



## A THERMOBALANCE SET-UP FOR NITRIDING IN AMMONIA GAS ATMOSPHERES

ASW KURNY\*

### ABSTRACT

*Nitriding of pure iron in ammonia gas atmospheres has been studied in the temperature range of 475-550°C by using a thermobalance. The effects were followed by optical metallography and X-ray diffraction techniques. The setup has been described and the results obtained have been discussed. The advantages of performing nitriding experiments in a thermobalance has also been outlined.*

### Introduction

The kinetics of nitriding in ammonia is usually followed by nitriding a large number of specimens for different times at a constant temperature and then finding out the weight gain<sup>1-2</sup>. In the present case, a thermobalance, which can directly give the weight changes, was used to follow the weight changes. One distinct advantage

of using a thermobalance for kinetic studies is that, it is a single specimen technique, i. e. isothermal kinetics at one temperature can be followed using only one specimen and the accuracy of the technique depends on the accuracy of measurement of the extension of spring during the process. Moreover, weight gain measurement is possible at very short time intervals, leading to a better fitting of the curves.

\* Associate Professor, Department of Metallurgical Engineering, BUET, Dhaka.

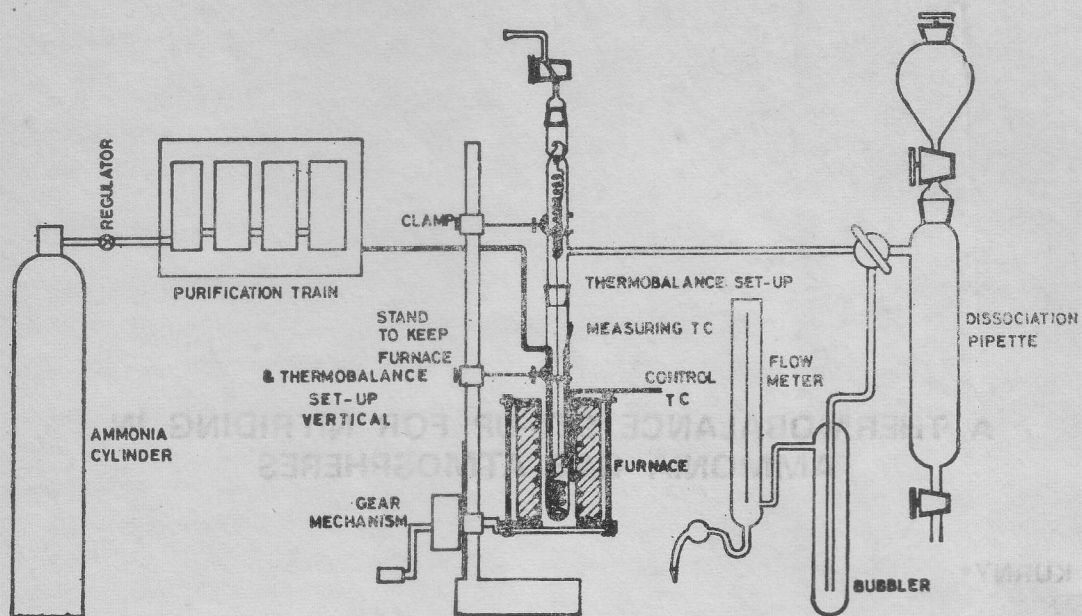


FIG. 1 EXPERIMENTAL SETUP FOR GAS-NITRIDING

### Experimental Details

The experimental set up for gas nitriding is illustrated in Fig. 1. The thermobalance (Fig. 2) consists of a three piece assembly joined by standard ground glass joints. The lower piece is made of transparent quartz tube connected to a pyrex tube through a graded seal. This part has an opening for gas inlet and an opening for the thermocouple. The gas inlet extends to the bottom and takes the form of a coil spiral with small holes on the bottom-most coil of the spiral. The thermocouple is protected from nitridation by a thermocouple protection tube closed at one end which extends upto the top of the spiral. The mid-section of the assembly is the

thermobalance tube, housing the spring from which the specimens are suspended by means of quartz fibres. This part also contains the gas outlet. The third and the top-part has an additional outlet for flushing the system with ammonia before the initiation of nitriding and is provided with a stopcock for sealing the top during nitriding.

