Thermochimica Acta, 134 (1988) 395–400
Elsevier Science Publishers B.V., Amsterdam

WEIGHING IN FREE SUSPENSION AND ITS APPLICATION IN THERMOGRAVIMETRY AND IN THE DETERMINATION OF SURFACE AREAS AND THE DENSITY OF POROUS SOLIDS

TH. GAST[1], E. HOINKIS[2], U. MÜLLER[3], E. ROBENS[3]

1 Institut für Meß- und Regelungstechnik der Technischen Universität, Budapester Straße 46-50, 1000 Berlin 30, Federal Republic of Germany
2 Hahn-Meitner-Institut, Postfach 390128, Glienicker Straße 100, D-1000 Berlin 39, Federal Republic of Germany
3 Institut für Anorganische und Analytische Chemie der Johannes-Gutenberg-Universität, Postfach 3980, D-6500 Mainz, Federal Republic of Germany

ABSTRACT

The magnetic suspension balance is described and new developments are presented. The advantage of gravimetry in the determination of surface area is discussed in comparison with the volumetric method. As an example of the application of gravimetric measurements the oxidation kinetics of a POCO-graphite in CO_2 at 1000 °C and the determination of the specific surface area before and after oxidation are described.

THE ELECTROMAGNETIC SUSPENSION BALANCE

The suspension balance (Fig. 1) consists of a conventional balance with the sample suspended by magnetic force at a distance of about one centimeter below an electromagnet. There are several ways of establishing and controlling suspension. Most practical application obtained the controlled ferromagnetic attraction: An upper bar magnet suspended from the beam of an electromagnetic balance carries a lower magnet with a pan. A nonmagnetic, preferably dielectric, wall between the attracting poles separates the reaction chamber from the balance. The distance of the magnets is measured by an inductive sensor while a superimposed control loop keeps the controlling power at a minimum. Hermetically sheltered from the atmosphere and the measuring system, the sample can be

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50 © 1988 Elsevier Science Publishers B.V.

treated with corrosive gases under variable temperature and pressure.

In the development of electromagnetic balance, progress in sensor technology and permanent magnetic materials, electrical components, and circuitry have extended the range of electromagnetic compensation from a small fraction of the measurement range to full capacity. The balance beam could be replaced by a system of parallel levers, which guide the balance pan in a vertical path of deflection. In prototypes any mechanical guidance could be omitted and replaced by artificially stabilized magnetic attraction or repulsion which can also be combined. With magnets of rare earth-cobalt and neodynium iron boron [1] the maximum energy product has been increased to the tenfold compared with ALNICO. Due to the small diameter of the magnets, an enclosure for the lower magnet can be made which withstands pressures up to 5 kbar without distance control from the outside being obstructed.

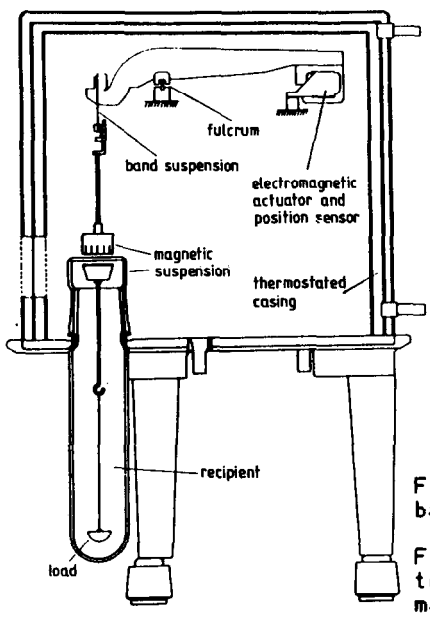


Fig. 1. Suspension system according to Gast based on controlled ferromagnetic attraction with supporting electromagnetic balance. Manufacturer Sartorius-Werke GmbH, D-34 Göttingen.

