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Powder metallurgy — Hot isostatic pressing — Argon detection using gas chromatography and mass spectrometry techniques

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Foreword

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This document was prepared by Technical Committee ISO/TC 119 *Powder metallurgy*, Subcommittee SC 3, *Sampling and testing methods for sintered metal materials (excluding hardmetals)*.

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

It is essential to detect argon in powder metallurgy hot isostatic pressing (PM HIP) material in order to ensure the desired performance of the PM HIP component. Argon from the production of powder can remain in the powder grains. Argon from the powder filling processes can remain in the voids between powder grains and become trapped during consolidation. Can imperfections can result in ingress of argon from the HIP chamber and potentially introduce, or increase the level of, argon.

Argon in the resulting metal powder produced component can be detected using the techniques included in this document

Powder metallurgy — Hot isostatic pressing — Argon detection using gas chromatography and mass spectrometry techniques

IMPORTANT — It is the responsibility of the purchaser of the PM HIP service to specify in the purchase order if an argon detection test is needed. If so, the agreed argon limit shall be specified.

1 Scope

This document specifies a gas chromatography and a mass spectrometry method of detecting the presence of argon in metal powder produced components, consolidated by hot isostatic pressing.

This document specifies the calibration and functionality test for the equipment covered. It also specifies methods for sampling, sample preparation and sample test procedure of PM HIP components to detect argon presence.

Components produced by additive manufacturing are not covered in this document.

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 terminological 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
blank test
test performed without sample in the same manner as, and parallel with, a test using an analytical sample

[SOURCE: ISO 11323:2010, 8.13]

3.2
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

Note 1 to entry: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system, often mistakenly called “self-calibration”, nor with verification of calibration

Note 3 to entry: Often, the first step alone in the above definition is perceived as being calibration.

[SOURCE: ISO/IEC Guide 99:2007, 2.39]

3.3
can
capsule
canister
container used to encapsulate the powder during the pressure consolidation process

Note 1 to entry: It is partly or fully removed from the final part.

3.4
detection limit
smallest actual amount of an analyte that can be detected by a measuring method

[SOURCE: ISO 20553:2006, 3.14, modified — "measurand" has been replaced by "analyte".]

3.5
functionality test
assessment of the performance of a measuring system, based on specific parameters

[SOURCE: ISO/TS 14907-1:2015, 3.10, modified — measurand has been replaced by analyte]

3.6
gas chromatograph
device that physically separates components of a mixture in the gaseous phase and measures them individually with a detector which signal is processed

[SOURCE: ISO 14532:2014, 2.4.3]

3.7
mass spectrometer
instrument which separates ionized particles of different *mass/charge ratios* (3.8) and measures the respective ion currents

[SOURCE: ISO 3529-3:2014, 2.5.1]

3.8
mass/charge ratio
mass of a charged particle in atomic mass units divided by its elementary charge

3.9
powder metallurgy hot isostatic pressing
PM HIP
process for simultaneously heating and forming a compact in which the powder is contained in a sealed formable enclosure usually made from metal and the so-contained powder is subjected to equal pressure from all directions at a temperature high enough to permit plastic deformation and consolidation of the powder particles to take place

[SOURCE: ASTM A988/A988M – 15A]

3.10
reference sample
material or substance which property values are sufficiently homogeneous and well established to be used for the *functionality test* (3.5) of an apparatus, the assessment of a measurement method, or for assigning values to materials

3.11
solvent cleaner
liquid cleaning substance that is either ethanol, CH_3CH_2OH, acetone, $(CH_3)_2CO$ or iso-propanol, $CH(CH_3)_2OH$

