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Corrosion of metals and alloys — Measurement of the electrochemical critical localized corrosion potential (E-CLCP) for Ti alloys fabricated via additive manufacturing method in simulated biomedical solutions

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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

Ti alloys such as Ti-6Al-4V are considered to be the most promising biomedical materials. Due to a unique combination of high strength, low modulus, lower density, and outstanding corrosion resistance, their applications have become more widespread in a wide range of industries, e.g. aerospace, automobile, marine and biomedical fields. Especially the medical grade Ti alloys are implanted in patients worldwide every year and also have a significantly higher strength to weight ratio than competing stainless steels. It is well established that Ti alloys have excellent corrosion resistance to all body fluids and tissue and are thus completely biocompatible. These Ti alloys are conventionally produced by wrought or cast processes which are the subtractive manufacturing (SM) methods, but recently the new additive manufacturing (AM) method is emerging, called “3D printing”. This new methodology has gained worldwide attention as a way to cut costs and improve efficiency. Comparing SM with AM, the ratio of the mass of the starting, raw material to the mass of the final, finished part can be as high as 20:1. In terms of mechanical view point, both strength and ductility of Ti alloys such as Ti-6Al-4V fabricated by AM are comparable to or above their properties made by conventional manufacturing methods, because of their unique microstructure. However, the resistance to corrosion of Ti alloys produced by AM is still unknown, whether it is comparable to those of the conventionally manufactured Ti alloys or not, because of their defects such as porosity, the formation of martensite phase resulting from the rapid solidification, and directional difference with the stacking. Therefore, the new standards should be made how to evaluate the resistance to localized corrosion on the stacked alloys produced by AM methods. For this use, the measurement method such as electrochemical critical localized corrosion temperature (E-CLCT) has been adopted as ISO 22910. However, at the normal ranges of pH and temperatures corresponding to human body, the use of E-CLCT measurement method should be limited because of the temperature scan during testing. Therefore, electrochemical critical localized corrosion potential (E-CLCP) is newly introduced and proposed as a new criterion for the evaluation of the resistance to the localized corrosion on the biomedical AM Ti alloys in human body environments. This new test method is controlled by potentiostat through potentiodynamic – galvanostatic-potentiostatic polarization processes and electrochemical polarization cell is used in the artificial physiological fluids.

Corrosion of metals and alloys — Measurement of the electrochemical critical localized corrosion potential (E-CLCP) for Ti alloys fabricated via additive manufacturing method in simulated biomedical solutions

1 Scope

This document specifies the procedures for testing the resistance to localized corrosion of biomedical Ti alloys fabricated via additive manufacturing (AM) method. This document defines the method of measuring the electrochemical critical localized corrosion potential (E-CLCP) of the AM Ti materials in aqueous environments, including biomedical solutions, for comparative evaluation of resistance to localized corrosion.

2 Normative references

There are no normative references in this document.

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
electrochemical critical localized corrosion potential
E-CLCP
highest potential at which repassivation occurs, as indicator of the resistance to propagation of localized corrosion of AM Ti alloy specimen

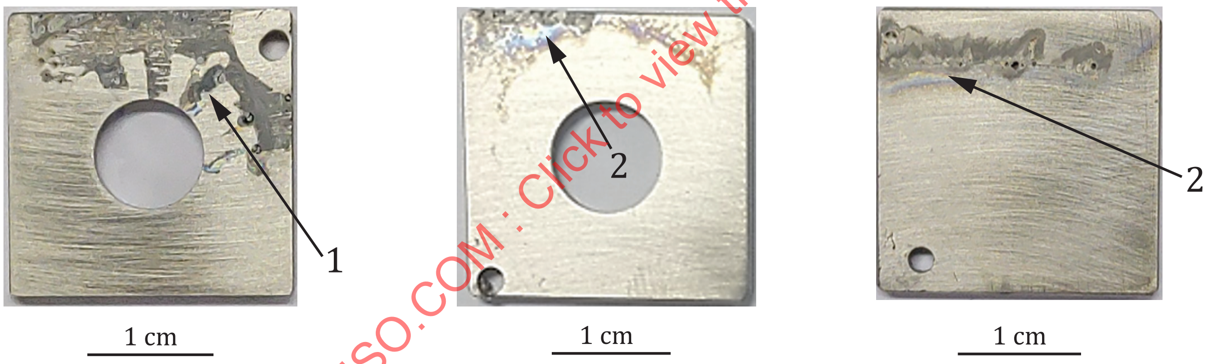
Note 1 to entry: The more noble the potential, the greater the resistance to localized corrosion.