The whole setup along with a vertical tube furnace, made by winding nichrome on a heavy duty mullite tube, for heating the specimen is mounted vertically on a stand. This stand has a manually operated gear-mechanism for lifting or lowering the furnace. The lower quartz tube is



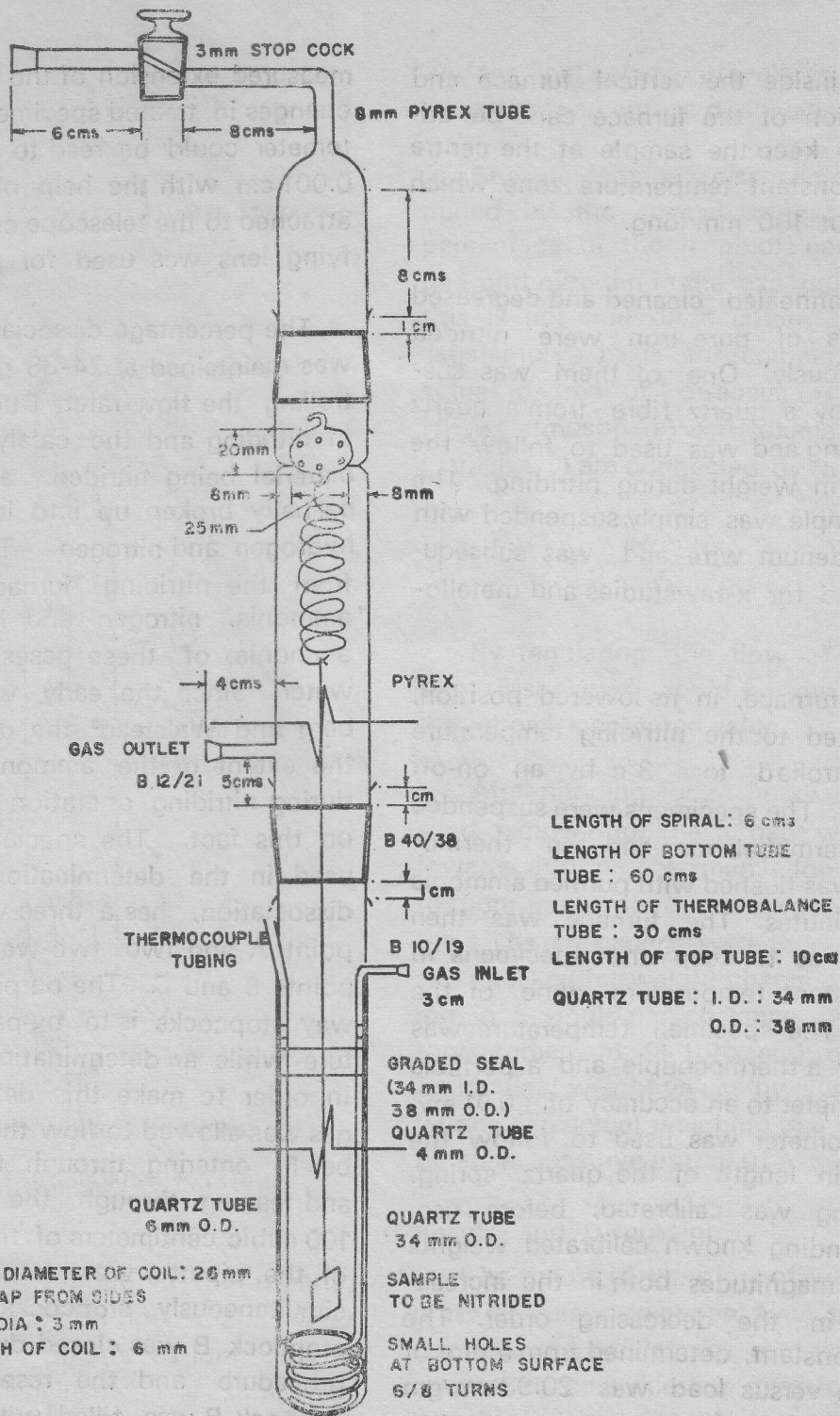


FIG.2 THE THERMOBALANCE ASSEMBLY

located inside the vertical furnace and the position of the furnace can be adjusted to keep the sample at the centre of the constant temperature zone, which was about 100 mm long.

Two annealed, cleaned and degreased specimens of pure iron were nitrided simultaneously. One of them was suspended by a quartz fibre from a quartz fibre spring and was used to follow the changes in weight during nitriding. The other sample was simply suspended with a molybdenum wire and was subsequently used for x-ray studies and metallography.

