CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

In this work, the graphite labeled as Micro 850 was obtained from Asbury Graphite Mills. The Micro 850 graphite was highly graphitic, of high purity, and was of uniform disk-shaped sizes. The properties of such graphite sample are illustrated in Table 1. Nitric oxide (NO) used for gasification reaction was in a purity of 99.5% and was supplied by Intergas Co., Ltd. Nitrous oxide (N_2O) used for gasification reaction was of 99.5% purity. Helium used as diluent and carrier gas for gas chromatographs (GC) was in an ultra high purity of 99.999%. The two latter gases were obtained from Thai Industrial Gases Public Co., Ltd.

Table 3.1 Physical properties of Micro 850 graphite sample used.

Property	Value
BET*, m^2/g	15.5
Average diameter*, μm	4.00
Average thickness**, μm	0.06
Basal plane surface area**, m^2/g	15.05
Edge plane surface area**, m^2/g	0.45

* these values are obtained from the manufacturer.

** these values are obtained from calculation.

3.2 Experimental Apparatus

The apparatus for studying the intrinsic kinetics of graphite gasification in NO and N_2O is schematically shown in Figure 3.1. The experimental system is divided into 4 parts: a gas mixing section, an oxygen removal unit, a TGA reactor, and a gas analysis section.

3.2.1 Gas Mixing Section

NO, N_2O, and He were supplied from cylinders. For each cylinder, a regulator was installed to control the delivery pressure of gas. A two-stage stainless-steel regulator with CGA 330 connection was used for a NO cylinder. A brass regulator with CGA 326 connection was used for a N_2O cylinder. A brass regulator with CGA 580 connection was used for a He cylinder. The operating pressures of all gases were designated at 30 psia. In order to prevent side reactions, moisture and oxygen as impurity in the He gas were removed by installing a moisture trap and an oxygen trap, respectively, in line.

Each gas was passed through a NUPRO 7 micron filter to remove contaminants. The flow rates of each stream were controlled by Side-Trak Model 840 mass flow controllers. Either NO or N_2O was homogeneously mixed with He in a mixing chamber. Next, residual oxygen as impurity, which contaminates the reactant gas, would be disposed by an oxygen removal unit.

3.2.2 Oxygen Removal Unit

The reactant gas having a residual amount of oxygen as a contaminant was passed to a stainless steel reactor having a diameter of 0.5 inch which was packed with an amount of copper flakes in order to remove such residual oxygen. The oxidation temperature of commercial copper was 550 ^{o}C. To ensure that the residual oxygen was completely removed, the oxygen concentration had been analyzed by GC. The flow rate of gas was controlled