3.2
cyclic potentiodynamic polarization
CPP
electrochemical test method to evaluate the resistance to propagation of localized corrosion through the measurement of repassivation potential

3.3
electrochemical critical localized corrosion temperature
E-CLCT
lowest temperature on the surface of AM Ti alloy specimen at which stable propagating localized corrosion occurs under specified test conditions

4 Principles

This test method specifies a determination of the electrochemical critical localized corrosion potential (E-CLCP) for localized corrosion from the reciprocating anodic polarization of biomedical AM Ti alloys in artificial physiological fluid environments. E-CLCP of AM Ti alloys is a criterion for the evaluation of the resistance to localized corrosion on the biomedical AM Ti alloys in artificial human body environments. This test method, which is a complement to the cyclic potentiodynamic polarization (CPP), combines techniques such as potentiodynamic, galvanostatic, and potentistatic polarization methods. CPP is used as first fast screening method while E-CLCP test method is used for fine-tuning the repassivation potential for localized corrosion. The electrolyte for this method can be used with the artificial physiological fluids such as in Ringer, Hanks and saliva solutions. This test method is originally designed to provide the repassivation potential for crevice corrosion resistance alloys in a wide range of environments. The crevice corrosion tool assembly such as crevice former and crevice washers were used to mount on the test samples. This crevice assembly allows crevice corrosion to be induced in a contacted test specimen by applying certain torques. However, in the case of AM Ti alloys, the layer-by-layer corrosion initiates from the edges of the specimen rather than the locations underneath the crevice former as shown in Figure 1. Therefore, in order for the determination of the localized corrosion resistance of AM Ti alloys, crevice assembly is not necessary at all. ISO 22910 provides the alternative test method to determine the electrochemical critical localized corrosion temperature (E-CLCT) by means of a potentiostatic technique using a temperature scan. The anodic applied potential is held constant during the whole temperature scan. The current is monitored during the temperature scan. E-CLCT shall be measured as the temperature where the current increases rapidly. The higher E-CLCT, the more resistance to localized corrosion. However, for the measurement of the localized corrosion resistance for biomedical AM Ti alloys in artificial physiological fluids, E-CLCP without the temperature scan is a better method than E-CLCT obtained by the temperature scan during testing. In terms of the resistance to localized corrosion of biomedical AM Ti alloy, E-CLCP measurement is confined to the 37,0 °C which is the human body temperature during testing. As much as E-CLCT, E-CLCP also does not need to use the crevice former, i.e. the component of the crevice corrosion test tool assembly. The more noble E-CLCP value of biomedical AM Ti alloys, the more resistance to localized corrosion resistance in the artificial physiological fluids.



a) Crevice corrosion beneath the crevice former for SM Ti-6Al-4V

b) Layer-by-layer corrosion for AM Ti-6Al-4V with the crevice former and a hole at the centre[a]

c) Layer-by-layer corrosion of AM Ti-6Al-4V without the crevice former and a hole at the centre of a specimen

Key

1 crevice corrosion

2 layer-by-layer corrosion

[a] The occurrence of layer-by-layer corrosion is noticeable in the vicinity of edges instead of underneath the crevice former.

Figure 1 — Shapes of Ti-6Al-4V alloys observed after E-CLCP tests

5 Apparatus

5.1 Potentiostat

The potentiostat shall be capable of controlling the electrode potential to within ±1 mV of a preset value.

This potentiostat should have the electrode potential-measuring instrument with a high impedance of the order 10^{11} Ω to 10^{14} Ω and the current-measuring instruments capable of measuring a current to within 2 % of the actual value.

