G-01-01
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INTERNATIONAL STANDARD 886

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION •МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Aluminium and aluminium alloys — Determination of manganese — Photometric method (Manganese content between 0,005 and 1,5 %)

First edition — 1973-11-15

UDC 669.71 : 546.711 : 543.42 Ref. No. ISO 886-1973 (E)

Descriptors : aluminium, aluminium alloys, chemical analysis, determination of content, manganese, photometry.

Price based on 5 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, International Standard ISO 886 replaces ISO Recommendation R 886-1968 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

Australia
Austria
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Israel
Italy
Japan
Netherlands
Norway
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South Africa, Rep. of
Spain
Sweden
Switzerland
Thailand
Turkey
U.S.A.
U.S.S.R.
Yugoslavia

The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

United Kingdom

Printed in Switzerland

Aluminium and aluminium alloys – Determination of manganese – Photometric method (Manganese content between 0,005 and 1,5 %)

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method for the determination of manganese in aluminium and aluminium alloys.

The method is applicable to the determination of manganese content between 0,005 and 1,5 %.

The method does not apply completely to the following special cases :

a) alloys with a silicon content higher than 10 % and a manganese content less than 0,1 % (see Annex);

b) aluminium alloys containing tin, antimony, bismuth, zirconium, etc. (In this International Standard these special cases are not treated.)

2 PRINCIPLE

Attack of the sample with sodium hydroxide. Acidification by sulphuric and nitric acids.

Oxidation of manganese(II) to manganese(VII) by means of potassium periodate (acidity of solution over 3,5 N approximately), in the presence of phosphoric acid.

Photometric measurement at a wavelength of about 525 nm.

3 REAGENTS

For the preparation of solutions and during the analysis, use doubly distilled water.

3.1 Water free from reducing agents

Heat to boiling, water acidified with 10 ml per litre of the sulphuric acid (3.4); add a few crystals of potassium periodate (KIO_4) and continue boiling for about 10 min.

3.2 Sodium hydroxide, 200 g/l solution.

In a nickel dish dissolve 200 g of sodium hydroxide (NaOH) in water and, after cooling, make up the volume to 1 000 ml. Keep in a plastics container.

3.3 Sulphurous acid solution

Pass a current of sulphur dioxide gas (SO_2) through water until saturation point is reached.

3.4 Sulphuric acid, ρ 1,48 g/ml, approximately 17,5 N solution.

Carefully add 500 ml of sulphuric acid (ρ 1,84 g/ml), approximately 35,6 N, to water, cool and make up the volume to 1 000 ml.

3.5 Sulphuric acid, ρ 1,84 g/ml, approximately 35,6 N solution.

3.6 Nitric acid, ρ 1,40 g/ml, approximately 15 N solution.

3.7 Hydrofluoric acid, 40 % (*m/m*) solution (ρ approximately 1,14 g/ml).

3.8 Fluoroboric acid solution

In a plastics flask mix 800 ml of saturated boric acid solution at 20 °C with 200 ml of the hydrofluoric acid (3.7).

3.9 Phosphoric acid, ρ 1,71 g/ml, approximately 45 N solution.

3.10 Potassium periodate, 50 g/l solution.

Dissolve 50 g of potassium periodate (KIO_4) in water, add 200 ml of the nitric acid (3.6) and make up the volume to 1 000 ml with water.

3.11 Sodium nitrite, 20 g/l solution.

Dissolve 2 g of sodium nitrite ($NaNO_2$) in a little water and make up the volume to 100 ml.

3.12 Manganese standard solution, 1 g/l (1 ml contains 1 mg of Mn),

prepared by one of the following methods.

