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THERMOGRAVIMETRY SYSTEM DESIGNED FOR USE IN DISPERSION STRENGTHENING STUDIES*

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ABSTRACT

A thermogravimetry system, designed to study the reduction of oxides in metal and alloy powders to be used in dispersion strengthened materials, is described. The apparatus was devised for use at high temperatures with controlled atmospheres. Experimental weight change and moisture evolution results for the thermal decomposition of calcium oxalate monohydrate in dry helium, and experimental weight change results for the reduction of nickel oxide in dry hydrogen and hydrogen containing 15,000 p.p.m. water vapor are presented. The system is currently being successfully applied to the evaluation of the reduction characteristics and the removal of impurities from metals and alloys to be used for dispersion strengthening.

SUMMARY

A thermogravimetry system was designed and constructed to permit the study of the reduction of surface oxides on metal and alloy powders to be used in the fabrication of dispersion strengthened materials. The apparatus was specifically devised for use at high temperatures (up to 1000°C) with controlled atmospheres. Components described in detail include: balance; furnace; temperature control, measurement, and programming equipment; vacuum system; gas flow and control system; and moisture detection and control. The system was evaluated in terms of stability, reproducibility, and accuracy. In order to check out the system for use with inert atmospheres, the thermal decomposition of calcium oxalate monohydrate was studied in dry helium at heating rates of 2.5, 5, and 10°C per min. The results obtained were consistent with those reported in the literature. Operation under a reducing atmosphere was evaluated by studying the hydrogen reduction of nickel oxide. This was carried out at a heating rate of 5°C per min in both dry and wet (15,000 p.p.m. water vapor) hydrogen. The system is currently being used to study the reduction of a variety of impurity metal oxides from powders which have potential for use in the production of dispersion strengthened materials.

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INTRODUCTION

The effectiveness of dispersion strengthened products depends on the distribution of fine stable oxide particles in a metal or alloy matrix. It has been shown in a previous study[1] that the stability of these products and the maintenance of long time high temperature strength depends on the cleanliness of the matrix. The presence of matrix oxides tends to aggravate the agglomeration of the added stable oxide which in turn decreases the strength of the material. Thus, the removal of matrix oxides is a critical feature in the processing of dispersion strengthened products.

Thermogravimetry (TG) has been used for many years to determine the behavior of different materials at various temperatures in different environments. TG involves the continuous weighing of a sample while it is being heated in a selected atmosphere or environment at a constant, preferably linear, heating rate. The weight change *vs.* temperature curve can be obtained automatically. Such curves can give information about the thermal stability of the original sample and any intermediate compounds that may form. And they can also reveal the temperature at which compounds are decomposed or reduced. The environment surrounding the sample may be self generated or controlled and includes inert gases, reactive gases, air or vacuum. The TG system is adaptable to study the optimum conditions for cleaning and removing impurity oxides from metal powders used for dispersion strengthening or other studies. The apparatus of concern in this paper is not only suitable for studies of oxide reduction, but also for measurement of carburization, decarburization and reactions of materials with corrosive atmospheres such as the hydrogen halides.

One objective of this report was to describe the features of a TG system which was designed and assembled for use in studying the cleaning of metal and alloy powders to be used in the fabrication of dispersion strengthened materials. Another objective was to check the performance of the apparatus by studying the thermal decomposition of calcium oxalate monohydrate in dry helium and the reduction of nickel oxide in both dry and wet hydrogen.

A sample of calcium oxalate monohydrate was heated in dry helium at linear heating rates of 2.5, 5, and 10°C per minute. Weight change and moisture evolutions were simultaneously observed and recorded. In addition weight changes in nickel oxide heated in dry hydrogen and hydrogen containing 15,000 p.p.m. water vapor, at a linear heating rate of 5°C per min were also determined. Blank crucible calibration curves were run for buoyancy compensation in dry helium and dry hydrogen at linear heating rates of 2.5, 5, and 10°C per min.

APPARATUS AND PROCEDURE

Apparatus. — The primary components of the TG apparatus are the microbalance and the reaction tube assembly shown schematically in Fig. 1.

The microbalance is enclosed in a belljar which is sealed to the aluminum balance base with an elastomer "O" ring. The entire assembly rests on a cementfilled laboratory table. An opening in the balance base leads to the sample which is located in a quartz crucible. The crucible is suspended from the balance with a segmented quartz fiber. The sample crucible is contained in a quartz reaction tube which is heated externally by a resistance furnace. The quartz tube is attached to the balance base with a flanged stainless-steel tube or "spool piece". The spool piece also serves as a heat sink which helps to prevent overheating of the balance mechanism during operation at elevated temperatures. The balance is additionally protected from heat by use of a radiation shield located in the top portion of the spool piece. Two other openings in the balance base lead to a vacuum system and a purge gas system. A more detailed description of the apparatus and operational procedures is given in the Appendix.