4 Equipment for argon detection

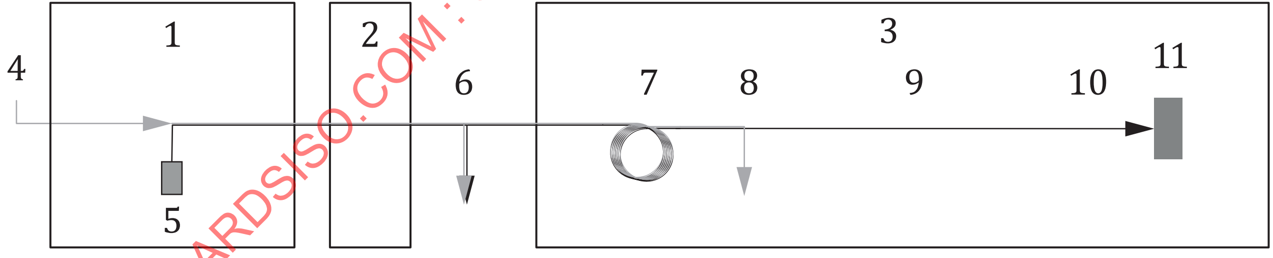
4.1 Gas chromatography

4.1.1 Principle

Gas chromatography (GC) is a separation technique where the mobile phase is gaseous. When GC is used as analytical technique, a known amount of sample is evaporated and dissolved into the mobile phase, also called the carrier gas. The sample compounds are carried by this mobile phase through a chromatographic column and further through detectors. Due to different specific interactions between the sample compounds and stationary phase (stationary phase is usually a chemical that can selectively attract components in a sample mixture), the sample compounds are retained individually and “travel” through the column with different velocities. This leads to a separation of individual components in time. The so-called retention time is the amount of time that elapsed from injection of the sample to the recording of the peak maximum of the component band (peak). When using non-specific detectors, the retention time is the only indication in chromatography for the correct identification of an individual sample component.

4.1.2 Apparatus and reagents

The carrier gas for argon detection shall be helium with purity ≥ 99,9999 % by volume. Measurement starts with fusion of a test portion in a graphite crucible under helium gas at a temperature of about 2 200 °C. The instrument samples a known volume of gas which subsequently enters the column(s) where the gases are separated. The apparatus shall, by an integrated function, correctly identify the signal which belongs to the separated argon. As an example, in Figure 1, a time relayed valve ejects all other gases to leave-out argon as the only analyte producing a signal. However, the chromatograph column may not be able to separate argon from all gases that may originate from the test sample. In that case, it can be necessary to integrate into the apparatus a separation and/or chemical conversion step prior to the gas stream entering the chromatograph column. The argon is ionized by an ionization source in a chamber followed by detection and quantification by the detector. An illustration of an apparatus is shown in Figure 1.



Key

1	furnace
2	particle filter
3	gas chromatograph
4	helium carrier gas
5	test sample
6	sampling valve (gas sample)
7	gas chromatograph column
8	relayed valve
9	ion source
10	ionized argon
11	detector

Figure 1 — Example illustration of a gas chromatography apparatus

4.1.3 Equipment detection limit

The detection limit of the equipment shall at most correspond to a content of 0,02 µg/g argon in a test sample prepared according to Clause 6.

NOTE 1 The detection limit does not correspond to the lowest level that can be quantified with statistical certainty.

NOTE 2 0,02 µg/g is sometimes referred to as 0,02 mg/kg, 0,02 ppm by mass or 20 ppb by mass.

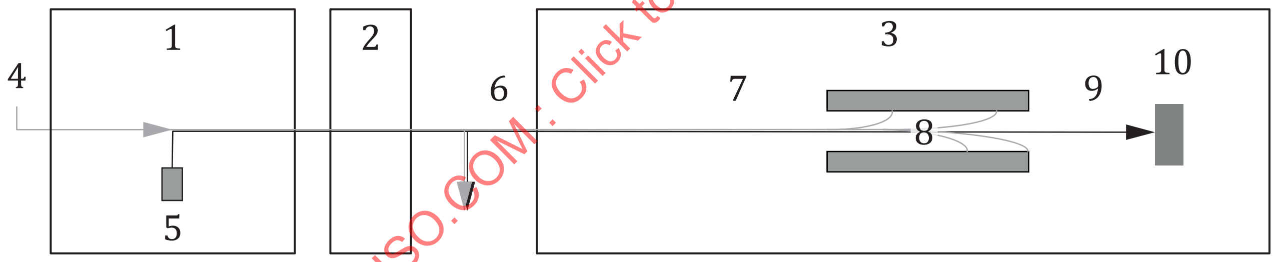
4.2 Mass spectrometry

4.2.1 Principle

Mass spectrometry (MS) is an instrumental method to identify and quantify chemical compounds or elements. It involves a sample that is being dissolved in a carrier gas. The carrier gas carries the compounds through the instrument to the detector. After ionization, the instrument detects extracted argon based on the mass/charge ratio.

