MASS AND ENERGY TRANSFER STUDY OF THE DECOMPOSITION OF NH_3 IN AN INDUCTION PLASMA REACTOR

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Abstract

The thermal decomposition of NH_3 introduced into an induction plasma reactor, operating below atmospheric pressure, is investigated. Thermodynamics are first used to predict the decomposition products of the ammonia and to determine the minimum temperature required for complete decomposition. Experimentally, a cold wall reactor is used into which ammonia is injected axially. The temperature profiles of the plasma stream are evaluated by means of an enthalpy probe and the concentrations profile of the reactive and the plasma gas are measured in the mixing zone with the use of the same enthalpy probe connected to a quadrupole mass spectrometer. Conclusions on the mass and energy transfer mechanisms are drawn by a comparison of the measured profiles of concentration and temperature of the ammonia with those obtained during the injection of the stoichiometricly equivalent N_2/H_2 mixture. The investigation results show that ammonia decomposition is strongly affected by the mass and energy transfer phenomena.

1. Introduction

The production of silicon nitride through the gas phase reaction of ammonia and silicon tetrachloride is receiving growing interest. Recently, this reaction route has been performed in an induction plasma reactor and many authors(1,2,3) have recorded obtaining very different yields and crystalline content of the product. The major difference between these authors work that can account for these differences appears to lie in the manner by which the reactant ammonia decomposes in the plasma, in turn determined by the mass and energy transfer phenomena occuring in the reactor.

Until recently, no systematic study of the mass transfer and energy transfer phenomena in this system had been undertaken. Soucy et al (5) has earlier demonstrated experimentally that, at plasma temperatures, molecular diffusion is the controlling mass transfer mechanism because of the high viscosity of the gases present in the hot discharge. Furthermore, other authors(4,5,6) have examined mass transfer in order to understand the fundamental mechanisms during injection of a cold gas into a hot plasma. From an initial stand point, this phenomena could be rate limited for many reactive systems. Most of the prior work has been carried out with the injection of cold helium (an atomic gas) and with nitrogen or hydrogen (diatomic gases). Soucy and al(7) have worked on the influence of mass transfer effects on the decomposition of ammonia in an induction plasma reactor. Preliminary results suggests that the decomposition reaction seems to be mass transfer limited. Such a conclusion was arrived at studying the gas mixing length inside the reactor, involving the measurement of the central composition profile up and down the reactor. The radial diffusion effect was not studied and the gas temperature profiles could not be obtained due to the design of the reactor involved.

The present paper describes the results of our study of mass and energy transfer in decomposition of NH_3 injected axially in an induction plasma reactor. Composition, temperature and velocity of the plasma are all measured radially, at three different levels in the reactor after the torch exit, with the enthalpy probe that has previously proven to be a robust and reliable diagnostic tool(8,9,10). The ammonia is sequencially replaced by an equivalent volume of H_2 and N_2 and the ratio (3 to 1) of these two species corresponds to the stoichiometric decomposition products of ammonia. This mixture is helpfull in determining the effects of a reactive gas on the plasma stream in which the heat of dissociation replaces the endothermic heat of decomposition.

2.0 Thermodynamic considerations

To provide a basis for understanding the decomposition of ammonia, a simple thermodynamic equilibrium computation was carried out with the system Ar-H-N. A fortran program(11) using a Gibbs free energy minimization scheme was used to determined the equilibrium composition of the system involved over the temperature range of 300 to 3000 K. After a few simulations, the following species were considered in the energy minimization calculations: NH_3, NH_2, NH, N_2, N, H_2, H and Ar. The Janaf's tables(12) were used for the values of the Gibbs free energy at different temperatures. The initial mixture required for the calculation is corresponding to plasma operating conditions with injection of ammonia: 85% Ar, 10% NH_3 and 5% H_2. The calculations illustrated in Fig. 1 show that ammonia decomposes between 500-700 K.

