid to measure pitting potential of aluminium and aluminium alloys in chloride solutions

Méthode à deux électrodes utilisant l'acide acétique pour mesurer le potentiel de piqûre de l'aluminium et des alliages d'aluminium dans des solutions de chlorure

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

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Foreword

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This document was prepared by Technical Committee ISO/TC 156, *Corrosion of metals 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

Aluminium and aluminium alloys show excellent corrosion resistance in near-neutral environments as a result of the formation of an oxide or hydroxide film on their surface, thereby achieving passivation. However, if the environment contains the chloride ion, the passive film will be broken, and localized corrosion, such as pitting corrosion, can occur. Aluminium-clad material is used to prevent localized corrosion by galvanic protection. In this method, the underlying core aluminium is protected by a sacrificial layer whose pitting potential is lower than that of the core aluminium. Therefore, in order to estimate the performance of galvanic protection, it is important to obtain the pitting potential.

Although anodic polarization curve measurement is one method for obtaining the pitting potential, the method described in the test method in this document has several advantages in that it causes less specimen damage, has a shorter measurement time and smaller specimen area, multiple measurements are possible, and a two-electrode system is used. In an anodic polarization curve measurement, the specimen is severely corroded due to excessive polarization. The method described in this document causes less specimen corrosion, as the degree of polarization is small because the potential is maintained near the pitting potential. This makes it possible to conduct repeated etching and measurements with the same specimen, which is particularly useful for measurement of the depth profile of the pitting potential in thin clad materials. As a method for measuring the corrosion potential of aluminium alloys, ASTM G69 was established in 1997. ASTM G69 is widely used, substantially to obtain the pitting potential without the anodic polarization curve measurement. In ASTM G69, 1 M (a mass fraction of 5,85 %) of sodium chloride is used as the solution and hydrogen peroxide is used as the oxidant. The test method in this document, where a sodium chloride mass fraction of 5 % is used as the solution and acetic acid is used as the oxidant, also has advantages over ASTM G69. In particular, it causes less specimen damage and has a more stable oxidant with a buffer action.

Two-electrode method using acetic acid to measure pitting potential of aluminium and aluminium alloys in chloride solutions

1 Scope

This document specifies a test method for the measurement of the pitting potential of aluminium and aluminium alloys in sodium chloride solution of a mass fraction of 5 %, with a fixed concentration of acetic acid as the oxidant, using a two-electrode system. This document provides a simple method for ranking aluminium alloys and is especially useful for evaluating galvanic protection performance of thin clad materials because the test method causes little specimen damage.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

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/

4 Field of application

This test method can be used to estimate the corrosion resistance of aluminium alloys in chloride environments, the galvanic corrosion between an aluminium alloy and other metals, and the galvanic protection of aluminium products. In particular, it is useful for estimating the galvanic protection performance of aluminium-clad materials used in heat exchangers in the automotive and air-conditioning fields.

5 Comparison with conventional methods

5.1 Anodic polarization curve measurement

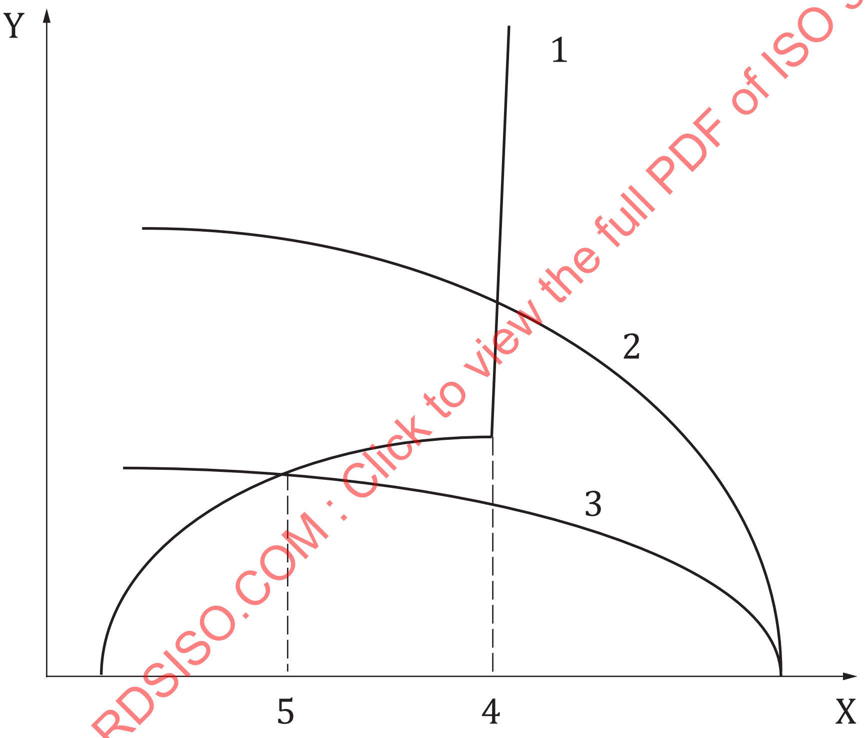
This test method has several advantages compared to the anodic polarization curve measurement, including less specimen damage, a shorter measurement time and smaller specimen area, the possibility of multiple measurements, and the use of a two-electrode system. In an anodic polarization curve measurement, the specimen is severely corroded due to excessive polarization. The method described here causes less specimen corrosion, as the degree of polarization is small because the potential is maintained near the pitting potential. This makes it possible to perform repeated measurements with the same specimen, which is particularly useful for the measurement of the pitting potential at intervals of around 10 µm.