The furnace, in its lowered position, was heated to the nitriding temperature and controlled to  $\pm 3^\circ\text{C}$  by an on-off controller. The specimens were suspended in the thermobalance and the thermobalance was flushed with purified ammonia for 15 minutes. The furnace was then raised so as to keep the specimens in the constant temperature zone of the furnace. The specimen temperature was noted by a thermocouple and a portable potentiometer to an accuracy of  $\pm 0.01$  mv. A cathotometer was used to follow the changes in length of the quartz spring. The spring was calibrated, before use, by suspending known calibrated weights of small magnitudes both in the increasing and in the decreasing order. The spring constant, determined from a plot of extension versus load was 20.93 cm/gm and was used for conversion of the

measured extension of the spring to weight changes in treated specimens. The cathotometer could be read to an accuracy of 0.001 cm with the help of a vernier scale attached to the telescope carrier. A magnifying lens was used for precise readings.

The percentage dissociation of ammonia was maintained at 24-38 percent by controlling the flow-rate. Due to temperature of nitriding and the catalytic effect of the material being nitrided, ammonia gas is partially broken up into its constituents hydrogen and nitrogen. Thus exit gases from the nitriding furnace consist of ammonia, nitrogen and hydrogen. Only ammonia, of these gases, is soluble in water. Since the early work of Homerberg and Walstead<sup>3</sup> the determination of the extent of the ammonia dissociation during nitriding operation has been based on this fact. The special pipette (Fig. 3) used in the determination of extent of dissociation, has a three-way stopcock at point A and two two-way stopcocks at points B and C. The purpose of the three way stopcocks is to by-pass the gas mixture while a determination is being made. In order to make this determination, the gas was allowed to flow through the chamber F, entering through the stopcock A and leaving through the stopcock C. A 100 cubic centimeters of the gases (volume of the pipette) was trapped by closing simultaneously stopcocks A and C. The stopcock B was closed during the above procedure and the reservoir above the stopcock B was filled with water. After



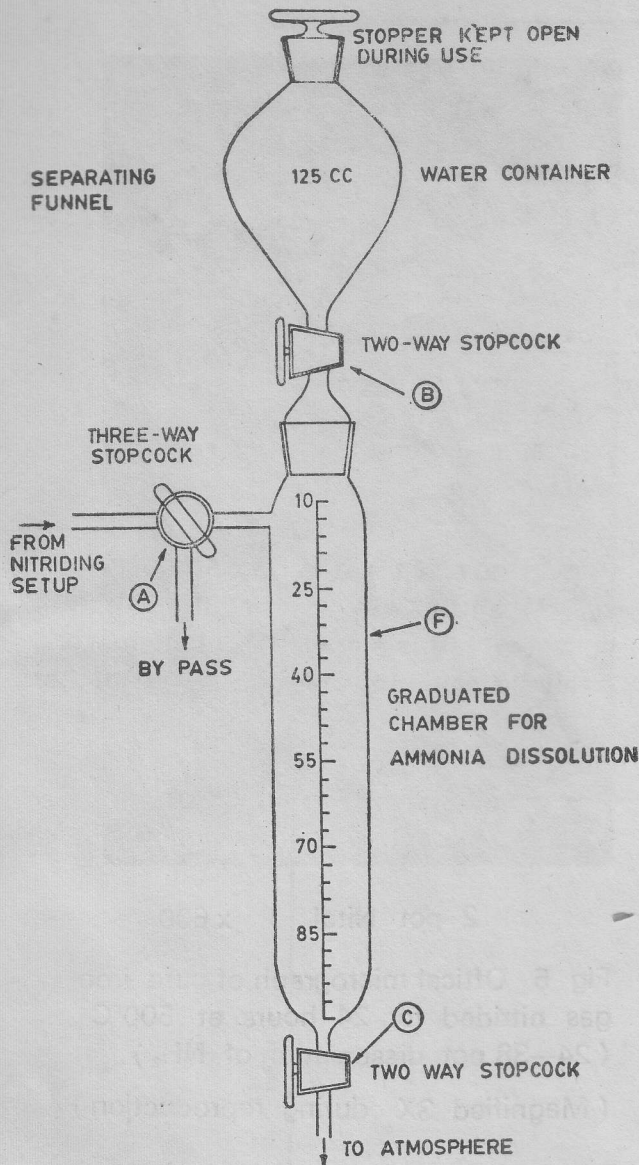


FIG 3 THE DISSOCIATION PIPETTE

the gases were trapped in the pipette, the upper stopcock was opened and water flowed into the pipette as long as any ammonia gas remained. The difference between the initial gas volume (100 cc)

and the final volume of water in the pipette gave the percentage dissociation.

