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Metallic powders — Determination of oxygen content by reduction methods —

Part 1:
General guidelines

Poudres métalliques — Dosage de l'oxygène par les méthodes de réduction —

Partie 1: Directives générales

Reference number
ISO 4491-1 : 1989 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4491-1 was prepared by Technical Committee ISO/TC 119, *Powder metallurgy.*

ISO 4491 consists of the following parts, under the general title *Metallic powders — Determination of oxygen content by reduction methods*:

- *Part 1: General guidelines*
- *Part 2: Loss of mass on hydrogen reduction (hydrogen loss)*
- *Part 3: Hydrogen-reducible oxygen*
- *Part 4: Total oxygen by reduction-extraction*

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Introduction

In powder metallurgy, the purity of the powders is an important parameter for the manufacture of sintered metals. Among the various impurities which may be present in a powder, oxygen plays a particular role as it is always present in any metal or alloy powder, and in amounts greater than those encountered in compact metals. Oxygen is mostly combined in the form of oxides which appear in the following ways:

- Oxide film coatings on particle surfaces, spontaneously formed by oxidation of the metal by air or moisture during powder preparation and during handling and storage.

- Oxide inclusions, being either oxides of the main metal remaining locally unreduced during the production process (in the case of reduced powders), or other oxide impurities originating from the raw material and/or from the equipment (e.g. refractory ceramics from melting furnace in atomization processes).

In practice, oxygen contents in metallic powders lie mostly in the range 0,1 % (m/m) to 1 % (m/m).

The determination of oxygen content can be made by means of many physical or chemical methods, for example

a) specific methods, such as activation analysis or mass spectrometry, in which the element O is directly determined;

b) reduction methods, in which oxides present are, totally or partially, reduced by hydrogen or by carbon. Oxygen content is related, either to the loss of mass of the sample through reduction, or to the amount of water or CO/CO_2 produced by the reaction;

c) separation methods, in which

  - either the oxide phase is selectively dissolved and determined chemically (for example in copper powder, where copper oxide is dissolved by hydrochloric acid);

  - or the metal phase is selectively dissolved, and the insoluble residue (assumed to be oxide) is evaluated (for example in aluminium powder, aluminium is dissolved in bromine-methanol reagent, leaving aluminium oxide).

The present International Standard considers only reduction methods, as these are commonly used in laboratories for analysing a great variety of metal powders.

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Metallic powders — Determination of oxygen content by reduction methods —

Part 1 :
General guidelines

1 Scope

This part of ISO 4491 is the first part of a series dealing with the determination of oxygen content in metallic powders by reduction methods. It gives general guidance to these methods, and gives some recommendations for the correct interpretation of the results obtained.

The test methods are applicable generally to all powders of metals, alloys, carbides and mixtures thereof. The constituents of the powder shall be non-volatile under the conditions of test. The powder shall be free of lubricant or organic binder.

However, there exist certain limitations which depend upon the nature of the analysed metal. These limitations are discussed in clause 4.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 4491. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 4491 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 4491-2 : 1989, *Metallic powders — Determination of oxygen content by reduction methods — Part 2: Loss of mass on hydrogen reduction (hydrogen loss).*

ISO 4491-3 : 1989, *Metallic powders — Determination of oxygen content by reduction methods — Part 3: Hydrogen-reducible oxygen.*

ISO 4491-4 : 1989, *Metallic powders — Determination of oxygen content by reduction methods — Part 4: Total oxygen by reduction-extraction.*

3 Sampling

For sampling of the powder the procedures given in ISO 3954 : 1977, *Powders for powder metallurgical purposes — Sampling,* are recommended.

The powder shall be tested in the as-received condition.

Metallic powders are frequently reactive substances with respect to air and moisture. Therefore, particular attention shall be given to adequate conditions for handling and storage of the test sample. The test portion shall be taken immediately prior to the analysis.

4 Meaning of the results according to the method used

4.1 Hydrogen as a reducing agent

4.1.1 At the test temperatures prescribed in the determination, only the following metals have oxides totally reducible by hydrogen :

Fe, Ni, Co, Cu, Ag, Sn, Pb, W, Mo, Re

All other common oxides are not reducible, in particular Al_2O_3, SiO_2, ZrO_2 and other oxides of alkali, alkali-earth and most rare-earth metals. Oxides of chromium, manganese, titanium, and vanadium may be partially reducible.

4.1.2 However, other reactions with constituents of the powder take place during the reduction process:

a) Water vapour and/or hydrocarbons present in the sample, and also gases, which possibly by adsorption or occlusion are contained in the powder, are released during heating.

b) Elements, such as carbon, nitrogen, sulfur, phosphorus, free or combined in the powder, may be completely or partially removed, either because they are volatile or because they react with hydrogen or with oxides in the powder, forming volatile compounds.

c) Some metals present in the powder, such as lead, tin, cadmium, zinc, may be partially or completely volatilized, depending on the test conditions.

d) Carbon present in the powder can also reduce oxides under the specified test conditions, and possibly also oxides that normally are not reduced or are only partially reduced by hydrogen, such as chromium, manganese and vanadium oxides.

e) Alloy powders containing metallic elements with high affinity for oxygen, such as chromium, manganese, silicon, aluminium and titanium, may be oxidized during the test by reaction with the atmosphere or with less refractory oxides, entailing an apparent decrease of measured oxygen content.

