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THERMOGRAVIMETRIC APPARATUS FITTED INTO THE OPTICAL FIBRES PRODUCTION MCVD LINE

J. Wójcik, M. Makara, B. Janoszczyk and K. Poturaj

Laboratory of Optical Fibre Technology, Maria Curie-Sklodowska University, 20031 Lublin, Poland

Abstract

An apparatus for thermogravimetric measurements is presented. This device gives the possibility of investigation reaction as well as other processes taking place in aggressive atmosphere into the atmosphere composed of high purity gases. High flexibility of the apparatus fitted into the MCVD line for optical fibres preparation provides a wide range of measurement possibilities.

Keywords: MCVD line, optical fibres, TG

Introduction

There are known many methods of silica optical fibres manufacturing: MCVD (Modified Chemical Vapour Deposition), PCVD (Plasma Activated Vapour Deposition), OVD (Outside Vapour Deposition), VAD (Vapour Axial Deposition) etc. The main chemical process characterizing these methods – glass synthesis – takes place in closed or almost closed chambers. The great advantage of these methods is the high purity of glass obtained. However the yield of glass synthesis is rather low. The effectiveness of glass production is especially important in the case of optical fibres for telecommunication use.

The glass synthesis by the sol–gel method is more effective (by some orders of magnitude) than by the methods mentioned above. Unfortunately, many processes from the raw materials to the transparent glass run in the contact with atmosphere, therefore the possibility of contamination of intermediate product and final glass by e.g. atmospheric dust is very probable.

A typical process of glass preparation by the colloidal sol–gel method is composed of the following stages: synthesis of raw materials, formation of porous preform, purification and consolidation. The purification process (usually by chlorination) is carried out first of all in order to dehydroxylate the preform but the transition elements are also removed at same time from the preform [1, 2].

The transition elements can be introduced into the glass practically in each stage of the synthesis. They can be present either on the surface of silica parti-

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cles or inside them as the inclusion in these particles or as the homogeneous impurities. The form of these impurities depends on the form and time of their introduction to the raw materials and to the silica gel. It is very important to know the form of impurities because the methods of purification must be chosen in accordance with this form. The main questions concerning the purification of the preform obtained by the sol–gel method are: i) whether it is possible purify the glass to the level of 0.1 ppb of transition elements, and ii) if it is not possible, which stages of glass production must be carried out in the closed vessels protecting the reactants from the outside impurities. The researches on the preparation of the silica glass rods and tubes for optical fibres technology by sol–gel method are carried out in our Laboratory. One of main problems concerning this technology is the purity of silica glass. Therefore, we have made the attempts to investigate the process of transition elements removed of from silica glass by chlorinating porous preforms. The investigations were focused on the iron and copper contamination of silica glass, because these elements occur at the highest concentration in atmospheric dust [3, 4].

In this paper the thermogravimetric apparatus, which provides the possibility for studying the chlorination process at high temperature, is described. The apparatus works as a part of MCVD optical fibres preform lathe. Also, the results of the tests of the apparatus are given.

Experimental

As it was mentioned above the chlorination process of SiO_2 obtained the by sol–gel methods is usually carried out at high temperature and with very reactive compounds containing chlorine atoms. Thus a problem of choosing materials resistant to high temperature and corrosion appeared. The silica glass was chosen as a material for these parts of the apparatus which works at high temperature. The other parts were made of PTFE. The ceramic materials and stainless steel were used for constructing the outer owen.

Also the spiral balance and pan containing the sample under investigation were made of silica glass. It was assumed that the thermobalance pan would have a mass of 1.5 g and the maximal mass of the sample could equal to 1 g. Thus, the greatest value of the spiral loading can be 2.5 G. These conditions as well as the quartz glass tube dimension in which the spiral was to be placed led us to calculate the optimal parameters of the spiral: length –4.5 cm and a diameter 2.5 cm. Such a spiral should be elongated up to 12.5 cm under the loading of 2.5 G, therefore it should consist of 15 coils. A diameter of the quartz fibre used was 329 μm.

The spiral with a pan was placed in the tube of silica glass. The tube was divided into two parts by the taper pipe which limits the convection of gases and

heat transfer from the bottom to the upper zone of the tube. The bottom part of the tube can be heated up to 1000°C by the resistance furnace. As it is seen in Fig. 1, in the heated zone a pan with the investigated sample is placed and a spiral is situated relatively far from the source of heat, in order to avoid the influence of temperature on its elongation. In our apparatus the space containing the spiral was not thermostated as it was recommended by Mrowec [5, 6], because the flow of gases through the tube thermostated the spiral sufficiently.