4.2.2 Apparatus and reagents

The carrier gas for argon detection shall be helium with purity ≥ 99,9999 % by volume. Measurement starts with fusion of a test portion in a graphite crucible under helium gas at a temperature of about 2 200 °C. The gases are ionized by an ionization source in a chamber. Subsequent detection and quantification of the extracted argon (mass/charge ratio of 40) is made by a mass spectrometer. However, a chemical compound or element that originates from the test sample may give rise to an overlapping signal with the extracted argon. In that case, it can be necessary to integrate into the apparatus a separation and/or chemical conversion step prior to the ionization. An illustration of an apparatus is shown in Figure 2.



Key

1	furnace
2	particle filter
3	mass spectrometer
4	helium carrier gas
5	test sample
6	aliquot (gas sample)
7	ion source
8	mass selector
9	ionized argon
10	detector

Figure 2 — Example illustration of a mass spectrometry apparatus

4.2.3 Equipment detection limit

The detection limit of the equipment shall at most correspond to a content of 0,02 µg/g argon in a test sample prepared according to Clause 6.

NOTE 1 The detection limit does not correspond to the lowest level that can be quantified with statistical certainty.

NOTE 2 0,02 µg/g is sometimes referred to as 0,02 mg/kg, 0,02 ppm by mass or 20 ppb by mass.

5 Calibration and functionality test

5.1 General

Calibrate the detector according to the recommendations of the equipment supplier and at each of the following occasions:

a) after it is installed and commissioned;

b) after replacement of critical parts or components of the equipment;

c) whenever the equipment functionality test significant deviates from expected values.

Functionality test of the apparatus shall be carried out at each of the following occasions:

1) daily, before detection;

2) after calibration;

3) after replacement of the carrier gas container;

4) whenever inaccuracy of the instrument is suspected.

5.2 Gas chromatograph

5.2.1 Calibration

Calibration consists of dosing through the apparatus, a gas mixture with a known pressure and a known level of argon (which is detectable but not high). Apart from argon, the gas mixture shall consist of helium with a low level of impurities. The gas mixture (helium + argon) shall be of purity ≥ 99,9995 % by volume.

The integrated detector response signal of the instrument shall be correlated to the known level of argon in the calibration gas mixture.

5.2.2 Functionality test

Functionality of the apparatus shall be ensured prior to detection. The functionality test shall be performed through measurement of at least one blank sample and at least one reference sample. If the measured values from the blank sample and/or reference sample deviates from the expected values, the source of the error shall be investigated and eliminated.

Single reference samples shall have a detectable argon content and a mass of 0,7 g ± 0,2 g with a non-slender geometry (square, round, or equivalent form).

If the measured result of the blank sample and the reference sample are satisfactory, the test procedure may commence.

NOTE The measurement of a blank sample is sometimes referred to as a blank test. The blank test can either be performed using no sample or using a sample without presence of argon.

5.3 Mass spectrometer

5.3.1 Calibration

Calibration consists of dosing through the apparatus, a gas mixture with a known pressure and a known level of argon (which is detectable but not high). Apart from argon, the gas mixture shall consist of helium with a low level of impurities. The gas mixture (helium + argon) shall be of purity ≥ 99,9995 % by volume.

The integrated detector response signal of the instrument shall be correlated to the known level of argon in the calibration gas mixture.

5.3.2 Functionality test

Functionality of the apparatus shall be ensured prior to detection. The functionality test shall be performed through measurement of at least one blank sample and at least one reference sample. If the measured values from the blank sample and/or reference sample deviates from the expected values, the source of the error shall be investigated and eliminated.

Single reference samples shall have a detectable argon content and a mass of 0,7 g ± 0,2 g with a non-slender geometry (square, round, or equivalent form).

If the measured result of the blank sample and the reference sample are satisfactory, the test procedure may commence.

NOTE The measurement of a blank sample is sometimes referred to as a blank test. The blank test can either be performed using no sample or using a sample without presence of argon.