The percentage dissociation, determined by the special pipette, is the percentage of the insoluble gases, hydrogen and nitrogen in the exit gases. While this is not true dissociation, this gives a satisfactory basis for comparison. The actual degree of dissociation ( $\alpha$ ) (for  $NH_3=1$  atmosphere) and volume of  $N_2+H_2$ , ( $V_{N_2+H_2}$ ) are connected by the formula<sup>4</sup>,

$$\alpha = \frac{V_{N_2+H_2}}{2 - V_{N_2+H_2}}$$

By regulating the flow of ammonia, this dissociation could be maintained at the above mentioned value.

After nitriding for 24 hours at the desired temperature, the furnace was quickly lowered and the specimen allowed to cool to room temperature in a stream of ammonia. The specimens were then taken out and checked for weight changes by weighing in a single pan balance. A satisfactory agreement ( $\pm 0.15$  mg.) was noted in the final weight values by spring calculations and actual weighing in a single pan balance, sensitive upto 0.01 mg.

### Results and Discussion

The nature of the plots of weight gain/unit area versus treatment time and weight gain/area versus square root time (Fig. 4) show that the process is diffusion controlled. It is also evident that the kinetics of

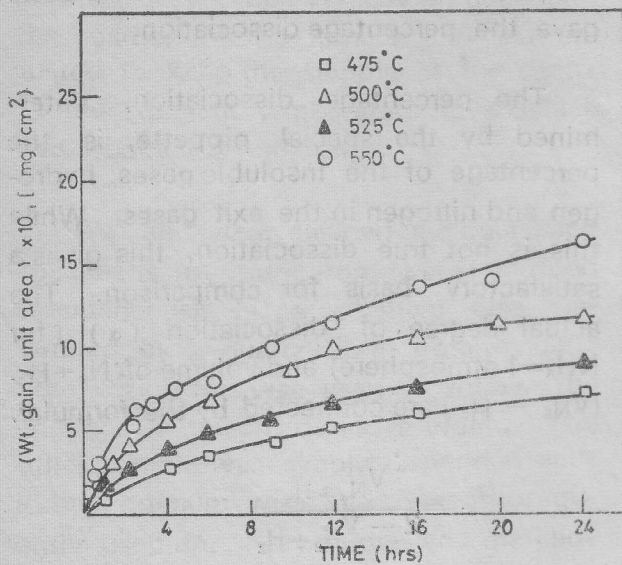


FIG. 4 THERMOGRAVIMETRIC DATA ON GAS NITRIDED ARMCO IRON [ Dissoc<sup>n</sup> of NH<sub>3</sub> : 24-38 pct ]

nitriding can be followed by using a thermobalance. However, because of the higher partial pressures of nitrogen used in these experiments, a mixture of nitrides formed and therefore further treatment of this data to calculate the activation energy could not be done.

Optical metallographic studies on sections orthogonal to nitrided surface (Fig. 5) show that the specimens were properly nitrided. An unetched compound layer together with the nitride needles could be clearly seen on the micrograph. Etching techniques did not reveal the depth of penetration. Attempts were, therefore, made to determine the depth of penetration by the microhardness measurement techniques. However, microhardness measurements also could not be used to



2 pct Nital x 600

Fig 5 Optical micrograph of pure iron gas nitrided for 24 hours at 500°C ( 24-38 pct dissociation of NH<sub>3</sub> ) ( Magnified 3X during reproduction )

determine the depth of penetration of nitrogen, because the matrix was very soft. Low loads caused very small indentation leading to poor accuracy in microhardness measurements while higher loads, in fact, measured the hardness of the layers below.



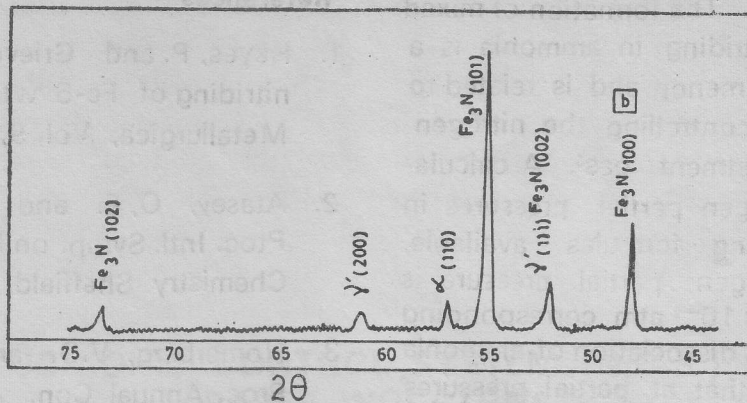


FIG. 6 X-RAY DIFFRACTION PATTERNS OF ARMCO IRON GAS NITRIDED FOR 24 HRS AT 525°C.

