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Copper alloys — Determination of aluminium as alloying element — Volumetric method

Alliages de cuivre — Dosage de l'aluminium comme élément d'alliage — Méthode volumétrique

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FOREWORD

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Copper alloys — Determination of aluminium as alloying element — Volumetric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a volumetric method for the determination of aluminium in copper alloys.

The method is applicable for the determination of aluminium as an alloying element in all types of copper alloys listed in ISO Recommendations or International Standards.

2 PRINCIPLE

Determination of aluminium by chelatometric titration at pH about 6, following a sodium fluoride demasking procedure, and using a voltametric indication.

3 REAGENTS

All the reagents shall be of the analytical grade. Distilled or deionized water shall be used.

3.1 Nitric acid

Mix 50 ml of nitric acid (ρ 1,40 g/ml) with 50 ml of water.

3.2 Disodium salt of ethylenediaminetetra-acetic acid (EDTA), 0,2 M solution.

3.3 Hexamethylentetramine.

3.4 Copper, 0,05 M solution.

Dissolve 3,177 g of copper (copper content > 99,9 %) in 20 ml of nitric acid (3.1) and dilute to 1 l.

3.5 Sodium fluoride, 25 g/l solution.

3.6 Manganese solution containing 4,55 g of $Mn(NO_3)_2 \cdot 4H_2O$ per litre (1 ml contains 1 mg of manganese).

3.7 Hydrochloric acid

Mix 50 ml of hydrochloric acid (ρ 1,19 g/ml) with 50 ml of water.

3.8 Hydrogen peroxide, 30 % (*m/m*) solution.

3.9 Cupferron solution.

Dissolve 10 g of cupferron with 100 ml water.

3.10 Chloroform.

3.11 Perchloric acid (ρ 1,74 g/ml).

3.12 Nitric acid (ρ 1,40 g/ml).

4 APPARATUS

4.1 Normal laboratory apparatus.

4.2 Potentiometer in connection with a device for a voltametric indication, i.e. for polarizing the electrodes with a constant current (2 to 10 μA).

This attachment can be made in a simple way using for example an accumulator or a storage battery of 2 V in series with a 1 MΩ resistor and the electrodes. The potentiometer shall be in parallel with the electrodes.

4.3 Double platinum electrode, made of 1 mm diameter platinum wire, sealed in a glass tube directly or after welding on a copper wire in such a way that each wire electrode is about 0,4 cm long with a free geometric surface of about 10 mm^2.

5 SAMPLING

Carry out the sampling in accordance with the requirements of ISO . . .[1]

6 PROCEDURE

6.1 For alloys free of titanium and zirconium

6.1.1 *For aluminium contents of 4 to 12 % (m/m)*

6.1.1.1 Weigh 0,200 0 g of the finely divided sample into a 250 ml tall-form beaker, add 5 ml of water and 3 ml of the nitric acid (3.1) and heat gently until the test portion has dissolved. Evaporate the solution obtained to about 1 to 2 ml and dilute with 25 ml of water.

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[1] In preparation.

In the case of analysis of tin rich alloys, the tin oxide (SnO_2) precipitated during dissolving has to be filtered off. This precipitate is free of aluminium and may be rejected.

6.1.1.2 Add 1 ml of the manganese solution (3.6), 22 ml of the EDTA solution (3.2) and sufficient hexamethylentetramine (3.3) to give a pH value of 6,0 to 6,2. (The manganese solution may be omitted if the sample contains 0,5 % or more of manganese.) Boil for 5 min. Cool to room temperature and titrate the excess EDTA present with the copper solution (3.4) employing voltametric indication using the polarized double platinum electrode (4.3).

The copper solution shall be added drop by drop, rapidly at first and near the end-point in 1 drop steps. The end-point is indicated by a sharp potential break of more than 100 mV per drop (note the volume used, V_1). To the solution titrated in this way add 20 ml of sodium fluoride solution (3.5). Check the pH value and if necessary correct it by adding a few drops of nitric acid (3.1). Boil for 2 min. Cool again to room temperature and, using the same burette without refilling, titrate the liberated EDTA (primarily bonded to aluminium) with the copper solution (3.4) in the same manner as described above (total volume used V_2).

