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Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Part 9: Determination of sulfur content by the bomb method

原铝生产用炭素材料 煤沥青 第9部分：氧弹燃烧法测定硫含量

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Note on the printed English title

The front page of the document prints the English title as Carbonaceous materials used in the production of aluminium-Pitch for electrodes-Part 9: Determination of sulful content by the bomb method. The word sulful is a misprint for sulfur: the reference to ISO 9055:1988 printed immediately below it on the same page reads sulfur content. The title given in this record is the corrected one.

2 Normative references

The following documents are indispensable for the application of this document. For dated references only the edition cited applies; for undated references the latest edition, including any amendments, applies.

The only document listed is ISO 6257, Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Sampling.

3 Principle of the method

The test portion is burned in a steel bomb containing pressurised oxygen; the bomb is washed out, the various oxides of sulfur are collected and converted to barium sulfate, and the determination is made gravimetrically.

4 Reagents

Only analytical grade reagents and distilled water, or water of equivalent purity, are used in the analysis.

4.1 Hydrochloric acid: a solution of density about 1.19 g/mL and concentration about 37 % (mass fraction). 4.2 Saturated bromine water. 4.3 Barium chloride solution, 85 g/L: 100 g of barium chloride ($BaCl_2.2H_2O$) is dissolved in water and diluted to 1 000 mL. 4.4 Sodium carbonate solution, 50 g/L: 135 g of sodium carbonate decahydrate ($Na_2CO_3.10H_2O$), or an equivalent mass of sodium carbonate, is dissolved in water and diluted to 1 000 mL. 4.5 Oxygen: free from very readily combustible matter and from sulfides, usable at a pressure of 4.053 MPa. 4.6 White oil: liquid paraffin B.P. or another equivalent material.

5 Apparatus

5.1 Bomb: capacity not less than 300 mL, leak-free throughout the determination and allowing the solution in the vessel to be transferred quantitatively. The inner surface of the bomb is made of stainless steel or of any other material not affected by the combustion process or its products. The materials assembled with the bomb, such as the head gasket and the lead seal, shall withstand heat and chemical attack; where they cannot withstand them, they will affect the sulfur content of the liquid in the bomb.

5.2 Platinum sample cup: outside diameter at the bottom 24 mm, outside diameter at the top 27 mm, height 12 mm, mass 10 g to 11 g. 5.3 Platinum heating wire: about 0.4 mm in diameter. 5.4 Ignition circuit: able to supply enough current to ignite a cotton wick or a nylon thread without melting the heating wire. The current is not to be taken directly from the mains and the voltage shall not exceed 25 V. Warning: the switch of the ignition circuit is normally to be left open and is closed only when the operator is using it.

5.5 Cotton wick or nylon thread. 5.6 Emery polishing paper: No. 00 or equivalent. 5.7 Unground chromium(III) oxide paste. 5.8 Cooling water bath. 5.9 Ceramic filter crucible: P10 series, pore size 4 micrometre to 10 micrometre.

6 Sampling and sample preparation

6.1 Sampling: the pitch sample is taken according to ISO 6257.

6.2 Sample preparation: where the sample is on the hard side, the whole sample is ground

in a mortar to a particle size below 200 micrometre. Where the sample is soft and unsuitable for grinding, it is melted and mixed, the melting temperature being kept at not more than 150 °C and the melting time at not more than 10 min; the test portion may then be taken from the melted sample.

7 Procedure

7.1 A 100 mm length of the heating wire of 5.3 is cut off, its middle part, about 20 mm, is coiled and the free ends are connected to the terminals. The coiled part is placed above the sample cup of 5.2 and close to one side, and a bundle of cotton wick or nylon thread of 5.5, long enough to reach into the sample cup, is inserted between the two turns of the coil. 5 mL of the sodium carbonate solution of 4.4 is put into the bomb, which is then turned so that its inner surface is wetted by the solution. The test portion is weighed into the sample cup as laid down in Table 1 and, where needed, a weighed amount of white oil may also be added, to 0.1 mg; where white oil is used, a short quartz rod may be used to stir and mix, and the cotton wick or nylon thread may be left in the sample cup during the combustion. Warning: the total mass of the test portion and of the white oil, or other low-sulfur combustible matter, shall not exceed 0.8 g. Table 1, which carries no caption in the printed text, has three columns, sulfur in per cent, mass of test portion in grams and mass of white oil added in grams, and two rows: for sulfur of 5 or less, 0.6 to 0.8 of test portion and no white oil; for sulfur over 5, 0.3 to 0.4 of test portion and 0.3 to 0.4 of white oil.