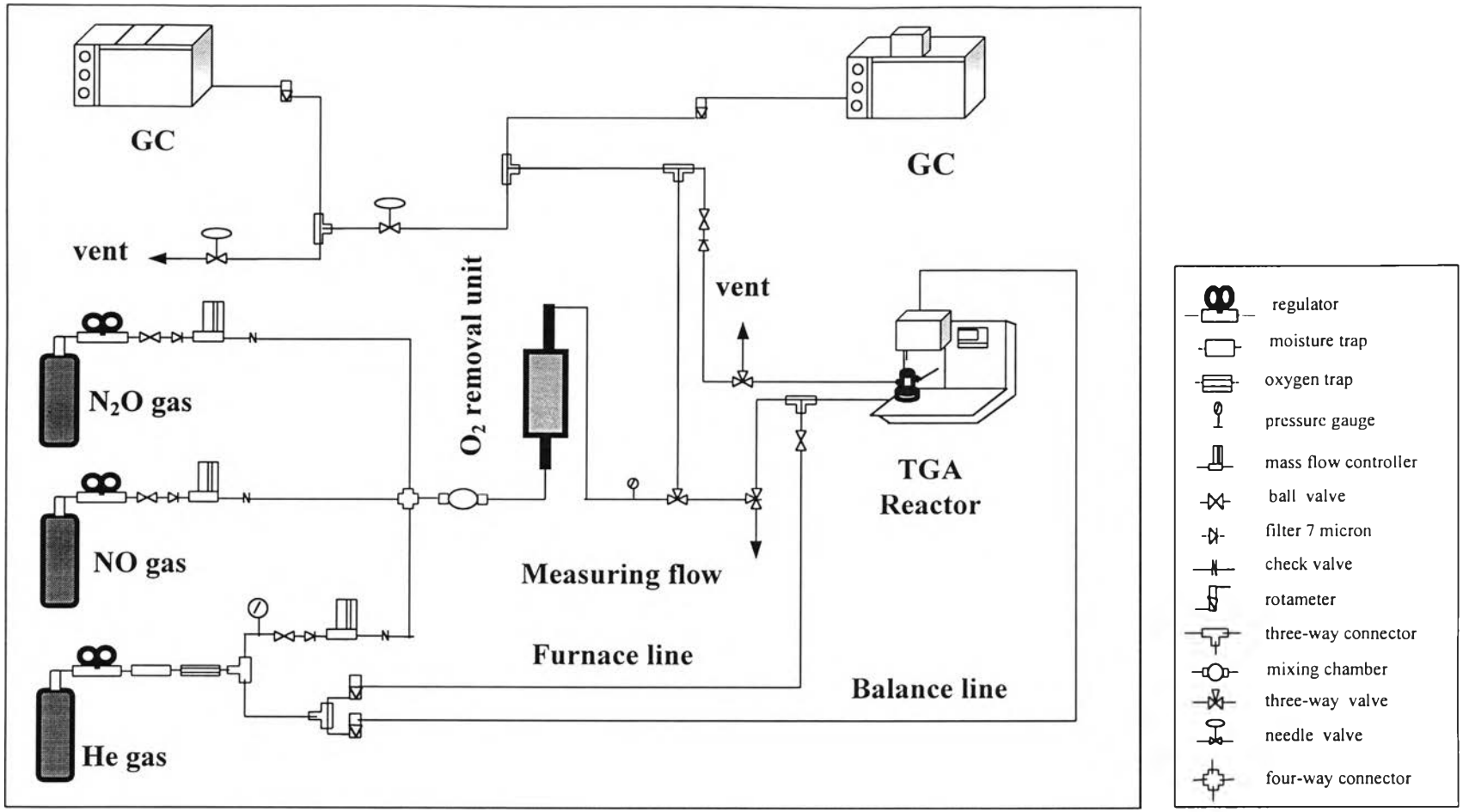

Figure 3.1 Schematic diagram of the experimental apparatus used.

by a rotameter prior to passing through a GC. Then, the reactant gas was fed into a TGA reactor.

3.2.3 TGA Reactor

The apparatus used for measuring graphite gasification rate in NO or N_2O was a 2950 Du Pont Thermogravimetric analyzer (TGA), of which sensitivity was 0.1 μg, as revealed in Figure 3.2. It measured the amount and rate of weight change in graphite when reaction occurred in a controlled atmosphere.

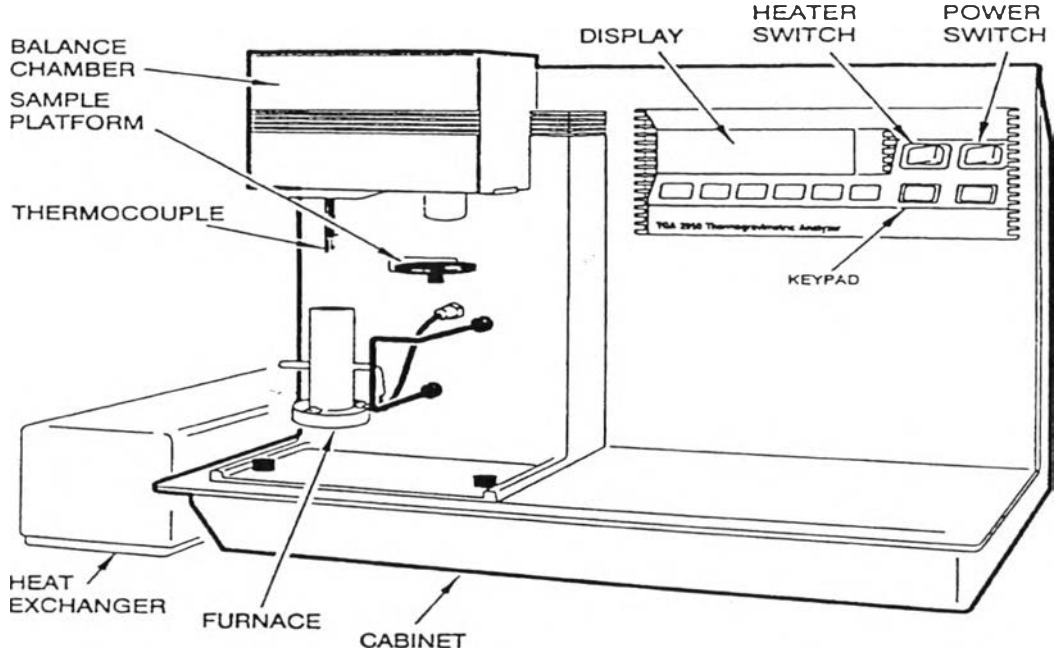

Figure 3.2 The parts of the TGA 2950 Module (Du Pont Company, 1990).

3.2.4 Gas Analysis Section

The product gases were withdrawn from the TGA reactor and divided into two streams – one stream was continuously fed through a Hewlett Packard 5890 series II gas chromatograph comprised of a thermal conductivity detector (TCD). The other stream was progressively passed through a FISONS 8000 series gas chromatograph equipped with a TCD as well.

