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Dedicated to Professor Dr. Sorin Dan Anghel on His 65th Anniversary

FORMATION OF AMMONIA IN A LINEAR PLASMA REACTOR

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ABSTRACT. A study of ammonia formation in DC plasma discharge is presented in function of gas composition and working temperature by using a laboratory scale plasma nitriding reactor. The nitriding process took place in case of a Hollow Cathode (HC) configuration with treated part on Anodic Potential (HCAPN). It was found that in the temperature range of 500-700 K the yield of ammonia was directly proportional with the discharge current and the coefficient of efficiency was found to be constant. This indicates that ammonia formation in low temperature plasma discharge is electrochemical in nature. During our experiments nitride layers was formed on both the cathode and the inner anode. This indicates that the neutral ammonia molecules have a nitrogen carrying role in the plasma nitriding process.

Keywords: *linear plasma reactor, plasma nitriding, active screen, hollow cathode, anodic potential, formation of ammonia, nitrogen mass transfer.*

1. INTRODUCTION

The study of the formation of ammonia in DC gas discharge has a long history. Brewer and Westhaver [1] have begun its investigation before the 1930's. They detected ammonia in a DC gas discharge containing a mixture of three parts hydrogen and one part nitrogen. The amount of ammonia formed was found to be directly proportional to the current of the discharge and independent of the gas pressure.

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They removed the ammonia formed from the discharge space by freezing. According to Auner's patent [2] from 2013, ammonia can be produced using a gas a mixture of three parts hydrogen and one part nitrogen in a low power (10 W) gas discharge between two electrodes inside of a quartz tube. This method simultaneously superimposes a high frequency discharge (2.45 GHz, 800 W, 1 msec impulse and 19 msec pauses). The formed ammonia is then frozen in a trap at 77 K, dissolved in water and quantitatively analyzed. Burlakov and others [3] detected ammonia in an active screen plasma nitriding (ASPN) industrial installation. They found that the maximum amount of ammonia (1.2% vol. of the incoming gas mixture supply) is produced when the supplied gas mixture has a ratio of hydrogen to nitrogen is 1:1. They observed that the amount of ammonia formed decreased with the increase of the temperature. They concluded that the role of NH_3 in the ASPN process was not well-defined and needed further study. Skalecki and others [4] studied the influence of plasma treatment parameters, and of the nitrogen to hydrogen ratio on the atmosphere and on the formation of ammonia during plasma nitriding. By correlating the measured ammonia with the treatment parameters, they could predict the ammonia-content of the exhaust gas. Furthermore, they were able to calculate the plasma nitriding potential based on the ammonia content. They also established the correlation of this nitriding potential to the formation of ε and γ' nitride phases. This paper presents the results of our study of the formation of ammonia in a DC plasma discharge, in function of gas composition and the working temperature by using a laboratory scale plasma nitriding reactor. We controlled the temperature by concurrently changing the applied voltage and the current intensity. Similarly, we studied the relationship between the amount of ammonia formed and the intensity of the current. It should be noted that the total electric current in the discharge is formed by the sum of electron and ionic currents. For temperatures at the low end of the nitriding process temperature scale we observed a strictly direct proportionality between the total electric current and the amount of ammonia formed (μmols/sec). We determined that over the threshold temperature of 780 K, the decomposition rate of the formed ammonia exceeds its formation rate. Presumably, the decomposing ammonia was a nitrogen transporting medium of the anodic nitriding process.

2. EXPERIMENTAL EQUIPMENT AND PROCEDURE

The studies were performed in a laboratory scale plasma nitriding reactor with a diameter of 0.25 m and length of 1.0 m. The hydrogen-nitrogen mixture has been supplied by a gas generator furnished with two flow-meters. Through pin-valves

the gases passed through a low pressure mixer, where they were well mixed as ideal gases. From the mixer the gas mixture entered the reactor and passed by the electrodes made of unalloyed steel. The gases were then removed from the reactor using a vacuum pump. This gas then was passed through a water-trap with a set amount of water, which dissolved and retained the ammonia from the gas mixture. The dissolved ammonia then was determined volumetrically.