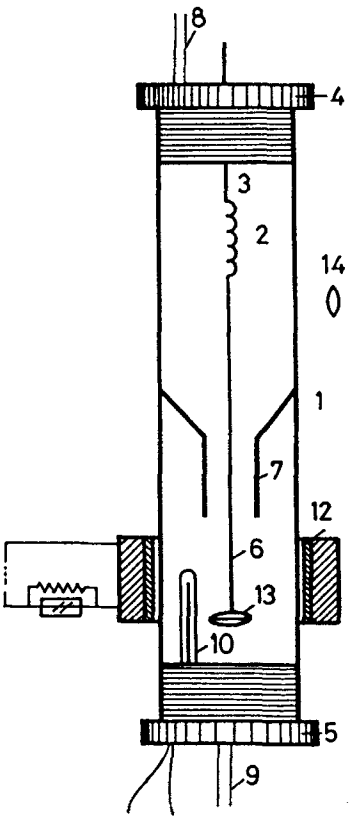

Fig. 1 Scheme of the thermogravimetric apparatus. 1-silica glass tube, 2- silica glass spiral balance, 3- silica glass hanger, 4,5- teflon plugs, 6- silica glass pull rod, 7- taper pipe, 8- gases inlet, 9- gases output, 10- thermocouple, 11- thermoregulator, 12- pipe resistance furnace, 13- pan for a sample, 14- cathetometer lens

The upper part of tube is closed with a teflon plug (4, Fig. 1) with two holes. A rod made of silica glass being a hanger for the spiral passes through the hole in the plug axis and the gases are brought inside the tube through another hole (8). The silica glass rod can be moved in the plug and can regulate the position

of the spiral and pan (13). The pan is connected with the spiral with a thin silica glass rod which goes through the taper pipe (7). The bottom of the tube is also closed with a PTFE plug (5) which has a hole to carry away the reactive gases (9) and another one with a silica glass capillary including thermocouple (10) to measure temperature in the reaction zone near the pan (13).

The tube and furnace are mounted on a stand excluding vibrations of the system. The stand construction enables easy displacement of the furnace along the tube. This makes it possible to obtain a stable position of the sample in the high temperature zone.

The changes of the spiral elongation are recorded by means of a cathetometer. As a point of reference a platinic wire, 40 μm in diameter is used, stretched at the bottom end of the spiral. The change of the wire position by 0.01 mm can be observed, which corresponds to the change of sample mass equal to 1.2×10^{-4} g.

The thermogravimetric balance described above was joined to the MCVD system existing in the Laboratory of Optical Fibres Technology. This apparatus contains the chlorination dosage and gas flow regulations systems, indispensable for the chlorination process investigation. The block of whole system is presented in Fig. 2.

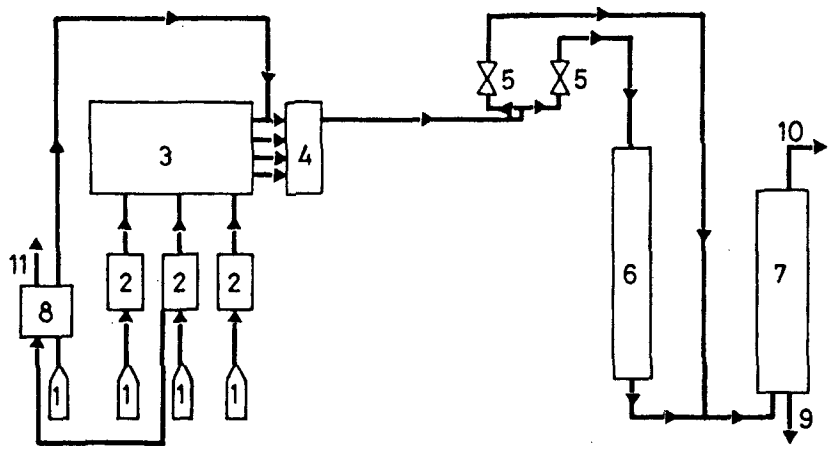

Fig. 2 Block scheme of the TG apparatus – MCVD line systems. 1- cylinders with gases, 2- gas purifiers, 3- mass flow controllers, 4- saturators, 5- rotameters, 6- thermogravimetric apparatus, 7- neutralization column, 8- system of chlorine flow regulation, 9- output to sewer pipe, 10- output to atmosphere, 11- output of washing, neutral gas to neutralizator (7)

Gases are carried from the cylinders (1) through purifiers (2) to the system regulating oxygen, argon and helium flow. A block of thermostated saturators (4) filled with $SOCl_2$ and CCl_4 is fitted to the output system through electromagnetic three-way valves. The system enables passage of helium, argon or oxygen

through a given saturator with a definite rate and at desired temperature. In this way, the flow rate of O_2, He and Ar mixture as well as the concentration of chlorinating agent can be precisely determined. In the case of chlorine application dosage of this chlorinating agent is made using a separate flow system (8). Then a system of gas flow regulators (3) ensure a dosage of oxygen and helium and (4) is not used.