5.2 Corrosion potential

ASTM G69 provides a method for measuring the corrosion potential of aluminium alloys and is widely used to obtain the pitting potential without an anodic polarization curve measurement. In ASTM G69, 1 M of sodium chloride is used as the solution and hydrogen peroxide is used as the oxidant.

6 General principles

In this test method, acetic acid is added to the sodium chloride solution of a mass fraction of 5 % as an oxidant at a concentration in which the corrosion potential is always above the pitting potential of the range of aluminium alloys investigated. On the basis that the current pitting of these alloys increases without much change in potential (see Figure 1), the corrosion potential at which the cathodic reduction of protons intersects the anodic curve reflects the pitting potential of the alloy (to a reasonable approximation). This assumes that there is no effect of the alloy on the cathodic current if the latter is activation controlled. Thus, a simple measurement of the corrosion potential using a working and reference electrode provides a measure of the pitting potential.



Key

X	electrode potential
Y	current density
1	anodic polarization curve in sodium chloride with and without acetic acid
2	cathodic polarization curve in sodium chloride with acetic acid
3	cathodic polarization curve in sodium chloride without acetic acid
4	corrosion potential = pitting potential
5	corrosion potential < pitting potential

Figure 1 — Effect of acetic acid on corrosion potential

In pitting tests by a conventional anodic polarization measurement, the potential is commonly driven to values significantly above the pitting potential and the specimen can be severely corroded. The method described in this document causes less specimen corrosion, as the degree of polarization is small because the potential is maintained near the pitting potential.

ASTM G69 also describes a method for measuring the corrosion potential of aluminium alloys, in 1 M of sodium chloride, using a two-electrode system but with H_2O_2 as the oxidant. The test method in this document provides advantages over ASTM G69. In particular, it causes less specimen damage and has a more stable oxidant with a buffer action.

7 Apparatus

The measuring apparatus shall be a combination of the following. Figure 2 provides an example of a test apparatus.

7.1 Potentiometer

An internal resistance of potentiometer shall be larger than 10^9 Ω.

7.2 Working electrode

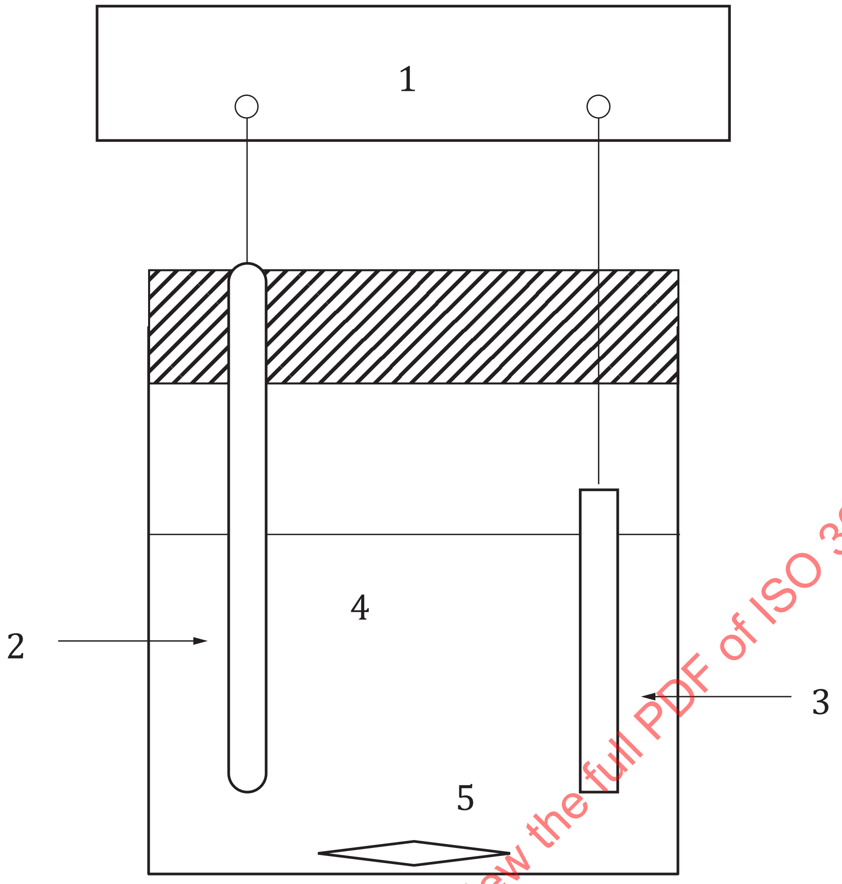
The working electrode should be taken from the test material with the test area of 1 cm^2. The other area shall be masked by or embedded in an inert material such as resin.