An analysis of x-ray patterns of pure iron gas-nitrided for 24 hours (Fig. 6) showed that at all temperatures investigated, the layers consist of higher nitrides.

The formation of higher nitrides during nitriding in ammonia is related to the high partial pressures of nitrogen. The results obtained are in good agreement

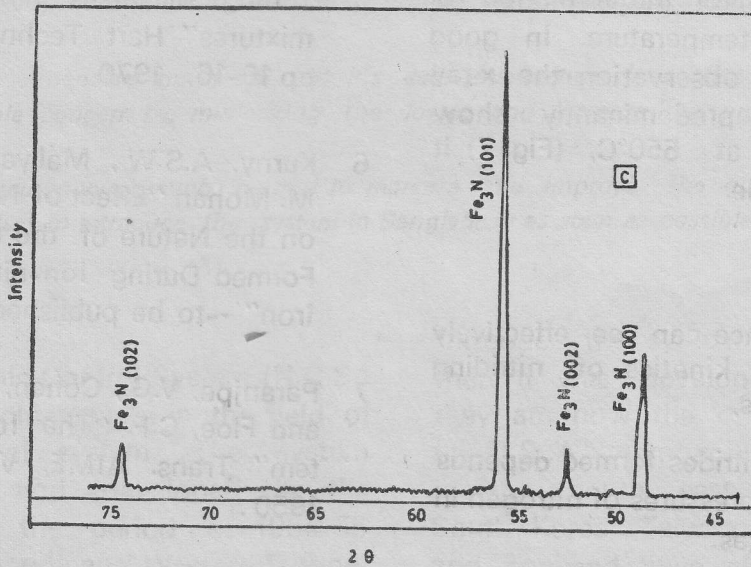


FIG. 7. X-RAY DIFFRACTION PATTERN OF ARMCO IRON GAS NITRIDED FOR 24 HR AT 550°C

with other studies. The formation of mixed nitrides during nitriding in ammonia is a well-known phenomenon and is related to the difficulty in controlling the nitrogen potential of the treatment gas<sup>5</sup>. A calculation of the nitrogen partial pressures in gas nitriding, using formulas available, shows that nitrogen partial pressure is  $6 \times 10^{-3}$  atm or  $9.5 \times 10^{-2}$  atm corresponding to 24 or 38 percent dissociation of ammonia. It may be noted that at partial pressures of nitrogen less than  $7.14 \times 10^{-3}$  atm, only  $\gamma$ -nitride formed during ion-nitriding of pure iron<sup>6</sup>. At 525°C the diffraction lines belonging to the Fe<sub>3</sub>N-phase is more intense, signifying that under such treatment conditions, the Fe<sub>3</sub>N nitride is predominant. This could be because of extended phase field of the  $\epsilon$ -nitride at these temperatures. It can be seen from the Fe-N system<sup>7</sup> that less nitrogen is required for the formation of  $\epsilon$ -nitride at higher temperature. In good agreement with this observation the x-ray pattern at 525°C predominantly show  $\epsilon$ -nitride whereas at 550°C, (Fig. 7) it shows only  $\epsilon$ -nitride.

### Conclusions

1. A thermobalance can be effectively used to follow kinetics of nitriding in ammonia gas,
2. Nature of the nitrides formed depends on the partial pressures of nitrogen in the treatment gas.

### References

1. Hayes, P. and Grieveson, P. "The nitriding of Fe-5 wt % Me", *Scripts Metallurgica*, Vol. 9, pp 39-50, 1975.
2. Atasey, O. E. and Kirkwood D. H. *Proc. Intl. Symp. on Metallurgical Chemistry Sheffield*, 1971.
3. Homerberg, V.O. and Walsted, J.P., *Proc. Annual Con. Am. SOC, Steel Treating*, Cleveland, Sept 13, p. 75, 1929.
4. Bebruchev, L.V., Kaplun, R.I., Morshstein, I.M., Smirnov, A.V. and Kuleshov, Yu.S. *Protective coatingen Metals* Vol.1, p. 52, 1969.
5. Minkevic A.N. and Sorokin Yu.V. "Nitriding of Steels in nitrogen-ammonia mixtures" *Hart Techn Mitt*, Vol. 25, pp.10-16, 1970.
6. Kurny, A.S.W., Mallya, R.M and Rao, M. Mohan "Effect of Nitrogen Pressures on the Nature of the Compound Layer Formed During Ion-nitriding of Armco Iron" --to be published
7. Paranjpe, V.G., Cohen, M., Bever, M.B. and Floe, C.F. "The Ion-nitrogen System" *Trans. AIME*, Vol. 188, p. 261, 1950.