4.1.3 In the **loss in hydrogen method** (ISO 4491-2), the loss of mass of the test portion, when submitted to a specified heat treatment in hydrogen, is measured. Originally this test was considered to give an estimate of the oxygen content of a metal powder, the oxide of which is reducible by hydrogen. However, with the advent of more complex or alloyed powders, all the reactions considered above (4.1.2) may contribute, positively or negatively, to the measured loss of mass. Therefore this test method is purely conventional and its reproducibility requires a scrupulous respect of the operating procedure. This method is commonly used in routine control of powders of certain defined metals as stated in ISO 4491-2.

4.1.4 In the method **determination of oxygen emanating from hydrogen-reducible oxides** (ISO 4491-3), the quantity of water formed by hydrogen reduction of these oxides is measured by titration. In comparison with the loss in hydrogen method, this method is more specific for the following reasons:

- The interference of moisture and adsorbed gases is prevented by pre-treatment at low temperature. With a slight modification of the procedure, it is possible to determine the water content of the sample.
- The interference of metalloids and of volatile metals is avoided.

However, interference of carbon present in the sample may have to be taken into account. Some part of the metal oxides, which otherwise may have been reduced by hydrogen, are reduced by carbon, producing carbon monoxide or dioxide, which are not measured by water titration. Consequently a lower result will be obtained. Therefore two alternative methods are specified:

- Method 1: Oxygen content corresponding to hydrogen-reducible oxides, without taking into account carbon interference. This method is applicable in practice when the sampled powder is known to be almost free of carbon [for example $C < 0{,}02\ \%\ (m/m)$] or the carbon present is in an unreactive form. Then the result represents the oxygen content from hydrogen-reducible oxides.
- Method 2: Oxygen content corresponding to hydrogen-reducible oxides, taking into account carbon interference. In this method the $CO + CO_2$ gases released by carbon reduction of some of the oxides and contained in the H_2 carrier gas, are quantitatively converted to methane and water on a nickel catalyst at 380 °C. The total water determined represents the oxygen content emanating from hydrogen-reducible oxides, irrespective of whether the actual reduction has taken place by means of hydrogen or carbon.

NOTE — With reference to 4.1.2 d), certain oxides may be partially reduced by carbon. i.e. oxides which otherwise would not be reduced by hydrogen. In such a case, the test conditions shall be subject to a special agreement and interpretation of the result should be made with great care.

4.2 Carbon as a reducing agent: reduction-extraction method

This method (ISO 4491-4) is based on the reduction of the sample by graphite at very high temperature (2 000 to 3 000 °C), either under vacuum, or in a flow of pure inert gas (for example argon). Depending on the metal analysed, the operating conditions are chosen so that all the oxides, even the most refractory ones, are reduced totally. Any interference is completely excluded and the result represents accurately the total oxygen content of the sample.

5 Practical application of the standard methods

The following table gives a summary of the applicable methods, depending on the type of powder analysed and on the nature of the oxygen which shall be determined. It should be emphasized that a combination of several methods can bring precise information, for example:

- on the "hydrogen-reducible" and "hydrogen-irreducible" oxygen, i.e. the presence of refractory oxides in "hydrogen-reducible" metals;
- on the internal effect of carbon, when present, on the reduction of oxides.

An interesting alternative is to carry out the total oxygen determination on a test portion already reduced by hydrogen (by means of a loss in hydrogen test or a hydrogen-reducible oxygen test). In this way the content of oxygen not reduced by hydrogen (and by internal carbon) under the conditions of hydrogen reduction can be determined.

6 Summary of the implementation of methods for oxygen determination by reduction

Two cases are considered:

a) Metals of oxides which are reducible by hydrogen ("H reducible") and which may possibly contain carbon, for example:

Fe, Ni, Co, Cu, Ag, Sn, Pb, W, Mo, Re

When such a metal is reduced by hydrogen, the behaviour of the oxygen and carbon content is represented by the following analytical results

$$\text{content of oxygen} \left\{ \begin{array}{ll} \text{contained in hydrogen reduced oxides} & O_H \\ \text{contained in carbon reduced oxides} & O_C \\ \text{from remaining (unreduced) oxides} & O_r \end{array} \right.$$

content of carbon having reacted C_O

b) Any metal (containing carbon or not)

When reduced totally by graphite (reduction-extraction method), the total oxygen content (O_t) is measured.

Table 1 — Content determined depending on method used

Powder	Method				
	Hydrogen loss	Hydrogen-reducible oxygen		Reduction-extraction	
		Direct method	With correction for carbon	On initial sample	On sample reduced by hydrogen
Metals with hydrogen-reducible oxides:					
not containing carbon	O_H	O_H	O_H	$O_t = O_H + O_r$	O_r
containing carbon	$O_H + O_C + C_O$	O_H	$O_H + O_C$	$O_t = O_H + O_C + O_r$	O_r
Any other metal				O_t	
NOTE — In this table, interference by moisture, adsorbed gases, volatile and reoxidizable metals, is assumed to be absent.					

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