V_{SCE} is the potential measured using a saturated calomel electrode (0,242 volts versus the standard hydrogen electrode). The upper limit on the controllable voltage of the potentiostat is 9 V_{SCE}. If localized corrosion does not occur up to 9 V_{SCE}, the test should be terminated.

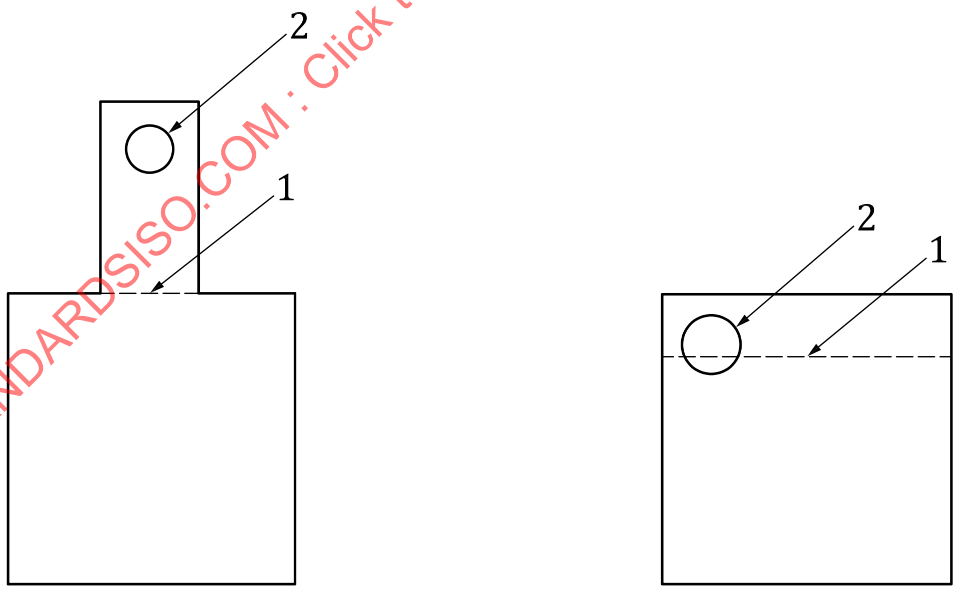
5.2 Heating bath with temperature controller

The heating bath is a vessel capable of providing temperatures of 37,0 °C ± 1 °C.

The temperature controller should be capable of holding the temperature of the surface of the specimen at 37,0 °C ± 1 °C.

5.3 Specimen holder and connections

Different experimental setups and connections can be used. Some examples of specimens and how to connect them electrochemically are given in Figure 2. Any part of the specimen holder or the connection of the electrode shall be designed to ensure no corrosion occurs in the connecting point. The connections are studiously avoided from exposure to the solution in order to prevent from the possible site for localized corrosion. If necessary, the coating sealant can be used on the connections. The minimum exposed specimen volume of 10 mm × 10 mm × 1 mm shall be used.