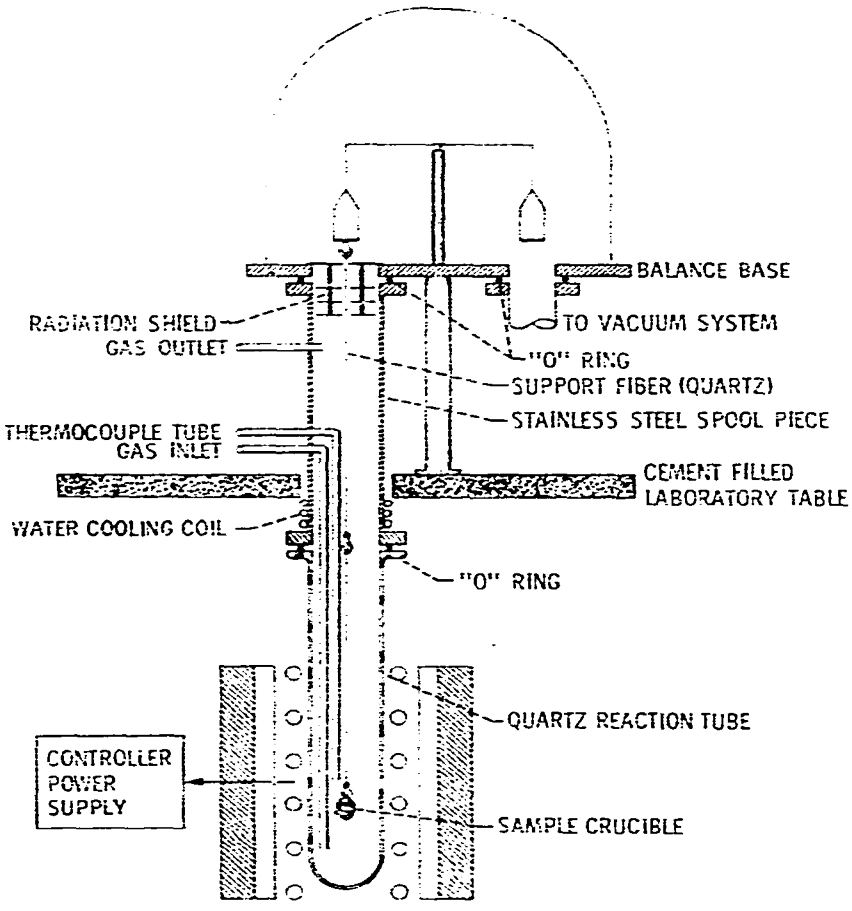

Fig. 1. Reaction tube assembly.

Procedure. — In using the apparatus, a sample is weighed into the crucible to the nearest 0.1 mg. The weight of material used is predetermined from formula weight, chemical analysis, or by a trial run in the TG apparatus to give a weight change close to 10 mg during heating. The crucible is attached to the quartz support fiber which is suspended from the balance. The crucible and sample are then "balanced out" with tare weights. After establishing equilibrium with the reaction gas and purge gas flow, heating is begun. Temperature, weight loss, and water evolution are recorded automatically. For reasons described in the Appendix, the moisture evolution is reported in qualitative terms.

Before carrying out an experimental run, a blank crucible or buoyancy calibration run was conducted with the same environment and heating conditions to correct for changes in density of the flowing gases and other fluctuations that occur as a result of heating. The buoyancy correction is described in greater detail in the Appendix. Typical blank crucible calibration runs with helium purge gas and helium reaction gas as well as helium purge gas and hydrogen reaction gas are shown in Figs. 2 and 3. A separate temperature *vs.* time curve was also run simultaneously with each experimental run. A linear temperature–time curve is indicative of uniform heating condi-