7.3 Reference electrode

The reference electrode should be a saturated silver/silver chloride electrode (SSE). Other reference electrodes, i.e. saturated calomel electrode (SCE), can be used. The potentials of these electrodes relative to the standard hydrogen electrode at 25 °C are given in ISO 17474.

7.4 Stirrer

The stirrer and stirrer bar are used to stir the solution at a speed of at least 60 rpm. Stirring is important for stable measurement of the corrosion potential, as in measurements of pitting potential, because stirring accelerates the cathodic reaction by acetic acid and reduces local differences in the solution between the anode site and cathode site.



Key

1	potentiometer
2	reference electrode
3	working electrode
4	solution
5	stirrer bar

Figure 2 — Example of test apparatus

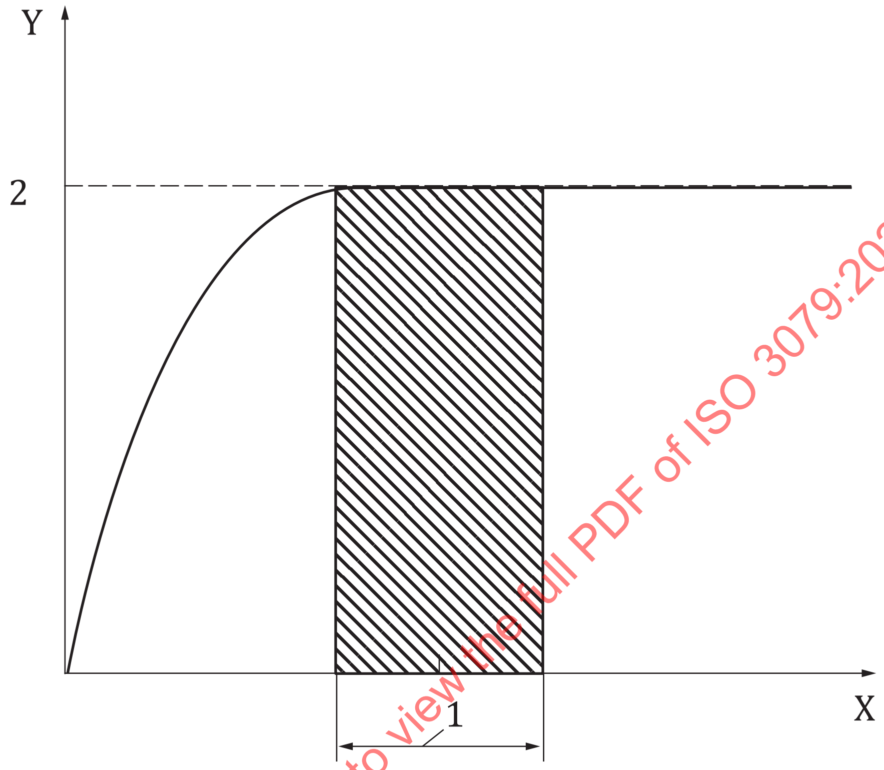
8 Specimen

The specimen shall be taken from a test material with the test area of 1 cm^2. The other area of the specimen shall be masked by or embedded in an inert material such as resin. There is a possibility of a crevice attack in the resin. The aluminium and resin should be closely attached so that there is no gap between them.

9 Test procedure

9.1 Solution

The solution shall be prepared using reagent-grade chemicals and high purity water. The solution is prepared by creating an aqueous solution with a sodium chloride and glacial acetic acid or diluted acetic acid. The ratio of the volume of the solution to the test area of the specimens shall be at least 100 ml/cm^2. The chloride ion concentration, which strongly influences the value of pitting potential, is adjusted with a sodium chloride mass fraction of 5 %. To determine the appropriate concentration of acetic acid, immerse the specimen and the reference electrode and connect them via a potentiometer in a sodium chloride solution, repeating the addition of acetic acid to the solution and the measurement of corrosion potential after 30 min of stirring, up to constant corrosion potential. The appropriate concentration of acetic acid is the concentration where corrosion potential becomes constant (see Figure 3). 1 ml/l glacial acetic acid is enough to measure the pitting potential in a sodium chloride mass fraction of 5 % for almost all aluminium alloys except for highly pure aluminium.