3.12.1 In a tall-form beaker of suitable capacity (for example 400 ml) dissolve 2,877 g of very pure potassium permanganate ($KMnO_4$) in about 200 ml of water and add 20 ml of the sulphuric acid (3.4). Reduce the permanganate solution by adding a few crystals of sodium sulphite or hydrogen peroxide (36 % (*m*/*m*)). Boil the solution to remove excess SO_2 or H_2O_2, cool, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

3.12.2 In a tall-form beaker of suitable capacity (for example 600 ml) dissolve 1 ± 0,001 g of electrolytic manganese (purity above 99,9 %) with 20 ml of the sulphuric acid (3.4) and about 80 ml of water. Boil the solution for a few minutes. Cool, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

NOTE – Free the electrolytic manganese from any surface oxide by placing a few grams of the metal in a glass beaker, of about 250 to 300 ml capacity, containing 30 to 40 ml of the sulphuric acid (3.4) and about 100 ml of water. Shake and, after a few minutes, decant the acid solution and introduce into the beaker double distilled water. Repeat the decantation and washing with double distilled water several times; then place the metallic manganese in acetone and shake. Decant the acetone, dry the metal in a hot air oven at 100 °C for about 2 min and allow it to cool in a desiccator.

3.13 Manganese standard solution, 0,1 g/l (1 ml contains 0,1 mg of Mn).

Transfer 100,0 ml of the manganese standard solution (3.12) to a 1 000 ml volumetric flask, make up to volume and mix.

4 APPARATUS

4.1 Ordinary laboratory apparatus.

4.2 Hotplate fitted with a mechanical or magnetic stirrer.

4.3 Spectrophotometer, or

4.4 Photoelectric absorptiometer.

5 SAMPLING

5.1 Laboratory sample[1]

5.2 Test sample

Chips not more than 1 mm thick obtained by milling or drilling.

6 PROCEDURE

6.1 Test portion

Mass of test portion : 1 ± 0,001 g.

6.2 Preparation of the calibration curve

6.2.1 *Preparation of the compensating solution (Term 0)*

In a platinum dish, place 7 ml of the sulphuric acid (3.4) and 8 ml of the nitric acid (3.6) and evaporate to dryness (do not calcine). Take up the residue in a little warm water, add 8 ml of the sulphuric acid (3.4), 2 ml of the nitric acid (3.6) and 5 ml of the phosphoric acid (3.9). Transfer the solution to a vessel of suitable capacity (for example 250 ml). Dilute to approximately 70 ml with water and continue according to the procedure described in 6.2.3.

6.2.2 *Preparation of the standard matching solutions*

Introduce into a series of six vessels of suitable capacity (for example 250 ml to 300 ml), respectively : 1,0 – 2,0 – 5,0 – 10,0 – 15,0 and 20,0 ml of the manganese standard solution (3.13), corresponding respectively to 0,1 – 0,2 – 0,5 – 1,0 – 1,5 and 2 mg of manganese. To each vessel add 15 ml of the sulphuric acid (3.4), 10 ml of the nitric acid (3.6) and 5 ml of the phosphoric acid (3.9) and make up the volume to about 70 ml with water.

6.2.3 *Development of the colour*

Place the vessels specified in 6.2.1 and 6.2.2 on a hot-plate fitted with a stirrer and bring the solutions to the boil. (Stirring by means of a mechanical or magnetic stirrer during heating and during boiling enables splashing to be avoided.) Then add to each solution 10 ml of the potassium periodate solution (3.10) and continue boiling until the characteristic colour develops.

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[1] The sampling of aluminium and aluminium alloys will form the subject of a future International Standard.

Boil for another 5 min (15 to 30 min if the concentration of manganese is less than or equal to 0,2 mg of manganese in 100 ml of solution). Cool to room temperature, transfer the solutions into as many 100 ml volumetric flasks, previously rinsed with treated water (3.1), and make up to volume with the treated water (3.1).

6.2.4 *Photometric measurements*

Carry out the photometric measurements using the spectrophotometer (4.3) at a wavelength of about 525 nm or the photoelectric absorptiometer (4.4), fitted with suitable filters, after having adjusted the instrument to zero absorbance against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.11) and repeat the measurement (Δ_{Ed}). In order to obtain the value of the absorbance due to the manganese introduced, calculate for each dilution the differences.

$$[(\Delta_{Ec} - \Delta_{Ed}) - (\Delta_{Tc} - \Delta_{Td})]$$

where Δ_{Tc} and Δ_{Td} are the values of absorbance corresponding to the term 0, coloured and decolourized.