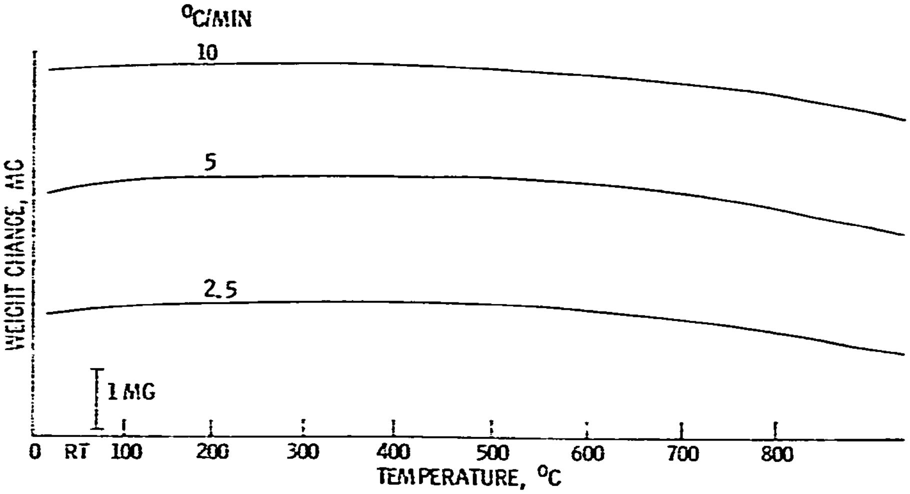

Fig. 2. Apparent weight change of empty quartz crucible during heating in helium at various linear heating rates: reaction gas, helium at 150 cc per min; purge gas, helium at 50 cc per min.

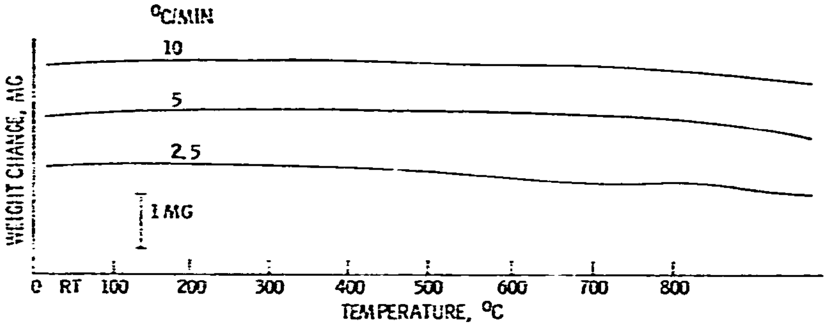

Fig. 3. Apparent weight change of empty quartz crucible during heating in hydrogen at various linear heating rates: reaction gas, hydrogen at 150 cc per min; purge gas, helium at 50 cc per min.

tions and is required to assure reproducibility and to obtain reliable weight change curves. Linear heating rate curves at 2.5, 5, and 10 °C per min are shown in Fig. 4.

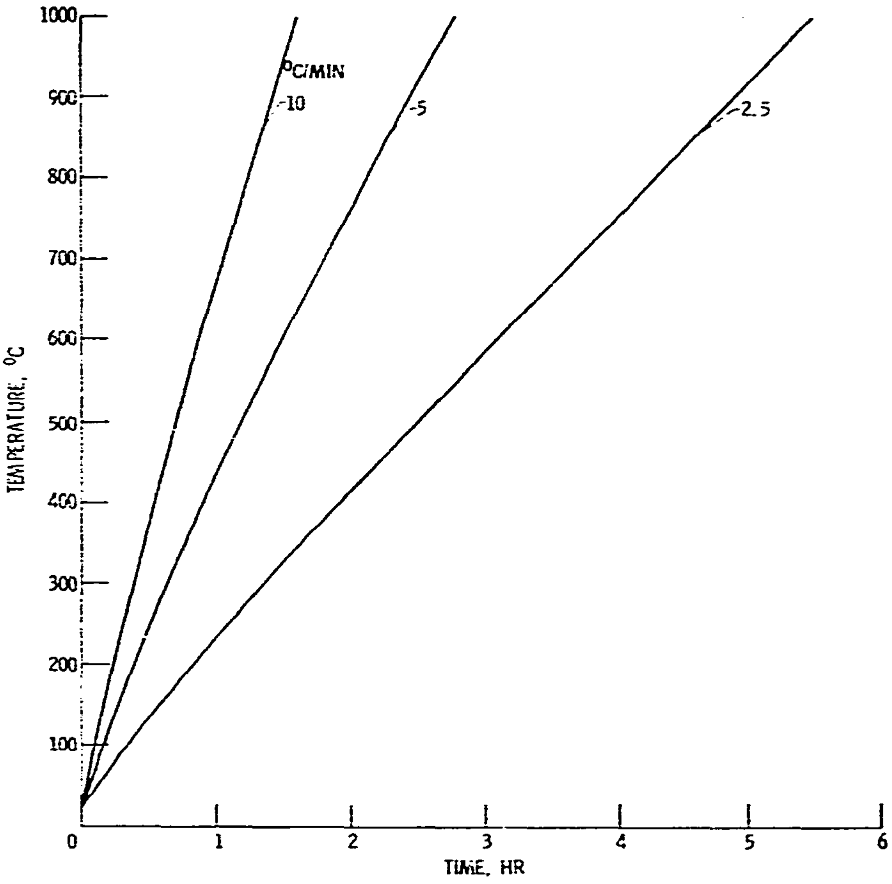

Fig. 4. Change of temperature with time at various heating rates.