Key

X	acetic acid concentration, in ml/l
Y	corrosion potential
1	appropriate concentration
2	pitting potential

Figure 3 — Effect of acetic acid concentration on corrosion potential

9.2 Test set-up

9.2.1 The temperature of the solution shall be 25 °C ± 1 °C. The test solution shall be agitated by stirring at a speed of at least 60 rpm.

9.2.2 As a pre-treatment, immerse the specimen in a sodium hydroxide aqueous solution of 50 g/l at a temperature of 60 °C for 30 s. Then, rinse the specimen with distilled water or ion-exchanged water. Next, immerse the specimen in a nitric acid aqueous solution of a mass fraction of 30 % at a temperature of 25 °C ± 5 °C for 60 s. Then, immerse the specimen in distilled water or ion-exchanged water and rinse the specimen. After pre-treatment, immediately immerse the specimen in the solution while still wet.

9.2.3 Connect the specimen and the reference electrode via a potentiometer and measure the potential. Measurements shall be performed at intervals of 1 min. The duration of the test shall be 60 min.

9.3 Evaluation

9.3.1 The corrosion potential is the arithmetic average value of the measured values from 30 min to 60 min. The number of repeated tests required is more than two.

9.3.2 Examine the pits on the test area (see Figure 4) and check that there is no crevice attack under the resin after the test.

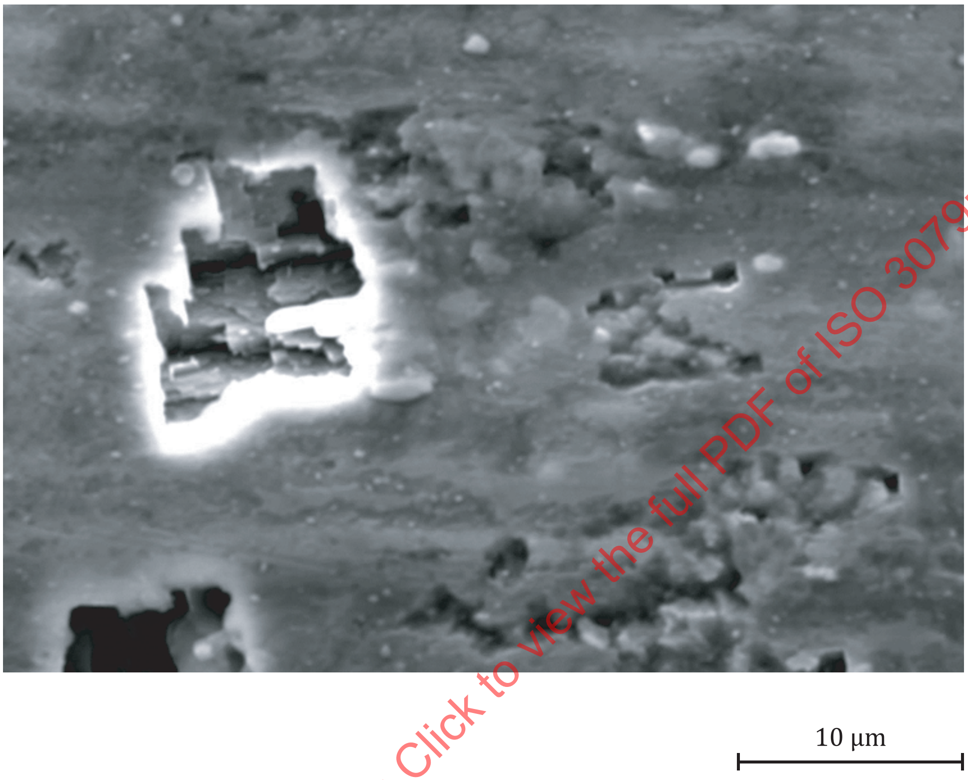


Figure 4 — Pits on surface of specimen after measurement

10 Test report

The test report shall include at least the following information:

a) reference to this document, i.e. ISO 3079:2022;

b) the composition of the specimen, and its temper;

c) the composition of the solution;

d) the pH of the solution;

e) the ratio of the volume of the solution to the test area of the specimen;

f) the temperature of the solution;

g) the agitation rate of the solution;

h) the pre-treatment of the specimen;

i) the duration of the measurement;

j) the type of reference electrode;