Each of the chromatographs used for the gas analysis possessed its column and condition as follows:

1. The Hewlett Packard 5890 series II GC was installed with a Porapak Q column for the analysis of CO_2 and N_2O. The conditions used include in the following:

-The column temperature was operated isothermally at 55 °C.

-The detector temperature was used at 180 °C.

-The injector temperature was constant at 120 °C.

-The helium flow rate was 25 ml/min.

2. The FISONS 8000 series GC was equipped with a molecular sieve 13 column for the analysis of N_2 and NO. The followings are the conditions used for the analysis of gas.

-The column temperature was maintained isothermally at 30 °C.

-The detector temperature was employed at 140 °C.

-The Injector temperature was stood at 160 °C.

-The flow rate of helium gas used as carrier gas was 25 ml/min.

3.3 Experimental Procedure

The measurements of reactivity of the graphite were performed in the TGA reactor as described previously. For the study of carbon-nitric oxide reaction the graphite sample was weighed in an accuracy weight of 5 mg while in that of 7 mg for the study of carbon-nitrous oxide. The accurately weighed graphite in the sample pan was suspended in the heated zone of the TGA, and the temperature in the vicinity of the sample was measured by the thermocouple as depicted above.

Prior to each run, the graphite sample was degassed at 120 °C in He for 2 hours in order to remove the physically adsorbed gases and to clean the surface. A flow distribution of helium was set at 40 and 60 ml/min in balance

chamber and furnace chamber purge, respectively. After degassing and surface cleaning, the sample was heated to the desired reaction temperature with a ramp rate of 10 °C/min in a He flow. Whenever the desired reaction temperature was reached, NO or N_2O gas as desired concentration was switched instead of He in furnace chamber and passed through the TGA reactor with a flow rate of 60 ml/min to react with the degassed sample. During the reaction, the product gases were continuously analyzed by GC. After a certain time of reaction, the reaction gases were switched back to helium and the temperature was allowed to drop to ambient temperature quickly in order to reduce any post-reaction.

3.4 Intrinsic Kinetic Parameters

In the present work, due to the fact that the edge sites on graphite surfaces are active sites, the gasification rates of graphite in NO or N_2O would be determined in terms of the rate per active site or TOF. The graphite gasifications by NO or N_2O were studied under isothermal conditions. Both of them were studied at temperatures from 500 °C up to 750 °C, at NO concentration of 6%, 20%, 40%, and at N_2O concentration of 6%, 12%, 20%. The total flow rate of gases passed through the TGA reactor was maintained at 100 ml/min. The reactions occur under an atmospheric pressure. Because the reaction rate changed to some extent at both very low and very high burn-off levels, only reaction rates between 10% and 20% burn-off were used.

3.4.1 TOF as a Function of Reaction Temperature

In order to study the effect of temperature on TOF and to determine activation energies, the TOFs at different temperatures in the range of 500-750 °C except at a fixed NO or N_2O concentration were obtained. The concentrations of NO investigated were 6%, 20%, 40% and those of N_2O were

studied at 6%, 12%, 20%. The reaction rates obtained were between 10% and 20% burn-off.

3.4.2 TOF as a Function of NO or N_2O Concentration

In order to investigate the effect of NO or N_2O concentration on TOF and to determine the reaction order. The TOFs at different concentrations of NO or N_2O but at a fixed temperature in the range of 500-750 °C were attained. The concentrations of NO investigated were 6%, 20%, 40% and those of N_2O were studied at 6%, 12%, 20%. The reaction rates, which were brought to further calculate the reaction order, were between 10% and 20% burn-off levels.

The experimental conditions for studying the graphite gasification in nitric oxide and nitrous oxide are shown in the Table 3.2 and Table 3.3.

Table 3.2 The experimental conditions for studying the graphite gasification in nitric oxide.

Condition	Quantity
Weight of Micro 850 graphite, mg	5
Isothermal reaction temperature, °C	500- 750
The concentration of NO diluted in He, %	6, 20, and 40
Total flow rate, ml/min -Furnace chamber purge (NO reactant gas), ml/min -Balance chamber purge (Helium gas), ml/min	100 60 40
Heating rate, °C/min	10
Total pressure, atm	1

Table 3.3 The experimental conditions for studying the graphite gasification in nitrous oxide.

Condition	Quantity
Weight of Micro 850 graphite, mg	7
Isothermal reaction temperature, °C	500- 750
The concentration of NO diluted in He, %	6, 12. and 20
Total flow rate. ml/min -Furnace chamber purge (N_2O reactant gas), ml/min -Balance chamber purge (Helium gas), ml/min	100 60 40
Heating rate, °C/min	10
Total pressure. atm	1