In addition to the six blank crucible calibration runs, a total of five experimental runs were made. Three of the five experimental runs were done with calcium oxalate monohydrate. Fisher "certified" reagent grade material was used. X-ray analysis indicated the presence of a trace of CaO and a significant amount of $CaCO_3$. Chemical analysis indicated that there was about 3% $CaCO_3$ present. Calcium oxalate monohydrate was chosen for use in evaluating the operation of the TG system. The use of this material was predicated by the large number of TG studies which have used it, and particularly the study of Simons and Newkirk[2] which indicated its usefulness for judging the performance of a TG system. The three runs were carried out in dry helium at linear heating rates of 2.5, 5, and 10 °C per min. The helium flow rate was 150 cc per min and the maximum temperature was 900 °C.

The remaining two experimental runs were done with nickel oxide. Here again Fisher "certified" reagent grade material was used. X-ray analysis showed no impurities in the material. Nickel oxide was chosen for use in evaluating the performance of the TG system with reducing atmospheres particularly hydrogen. Nickel oxide was selected because it can be easily reduced in a single stage with hydrogen at low temperature. Two runs were made at a linear heating rate of 5 °C per min. The hydrogen flow rate was 150 cc per min and the maximum temperature was 800 °C. One of the nickel oxide runs was in dry hydrogen and the other in hydrogen containing 15,000 p.p.m. water vapor.

RESULTS AND DISCUSSION

A TG apparatus for use in powder metallurgy studies has been designed and assembled. The stability, reproducibility, and accuracy of the system when used with either inert (helium) or reducing (dry or wet hydrogen) atmospheres makes it uniquely suitable for the study of the reduction of surface oxides and other impurities present in materials to be used in dispersion strengthening studies. One of the most important factors when dealing with the fabrication of dispersion strengthened materials is

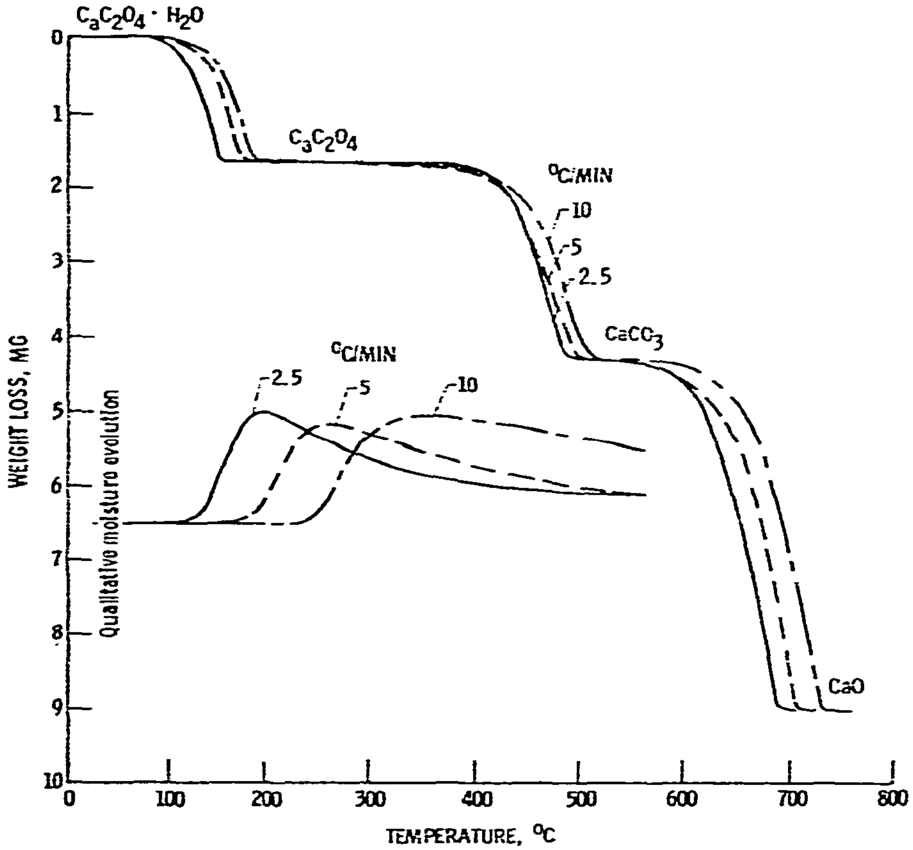

Fig. 5. Thermal decomposition of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) showing weight loss and moisture evolution as a function of temperature at three linear heating rates: sample weight, 14.8 mg; atmosphere, dry helium; flow rate, 150 cc per min.

impurity contamination. And a tool which will aid in the selection of proper and effective cleaning procedures or treatments is extremely valuable.