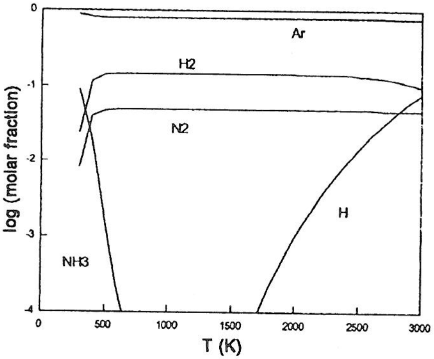

Figure 1 Equilibrium composition of the Ar-N-H system at 300 torr

3.0 Experimental set-up

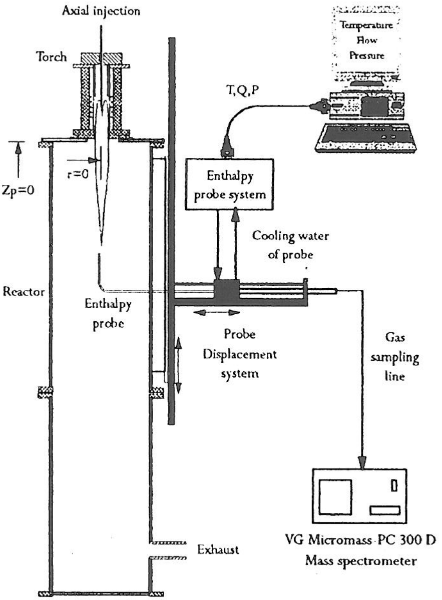

Figure 2 Experimental set-up

The experimental set-up for the present study is illustrated in Fig. 2, and consists of three majors components: an induction plasma torch installed on the top of a cylindrical reactor (0.6 m i.d., 2.74 m long), an enthalpy probe system and a mass spectrometer. The induction torch used was a TEKNA PL-70 utilizing a water-cooled 70 mm i.d. ceramic tube as a plasma confinement tube. The 5-turn induction coil was powered by a 400 kHz, 100 kW Lepel r.f. power supply. Pure argon was used as the plasma gas while a mixture of argon and hydrogen was used as the sheath gas. The axial water-cooled injection probe was used to injected the ammonia or the N_2/H_2 mixture as appropriate. The tip of the injection probe is placed in the center of the discharge, corresponding to $Z_p = -80$ mm. The axial reference $Z_p=0$ is illustrated on Fig. 2 and is taken as the plane of the torch exit. The enthalpy probe system consists of a high-pressure water-cooled probe (6.35 mm o.d. and 2.7 mm i.d.), a probe displacement system fitted with a steper motor, a gas sampling line and a PC probe acquisition and control unit interfaced with Labview software. The displacement system allows a complete 2-D sweep of the plasma stream. The enthalpy probe allows measurements of stagnation pressure at the tip of the probe and the enthalpy of the gas. For further information on the capacities/performance of the enthalpy probe, refer to Rahmane and al.(8). Finally, in order to calculate the velocities and the temperatures of the plasma stream, the gas composition is needed to complete the information derived by means of the enthalpy probe. In the present system, the gas sample line is connected to a VG micromass -PC 300D mass spectrometer, pre-calibrated with a multi-point sequence to give a maximum of ±1% error in the composition of each species.

4.0 Result and discussion

A number of induction plasma reactor parameters were held constant throughout the study. Thus, 115 lpm of argon was used for the plasma gas and 50 lpm of argon and 10 lpm of hydrogen were used for the sheath gas. Reactor pressure of 300 torr and 75 kW plasma plate power were employed for all experiments. The following parameters were varied:

- flow rates of NH_3, 10 and 20 lpm (STP)
- replacement of NH_3 by a mixture of H_2 and N_2

For the sake of comparison and discussion, the decomposition reaction run where 20 lpm of NH_3 was injected axially will be taken as a basis. Figures 3 and 4 present the radial temperature and composition profiles at the three selected levels in the reactor: Zp= 22mm, Zp= 72 mm and Zp= 172 mm. The abcissa represents the radial position where r=0 is taken as the centerline of the reactor. For the high temperature profile (Fig. 3(a)), the effect of injection of a cold, reactive gas is important. The temperature in the plasma on the centerline is cool in comparison to the maximum temperature obtained in this profile at r= 10mm. This high temperature gradient is similarly reflected in the composition profile at the same position (Fig. 4 (a)). As shown, radial diffusion of nitrogen is not observed beyond r=10 mm (the rise in composition of N_2 after 25 mm is related to recirculation patterns near the wall of the reactor) and limited diffusion is observed for the hydrogen (part of this hydrogen coming from the sheath gas). Then, in the high temperature region, the dominant mass transfer mechanism is molecular diffusion. The temperature profile, at Zp= 72 mm (Fig. 3(b)), is more uniform but the composition profile again shows mass transfer limitations. This suggests that energy transfer is occurring more rapidly than mass transfer. Finally, the flats profiles for both temperature and composition at the lower position (Fig. 3 (c) and Fig. 4 (c), indicate that turbulent mixing has taken over from the laminar molecular diffusion. An axial concentration profile will be usefull to determine the mixing lenght in this system.

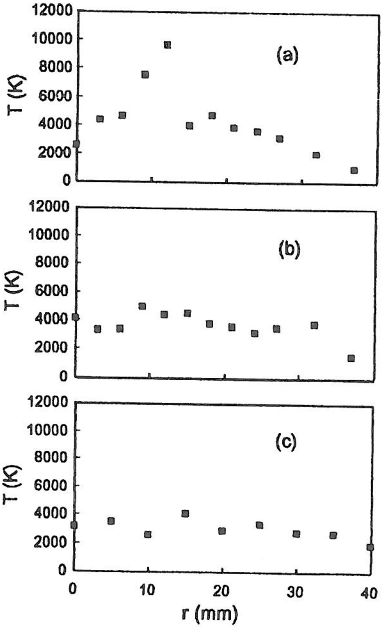

Figure 3 Radial temperature profiles at (a)Zp=22mm (b)Zp=72mm (c)Zp=172mm with 20 lpm of NH_3 injected

