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SUSPENSION BALANCE APPARATUS FOR THE INVESTIGATION OF THE OXIDATION OF REFRACTORY AND PLATINUM METALS AT HIGH TEMPERATURES AND LOW PRESSURES

HERMANN JEHN
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften
D-7000 Stuttgart, Germany (Fed. Rep.)

ABSTRACT. A magnetic suspension balance apparatus for oxidation studies at high temperatures and low pressures is described. The balance is mounted on a high-vacuum device with induction heating of the samples. Specific experimental problems of the investigation of gas-metal reactions at higher temperatures are discussed. Results are presented for the oxidation of Ir, Re, Mo, and W in oxygen, air, and water vapor at 1200–2300 °C and 10^{-4} to 1 mbar. These metals react with oxygen at high temperatures forming volatile oxides, the evaporation of which considerably increases the metal loss in oxygen-containing atmospheres, when compared with high vacuum annealing conditions.

GRAVIMETRIC STUDY OF GAS-METAL REACTIONS

Weight change measurement is one of the most frequently used methods to study the oxidation of metals and alloys, but also other gas-metal reactions like equilibria and absorption and degassing reactions can well be investigated gravimetrically. In fact, the microbalance technique offers an almost ideal tool for short and long period studies in static and flowing atmospheres and enables a large pressure and temperature range, to be covered, especially at lower temperatures. Usually the samples are mounted to a balance within a reaction chamber made of glass or ceramic and heated in a furnace. The gas reacts only with the sample positioned in the hot zone, because of the inactivity of the chamber material. At higher temperatures, however, this indirect heating technique cannot be used any longer for lack of proper furnaces or of non-reacting construction materials. Therefore, gravimetric measurements have to be done in high vacuum or in an inert atmosphere and thus are limited to relatively few processes.

In the case of gas-metal reactions only the sample itself must be heated since the gases react also with any metallic heating element or shielding construction material. This is especially true for oxygen-containing atmospheres, where the oxidation leads to the formation of solid, liquid, or volatile oxides. Detrimental effects also can arise due to the solution of gases in the metal and the embrittlement caused by this. Thus, the only applicable heating technique is induction heating by a high-frequency electromagnetic field. Only the sample itself is heated and the temperature can be increased up to the melting point of the metal. The induction coil and the reaction chamber are water-cooled and thus non-reacting. These conditions of hot specimen and cold walls have to be taken into consideration when the reactions are discussed. At lower pressures the gas atmosphere has the temperature of the wall and evaporating

species (metal atoms or oxide molecules) are condensed on the cold parts. On the oth hand, these conditions are realistic with respect to practical application of high- temperature metals and alloys where often hot parts are working in cooled devices.

Combining induction heating and microbalance technique, no continuous measurement of the weight change with high accuracy is possible because of the comparatively lar electromagnetic forces acting on the sample [1]. The weight change can only be measure stepwise when the induction heating is switched off and the sample cools down. This disadvantage reduces the general applicability of the induction-heating microbalance technique. Only such processes can be studied in which the interruption of heating a the cooling of the sample don't affect the reaction, e.g. oxidation processes formin oxide scales which transform or crack off during cooling cannot be studied, while so solution reactions and equilibria in metal-gas systems or degassing reactions in the absence of a compound scale can be examined satisfactorily.

In principle, all types of balances with sufficient accuracy are appropriate for t investigation of the reactions of metals with gases. The balance is normally mounted entirely within the reaction chamber. This is especially true for the ultrasensitive microbalances ($< 1/\mu g$). That construction limits their use to atmospheres which don corrode the balance construction materials (e.g. N_2, O_2, H_2, CO, ...). In the case o highly aggressive atmospheres (e.g. NH_3, H_2S, Cl_2, acid vapors, ...) the magnetic su pension balance offers a unique possibility for weight change measurements since no mechanical connection exists between sample and balance, and the weighing system and reaction chamber are completely separated.

SUSPENSION BALANCE APPARATUS

For the measurement of weight changes during the reaction of metals with gases tw devices with suspension balances have been construced.