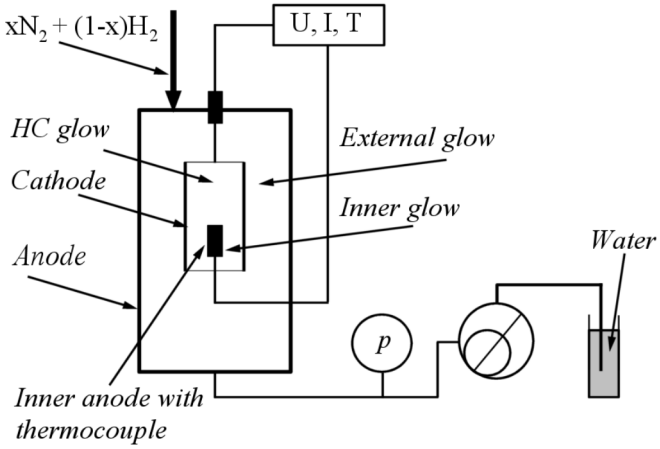

Fig. 1. The diagram of the experimental equipment

In order to increase the amount of ammonia formed, we created a composite discharge space formed by a hollow cathode (0.085x0.2 m) and an auxiliary anode with a thermocouple, placed inside the lower part of the hollow cathode. See Fig. 1. This setup created two abnormal discharges. The first was between the external surface of the hollow cathode and the walls of the reactor (anode). The second one was between the internal wall of the hollow cathode and the auxiliary anode. In addition to these two abnormal discharges, an HC glow discharge was formed in the upper side of the hollow cathode, the anode being the wall of the reactor and the auxiliary anode.

The reactor has been outfitted with a rotary vane pump with a nominal pumping speed of $15 m^3/h$ or $4.166 \cdot 10^{-3}$ m^3/s. In function of the volume of the incoming gas supply, the equilibrium pressure was between 200-300 Pa. Varying the voltage of the plasma discharge between 400 to 950 V, the maximum value of the current density has been 22 A/m^2. Under these conditions the electron temperature was 10^4 K in the proximity of the anode, while the concentration of electrons was $5 \cdot 10^{14}$ m^{-3}.

3. SAMPLING AND ANALYSIS

The gas mixture exiting the pump was driven through a porous ceramic filter into a known volume of water (250 ml) where the ammonia has been absorbed. Then the samples were stored in airtight containers while awaiting chemical analysis.

The amount of ammonia absorbed during the sampling process has been determined by titration using a hydrochloric acid 0.1 N. A 25 ml ILMABOR Schellbach burette was used to measure the amount of hydrochloric acid solution. Methyl-orange was used as an indicator, its color change occurring at around pH 3.1-4.4. For every experimental setup, we took three samples and we used their averages for our calculations. It should be noted that the values were standardized by dividing the absolute amount of ammonia formed with the sampling time (mMol/sampling time). This standardized amount was transformed into µMol/sec or into volumetric percent of the incoming gas mixture - as was needed.

During the first series of experiments, we studied the precision of the analysis methodology i.e. the sample collection and the titration itself. Our assumption was that the absolute amount of ammonia formed in identical conditions had to be proportional with the sampling time.

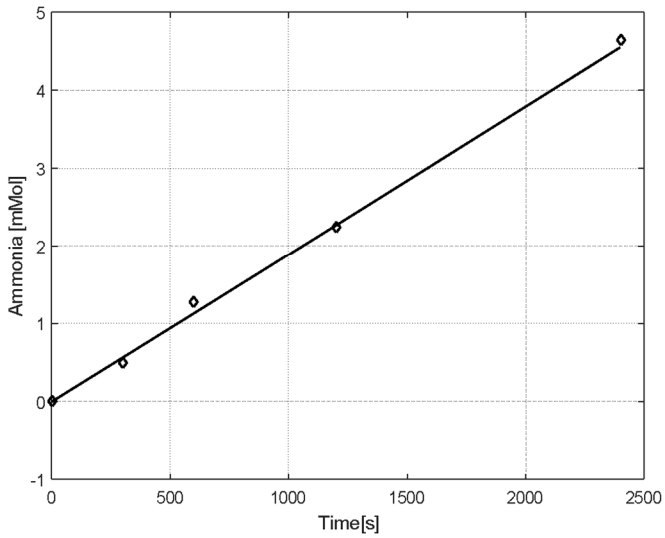

Fig. 2. The absolute amount of ammonia formed in function of sampling time (T=800 K, $Q_v=10^{-5}$ m^3/sec)

