BRITISH STANDARD

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Aerospace series — Titanium and titanium alloys — Test method — Chemical analysis for the determination of hydrogen content

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National foreword

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Luft- und Raumfahrt - Titan und Titanlegierungen - Versuchsmethode - Chemische Analyse zur Bestimmung des Wasserstoffanteils

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Contents

Foreword

This document (EN 3976:2006) has been prepared by the Aerospace and Defence Industries Association of Europe - Standardization (ASD-STAN).

After enquiries and votes carried out in accordance with the rules of this Association, this Standard has received the approval of the National Associations and the Official Services of the member countries of ASD, prior to its presentation to CEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2007, and conflicting national standards shall be withdrawn at the latest by June 2007.

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Introduction

This standard is part of the series of EN metallic material standards for aerospace applications. The general organization of this series is described in EN 4258.

1 Scope

This standard specifies the requirements for chemical analysis using Inert Gas Fusion Thermal Conductivity Method for the determination of the hydrogen content of titanium and titanium alloys for aerospace applications.

The method applies to hydrogen contents ranging from several micrograms per gram to several hundreds of micrograms per gram.

It shall be applied when referred to in the EN technical specification or material standard unless otherwise specified on the drawing, order or inspection schedule.

NOTE The absolute method not used in routine inspection is solid state hot extraction under vacuum followed by measurement of volume and pressure. Due to its complexity, it is only summarized in Annex A.

2 Normative references

The following referenced documents are indispensable for the application 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 Guide 30:1992, *Terms and definitions used in connection with reference materials.*

ISO Guide 31, *Reference materials — Contents of certificates and labels.*

ISO Guide 35, *Reference materials — General and statistical principles for certification.*

EN 2003-10, *Aerospace series — Titanium and titanium alloys — Test methods — Part 10: Sampling for determination of hydrogen content.* 1)

EN 4258, *Aerospace series — Metallic materials — General organization of standardization — Links between types of EN standards and their use.*

EN 4259, *Aerospace series — Metallic materials — Definition of general terms.* 1)

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1) Published as ASD Prestandard at the date of publication of this standard.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
general terms
definition, see EN 4259

3.2
certified reference material (C.R.M.)
definition, see ISO Guide 30

4 Health and safety

Resources, test pieces, test samples, test materials, test equipment and test procedures shall comply with the current health and safety regulations/laws of the countries where the test is to be carried out.

Where materials and/or reagents which may be hazardous to health are specified, appropriate precautions in conformity with local regulations and/or laws shall be taken.

5 Principle

5.1 General

The test consists of thermally decomposing the hydrogenated compounds (mostly as metallic hydrides) present in the titanium or titanium alloys.

The degassed hydrogen is sent, in a stream of supporting inert gas, into the detection system (thermal conductivity cell) which allows a quantitative measurement of hydrogen content (comparative).

Two extraction modes are considered, with respect to the use (or not) of a melting flux. (Table 1).

Table 1

Method	Extraction Mode	Temperature	Supporting Gas
1	With flux	1 800 °C	Nitrogen or Argon
2	Without flux	2 100 °C	Argon

5.2 Method 1

The role of melting flux is to liquefy the mixture (thus facilitating the gas extraction) and to avoid an eventual formation of nitrides. Fusion is performed in a graphite crucible at a temperature of around 1 800 °C:

— either in a nitrogen supporting gas which allows the nitrogen in the sample to be disregarded with the carbon monoxide which, with the nitrogen, has a very small difference in conductivity. (The excess of carbon and the temperature at which melting is performed prevents any carbon dioxide from forming; it is necessary, however, to foresee a way of trapping small quantities of this gas eventually present by using, for example, a molecular sieve);

— or in an argon supporting gas which prevents nitrides forming and results in a better sensitivity since argon has a greater difference in conductivity compared to hydrogen. A separation of nitrogen and carbon oxides is necessary as well as, in the case of using a high frequency furnace, an adapted frequency to avoid discharges by ionization.

5.3 Method 2

Fusion is performed in a graphite crucible at a temperature of around 2 100 °C and shall be carried out in an argon supporting gas (nitrogen in this case would cause formation of nitrides).

6 Testing requirements

6.1 Resources

6.1.1 Equipment

There are numerous models of apparatus but they all generally include the following elements:

- Device for introducing samples;
- Heating device (induction furnace or resistance furnace);
- Sweeping system using supporting gas;
- System for separating gases (if necessary);
- Thermal conductivity cell.

Where a high frequency furnace is used with an argon supporting gas, the frequency shall be adapted to avoid discharges by ionization.

6.1.2 Materials/Reagents

6.1.2.1 Certified Reference Materials (titanium base alloys with certified hydrogen content)

According to ISO Guides 31 and 35 these C.R.Ms. should be produced by a certifying body, traceable to S.I. Units by demonstrated methods and accompanied by a certificate.

The certified hydrogen content value shall be accompanied by an uncertainty at a stated level of confidence.