Fig. 1 shows the commercial SARTORIUS magnetic balance, of which two types have been used having an accuracy of 0.1 mg (type 4200) and $10/\mu g$ (type 4201). The weighi range reaches up to 10 g and the weight of the sample can reach up to 30 g. This hig sample weight in relation to the accurcy enables weight change measurements in the o der of 5×10^{-4} and 5×10^{-5} %, respectively. The temperature of the weighing system can be stabilized by means of a circulation thermostat, if necessary. The sample is connected to the beam by an electronically stabilized magnetic field between two magnets in a distance of about 5 mm, one below and one above a window of the receive i.e. inside and outside the reaction chamber. The balances have a special lock position where the beam is fixed without interruption of suspension, in which they have been hold during the heating periods.

The vacuum microbalance system (schematically shown in Fig. 2) consists of a receiver made from Duran glass and provided with an effective pumping system, ionization gauge, needle valve for gas inlet, windows for the balance connection and the temperature measurement by an optical micropyrometer, and a conical water-cooled

feedthrough for the high-frequency current. A photograph of this system is shown in Fig. 3. In a second system, the receiver is made of metal which is shown in Fig. 4. The vacuum chambers have to be water-cooled because of the high annealing temperatures. For the experiments performed in the present studies, a usual high-vacuum device (background pressure 10^{-6} mbar) was sufficient. The same construction scheme can, of course, used also for ultra high vacuum technique.

TYPICAL MEASUREMENTS

In the present investigations the systems have been used to study the oxidation of refractory and platinum metals in low-pressure oxygen and oxygen-containing atmospheres. In the high-temperature reaction of oxygen with these metals volatile oxides are formed, the evaporation of which considerably increases the metal loss, when compared with high-vacuum conditions. From the pressure and temperature dependent weight loss the recession rates can be calculated, which give a direct information on the life time of heating or construction element under certain environmental conditions, or on the other hand the limits of the conditions to reach a certain life time at a given temperature.

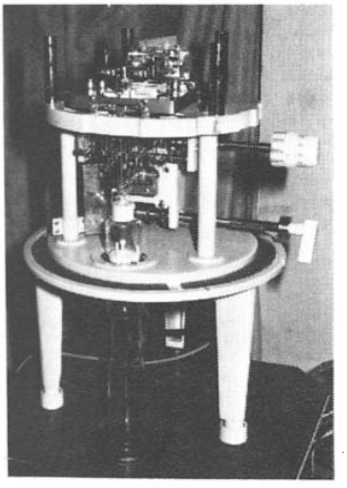

Fig.1. Magnetic suspension balance (SARTORIUS 4201)

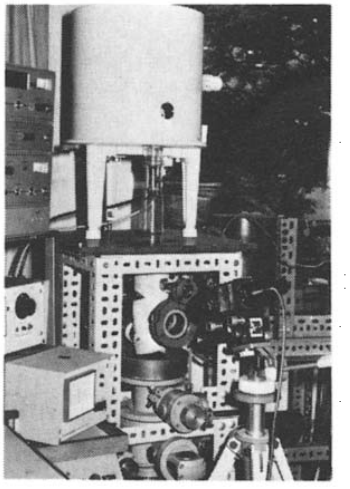

Fig.3. Balance and vacuum system (glass receiver)

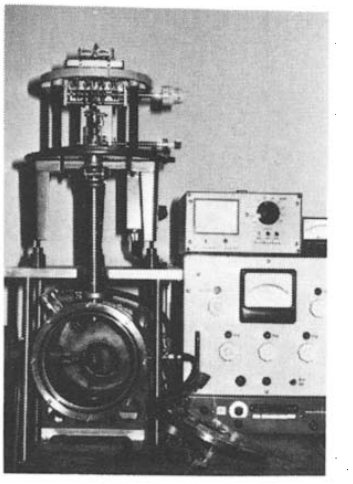

Fig.4. Balance and vacuum system (metal receiver)