NOTES

1 During the titrations the anode becomes coated with manganese oxide (MnO_2). This precipitate must be dissolved after each titration by dipping the electrode into a solution of hydrochloric acid (1 + 5) containing a few drops of hydrogen peroxide.

2 Evaluate the titration curves in the same way as for potentiometrically indicated titrations. Care must be taken that the small amount of titrating solution added in excess during the first titration (back-titration of the EDTA in excess) is added to the volume used in the second (titration of the primarily aluminium-bonded EDTA liberated by the sodium fluoride).

6.1.2 *For aluminium contents of 0,5 to 4 % (m/m)*

Weigh 0,500 0 g of the sample into a 250 ml tall-form beaker, add 5 ml of water and 5 ml of the nitric acid (3.1) and heat gently until the test portion has dissolved. Evaporate the solution obtained to about 1 to 2 ml, dilute with 25 ml of water, add 1 ml of the manganese solution (3.6) and 42 ml of the EDTA solution (3.2). (The manganese solution may be omitted if the sample contains 0,5 % or more of manganese.)

For the titration follow the procedure given in 6.1.1, beginning with the addition of the hexamethylentetramine.

If the aluminium content of the alloy is less than 1 %, use a microburette for the second titration.

6.2 For alloys containing titanium and zirconium

6.2.1 *For aluminium contents of 4 to 12 % (m/m)*

Weigh 0,200 0 g of the finely divided sample into a 250 ml tall-form beaker and dissolve with 25 ml of the hydrochloric acid (3.7) by adding a total amount of 5 ml of the hydrogen peroxide (3.8) in several small portions. Cool the solution during this operation. Destroy the excess peroxide by boiling for about 5 min. After cooling to room temperature, transfer the solution to a separating funnel of approximately 150 ml, using as little water as necessary for rinsing. The total volume of the solution shall amount to approximately 50 ml.

Depending on the amount of iron, titanium and zirconium present, add 2 to 5 ml of the cupferron solution (3.9) and 20 ml of the chloroform (3.10) and shake vigorously for about 1 min. After separation of the phases, draw off the organic phase and repeat the extraction of the aqueous phase using 1 ml of the cupferron solution and 10 ml of the chloroform. Repeat this extraction once more if the organic phase shows a yellowish colour at this step. Discard the chloroform phases. Transfer the aqueous solution, now free of iron, titanium and zirconium, to a 250 ml tall-form beaker and evaporate to about 5 ml. Add 5 ml of the perchloric acid (3.11) and 5 ml of the nitric acid (3.12) and destroy any organic matter which may be present by wet combustion. Fume the perchloric acid to about 1 ml, dilute with about 25 ml of water and filter off any insoluble matter.

Continue as indicated in 6.1.1.2.

6.2.2 *For aluminium contents of 0,5 to 4 % (m/m)*

Weigh 0,500 0 g of the sample into a 250 ml tall-form beaker and dissolve with 30 ml of the hydrochloric acid (3.7) by adding a total amount of 10 ml of the hydrogen peroxide (3.8) in several small portions. Cool the solution during this operation. Destroy the excess peroxide by boiling and continue as indicated in 6.2.1, using a larger amount of the cupferron solution, if higher amounts of iron, titanium and zirconium are present.

After fuming the solution with perchloric/nitric acid, and if necessary filtration, follow the procedure given in 6.2.1 for the titration.

If the aluminium content of the alloy is less than 1 %, use a microburette for the second titration.

7 EXPRESSION OF RESULTS

Calculate the aluminium content, as a percentage by mass, as follows :

- for procedures according to 6.1.1 and 6.2.1 :

$$\text{Al \% } (m/m) = 0{,}674\,5\,(V_2 - V_1)$$

- for procedures according to 6.1.2 and 6.2.2 :

$$\text{Al \% } (m/m) = 0{,}270\,(V_2 - V_1)$$

where

V_1 is the volume, in millilitres, of copper solution required for the titration before the demasking with sodium fluoride;

V_2 is the total volume, in millilitres, of copper solution required for the titration both before and after the demasking with sodium fluoride.

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 characteristics noted during the determination;

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

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