6.1.2.2 Reagents

During the analysis only reagents of recognised analytical quality shall be used.

- Nitric acid
  ρ_{20} = 1,38 g/ml
- Hydrofluoric acid
  Aqueous solution at 40 %, ρ_{20} = 1,13 g/ml
- 95 % or 96 % (v/v) ethanol
- Melting flux tin granules
- Absorbing reagents, separating columns as specified by the manufacturer of the equipment
- Carbon tetrachloride
- Diethyl oxide
- Acetone

6.1.2.3 Compressed gases

6.1.2.3.1 Supporting gases

- Nitrogen of a purity > 99,995 % (N + rare gases) with H2 < 0,1 ppm (v/v)
- Argon of a purity > 99,995 % with N < 0,5 ppm (v/v) and H2 < 0,01 ppm (v/v)

6.1.2.3.2 Calibration gases

- Hydrogen of a purity > 99,9999 %
- Helium of a purity > 99,9999 %

6.1.2.3.3 Gas for pneumatic devices

Compressed air "for laboratory use".

6.1.3 Qualification of personnel

Testing to the requirements of this test method shall only be undertaken and/or supervised by personnel who have demonstrated their competence by a suitable education and appropriate training and experience.

6.2 Test samples/test pieces

6.2.1 Location of samples

In the case of semi-finished products: as per EN 2003-10.

In the case of finished products: as per special agreement and availability.

6.2.2 Sampling method and preparation of test portion

Sampling is carried out by machining, in dry conditions, with no lubricant, using tools cleaned with solvents (sawing with a blade, the protecting paint of which has previously been removed by cleaning with solvents and abrasive paper, drilling, pelleting, excluding hot cropping) in conditions whereby any heating of the metal is avoided as far as possible.

NOTE Titanium is easily hydrogenated by the humidity in the air at temperatures above 300 °C.

Sampling in the form of chips shall only be envisaged in the case of absolute necessity (due to the risks of heating the sample for analysis and the difficulties in introducing it in the analyser).

Whatever its surface appearance, the sample for analysis shall be thoroughly cleaned with solvents to eliminate any potential pollutants such as paint, grease, etc.

The procedure is as follows:

- clean at ambient temperature with a solvent such as carbon tetrachloride, diethyl oxide (ether), acetone ...,
- if trichlorethylene is used, it shall be followed by one of the above solvents,
- drying in the air at about 60 °C or at ambient temperature under a slight vacuum.

Furthermore, on certain semi-finished industrial products, but never on finished products, cleaning may be completed by pickling at ambient temperature for several minutes using the following acid mixture as recommended by work carried out by the European Community Bureau of References:

- 4 volumes of nitric acid;
- 1 volume of hydrofluoric acid;

Then rinsed three times in water, three times in ethanol and dried in the air at about 60 °C or at room temperature in a slight vacuum.

As hydrogen content may be affected by this chemical dissolution, an additional pickling may be added in an acid mixture corresponding to a weight ratio nitric acid/hydrofluoric acid around 15, in order to remove 5 µm to 10 µm.

6.2.3 Mass of the sample for analysis

The necessary mass of the sample for analysis may vary according to the apparatus, but is generally about 250 mg.

NOTE It may be necessary to reduce sampling accordingly depending on the size of the crucibles compatible with certain types of apparatus.

Where the method 1 is used, the quantity of melting flux shall be about 15 times greater than that of the titanium alloy.

6.3 Testing procedure

6.3.1 General instructions

The detailed procedure depending on the apparatus used is specified on the manufacturer's instruction sheet and cannot be described in this standard.

Certain general considerations shall nevertheless be recalled.

According to the individual characteristics of each type of analyser, the following should be checked:

- the cleanness and the absence of deposits in the different circuits by obtaining correct and constant values for the various gas deliveries (in the case of apparatus with a supporting gas),
- the cleanness and effectiveness of the different filters, traps and absorbing systems.

It is absolutely necessary to maintain the same values for the delivery of the supporting gas, for the temperature of the measuring cell and for the intensity applied on the filament of the thermal conductivity cell in the analysing sequence as in the calibration sequence.

6.3.2 Calibration

The various apparatuses generally include a calibrating device by injecting one or several known volumes of pure hydrogen (adjusted according to variations in temperature and pressure). These known volumes are delivered from a compressed hydrogen cylinder by a pneumatic system (calibrated "cavities" and gas slide valves ...).

This procedure effectively calibrates the measuring system but does not enable the effectiveness of extraction and the eventual separation of degassed chemical substances to be evaluated.

It is therefore essential to complete this procedure by analysing the Certified Reference Materials. If the result differs considerably (> relative 5 %), the analytical conditions shall be changed: quantity of flux powder, setting of the power applied to the furnace, heating time ...

The use of the result obtained with the Certified Reference Material for an arithmetical correction of the value obtained with the sample to be analysed is to be avoided.