Decomposition of calcium oxalate monohydrate. — The results of heating this material at three different linear heating rates in dry helium are shown in Fig. 5. The weight change curves have been corrected for buoyancy effects as noted earlier. The first plateau in the curves of Fig. 5 represents the weight of the starting monohydrate; the second, that of calcium oxalate; the third, that of calcium carbonate; and the fourth, that of calcium oxide. The three weight losses shown in the figure are the result of the gaseous evolutions indicated by the following reactions:

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \tag{1}$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \tag{2}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{3}$$

Assuming that the starting material was pure calcium oxalate monohydrate, the calculated weight losses for the three reactions are 12.3, 19.2, and 30.1%, respectively. With 3% $CaCO_3$ in the starting material, as indicated by chemical analysis, the calculated weight losses are 12.0, 18.6, and 30.5%, respectively. These values compare favorably with the measured weight losses of 11.3, 17.9, and 31.8%, respectively.

It can be seen from Fig. 5 that as the rate of heating increased the evolution of gas as indicated by the weight loss starts and stops at higher temperatures. These results are in good agreement with those of Newkirk[3]. The validity of these results is also borne out in the first reaction by the qualitative moisture evolution curves which also started and stopped at higher temperatures with increased heating rates. It can also be noticed from the figure that, despite the fact that the weight loss reactions started and stopped at different temperatures with changes in heating rate, the weights at which the plateaus occurred were identical in the three runs. This uniformity in the plateau weight in three different runs with calcium oxalate monohydrate demonstrates the stability of the system and the reproducibility that can be achieved.

Reduction of nickel oxide. — The weight loss of nickel oxide on reduction in dry and wet hydrogen is shown in Fig. 6 as a function of temperature. The weight loss indicative of reduction begins at 278 °C and is complete at 368 °C in dry hydrogen and begins at 296 °C and is complete at 344 °C in wet hydrogen. In both cases no further weight loss was noted at temperatures up to 800 °C. The sample weight for these runs was 46.3 mg. The calculated weight loss for the complete reduction of nickel oxide according to the reaction

$$NiO + H_2 \rightarrow Ni + H_2O \tag{4}$$

is 9.88 mg. The total measured weight loss in both dry and wet hydrogen was 9.90 mg. Thus the calculated and measured values are in excellent agreement.

The main difference between the NiO reduction in dry and wet hydrogen was that the reduction with wet hydrogen started at a somewhat higher temperature and was complete at a lower temperature. The temperature differences were not great, however, being less than 25°C in either case.

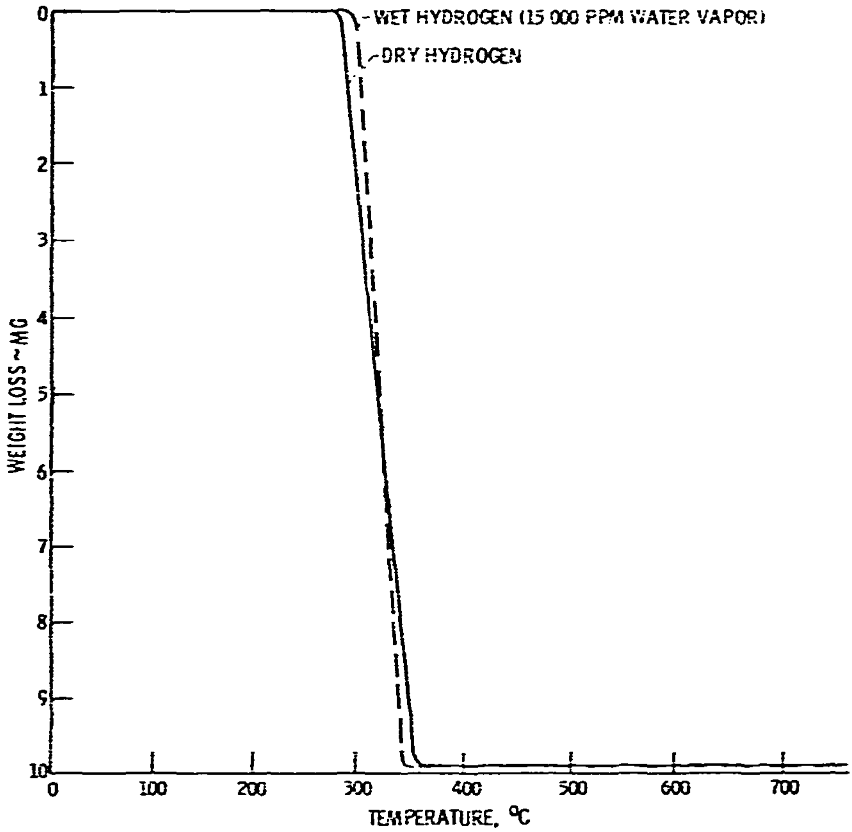

Fig. 6 Reduction of nickel oxide (NiO) showing weight loss as a function of temperature at a linear heating rate of 5°C per min: sample weight, 46.3 mg; atmosphere, dry hydrogen and hydrogen containing 15,000 p.p.m. water vapor; flow rate, 150 cc per min.