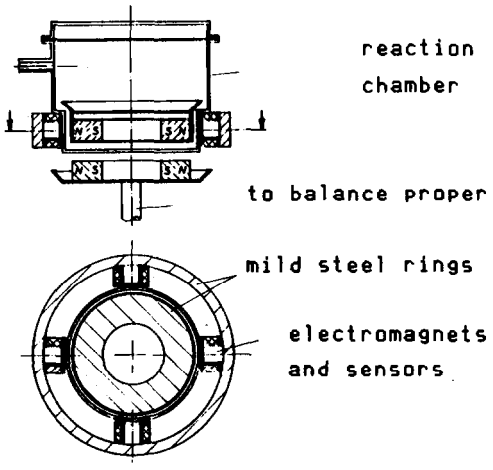
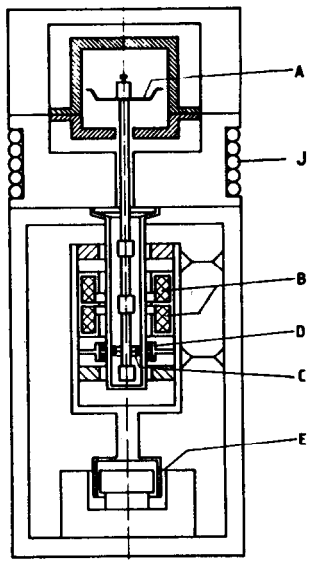


Fig. 2. Schematic drawing of a top pan balance with free magnetic suspension

The precision of the distance measurement could be considerably improved by the application of a phase locked loop. With the aid of an improved eddy current sensor, a frequency signal is obtained, which allows weighing without external balance with an uncertainty of 1×10^{-5} [2]. Using a Hall probe as a distance sensor, restrictions of the type of the wall between the suspen-

sion magnets (poor conducting material) can be avoided. Vertical motion of the magnet induces a velocity signal in the control coil. It can be extracted for position control. Further improvement allows the coupling device to be used in addition to transmit data for other parameters, like the sample temperature [3].

These principles have been applied to balances with the sample below the measuring system as well as for top loaders (Fig. 2). A high pressure balance with very short balance beam, shown in Fig. 3, is in the process of development [4].



Figs. 3. principle drawing of a high pressure suspension balance according to Gast. A pan, B control coils, C metal ring, D sensor coils, E actuator coils, J thermostat

SURFACE AREA AND POROSITY DETERMINATION

Porous solids are usually characterized by the specific surface area and the pore size distribution which is determined from the adsorption isotherm of a gas, in particular of nitrogen at 77 K. From the isotherm the monolayer capacity is determined and using a known value of the cross-sectional area of the adsorbed molecule the specific surface area is calculated e.g. by application of the equation of Brunauer, Emmett and Teller (BET) [5]. Furthermore, using the Kelvin equation the distribution of pore volume with respect to pore size can be estimated. The sorption methods may be divided into two groups: with the volumetric methods the amount of gas removed from the gas phase is measured whereas with the gravimetric methods the increase in mass due to the uptake of the gas by the specimen is measured directly. We disregard in this context the gas-chromatographic method and others which, as secondary methods, require calibration.

The volumetric method is much simpler in instrumentation as well as in handling. The gas is introduced by a gas burette or a dosage pump. Continuously or step by step the pressure is increased and the gas consumed by adsorption on the sample is recorded. Therefore, a variety of commercial instruments are offered.

Instead of the dosage pump an expensive electronic microbalance and a pressure controller are needed for the gravimetric method (Fig. 4). The handling of the balance requires some skills. Both methods are comparable in sensitivity and accuracy. So, what are the advantages of the suspension balance?