In the case where the analytical equipment is not fitted with gas-calibration system, it is only possible to calibrate with CRMs for routine analysis; several CRMs shall be analysed in order to ensure the linearity of the response of the detector.

The analytic conditions: power of the furnace, heating times, quantity of melting flux …, should be set according to the manufacturer recommendations.

In the case where calibration by injecting known volumes of hydrogen is substituted by calibration with injections of known volumes of helium it is necessary to take into account the difference in sensitivity of the catharometer between the calibration process and the analysing process.

Where a same system for injecting volumes of gas is used, the calibration value for the delivery of identical supporting gases obtained when using hydrogen shall be multiplied by a corrective coefficient. This coefficient which depends on the properties of these two gases (thermal conductivity, mass per unit volume ...) is also influenced by the nature of the supporting gas (thermal conductivity ...) and the apparatus (in particular the temperature of the catharometer's filaments). In practice, it may, however, be considered constant and equal to:

$$k = 0,60 \pm 0,01$$

It may also be determined experimentally by the ratio of values obtained with the catharometer by successively injecting the same volumes of hydrogen or helium.

Since the calibration procedure with helium introduces a supplementary factor likely to influence the reproducibility criteria of the analysing method, laboratories using it should periodically carry out calibration with hydrogen.

6.3.3 Analysis

6.3.3.1 Method 1

The test is performed in two stages in the analyser:

- during a first phase the graphite crucible, filled with melting flux, is totally emptied of its hydrogen by heating in the supporting gas flow;
- during a second phase the sample for analysis is placed in the crucible, now degassed, and submitted to the thermal analysis cycle under the supporting gas flow. Measuring is carried out using the thermal conductivity cell.
  Depending on the apparatus, the sample for analysis may be introduced by a lock chamber or manually through a "curtain" of supporting gas after opening the analyser; in this case it is essential to allow the crucible to return at room temperature prior to carrying out the operation.

6.3.3.2 Method 2

The test is performed in two stages in the analyser:

- during a first phase the graphite crucible is totally emptied of its hydrogen by heating in the argon flow;
- during a second phase the sample for analysis is placed in the crucible, now degassed, and submitted to the thermal analysis cycle under the argon flow. Measuring is carried out using the thermal conductivity cell.
  Depending on the apparatus, the sample for analysis may be introduced by a lock chamber or manually through a "curtain" of supporting gas after opening the analyser; in this case it is essential to allow the crucible to return at room temperature prior to carrying out the operation.

6.3.4 Blank test

A blank test consists in carrying out the same operations with the same reagents and products as for analysis while omitting to introduce the sample for analysis.

The blank value is subtracted (manually or automatically) by the apparatus in the previous operations.

6.4 Expression of results

Generally the indication given by the measuring system is either a quantity of hydrogen or directly the concentration.

In all cases, the result shall be expressed in a concentration per unit mass with the unit used being the microgram per gram.

7 Test report

The test report shall contain the following information:

- reference to this standard;
- test method used;
- all information necessary for the identification of the sample(s) and laboratory performing the test;
- the results;
- date of test;
- any unusual detail noted during analysis;
- any operating not specified in this standard.

Annex A

(informative)

Solid State Hot Extraction under Vacuum Method

A.1 Principle

The test consists of thermally decomposing under vacuum the hydrogenated compounds (mostly as metallic hydrides) present in the titanium or titanium alloys.

The degassed molecular hydrogen is collected in an absolute measuring system (volume or pressure) which allows a quantitative evaluation of hydrogen content.

The degassing temperature shall be in the range 900 °C - 1 250 °C in order to avoid an uncomplete degassing of hydrogen ($T < 900$ °C) or an evolution of nitrogen ($T > 1\ 250$ °C).

The degassing time shall be prolonged till the constancy of the measure in order to ensure the total extraction.

A.2 Equipment

There are numerous models of apparatus (commercially or laboratory-build) but they all generally include the following elements:

- Device for introducing samples.
- Heating device.
- Vacuum extraction system.
- System for measuring the volume or pressure.

A.3 Calibration

This apparatus needs not theoretically to be calibrated. It is advisable, however, to periodically check its running by analysing titanium base CRMs.

A.4 Analysis

The test consists in introducing the test portion in the apparatus at room temperature, then in creating a vacuum, and when is reached, in heating to analysing temperature which shall be in the range 950 °C - 1 250 °C, and measuring the degassed volume or pressure.

According to the type of apparatus, measuring may be done continuously or at successive time intervals. Degassing and consequently the analysis is considered to be complete when the value of the signal reaches a maximum and no longer varies with time.

A.5 Blank test

The blank test consists in carrying out the same operation with the same temperature and time of degassing while omitting to introduce sample for analysis.

A.6 Expression of results

The value of degassed volume or pressure is directly converted by calculation in quantity of hydrogen and expressed in a concentration per unit mass with the unit used being the microgram per gram.

blank

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London
W4 4AL