CONCLUSIONS

A thermogravimetry or TG system for use with controlled atmospheres, including those with controlled moisture levels, has been assembled and evaluated. The stability and reproducibility of the system for use with inert atmospheres has been established by evaluating the thermal decomposition of calcium oxalate monohydrate in dry helium at three different linear heating rates, *i.e.*, 2.5, 5, and 10°C per min. The use of the system with reducing atmospheres, specifically hydrogen, and controlled moisture levels has been demonstrated by the reduction of nickel oxide at a linear heating rate of 5°C per min in both wet and dry hydrogen. Thus the apparatus is felt to be suitable for such studies as the hydrogen reduction and/or carbon reduction of impurity or surface oxides as well as with other potential reducing agents such as the hydrogen halides or metal hydrides. In fact the system is currently being successfully applied to the evaluation of the reduction characteristics of a variety of metal and oxide powders which have potential for use in the production of high temperature dispersion strengthened materials.

APPENDIX

Details of the apparatus and procedure

Balance. — An automatic deflection type Ainsworth model RV balance with a Bristol model AU-1 single pen recorder is used. The balance mechanism is enclosed in a belljar which is sealed to the aluminum balance base with an elastomer "O" ring. Since the apparatus is intended primarily for use at pressures slightly above atmospheric, a bolted aluminum ring is used to hold the belljar tightly against the "O" ring. This gives a seal which is gas tight at pressures up to approximately 100 kN/m^2 (15 psig). The operating pressure within the belljar is dictated by the back pressure of the oil filled bubbler on the outlet gas flow and is normally limited to approximately 7–14 kN/m^2 (1–2 psig).

The balance base contains three entry ports. One port is located under each pan of the balance and the remaining port is located at the rear of the balance. As shown in Fig. 1, the two front ports are used for the reaction tube assembly and for the vacuum system. The rear port is used for the inlet and outlet of the gas used to purge the balance mechanism during operation.

The remaining parts of the balance system are the sample crucible and support fiber. The sample crucible is a tapered quartz crucible 2.7 cm in diameter and 1.6 cm high. The crucible is suspended from the balance by an 80-cm long, 0.15-cm diameter quartz fiber. The fiber is in two sections to facilitate loading and to aid in the damping of vibrations. The crucible and sample are contained in a quartz reaction tube which is heated externally by a resistance furnace.

The quartz support fiber and crucible are counterweighted with nonmagnetic stainless steel tare weights located on the right hand pan of the balance. The tare weights are used to bring the system into initial equilibrium. The Ainsworth balance is capable of automatic weight switching of up to 400 mg in 10 mg increments. The weight change is automatically recorded on the Bristol strip chart recorder. With proper adjustment of the recorder sensitivity a full scale deflection of 10 mg is obtained.

The recorder chart width is 25.4 cm, this means that a weight change of 1 mg is equivalent to 2.54 cm of chart paper. The maximum deviation from this equivalency is about one line width. With a fine ball point pen the ink line width on the chart is approximately 0.02 mg. The normal reproducibility is one line width. Taking all factors into consideration (including the buoyancy correction to be described later) the absolute weighing accuracy of the system appears to be about ±0.1 mg.

Furnace: Temperature control, measurement, and programming. — The furnace power supply, temperature control, programmer, and all of the associated recorders are shown schematically in Fig. A-1. The samples are heated with a coiled vertically wound nichrome resistance furnace. The upper temperature limit of the furnace is approximately 1100°C. Power is supplied with a "silicon-controlled rectifier" power supply and controller. The controller is of the three mode type, *i.e.*, it is equipped with separately adjustable rate, reset, and proportional band. The use of a three mode controller was dictated by the need to be able to use different furnaces and to assure that completely linear temperature programs, with no undershoot or overshoot of temperature, could be obtained. To permit automatic unattended operation, the power supply is equipped with thermocouple break protection.