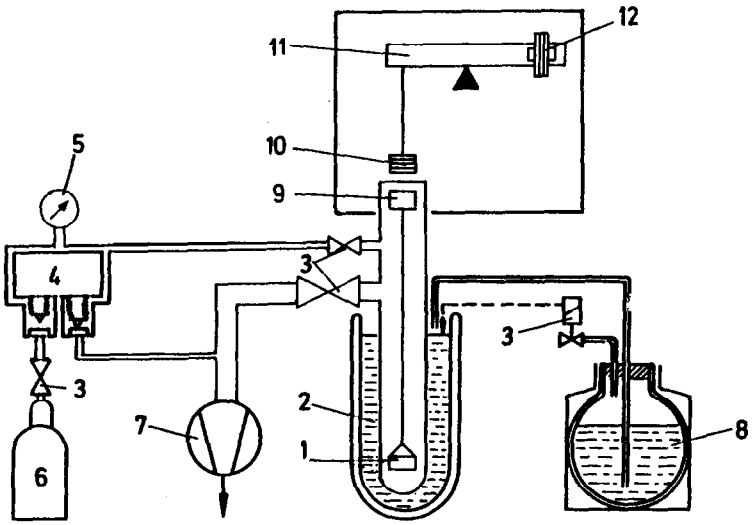


Fig. 4. Gravimetric apparatus for surface area and pore size measurements. 1 sample pan, 2 liquid nitrogen thermostat, 3 solenoid valves, 4 pressure controller, 5 manometer, 6 nitrogen cylinder, 7 vacuum aggregate (turbo molecular pump and rotary vane pump), 8 liquid nitrogen level controller, 9 suspension magnet, 10 electromagnet, 11 balance beam, 12 compensating electromagnetic measuring system.

Besides the direct measurement of the adsorbed mass, the most important advantage of gravimetry is the fact that it is possible to observe directly the modification of the sample during degassing and chemical reactions. Before starting adsorption measurements the surface area and the pore system of the sample must be thoroughly cleaned of adsorbed gases by heating in vacuum. A strong mass loss not joining a constant terminal value is a warning hint of sample damage. To avoid trial-and-error experiments, the IUPAC [6] recommends the control of sample preparation by using a thermobalance for volumetric measurements as well. Other advantages of the gravimetric method are that the density can be determined by buoyancy measurements and thermo-chemical reactions of the sample with the gas phase investigated by means of sequential thermogravimetric. With a suspension balance the gas phase can also be corrosive.

INVESTIGATION OF THE CORROSION OF A POCO GRAPHITE

In earlier investigations [7,8] of corrosion-induced changes in the surface area and porosity of graphitic matrix material we used an apparatus comprising a symmetric electronic balance, a turbo molecular pump and a diaphragm gauge. After degassing at about 1000 °C we determined the density by buoyancy measurement in nitrogen at room temperature and subsequently the nitrogen isotherm at 77 K to calculate the specific surface area and the pore radius distribution. Then the sample was oxidized at 900 °C in CO_2 to a mass loss of up to five percent and the measurements were repeated. Graphitic matrix materials consist of graphite grains and an ungraphitized polymeric carbon used as a binder. The latter contains many mesopores which are closed in the unmodified material but oxidation leads to the opening of these pores and a remarkable increase in the specific surface area.

In contrast POCO-graphites are highly graphitized materials which do not contain any binder carbon. POCO-graphites are used as a first wall protection in thermo-nuclear fusion reactors and corrosion induced changes in the surface area may alter the recycling of gases. A study of the dependence of surface area on burn-off was initiated.

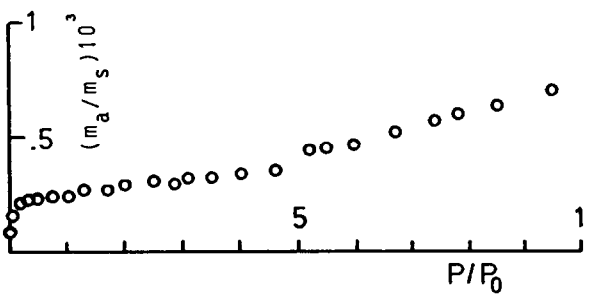


Fig. 5. Krypton adsorption isotherm at 90 K on POCO-graphite.