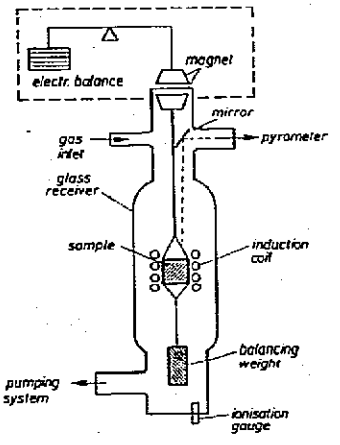

Fig.2. Microbalance apparatus (schematically)

Fig. 5. shows, as an example, the weight change of Ir specimens as a function of the annealing time. The linear weight loss increases with increasing pressure and temperature. From these

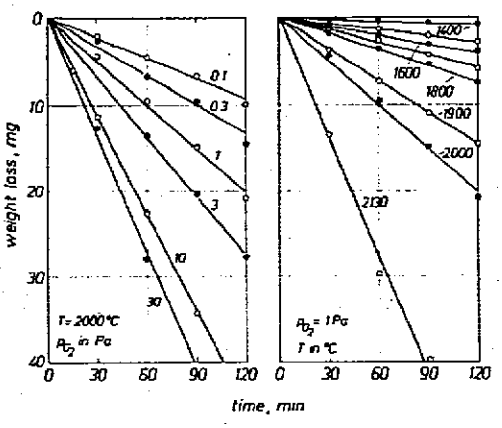

Fig.5. Weight change of Ir in oxygen (sample 10 mm diam, 1 mm thick)

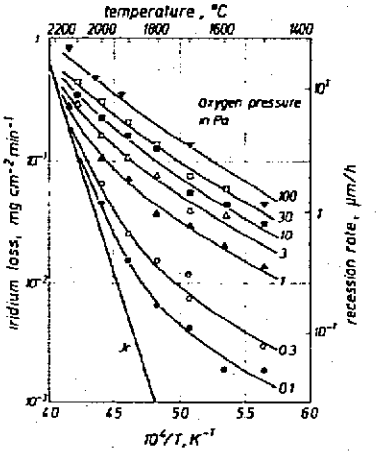

Fig.6. Ir-losses in oxygen

curves the volatilization rates (mg.cm^{-2}.min^{-1}) and recession rates (µm.h^{-1}), respe tively, have been calculated (Fig. 6). Each line in Fig. 5 is represented by one point in Fig. 6. Analogous measurements have been performed for the refractory meta Re [3], W [4], and Mo [5] in oxygen, air, and water vapor. As an example, Fig. 7 shows th recession rate of Re in water vapor. Fig. 8 gives a comparison of Ir, Mo, W, and Re high vacuum and in an oxygen atmosphere of 1.3×10^{-4} mbar. In all metal-gas systems t oxidation at high temperatures and low pressures leads to strongly enlarged metal losses by the additional oxide evaporation, which reach up to some orders of magnit especially in the lower temperature range. In the upper temperature range, the increase of the metal loss by oxide evaporation is less pronouced because the loss by pure metal evaporation reaches also higher values. The specific shape of the curves such as a continuous increase or the occurance of a maximum, depends on the differe evaporation characteristics of the volatile oxides. A discussion of further details is given elsewhere [2-5].

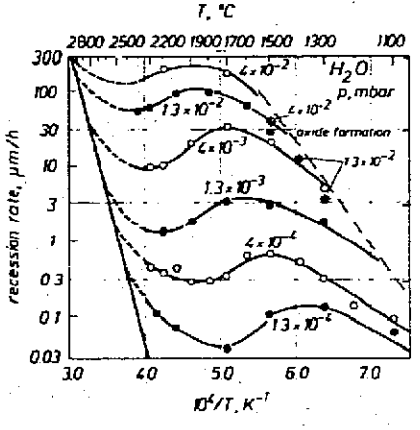

Fig.7. Re-losses in H_2O-vapor

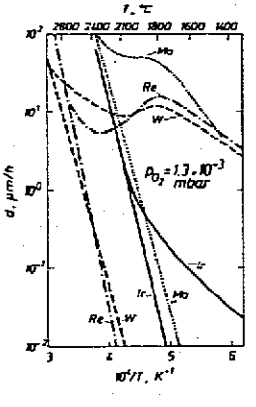

Fig.8. Metal losses in O_2

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