A gas mixture before entering the thermogravimetric apparatus passes through a system of two rotameters (5) with needle valves. It allows for rapid changes of mixture flow rate through the thermogravimetric apparatus (6) without the change of its composition. A part of gas stream gets into the reaction zone and then into the neutralization system (7), while the remaining part of gas stream by-passes the thermogravimetric apparatus (6) and goes directly into the neutralization system.

The described set of apparatus enables maintaining the optipurity level of inert gases, oxygen and chlorinating agents. The water content in gases is continuously monitored by a hygrometer and is usually equal to 10 ppm.

Some measurements in order to test the apparatus presented in Fig. 2 were carried out. At first, the mechanical stability of the whole thermogravimetric apparatus at room temperature was checked up. Then the apparatus was tested under the process conditions corresponding to those of the chlorination process at high temperature. Essential measurements were carried out with the Fe_2O_3 sample on the thermobalance pan without the flow of chlorine to determine the

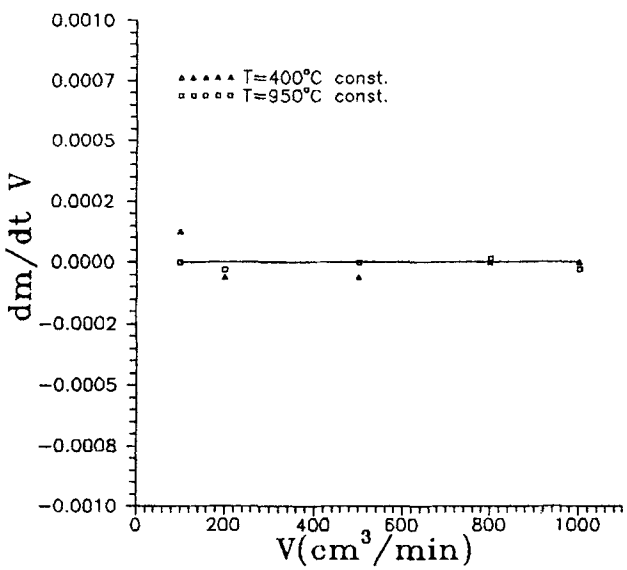

Fig. 3 The results of testing the apparatus with the SiO_2 sample. Atmosphere without the chlorinating agent, composed of, 20% O_2, 80% He. $dm/dt \times V$ means the change of the sample mass caused by 1 cm^3 of atmosphere flowing through the apparatus

apparatus stability at high temperature and with the flow of chlorine to determine the apparatus indications under the reaction course conditions.

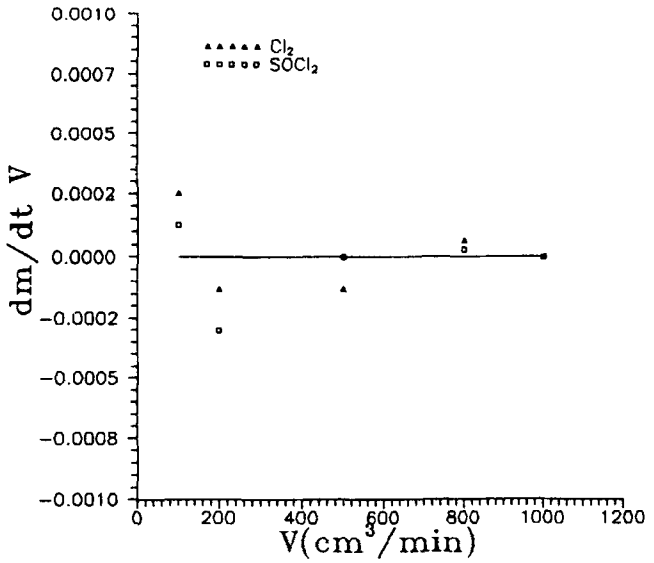

Fig. 4 The results of testing the apparatus with the SiO_2 sample. Atmosphere composed of 10% chlorinating agent (Cl_2 or $SOCl_2$), 10% O_2, 80% He