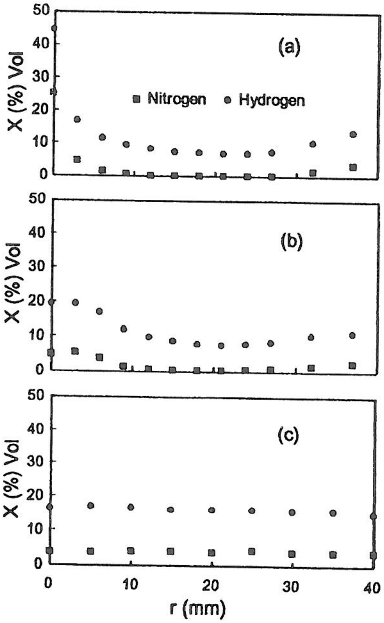

Figure 4 Radial composition profiles at (a)Zp=22mm (b)Zp=72mm (c)Zp=172mm with 20 lpm of NH_3 injected

Using the same reference, Fig. 5 represent the effect of lower flow rate of NH_3 on the plasma temperature. The axial position correspond to Zp=22 mm. As shown, the central temperatures are similar for both profiles. Differences occurs near the r=10 mm zone. In this zone, observation of the maximum temperature with 20 lpm NH_3 injection is found at r=12mm while at 10 lpm, the maximum occurs at r=9mm. This suggests that the cold zone is larger with greater flow rate of NH_3. Thus, for higher injection of reactive gas, radial penetration of the cold gas is more important.

To observe the effect of the endothermic heat of decomposition, an equivalent volume mixture is used to replace the injected ammonia. The composition of the mixture of N_2/H_2 corresponds to the stoichiometry of the decomposition of NH_3. Thus, to replace 20 lpm of NH_3, 15 lpm of H_2 and 5 lpm of N_2 are necessary. In Fig. 6, the radial temperature, velocity and nitrogen composition profiles at Zp= 72 mm for injection of NH_3 and the H_2/N_2 mixture are presented. The difference of the temperature profile could indicate that endothermic heat of decomposition has an important cooling effect. Nevertheless, further tests are needed where 40 lpm of H_2/N_2 is injected to simulate decomposition of 20 lpm of NH_3. Observation of the velocity (U) profile indicate that the central region is strongly affected by temperature (velocities are greater at higher temperature). Finally, the nitrogen composition profiles show that N_2 diffuses more rapidly, with NH_3

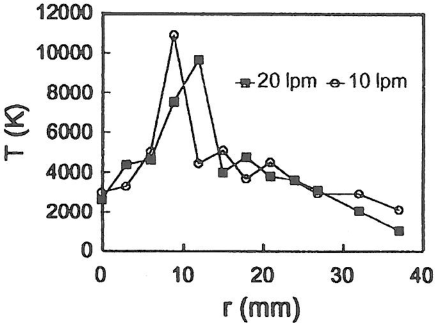

Figure 5 Radial temperatureprofiles at Zp= 22 mm for two differents NH_3 flow rates (10 and 20 lpm)

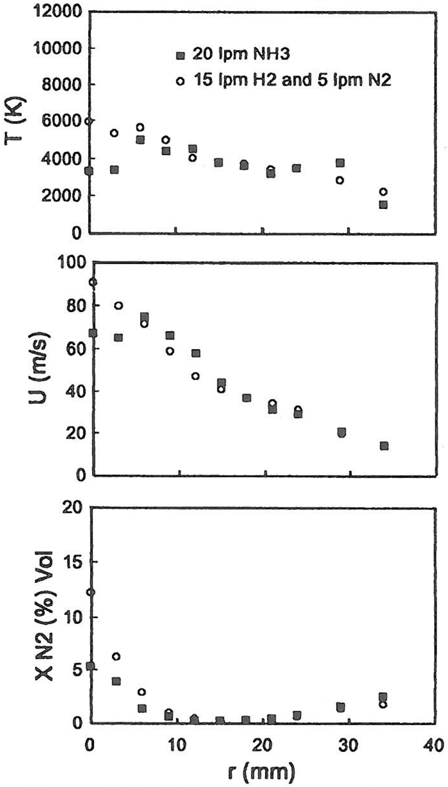

Figure 6 Radial temperature, velocity and nitrogen composition profiles at Zp=72 mm where NH_3 is replaced by H_2 and N_2

decomposition, near the centerline because the overall temperature is lower. So, convective transfer is more important than molecular diffusion in the center because of lower viscosity of the gases.

5. Conclusion

In this work, it has been demonstrated that mass and energy transfer are important factors to understand in order to maximize the quantity of NH_3 that can be decomposed and that transport phenomena is limited in the high temperature region by molecular diffusion. Furthermore, by increasing NH_3 flow rates, cooler central temperatures were observed. Finally, more tests need to be conducted to understand the effect of endothermic heat of decomposition of NH_3 on the mass and energy transfer mechnisms.

Acknowledgments

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