After the bomb has been used several times for sulfur determinations, a film can be seen on its inner surface. This passive layer can be removed by polishing the bomb from time to time. A suitable way of doing so is to turn it in a lathe at 300 r/min, polish the inner surface with the emery paper of 5.6, apply a coat of light machine oil to prevent deep cutting, then apply the chromium(III) oxide paste of 5.7 and water. This removes all the passive material except deep defects and gives a highly polished inner surface. Before the bomb is used, the oil and paste left by the polishing operation are washed off with soap and water. A test portion containing more than 20 mg of chlorine can corrode the bomb; to avoid corrosion, for test portions containing more than 2 % of chlorine by mass it is recommended that the mass of the test portion and the mass of white oil added be taken as laid down in Table 2. Table 2, likewise without a caption, has three columns, chloride content in per cent, mass of test portion in grams and mass of white oil added in grams, and four rows: 2 to 5, 0.4 and none; 5 to 10, 0.2 and 0.6; 10 to 20, 0.1 and 0.7; 20 to 50, 0.05 and 0.7. Where the test portion does not mix easily with white oil, some low-sulfur combustible diluent may be used instead, but the total mass of the test portion and of the non-volatile diluent shall likewise not exceed 0.8 g.

7.2 Charging with oxygen. The sample cup is put in place with the end of the pure cotton wick or nylon thread dipping into the test portion, the bomb is assembled and the cap is tightened to make it safe. Warning: charging with oxygen and ignition are forbidden while

the bomb is being shaken, is falling or is tilted. Oxygen is fed slowly into the bomb, so that the oil is not driven out of the cup, until the pressure reaches the value shown in Table 3. Table 3, without a caption, has three columns, bomb capacity in millilitres, minimum standard pressure in megapascals and maximum standard pressure in megapascals, and four rows: 300 to 350, 3.95 and 4.15; 350 to 400, 3.65 and 3.85; 400 to 450, 3.14 and 3.34; 450 to 500, 2.84 and 3.04. A note to the table states that the minimum pressure is there to supply the oxygen needed to ensure complete combustion and the maximum pressure is there for the safety of the apparatus.

7.3 Combustion. The bomb is immersed in the cooling water bath of 5.8 and connected to the terminals of the ignition circuit of 5.4, the circuit is closed and the sample is ignited. Warning: do not go near the combustion vessel until more than 20 s after ignition. After a further soak of at least 10 min in the cooling water bath the bomb is taken out. The pressure is released at a slow and even rate, the operation taking not less than 1 min, then the bomb is opened and its contents examined. Where a trace of unburnt pitch or a black deposit is seen, the determination is stopped and the bomb is cleaned thoroughly before it is used again.

7.4 Collection of the sulfur-bearing solution. A fine water spray is used to wash the inside of the bomb, the oil cup and the inner surface of the bomb cap, and the washings are collected in a 600 mL beaker marked at 75 mL. All deposits in the bomb are cleaned off with a rubber wiper. The bottom of the bomb is washed until a suitable indicator shows the wash liquid to be neutral; the volume of the washings will usually be more than 300 mL. 10 mL of the saturated bromine water of 4.2 is added to the washings in the beaker. The sample cup is placed in a 50 mL beaker and 5 mL of saturated bromine water, 2 mL of the hydrochloric acid solution of 4.1 and enough water to just cover the sample cup are added. The beaker is heated to just below the boiling point for 3 min to 4 min, then the solution is transferred to the beaker holding the washings. The sample cup and the 50 mL beaker are washed thoroughly with water and all deposits in the sample cup are cleaned off with a rubber wiper. The washings and the deposits from the 50 mL beaker and the sample cup are transferred into the washings in the 600 mL beaker. None of the washings is to be filtered, because filtration can cause the loss of the sulfur present in the insoluble matter.

7.5 Determination. The mixed washings are evaporated on a hotplate or other heater down to 200 mL. Heating is adjusted so that the solution is kept just boiling, then 10 mL of the barium chloride solution of 4.3 is added as a fine stream or drop by drop, the solution being stirred while it is added and for a further 2 min after the addition is complete. A grooved watch glass is placed over the beaker and gentle boiling is kept up until the solution has evaporated to a volume close to 75 mL. The beaker is taken off the hotplate or other heater and cooled for 1 h before filtration. The solution is filtered through ashless quantitative filter paper, see note 1. The precipitate is washed with water, at first by decantation and then on the filter, until the wash liquid is free of chloride. The filter paper and the precipitate are transferred to a crucible weighed to 0.1 mg and dried by gentle heating, see note 2, until