6 Sample preparation for argon detection

A test piece shall be removed from the PM HIP component. The test piece shall be extracted from the parent PM HIP material or from a sacrificial part integrated to the PM HIP can.

Single test samples with a mass of 0,7 g ± 0,2 g with a non-slender geometry (square, round, or equivalent form) shall be produced from the test piece. The samples shall be free from can material.

The technique to extract the test piece and to section the test sample is at the discretion of the provider of the PM HIP service.

7 Test procedure for argon detection

7.1 General

The samples shall be immersed or rinsed in a solvent cleaner (with adequate grade of purity for the purpose) to remove surface contaminations.

The dry mass of each individual test sample shall be determined and recorded using a precision scale with an accuracy of at least 0,001 g.

7.2 Test procedure using gas chromatography

The following procedure shall be followed:

- place a single use graphite crucible in the furnace using a crucible tong;
- degas while heating above 2 200 °C;
- cool the crucible for at least five seconds;
- manually place a single test sample prepared according to Clause 6 in the crucible; or in the test sample loading sluice, if such a utility is integrated into the apparatus;
- start the test;
- after the fusion and measuring cycle, remove the crucible and record the displayed value;
- prior to discarding spent crucible, the operator shall inspect the inside to ensure the sample is present and melted.

7.3 Test procedure using mass spectrometry

The following procedure shall be followed:

- place a single use graphite crucible in the furnace using a crucible tong;
- degas while heating above 2 200 °C;
- cool the crucible for at least five seconds;
- manually place a single test sample prepared according to Clause 6 in the crucible; or in the test sample loading sluice, if such a utility is integrated into the apparatus;
- start the test;
- after the fusion and measuring cycle, remove the crucible and record the displayed value;
- prior to discarding spent crucible, the operator shall inspect the inside to ensure the sample is present and melted.

8 Test report

When the purchaser has specified an argon detection test according to this document the provider of the PM HIP service shall provide a test report to the purchaser.

The test report shall, as a minimum, include the following information:

a) a reference to this document, i.e. ISO 5842:2022;

b) all details necessary for the identification of the parent PM HIP component;

c) expression of result as:

- approved (≤ agreed argon limit)

or

- not approved (> agreed argon limit)

d) date of test and authorized signature;

e) test equipment and laboratory identification.

Annex A
(informative)

Precision

A.1 Precision

An interlaboratory study of test samples was performed in 2019 and 2020, using the procedures described in ISO 5725-1 and ISO 5725-2. Each of the 12 laboratories made 14 tests of industry-made PM HIP material (non-cobalt tool steel grade). Of the 14 tests, each laboratory made 7 tests on material with a low-level content and 7 tests on material having a high-level content.

The labs used 2 types of equipment to perform the tests, gas chromatography technique and mass spectrometer technique, and the precision is presented for both tests together and separate.

There is no estimate of bias because there is no accepted reference material.

In Table A.1, the repeatability is presented as one standard deviation and the repeatability limit (*r*). The difference between two test results exceeds the repeatability limit (*r*) on average not more than once in 20 tests on identical test material, in the normal and correct operation of the method by one operator using the same apparatus within the shortest feasible time interval between the tests.

Table A.1 — Repeatability as standard deviations and limit for all laboratories, and separately for laboratories using either gas chromatograph (GC) or mass spectrometer (MS)

Tested samples	Number of laboratories	Mean argon content µg/g	Repeatability standard deviation s_r	Repeatability limit r
Low level	**12**	**0,047**	**0,010 µg/g**	**0,028 µg/g**
- only GC	5	0,045	0,009 µg/g	0,025 µg/g
- only MS	7	0,048	0,011 µg/g	0,031 µg/g
High level	**12**	**0,217**	**0,035 µg/g**	**0,098 µg/g**
- only GC	5	0,182	0,036 µg/g	0,101 µg/g
- only MS	7	0,241	0,035 µg/g	0,098 µg/g

In Table A.2 the reproducibility is presented as one standard deviation and the reproducibility limit (*R*). The difference between test results reported by two laboratories exceeds the reproducibility limit (*R*) on average not more than once in 20 reports on identical test material, in the normal and correct operation of the method.