6.1.5 *Plotting of the calibration chart*

Plot a graph having, for example, as abscissae the amounts of manganese, in milligrams, contained in 100 ml of standard matching solution and the corresponding values of absorbance as ordinates.

6.3 Blank test

Parallel to the analysis and using the same technique, carry out a blank test.

In a platinum dish, place 8 ml of the nitric acid (3.6) and 12 ml of the sulphuric acid (3.4) and evaporate to dryness (do not calcine). Take up the residue with a little warm water, add 2 ml of the nitric acid (3.6) and 18 ml of the sulphuric acid (3.4). Transfer the solution to a vessel of suitable capacity (for example 250 to 300 ml), add 40 ml of the sodium hydroxide solution (3.2) and mix. Heat until a clear solution is obtained, cool, add 5 ml of the phosphoric acid (3.9) and dilute to about 70 ml with water. Continue from this point according to the procedure described in 6.4.2.

6.4 Determination

6.4.1 *Preparation of the test solution*

Place the test portion in a platinum vessel of suitable capacity (for example 100 ml) and add, in small amounts, 40 ml of the sodium hydroxide solution (3.2). Cover the vessel with a platinum lid and heat gently to facilitate the attack. Move the lid slightly and evaporate with care until a syrupy consistency is reached. Cool, wash the lid and the walls of the vessel with the smallest possible quantity of warm water (for example 30 ml) and heat gently. Transfer the alkaline solution into a glass beaker of suitable capacity (for example 250 to 300 ml) containing 30 ml of the sulphuric acid (3.4) and 10 ml of the nitric acid (3.6). Carefully wash the platinum vessel and the lid with warm water and add the washings to the acid solution contained in the glass beaker.

If manganese hydroxide separates out and adheres to the walls of the platinum vessel, transfer into the vessel a little of the acid solution, add several drops of the sulphurous acid solution (3.3) and mix. Then again transfer the solution into the glass beaker and wash the platinum vessel with warm water.

Concentrate the solution to a volume of approximately 65 ml if the manganese content is less than 0,1 %.

For the determination of manganese contents greater than 0,1 % transfer the solution into a 100 ml or 250 ml volumetric flask, depending on the manganese content. Cool to 20 °C, make up to volume and mix. Depending on the assumed manganese content, the dilution of the main solution, the aliquot to be taken and the corresponding quantities of reagents to be added to the aliquot are given in the following table.

Assumed manganese content	Volume of main solution	Volume of aliquot to be taken	Corresponding mass of test portion	Volume of sulphuric acid (3.4)	Volume of nitric acid (3.6)
%	ml	ml	g	ml	ml
0,005 to 0,1	–	total	1	–	–
0,1 to 0,4	100	50	0,5	5	5
0,4 to 1	250	50	0,2	10	5
1 to 1,5	250	25	0,1	10	5

6.4.2 *Development of the colour*

Into a vessel of suitable capacity (for example 250 ml) introduce the aliquot taken and the corresponding quantities of the sulphuric acid (3.4) and the nitric acid (3.6). (For manganese contents below 0,1 % develop the colour reaction in the vessel in which the main solution was prepared.) Add 5 ml of the phosphoric acid (3.9), dilute to about 70 ml with water, then place the vessel on a hotplate fitted with a stirrer (see 8.3) and bring the solution to the boil. (Stirring by means of a mechanical or magnetic stirrer during heating and during boiling enables splashing to be avoided.) Then add 10 ml of the potassium periodate solution (3.10) and continue boiling until the characteristic colour develops.

Boil for another 5 min (15 to 30 min if the quantity of manganese present is less than or equal to 0,2 mg). Cool to room temperature, transfer the solution to a 100 ml volumetric flask previously rinsed with water (3.1) and make up to volume with treated water (3.1).