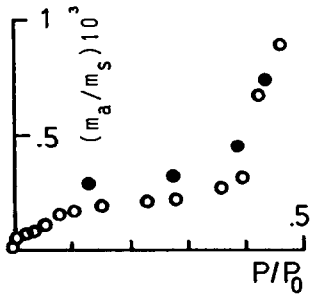


Fig. 6. Benzene adsorption isotherm at 298 K.

We now use a Sartorius suspension balance with a load capacity of 30 g and a sensitivity of 1 digit per 10 µg. We measured sorption isotherms with nitrogen at 77 K (Fig. 7), krypton at 90 K (Fig. 5) and benzene at 298 K (Fig. 6). The results of the density measurements by buoyancy are in good agreement with those of other methods. The krypton isotherm shows two steps. The nitrogen isotherm is of type H3 in the IUPAC classification with a hysteresis

extending to very low pressures. This indicates a pore system comprising mesopores and probably micropores. The specific surface area is therefore burdened with an error. As a result of a 1 percent corrosion in CO_2 at about 1000 °C the surface area increased about threefold. These investigations are to be continued.

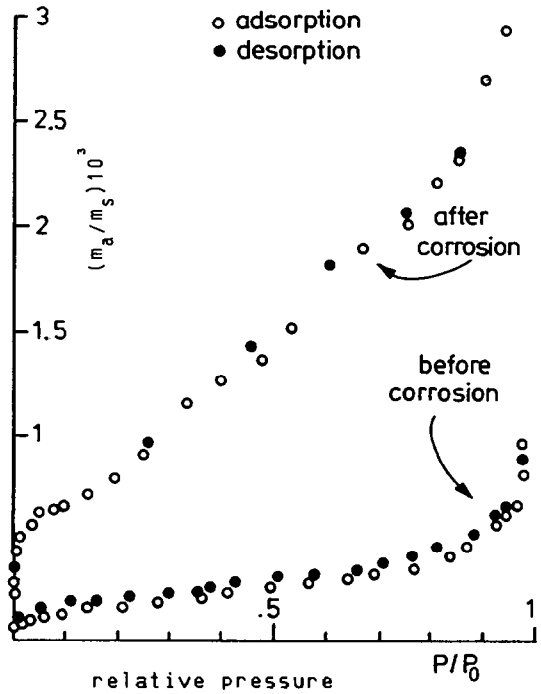


Fig. 7. Nitrogen adsorption isotherms at 77 K on POCO-graphite.

REFERENCES

1 W. Baran: Overview of applications of permanent magnets. In: K.J. Strnat (Ed.): Proceedings of the 8th International Workshop on Rare-Earth Magnets, Dayton, Ohio, USA, May 1985, p. 1-14.

2 Th. Gast, G. Luce: A directly weighing suspension balance with frequency variant output. In: H. Wieringa (ed.): Mechanical Problems in Measuring Force and Mass, M. Nijhoff, Dordrecht 1986

3 Th. Gast, H. Jakobs, G. Luce: Transmission of DTA-values from a magnetically suspended sample. Thermochimica Acta 82 (1984) 1-14

4 Anatech B.V., Pissummerweg 1, NL-6114 AH Susteren, Netherlands.

5 R.Sh. Mikhail, E. Robens: Microstructure and Thermal Analysis of Solid Surfaces. Wiley, Chichester 1983.

6 K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquérol, T. Siemieniewska: Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity." Pure & App. Chem. 57 (1985) 4, 603-619.

7 E. Hoinkis, W.P. Eatherly; P. Krautwasser, E. Robens: Corrosion- and irradiation-induced changes of a nuclear graphitic material, J. Nuclear Materials 141-143 (1986) 87-95.

8 E. Hoinkis: The volume of small micropores in unmodified, oxidized or irradiated graphitic matrix. In: K.K. Unger, J. Rouquérol, K.S.W. Sing, H. Kral (Eds.): Characterization of Porous Solids, Elsevier Amsterdam 1988.