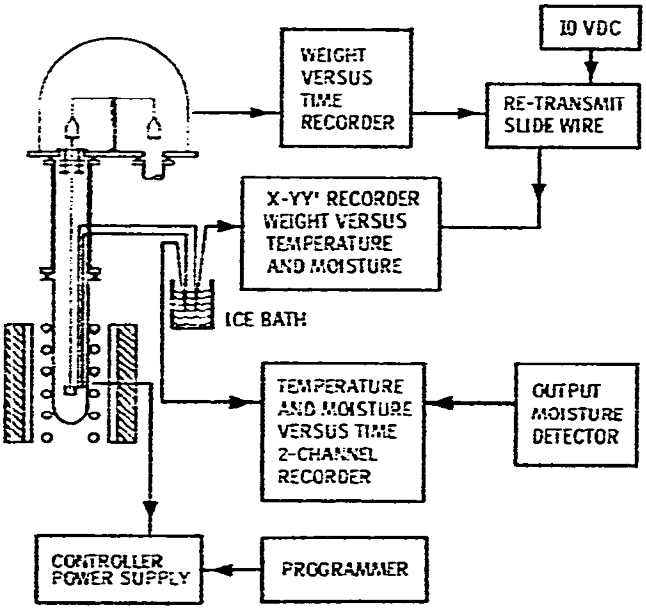

Fig. A-1. Temperature, weight, and moisture detection system.

Furnace temperature is controlled with an unsheathed platinum–platinum/13% rhodium thermocouple located approximately 0.5 cm from the outer wall of the reaction tube. The signal from this thermocouple is fed directly to the controller. The controller is ambient temperature compensated. The programmer is of the curve follower type. And with the furnace and thermocouple as described, various linear heating rates of less than one to greater than 20°C per min are possible.

Sample temperature is measured with a Chromel–Alumel thermocouple contained in a stainless steel protection tube which extends to within 0.5 cm of the sample crucible. Two couples are used and both are referenced to 0°C with an ice bath. The signal from one thermocouple is fed into one channel of a two channel strip chart recorder. The second thermocouple's signal is fed into the X-axis input of an X–YY′ recorder. The Y-axis input of the X–YY′ recorder is connected to the Bristol recorder associated with the balance weighing system. This interconnection is accomplished with a re-transmit slidewire which is powered with a precision 10 VDC power supply. The Y′ axis input of the X–YY′ recorder is connected to the reaction gas outlet moisture detector. This permits a continuous record of both weight change and moisture evolution as a function of sample temperature. The reaction gas outlet moisture detector is also connected to the two channel strip chart recorder mentioned above, thus giving also a continuous record of moisture evolution as a function of temperature. This apparent duplication of data taking is necessary because the X–YY′ recorder is independent of time and the linearity and uniformity of the heat application can only be observed by use of a time base strip chart recorder.

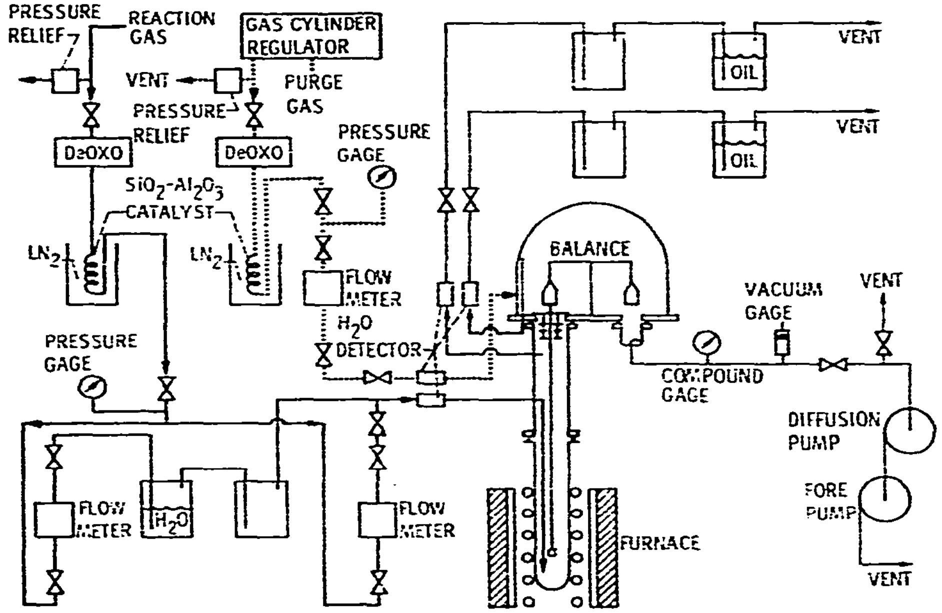

Fig. A-2. Reaction gas, purge gas, and vacuum system.

Vacuum system. — The vacuum is shown in Fig. A-2 and consists of a single stage oil diffusion pump backed with a mechanical roughing pump. The vacuum system is used primarily to remove air and moisture from the TG apparatus after the sample is inserted and prior to establishing the reaction gas and purge gas flows. A compound pressure-vacuum gage is used to give a rough estimation of the pressure in the system. For more precise vacuum measurements, which would be required if the system were to be operated under vacuum conditions, a cold cathode vacuum discharge gage is also included.