We used a classical direct current plasma nitriding (DCPN) setup with a central steel cathode (diameter 0.048 m and length 0.2 m). The incoming gas mixture volumes expressed at standard temperature and pressure (STP), were 150 ml/min N_2 and 450 ml/min H_2 i.e. the total volume of 10^{-5} m^3/sec gas mixture. The temperature of the cathode was 800 K and the sampling times were at 300, 600, 1200 and 2400 seconds. We used 250 ml of bidistilled water to absorb the ammonia from the exhaust gas mixture and a volume of 10 ml of this solution was used for volumetric analysis. The pressure of equilibrium in the reactor was 270 Pa. Based on the results of this experiment, shown in Fig. 2, we were able to state with confidence that the applied methodologies precision was good. The coefficient of determination of the regression line was R^2=0.9989.

In the following experiments the sampling times were set at 1200 seconds and we took three samples for each condition of equilibrium. The hollow cathode setup used in our experiments, see Figure 1, allowed the use of higher discharge currents and therefore the formation of larger amounts of ammonia. In doing so, we decreased the relative error of the analysis.

4. FORMATION OF AMMONIA IN FUNCTION OF THE COMPOSITION OF THE GAS MIXTURE

The formation of ammonia has been studied in gas mixtures of composition of $xN_2+(1-x)H_2$, where the x varied between 0 and 1. During the experiments the volumetric rate of the incoming gas mixture has been maintained at $6.5 \cdot 10^{-6}$ m^3/s and the temperature at 780 K. Based on our previous observations, this was the maximum temperature where the rate of decomposition of the ammonia on the steel electrodes was negligible.

The results of the experiments are presented in Fig. 3. It should be noted that the amount of ammonia formed has been given in terms of volumetric percentage (vol. %) of the incoming gas mixture.

The formation of ammonia started even in a pure hydrogen atmosphere. This phenomenon can be explained by the fact that the cathode was made of low-carbon steel which had been plasma nitrided for more than 100 hours during our previous experiments. The hydrogen dissolved the nitrogen from the ε iron nitride ($Fe_{2\text{-}3}N$) during the plasma discharge and it formed the ammonia.

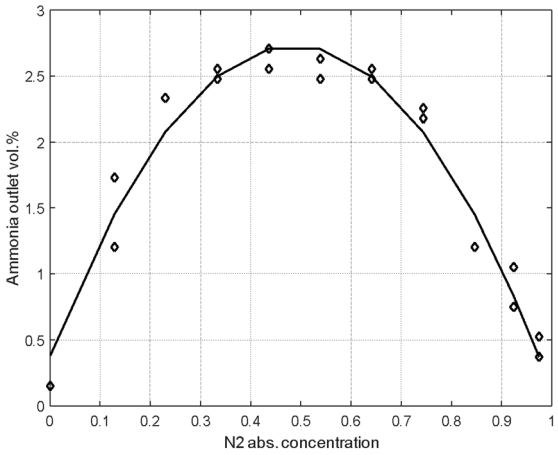

Fig. 3. Formation of ammonia from different gas mixture – $xN_2+(1-x)H_2$. ($T=780$ K, $Q_v=6.5\cdot10^{-6}$ m^3/s)