6.4.3 *Photometric measurements*

Carry out the photometric measurements according to the procedure described in 6.2.4 after having adjusted the instrument to zero absorbance against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.11) and repeat the measurement (Δ_{Ed}). The difference between these two values gives the absorbance due to permanganic acid.

At the same time, and under the same conditions carry out the photometric measurements relating to the blank test solution.

The absorbance due to the manganese of the test solution is given by the difference

$$[(\Delta_{Ec} - \Delta_{Ed}) - (\Delta_{Bc} - \Delta_{Bd})]$$

where Δ_{Bc} and Δ_{Bd} are the values of absorbance corresponding to the blank test solution, coloured and decolourized.

7 EXPRESSION OF RESULTS

By means of the calibration graph, determine the mass of manganese, in milligrams, corresponding to the value of the photometric measurement of the test solution.

Calculate the manganese content, as a percentage by mass, by the formula

$$\text{Mn } \% \ (m/m) = \frac{m_1 \times R}{10\, m_0}$$

where

m_0 is the mass of the test portion, in milligrams;

m_1 is the mass, in milligrams, of manganese found in the aliquot of the test solution;

R is the ratio of the volume of the test solution to the volume of the aliquot taken for the colour reaction.

8 TEST REPORT

The test report shall include the following particulars:

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

ANNEX

SPECIAL CASE OF ALUMINIUM ALLOYS WITH SILICON CONTENT HIGHER THAN 10 % AND MANGANESE CONTENT LESS THAN 0,1 %

A.1 PRINCIPLE

When the silicon content is higher than 10 % the silicon separates out as silica during the development of the colour reaction on the whole test portion (1 g). The sample is then attacked by a mixture of sulphuric, nitric and fluoroboric acids, the residue is filtered off and manganese present in it is recovered.

A.2 MODIFICATIONS TO THE GENERAL METHOD

A.2.1 *Replace 6.3* with the following :

Parallel to the analysis and using the same technique, carry out a blank test.

In a platinum dish, place 8 ml of the nitric acid (3.6) and 12 ml of the sulphuric acid (3.4) and evaporate to dryness (do not calcine). Take up the residue with a little warm water, add 2 ml of the nitric acid (3.6), 8 ml of the sulphuric acid (3.4) and 2 ml of the fluoroboric acid (3.8). Transfer the solution to a vessel of suitable capacity (for example 250 to 300 ml), add 5 ml of the phosphoric acid (3.9) and dilute to about 70 ml with water... Continue from this point according to the procedure described in 6.4.2.

A.2.2 *Replace 6.4.1* with the following :

Place the test portion in a vessel of suitable capacity (for example 250 to 300 ml) and add 20 ml of the sulphuric acid (3.4), 10 ml of the nitric acid (3.6) and 2 ml of the fluoroboric acid (3.8). Heat gently to complete dissolution of the test portion; once the reaction is finished, heat to boiling to eliminate nitrous fumes.

Dilute the solution to approximately 50 ml with warm water, add a little soaked filter paper and heat for several minutes. Filter the residue on a close texture filter and wash with warm water, collecting the filtrate in a vessel of 200 to 300 ml capacity. Introduce the filter with its content into a platinum crucible and ignite moderately at 500 to 600 °C until the combustion of the filter paper is complete. Allow to cool, add several drops of the sulphuric acid (3.5), 2 to 5 ml of the hydrofluoric acid (3.7) and finally nitric acid (3.6), drop by drop, until the solution becomes clear. Evaporate to dryness, calcine moderately, then take up the residue in a little warm water to which have been added a few drops of the sulphuric acid (3.4).

Heat to complete dissolution, filter if necessary and add the solution obtained to the main solution.

Concentrate the solution to about 65 ml, add 5 ml of the phosphoric acid (3.9)...

Continue from this point according to the procedure described in 6.4.2.