Reaction gas system. — The reaction gas system is shown schematically in Figure A-2. When the reaction gas is hydrogen, a Deoxo unit is used to react any oxygen present in the gas to form water vapor. The water vapor generated from this reaction plus any present in the incoming gas is then removed with an SiO_2–Al_2O_3 cracking catalyst at liquid nitrogen temperature. For other reaction gases, the cold trap temperature would be adjusted according to the gas liquefaction temperature.

The individual, or blended, thoroughly-dried gases are metered into the reaction tube with a precision (1% accuracy) flowmeter. Gas pressure is maintained at 35.5 kN/m^2 (5 psig) and measured with a 0–69-kN/m^2 (0–10-psig) gage. The gas to be used in the reaction tube enters via an inlet tube which passes through the wall of the spool piece (see Fig. 1) and extends downward parallel to the reaction tube wall, terminating about 3.5 cm below the sample crucible. In this manner the gas for the reaction is preheated before it comes into contact with the sample. The gas leaves the reaction tube through an outlet in the spool piece. It then passes through a surge reservoir, a bubbler filled with high vacuum diffusion pump oil, and then vents to atmosphere.

Purge gas system. — The purge gas (helium) is also dried with an SiO_2–Al_2O_3 cracking catalyst at liquid nitrogen temperature and then metered into the belljar (balance enclosure) with a precision (1% accuracy) flowmeter. The system is shown schematically in Fig. A-2.

The purge inlet flow is directed across the entry port located under the left hand balance pan. The purge outlet is located near the top of the belljar. In operation, the purge gas flow is adjusted so that a slight increase in flow causes an increase in the amount of gas leaving the reaction gas outlet bubbler. It is assumed that under this condition the balance mechanism sees essentially only purge gas. The main function of the purge gas is to protect the delicate balance mechanism from reaction products generated by samples under evaluation and also from possibly corrosive reaction gases.

Moisture detection and control. — The moisture level of the inlet and outlet gases (both reaction and purge gases) is measured with a gold–aluminum oxide capacitor hygrometer. When helium or hydrogen is dried as described previously, the moisture level of the incoming gas while detectable, is below the calibration limit of the hygrometer (0.03 p.p.m.). The moisture level of the reaction gas effluent can also be determined when the moisture level is above the minimum calibration level of the hygrometer. With moisture levels above about 0.5 p.p.m. the hygrometer can give quantitative measurements. With very low moisture levels such as those for the calcium oxalate monohydrate example of this paper, only a qualitative indication of evolved moisture is possible. Electronic amplification of the output signal from low level moisture evolution can be used to indicate the temperature at which moisture is evolved. Such indications are termed "qualitative moisture evolution".

If desired, moisture can be added to the reaction gas by diverting a portion of the gas stream through a water bubbler. Moisture levels of from 0.5 p.p.m. to saturation can be achieved and measured. A given moisture level can be controlled to ±5 p.p.m. at low moisture levels and to ±50 p.p.m. at high moisture levels.

Sample loading. — The sample to be run is weighed directly into a crucible on an analytical balance. Sample weights are determined to the nearest 0.1 mg. The weight of material used is generally predetermined to give an approximate weight change of 10 mg during heating. Formula weight, chemical analysis, or trial runs in the TG system are used to select the correct sample weight. For example, the reduction of nickel oxide (NiO) in hydrogen requires a sample weight of 46.7 mg to give a weight loss of 10 mg according to the reaction:

$$NiO + H_2 \rightarrow Ni + H_2O$$

The weighed crucible and sample is attached to the quartz support fiber. The reaction tube is put in place and the flange bolts inserted and tightened. The balance is then tared using the switching weights and the recorder is zeroed with the pen at the upper end of the scale. To aid in making this adjustment, the balance is equipped with a full scale zero adjustment. With this control at the midpoint of its adjustment it is possible to move about 6 mg in either direction.

To establish flow, the reaction tube and balance enclosure are first evacuated to a level of about 85 kN/m^2 (25 in. Hg) then backfilled with reaction gas and purge gas, respectively. At this point the appropriate 10-mg tare weights are added or removed by means of the automatic weight switching incorporated in the balance mechanism. The final zero is then set with the full scale zero adjustment, and after sufficient time with gas flow, the heating program is started.

Buoyancy correction. — When the same gas is used for the reaction gas and the purge gas, the density of the gas surrounding the heated sample and crucible is less than that surrounding the counterweights, the difference in gas density causes the sample to appear heavier than it really is. However, since the reaction gas enters from below the sample and flows upward, the sample has a tendency to appear lighter than it really is. With proper flow rates for the reaction and purge gases these two effects tend to cancel each other out. There still remains a variation due to temperature and a blank calibration run should be carried out under the identical conditions of heating rate and gas flow to be used in any weight loss determination. In many cases, the purge and reaction gases are not the same, and then calibration runs are mandatory.

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