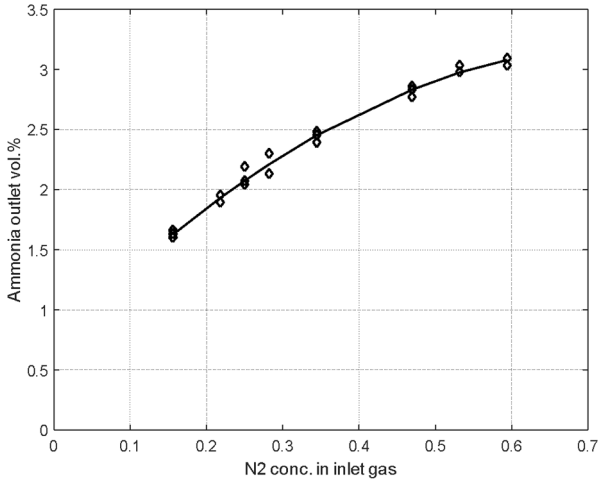

Fig. 4. The amount of ammonia in the outlet gas. ($T=780$ K, $Q_v=10.67\cdot10^{-6}$ m^3/s)

The maximum value of the curve occurs at the gas mixture of 0.5 N_2 + 0.5 H_2 and not at the expected theoretical ratio of 0.25 N_2 + 0.75 H_2, just as it has been observed by Burlakov [3] as well. By increasing the volumetric rate of the incoming gas mixture the maximum of the curve moved to the right as shown in Fig. 4. By increasing the volumetric rate of the incoming gas mixture by 60%, from $6.5\cdot10^{-6}$ m^3/s

to $10.67 \cdot 10^{-6}$ m^3/s, the maximum value of the curve moved past the 0.6 N_2 ratio and the amount of ammonia formed has increased substantially. Our assumption is that this behavior depended on the characteristics of the plasma reactor.

5. FROMATION OF AMMONIA IN FUNCTION OF TEMPERATURE

We studied the formation of ammonia in function of the equilibrium temperature. The composition ratio of the gas mixture was set to equal the ratio of nitrogen to hydrogen within the ammonia molecule (N_2 + $3H_2$). During our experimental runs, we kept the volumetric rate of the gas mixture at a constant value of Q_v=$10.67 \cdot 10^{-6}$ m^3/s. The results for the temperatures between 508 – 850 K are shown in Fig. 5.

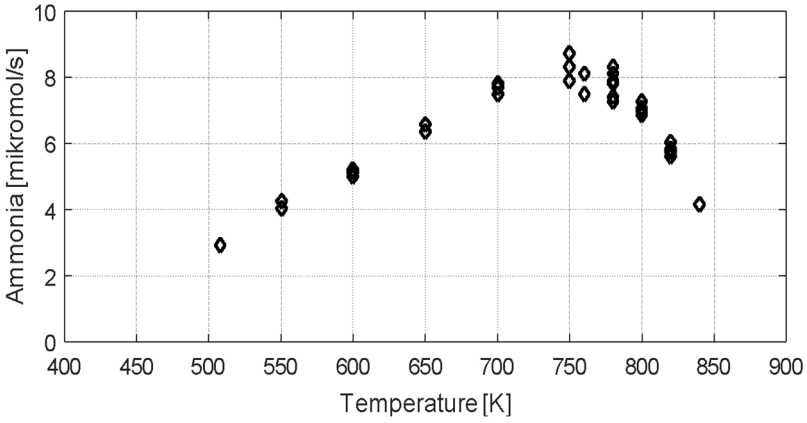

Fig. 5. Yield of ammonia in function of the equilibrium temperature (Qv=$10.67 \cdot 10^{-6}$ m^3/s; N_2/H_2=1/3).

The lowest equilibrium temperature we used was 508 K. At this temperature the negative light covers the entire surface of the cathode (the condition for an abnormal glow discharge). Up to 750 K, the yield in ammonia is directly proportional to the temperature. At higher temperatures, the yield decreases rapidly. We believe that this decrease is due to the thermal decomposition of the formed ammonia. This decomposition takes place on the surface of the cathode and inner anode, just like in the case of the decomposition that occurs during the classical gas nitriding process [7, 8]. It should be noted that during this process both the cathode and inner anode were nitrided.

