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Thermal decomposition of silver oxide

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This method has been used for the control of Ag_2O quality. The content of Ag_2CO_3, H_2O, organic substances and structure imperfections were followed. The observation of Ag_2O thermal decomposition was realized by means of an arrangement using a galvanic concentration cell with a solid electrolyte. The specimen was placed into a furnace and the carrying gas transfered the products of decomposition into an oxygen analyzer.

A method for potentiometric determination of oxygen using a solid ceramic electrolyte sensor with oxygen ionic conductivity was used for the indication and semiquantitative evaluation of products released during the thermal decomposition of silver oxide.

Solid electrolytes are often used for determining the oxygen concentration in gaseous atmospheres. This determination is carried out by means of a galvanic concentration cell. The solid electrolyte is a partition between the environment of known oxygen concentration and that of measured gas. The electromotoric force (E) of this galvanic cell is according to Nernst´s equation proportional to the log natural ratio of both concentrations:

$$E = \frac{R\,T}{4\,F} \ln \frac{p_1}{p_2}$$

R = universal gas constant

F = Faraday´c constant

T = absolute temperature

p_1, p_2 = partial oxygen pressures.

From the change of e.m.f. the oxygen concentration in measured environment can be calculated. Due to a very rapid response of this method, even rapid changes in O_2 content in gases released by thermal decomposition of products, can be indicated.

To investigate the Ag_2O decomposition we used an arrangement where the specimen is located in a decomposition furnace with the carrying gas. This gas transfers the released gases, occurring due to the decomposition, into an oxygen analyzer. The sensor is in the form of a ceramic tube made from zirconia solid state electrolyte with the platinum electrodes applied. It is placed in the furnace tempered to constant temperature.

The analysis is carried out in the following way: The carry-

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ing gas, in our case the nitrogen with the oxygen content below 0.1 vol.%, is transfered into the decomposition furnace where the temperature increases by 100° during 3 minutes. The specimen of 0.3 gr. is placed in a boat in a sintered ceramic tube. The temperature is measured using a thermocouple "chromel-alumel" placed in the specimen.

The carrying gas takes out the products of decomposition into an open-end tube heated up to 700 °C. The flowing speed of carrying gas is 20 l per hour. The change of oxygen content in the carrying gas results in changing the electromotoric force of the cell which is registered on the line-recorder. The initial cell voltage during the passage of pure carrying gas is about 100 mV, the surrounding air being the comparing environment of galvanic cell. As soon as the oxygen content in the carrying gas increases, the cell voltage decreases. If the oxygen during the Ag_2O decomposition is released, the e.m.f. minimum as low as the level of 10 mV takes place. In the case that the specimen consumes the oxygen from the carrying gas, e.g. by burning out the organic substances or when the inert oxygen-free gas is released, diluting the carrying gas, the oxygen content decreases and the cell e.m.f. increases. The use of nitrogen with a low oxygen content increases the method sensitivity, since even a small change in oxygen content develops a great change in the cell e.m.f. After passing through the analyzer the carrying gas is removed into the liquid seal.

The silver oxide theoretically is decomposed at the temperature of 455 °C. The EGA curve of pure oxide has only one minimum. The decomposition is endothermic and due to rather a high absorption of heat during the decomposition process the temperature of a thermocouple located in the specimen is delayed, in comparison with that of the furnace. According to the diagram of specimens with perfectly developed crystals the minimum is rather sharp.

For pure AgO there are two maxima on EGA curve. One being at 200 °C, the other one below 450 °C. The first one results in the decomposition of AgO to Ag_2O. In the second case Ag_2O is decomposed to Ag.

The application of EGA method results in defining the Ag_2O quality as the material for suitable cathodes for silver-zinc cells. Even for pure component its applicability is dependent on the condition of storage and preparation.

Ag_2O is a slightly alkali substance and when stored in the air its absorption of carbon oxide is rather high. The occurance of Ag_2CO_3 can be determined sensitively by EGA method. The effect of wide voltage maximum at about 260 °C appears already during the first day of the exposure in the air. During this period about 1 wt. % of Ag_2CO_3 is produced.

The humidity appears as the maximum with the peak above 100 °C. There often appear two maxima for precipitates which are typical for both Ag_2CO_3 and H_2O. Sometimes it happens that before a complete dehydration of the precipitate, this one is partly carbonized already.

If there is the presence of organic substances in silver oxide, this method records very sensitively the voltage maximum. Its peak is found in the diagram according to the type of organic material, since the oxidation temperature is different. It is usually recorded between 150 and 250 °C.

The behaviour of Ag_2O is rather different in the composition with graphite. In the intimate mixture Ag_2O decomposition is activated and passes in one or two steps, according to the amount of graphite and its preparation. For the graphite content above 2 % the exothermic decomposition takes place at about 300 °C and there is only one minimum on the curves. For a lower content of graphite or at slight blending there also appears a minimum at 450 °C, belonging to the decomposition temperature of pure Ag_2O. This happens always when the amount of heat, developed during the exothermic minimum, is so small that the decomposition temperature of pure Ag_2O is not reached.

The described effects in EGA diagrams are not exceptional and are expected. More interesting are, however, the possibilities offered by EGA for the evaluation of Ag_2O structural perfectness. During the precipitation of Ag_2O some defect oxides with smaller dimensions of an elementary cell can be prepared. This is indicated in X-ray diffractographs by a shifted maximum and by broading the lines for high theta angles. The defected Ag_2O is recorded on EGA curve by shifting the peak of decomposition minima towards lower temperatures and by broading the curve. The defects are explained by the introduction of Ag^{3+} into Ag_2O structure and by the formation of vacancies.

The described method has been proved as satisfactory, since it solves some main deficiencies found in the raw material, i.e. the presence of carbonates and the structural imperfections.