a) Type A specimen **b) Type B specimen**

Key

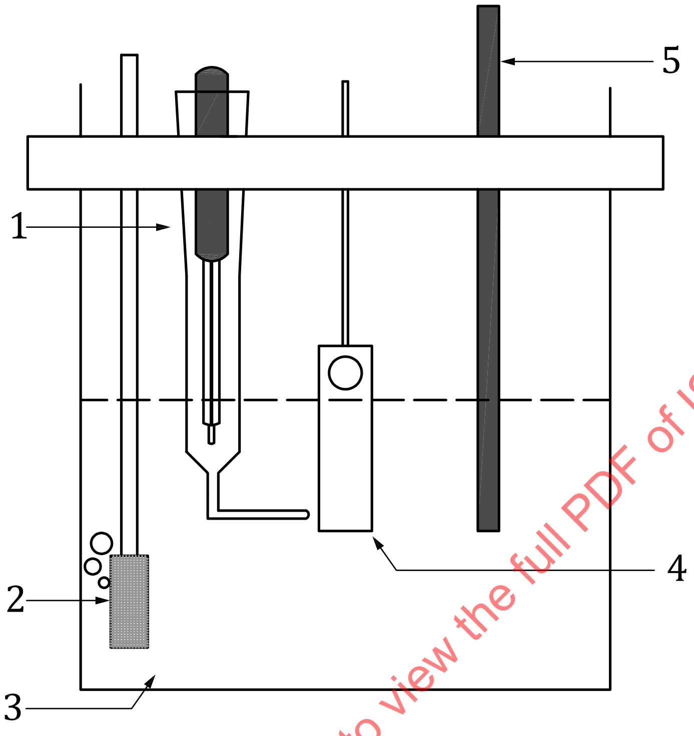
1 line of solution

2 electric connection

Figure 2 — Schematic figure of a specimen showing different possible connections of the electrode

5.4 Test cell

The test cell shall contain the test specimen, a Luggin capillary probe connected to an external reference electrode for measuring the electrode potential, an auxiliary electrode, a port for insertion of a temperature-measuring device and a facility for stirring the solution by bubbling gas through the solution. See Figure 3.



Key

1	reference electrode
2	bubbler
3	electrolyte
4	specimen
5	auxiliary electrode

Figure 3 — Schematic diagram of an E-CLCP cell

5.5 Auxiliary electrode and reference electrode

The auxiliary electrode is prepared from high-purity platinum larger than the area of the test specimen. The reference electrode shall be maintained at ambient temperature external to the test cell and connected to the test cell via a Luggin capillary probe. The commonly used reference electrode is the saturated calomel electrode.

6 Test solutions

For the test, the artificial physiological fluids are used such as Ringer, Hanks and saliva solutions defined by the end-user for the application.

7 Test specimen

Any specimen geometry compatible with the specimen holder can be used. Two different test surfaces of the specimen are used, which are made by the layers perpendicular to or parallel to the stacking direction, depending on the stacking direction via AM. A minimum test volume of 10 mm × 10 mm × 1 mm or higher shall be used. A less than 20 % ratio of side area (or rim area) to total area is desirable. Test specimen is wet-ground up to 600-grit SiC paper, clean with deionized water or double-distilled water and air-dried.

8 Procedure

8.1 Preparation of reference electrodes

The difference in potential between the reference electrode and two other validation electrodes shall be measured. If the potential difference is greater than 3 mV, the test electrodes shall be rejected.

8.2 Preparation of biomedical AM Ti alloy specimen

The specimen shall be prepared to ensure a reproducible surface finish.

The specimen shall be cleaned immediately prior to immersion in the solution by degreasing, rinsing in high-purity water, followed by ethanol or a similar solvent and air drying. After degreasing, care shall be taken not to contaminate the test surface of the specimen.

8.3 Preparation of solution

The solution shall be prepared using reagent-grade chemicals and high-purity water.

8.4 Setting up the E-CLCP test

The test method to determine the E-CLCP of AM Ti alloys in the environment of biomedical solutions comprises the following.

- The measuring apparatus consists of a potentio/galvanostat, an electrochemical polarization cell.
- For test solution, the artificial physiological fluids are used such as a Ringer, Hanks or saliva solutions.
- The temperature of the test solution is 37,0 ± 1 °C of human body temperature.
- The E-CLCP shall be measured as follows:

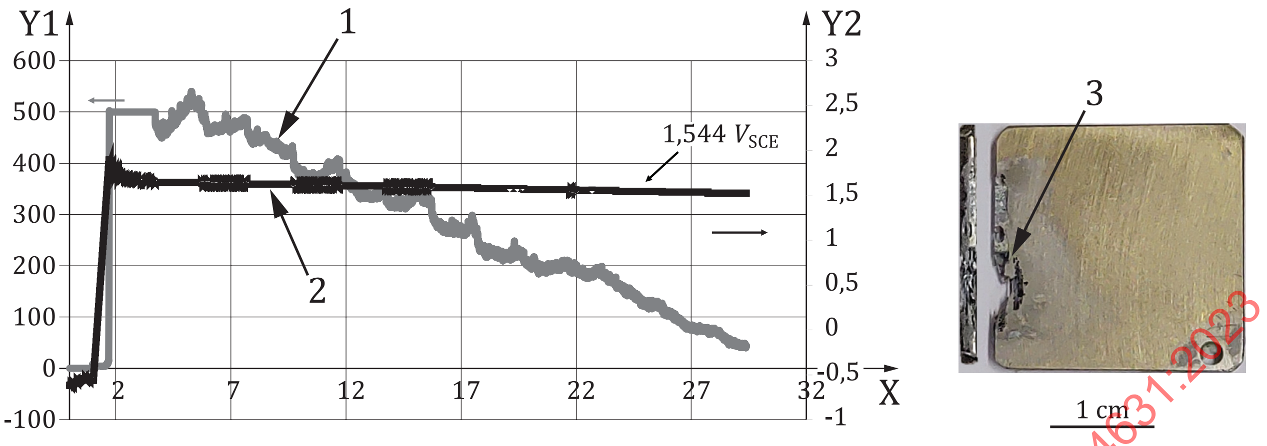
a) The shape of the test piece is the rectangular sheet type without a crevice part. The crevice former or crevice assembly shall not be used. However, for the comparison purpose, counterpart such as SM Ti alloys may be used as a crevice assembly.

b) The test piece is immersed into the solution except for the connection wire part in the gas phase.

c) Anodic polarization is performed with a potentiostat from an open circuit potential until an anodic current density reaches 500 μA/cm^2 by a potential equalization method of 1 mV/sec potential–sweep velocity.

d) After the anodic current density reaches 500 μA/cm^2, the method is immediately changed to constant current density, and the test is performed by holding for 2 h at 500 μA/cm^2.

e) In a reverse (cathode) direction, after holding a constant current density of 500 μA/ cm^2, immediately a constant polarization is held at an electrode potential of 10 mV lower than the electrode potential at that time. When an increase of the current density in the anodic direction is observed, a constant potential is held again at a potential 10 mV lower than that. This operation is repeated until an increase in the anodic direction of the current density is no longer observed by holding a constant potential for 2 h. If uncertainty exists concerning whether an increase in current density is clearly observed, the application should keep on, holding for at least three times more at a potential 10 mV lower than the present potential. If a clear increase in current density is not observed any more, this indicates the E-CLCP is obtained. Otherwise, the operation should be repeated until the precise E-CLCP is re-evaluated. The E-CLCP for biomedical AM Ti alloys is determined by the highest value where the increase in the anodic direction of a current density is no longer observed by constant holding for 2 h. See Figure 4.



a) Typical procedures of an E-CLCP test

b) Corresponding photograph showing layer-by-layer corrosion after testing

Key

X	time (hour)
Y1	current density ($\mu A/cm^2$)
Y2	potential (V_{SCE})
1	current density
2	potential
3	layer-by-layer corrosion

Figure 4 — Determination of the E-CLCP for biomedical AM Ti alloys in Ringer solution

NOTE 1 Some E-CLCP values can be found in Reference [3].

NOTE 2 Some E-CLCP and E-CLCT values can be found in Reference [4].

8.5 Ending test

The test shall be terminated when the E-CLCP has been determined.

The specimen shall be removed from the solution and rinsed in water, cleaned with ethanol, rinsed with high-purity water, cleaned with ethanol or a similar solvent and dried in air.

The specimen shall be inspected using an optical microscope to confirm whether pitting and crevice corrosion have occurred.

9 Examination and evaluation

The E-CLCP shall not be compared with values obtained using a different procedure. The E-CLCP of AM Ti alloys is specific to the test method used and should only be used as a comparative measure of performance.

Localized corrosion is generally of random nature, and thus the number of specimens required for experimental condition is preferably greater than three considering data scatter and analysis.

Annex A shows the validity of E-CLCP by the correlation between E-CLCP and E-CLCT. The two individual test results can be compared and evaluated.