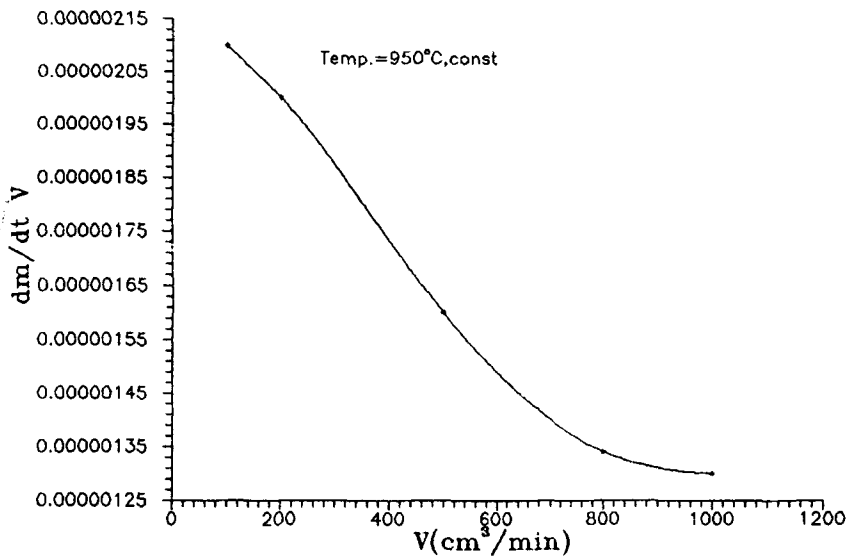

Fig. 5 The exemplary results of the Fe_2O_3 chlorination by chlorine. Atmosphere composition: 10% Cl_2, 10% O_2, 80% He

The influence of the gases flow rate on the apparatus behaviour was studied carrying out the experiments with a piece of fused silica placed on the thermobalance pan. The results of the test with the atmosphere composed of O_2 and He only are presented in Fig. 3, while in Fig. 4 the results of the experiment with chlorinating agents are shown. The conditions of the tests were as follows: composition of gas mixture: 80% He, 10% O_2, 10% of chlorinating agent; gas flow 0.5 $l \cdot min^{-1}$; temperature 950°C. The mass of Fe_2O_3 or fused silica sample did not exceed 1 g.

Results and discussion

The tests carried out showed that the described apparatus operated stable in the desired reaction conditions and its limit of detection was $\pm 1.3 \times 10^{-4}$ g. The whole set – the MCVD optical fibre preparation machine and the thermogravimetric apparatus – fitted to it – provide great possibilities of measurements. Such a system enables precise determination of gaseous atmosphere composition which can include a very aggressive chlorinating agent as well as maintenance of constant flow-rate and its smooth regulation without the change of atmosphere composition. It also provides high purity of gaseous reagents.

Conventionally, the thermogravimetric apparatus is used to study the kinetics of processes. Figure 5 presents the exemplary results of measuring a chlorinating rate of ferrum oxide with chlorine at 950°C as a function of gas mixture flow rate. It seems, that the obtained $dm/dt \times V$ *vs.* V relationships gives also, by the extrapolation to $V=0$, the possibility of determining the equilibrium constant of the investigated reaction.

Systematic studies of chlorination processes of transition metals are in progress and will be the subject of another article.

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References

1 R. Clasen, Glastech. Ber., 60, 4, (1987) 125.
2 J. B. Mac Chesney et al., Mat. Res. Bull., 22 (1987) 1209.
3 S. Morozow, Primienienije Chlora w Metalurgi Riedkich i Cwietnych Metalow, Nauka, Moskva 1968.
4 B. Jezowska-Trzebiatowska, S. Kopacz and T. Mikulski, The Rare Elements: Occurrence and Technology, Warsaw: Polish Scentific Publ., Elsevier, Amsterdam 1990.
5 S. Mrowec, Teria Dyfuzji w Stanie Stalym, Warszawa PWN, 1989.
6 S. Mrowec and A. Stoklosa, J. Thermal Anal., 2 (1970) 75.

Zusammenfassung — Es wird ein Gerät für thermogravimetrische Messungen vorgestellt. Dieser Apparat ermöglicht die Untersuchung von Reaktionen als auch anderen Prozessen, die in aggressiver Atmosphäre bis hin zu Atmosphären aus hochreinen Gasen ablaufen. Eine große Flexibilität der Apparatur, die bei der MCVD-Methode der Herstellung von Optoleiterfasern zum Einsatz kam, bietet einen weiten Bereich von Meßmöglichkeiten.