6. RELATIONSHIP BETWEEN THE YIELD OF AMMONIA AND CURRENT INTENSITY

We investigated the rate of ammonia formation as a function of current intensity for temperatures lower than the threshold temperature of 750 K. The composition and the volumetric rate of the gas mixture was N_2/H_2=1/3 and Q_v=10.67·10^{-6} m^3/s, respectively. It should be noted that the yield of ammonia (μmol/s) has been found to be directly proportional to the temperature at the temperature range at which we performed these tests.

In order to establish a relationship between the amount of ammonia formed and the current intensity, we compared the number of ammonia molecules formed in one second (yield) to the number of elementary electric charge carried by the electric current. We named this ratio coefficient of efficiency:

$$\eta = \frac{\nu \cdot N_A}{I \cdot n} = \frac{\nu \cdot N_A}{I \frac{1}{q}},$$

Where the ν was the amount of ammonia formed in unit time (mol/s), N_A is the Avogadro number 6.022·10^{23} molecules/mol, q is the elementary electron charge 1.602·10^{-19} C, and n is the number of elementary electric charge carried by 1 A current intensity.

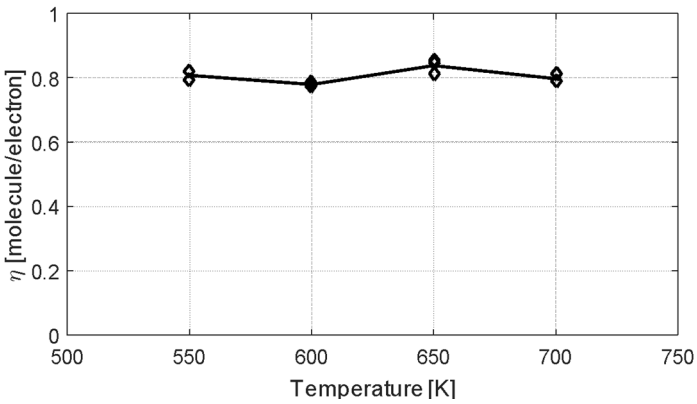

Fig. 6. Relationship of coefficient of efficiency of ammonia formation and temperature

The results of the experiment are summarized in Fig. 6. The coefficient of efficiency was found to be constant, 0.8 NH_3 molecule/elementary electric charge, at the temperatures used in our experiment, i.e. for temperatures below 750 K. We assume that this relationship continued to exist at temperatures higher than

the threshold temperature. This unvarying relationship between the number of ammonia molecules and the elementary electric charge indicates that ammonia formation in low temperature plasma discharge is electrochemical in nature.

7. CONCLUSIONS

Ammonia was formed in a linear plasma reactor using a gas mixture of nitrogen and hydrogen and by applying a DC glow discharge between the electrodes made of steel. From the standpoint of ammonia formation, the optimal composition of the gas mixture depended on the mechanical dimensions of the reactor, the volumetric rate of the supplied gas mixture, and the applied temperature. We studied the formation of ammonia at two different volumetric rates, i.e. at $6.5 \cdot 10^{-6}$ m^3/s and $10.67 \cdot 10^{-6}$ m^3/s. The maximum amount of ammonia was formed when the absolute concentration of nitrogen was between 0.5-0.7, depending on the incoming gas mixture volumetric rate. In the temperature interval of 500-700 K the yield of ammonia (μmol/s) was directly proportional with the discharge current. The coefficient of efficiency was found to be constant, 0.8 NH_3 molecule/elementary electric charge. This unvarying relationship between the number of ammonia molecules and the elementary electric charge indicates that ammonia formation in low temperature plasma discharge is electrochemical in nature. At temperatures above 750 K the amount of ammonia has decreased in the exhaust gas with the increase of the temperature. This temperature matched the lower limit of the classic gas nitriding process temperature. During our experiments nitride layers have been formed on both the cathode and the inner anode. This indicates that the neutral ammonia molecules have a nitrogen carrying role in the plasma nitriding process. The presence of iron atoms deriving from the cathode sputtering process makes it likely that the mechanism based on intermediary $FeNH_{2\text{-}3}$ molecules as proposed by Szabó, A [7] is correct.

9. ACKNOWLEDGEMENT

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